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*By Paul Foglino*



Cracking the  
**AP**<sup>®</sup>  
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2011 Edition

Paul Foglino

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# Introduction

## WHAT IS THE PRINCETON REVIEW?

The Princeton Review is an international test-preparation company with branches in all major U.S. cities and several abroad. In 1981, John Katzman started teaching an SAT prep course in his parents' living room. Within five years, The Princeton Review had become the largest SAT prep program in the country.

Our phenomenal success in improving students' scores on standardized tests is due to a simple, innovative, and radically effective philosophy: Study the test, not just what the test claims to test. This approach has led to the development of techniques for taking standardized tests based on the principles the test writers themselves use to write the tests.

The Princeton Review has found that its methods work not just for cracking the SAT, but for any standardized test. We've already successfully applied our system to the GMAT, LSAT, MCAT, and GRE, to name just a few. Obviously, you need to be well versed in chemistry to do well on the AP Chemistry Exam, but you should remember that any standardized test is partly a measure of your ability to think like the people who write standardized tests. This book will help you brush up on your AP Chemistry and prepare for the exam using our time-tested principle: Crack the system based on how the test is created.

We also offer books and online services that cover an enormous variety of education and career-related topics. If you're interested, check out our website at [PrincetonReview.com](http://PrincetonReview.com).



# 1

## Orientation

### **WHAT IS THE AP PROGRAM?**

The Advanced Placement (AP) Program bridges high schools and colleges by allowing high school students to do college-level work for college credit. The AP Chemistry Exam is one of more than 30 college-level examinations offered every year.

AP courses are offered by more than 10,000 high schools in the United States, Canada, and more than 60 additional countries. More than 3,000 colleges around the world offer college credit to students who perform well on AP tests. The specific score required for credit varies from school to school and from subject to subject.

The AP Program is coordinated by the College Board. The College Board is a national nonprofit organization composed of representatives from various schools and colleges. They see it as their mission to set educational standards.

The College Board appoints a development committee for each of the subjects. The development committee decides what should be covered in an AP course and how it should be covered on the AP test. The AP Chemistry development committee is composed of three high school chemistry teachers, three college professors who teach general chemistry, and an additional college professor who chairs the group. Each member of the development committee serves a three-year term.

The test is administered by the Educational Testing Service (ETS)—the same folks who bring you the SAT. ETS also plays a role in developing the test.

## WHAT IS THE AP CHEMISTRY EXAM?

The AP Chemistry Exam is a three-hour-long, two-section test that attempts to cover the material you would learn in a college first-year chemistry course. The first part, which counts for 50 percent of your grade, consists of multiple-choice questions. The second part, which counts for 50 percent of your grade, is composed of free-response questions, such as short essays and problems involving calculations.

The test is offered once every year in May. It's scored in June. The multiple-choice section is scored by computer and the problems and essays are scored by a committee of high school and college teachers. The problems and essays are graded according to a standard set at the beginning of the grading period by the chief faculty consultants. Inevitably, the grading of Section II is never as consistent or accurate as the grading of Section I.

When the grading is done, the results are curved and each student receives a grade based on a five-point scale. For the AP Chemistry Exam, the results break down as follows:

Grade	What It Means	Approximate % of Test Takers Who Get This Score
5	Extremely well qualified	15%
4	Well qualified	18%
3	Qualified	24%
2	Possibly qualified	18%
1	No recommendation	25%

Although standards vary from school to school, it's safe to say that most colleges will give credit for a 5, some will give credit for a 4 or 3, and very few will give credit for a 2.

## CRACKING THE MULTIPLE-CHOICE SECTION

### THE BASICS

Section I of the test is composed of 75 multiple-choice questions, for which you are allotted 90 minutes. This part is worth 50 percent of your total score.

For this section, you will be given a periodic table of the elements and you may NOT use a calculator. The College Board says that this is because the new scientific calculators not only program and graph but also store information—and they are afraid you'll use this function to cheat!

The first 15 multiple-choice questions, give or take a few, will be formatted with 5 answer choices followed by a series of questions (as shown on the next page).

#### Questions 1–4

- (A) O<sub>2</sub>
- (B) H<sub>2</sub>O
- (C) Ni
- (D) Fe
- (E) NaCl

1. This species contains ionic bonds. (E)
2. This species is a gas at standard temperature and pressure. (A)
3. This species is denser as a liquid than as a solid. (B)
4. This species contains a double bond. (A)

These are mostly straightforward, “you know it or you don’t” questions. Notice that an answer can be used once, more than once, or not at all.

The rest of the multiple-choice questions are in the standard question-and-answers format shown below.

16. Which of the following species is a gas at standard temperature and pressure?
  - (A) O<sub>2</sub>
  - (B) H<sub>2</sub>O
  - (C) Ni
  - (D) Fe
  - (E) NaCl

On the multiple-choice section, you receive 1 point for a correct answer, and  $\frac{1}{4}$  point is subtracted for an incorrect answer. There is no penalty for leaving a question blank.

Your raw score on this section will be just the number of questions you answered correctly minus one-fourth of the number of questions that you answered incorrectly. You can make a rough prediction of your overall score from your raw score on the multiple-choice section, assuming that you do about as well on the free-response section.

Roughly speaking,

- if you get a raw score of *at least* 50, you will probably get a 5
- if you get a raw score of *at least* 35, you will probably get at least a 4
- if you get a raw score of *at least* 25, you will probably get at least a 3

#### PACING

So you can get a 5 with a raw score of 50, a 4 with a raw score of 35, and a 3 with a raw score of 25. That’s a pretty generous curve. According to the College Board, the multiple-choice section of the AP Chemistry Exam covers more material than any individual student is expected to know. Nobody is expected to get a perfect or even near-perfect score.

What does that mean to you?



## Don't Answer All the Questions!

You can skip every third question and still get a 5. You can skip half the questions and still get a 4. You can skip two out of every three questions and still get a 3. Obviously, you should answer any question that you have a chance of getting right, but you should be aware that the grading curve gives you plenty of slack.

Okay, so you know that you can skip questions. How do you know which questions to skip?

## Use the Two-Pass System

Go through the multiple-choice section twice. The first time, do all the questions that you can get answers to immediately. That is, do the questions with little or no math and questions on chemistry topics in which you are well versed. Skip questions on topics that make you uncomfortable. Also, you want to skip the ones that look like number crunchers (even without a calculator, you may still be expected to crunch a few numbers). Circle the questions that you skip in your test booklet so you can find them easily during the second pass. Once you've done all the questions that come easily to you, go back and pick out the tough ones that you have the best shot at.

In general, the questions near the end of the section are tougher than the questions near the beginning. You should keep that in mind, but be aware that each person's experience will be different. If you can do acid-base questions in your sleep, but you'd rather have your teeth drilled than draw a Lewis diagram, you may find questions near the end of the section easier than questions near the beginning.

That's why the Two-Pass System is so handy. By using it, you make sure you get to see all the questions you can get right, instead of running out of time because you got bogged down on questions you couldn't do earlier in the test.

This brings us to another important point.

## Don't Turn a Question into a Crusade!

Most people don't run out of time on standardized tests because they work too slowly. Instead, they run out of time because they spend half the test wrestling with two or three particular questions.

You should never spend more than a minute or two on any question. If a question doesn't involve calculation, then either you know the answer, you can make an educated guess, or you don't know the answer. Figure out where you stand on a question, make a decision, and move on.

Any question that requires more than two minutes' worth of calculations probably isn't worth doing. Remember, skipping a question early in the section is a good thing if it means that you'll have time to get two correct answers later on.

## GUESSING

You get one point for every correct answer on the multiple-choice section. You lose  $\frac{1}{4}$  point for every wrong answer. Each question has five answer choices, so if you were to guess randomly on every single question, statistically you would get one out of five right. That's 15 right and 60 wrong.

$$(15 \text{ right} \times 1 \text{ point}) - (60 \text{ wrong} \times \frac{1}{4} \text{ point}) = (15) - (15) = 0$$

So guessing randomly neither helps you nor hurts you. Educated guessing, however, will help you.

## Use Process of Elimination (POE) to Find Wrong Answers

There is a fundamental weakness to a multiple-choice test. The test makers must show you the right answer, along with four wrong answers. Sometimes seeing the right answer is all you need. Other times you may not know the right answer, but you may be able to identify one or two of the answers that are clearly wrong. Here is where you should use POE to take an educated guess.

Look at this hypothetical question.

1. Which of the following compounds will produce a purple solution when added to water?
  - (A) Brobogdium rabelide
  - (B) Diblythium perjuvenile
  - (C) Sodium chloride
  - (D) Hynynium gargantuide
  - (E) Carbon dioxide

You should have no idea what the correct answer is because three of these compounds are made up, but you do know something about the obviously wrong answers. You know that sodium chloride, choice (C), and carbon dioxide, choice (E), do not turn water purple. So, using POE, you have a one-out-of-three chance at guessing the correct answer. Now the odds are in your favor. Now you should guess.

## If You Can Eliminate Even One Wrong Answer, Guess

In the example above, we eliminated two wrong answers, but even eliminating one wrong answer puts the odds in your favor. The guessing penalty ( $\frac{1}{4}$  point) assumes that you're taking a one-out-of-five guess, so even a one-out-of-four guess will gain points. Of course, the more wrong answers you can eliminate, the better.

## Guess and Move On

Remember, you're guessing. Pondering the possible differences between brobogdium rabelide and diblythium perjuvenile is a waste of time. Once you've taken POE as far as it will go, pick your favorite letter and move on.

Remember, the multiple-choice section is the exact opposite of the free-response section. It's scored by a machine. There's no partial credit. The computer doesn't know, or care if you know, why an answer is correct. All the computer cares about is whether you blackened in the correct oval on your score sheet. You get the same number of points for picking (B) because you know (A) and (E) are wrong and B is a nicer letter than C or D as you would for picking (B) because you fully understood the subtleties of an electrochemical process.

## ABOUT CALCULATORS

You will NOT be allowed to use a calculator on this section. That shouldn't worry you. All it means is that there won't be any questions in the section that you'll need a calculator to solve.

Most of the calculation problems will have fairly user-friendly numbers—that is, numbers with only a couple of significant digits, or things like “11.2 liters of gas at STP” or “160 grams of oxygen” or “a temperature increase from 27°C to 127°C.” Sometimes these user-friendly numbers will actually point you toward the proper steps to take in your calculations.

Don't be afraid to make rough estimates as you do your calculations. Sometimes knowing that an answer is closer to 50 than to 500 will enable you to pick the correct answer on a multiple-choice test (if the answer choices are far enough apart). Once again, the rule against calculators works in your favor because the College Board will not expect you to do very precise calculations by hand.

There may be a couple of real number-crunching problems on the test. If you can recognize them quickly, these are good ones to skip. There's no point in spending five minutes crunching numbers to get one problem right if that time could be better used in getting three others correct later in the test.

## CRACKING THE FREE-RESPONSE SECTION

Section II is composed of a series of six free-response questions, all of which are required. You will be allotted 95 minutes to complete this section, which is worth 50 percent of your total score. You get exactly 55 minutes for Part A, which is composed of three problems requiring calculation, then 40 minutes for Part B, which is composed of two essay questions and one question concerning chemical reactions.

### PART A — PROBLEMS

For Part A, you will be given a table of commonly used chemical equations, a table of standard reduction potentials, and a periodic table. You may use a calculator, which you will probably need.

#### The Equilibrium Problem

This is a multipart question involving calculation to determine some aspect of equilibrium.

This question will be divided into at least four or five parts, with partial credit available for correct answers on each part. The question is worth 20 percent of Section II. The average score for this question is usually less than half credit.

#### Two Additional Problems

Part A also includes two additional multipart questions that will involve calculation. These questions can come from any topic in the syllabus and one of them may be based in a laboratory setting. The test makers will probably do their best to include concepts from as many different chemistry topics as possible in the different parts of each problem.

These questions, like the equilibrium question, will be divided into at least four or five parts, with partial credit available for correct answers on each part. Each of these questions is worth 20 percent of Section II. The average score for these questions is usually less than half credit.

## CRACKING THE PROBLEMS

On Part A, you want to show the graders that you can do chemistry math, so here are some suggestions.

#### Show every step of your calculations on paper

This section is the opposite of multiple choice. You don't just get full credit for writing the correct answer. You get most of your points on this section for showing the process that got you to the answer. The graders give you partial credit when you show them that you know what you're doing. So even if you can do a calculation in your head, you should set it up and show it on the page.

By showing every step, or explaining what you're doing in words, you insure that you'll get all the partial credit possible, even if you screw up a calculation.

#### Include units in all your calculations

Scientists like units in calculations. Units make scientists feel secure. You'll get points for including them and you may lose points for leaving them out.

### **Remember significant figures**

You can lose one point per question if your answer is off by more than one significant figure. Without getting too bent out of shape about it, try to remember that a calculation is only as accurate as the least accurate number in it.

### **The graders will follow your reasoning, even if you've made a mistake**

Often, you are asked to use the result of a previous part of a problem in a later part. If you got the wrong answer in part (a) and used it in part (c), you can still get full credit for part (c), as long as your work is correct based on the number that you used. That's important, because it means that botching the first part of a question doesn't necessarily sink the whole question.

### **Remember the mean!**

So let's say that you could only complete parts (a) and (b) on the required equilibrium problem. That's 4 or 5 points out of 10, tops. Are you doomed? Of course not. You're above average. If this test is hard on you, it's probably just as hard on everybody else. Remember, you don't need anywhere near a perfect score to get a 5, and you can leave half the test blank and still get a 4!

## **PART B — REACTIONS AND ESSAYS**

You will not be allowed to use a calculator for Part B, which requires you to write balanced equations for chemical reactions and answer questions about chemical concepts.

### **Writing Chemical Equations**

For this section, you will be given a table of standard reduction potentials and a periodic table and you may not use a calculator.

You will be given 3 sets of chemical reactants and you will be asked to write the appropriate balanced equation for the reaction that will occur for each. Each reaction will be followed by a brief question that will focus on some aspect of the reaction.

Each reaction is worth 5 points; 1 point for reactants, 2 points for products, 1 point for balancing, and 1 point for the question; so you can earn a total of 15 points for this section. This part is worth 10 percent of Section II.

We'll talk about how to approach this section in Chapter 17.

### **Essays**

For the two essay questions, you will be given a table of commonly used chemical equations, a table of standard reduction potentials, and a periodic table. You may not use a calculator for this section, which is fine because there won't be any calculations.

The essays are multipart conceptual questions, with stress on understanding and explaining chemical concepts, rather than on doing calculations. These questions can come from any topic in the syllabus and one of them may be based in a laboratory setting. As in the problems, the test makers will probably try to include questions from as many different chemistry topics as possible. Partial credit will be given for correct answers on each part, and each question is worth 15 percent of Section II.

## **CRACKING THE ESSAYS**

This section is here to test whether you can translate chemistry into English. The term "essay" is a little misleading because all of these questions can be answered in two or three simple sentences, or with a simple diagram or two. Here are some tips for answering the two essay questions on Part II.

**Show that you understand the terms used in the question.**

If they ask you why sodium and potassium have differing first ionization energies, the first thing you should do is tell them what ionization energy is. That's probably worth the first point of partial credit. Then you should tell them how the differing structures of the atoms make for differing ionization energies. That leads to the next tip.

**Take a step-by-step approach.**

Grading these tests is hard work. Breaking a question into parts in this way makes it easier on the grader, who must match your response to a set of guidelines he or she has been given that describe how to assign partial and full credit.

Each grader scores each test based on these rough guidelines that are established at the beginning of the grading period. For instance, if a grader has 3 points for the question about ionization energies, the points might be distributed the following way:

One point for understanding ionization energy.

One point for explaining the structural difference between sodium and potassium.

One point for showing how this difference affects the ionization energy.

You can get all three points for this question if the grader thinks that all three concepts are addressed *implicitly* in your answer, but by taking a step by step approach, you improve your chances of *explicitly* addressing the things that a grader has been instructed to look for. Once again, grading these tests is hard work; graders won't know for sure if you understand something unless you tell them.

This leads us to an obvious point.

**Write neatly.**

Even if writing neatly means working at half-speed. You can't get points for answers if the graders can't understand them. Of course, this applies to the rest of the free-response section as well.

**The graders will follow your reasoning, even if you've made a mistake**

Just like in the problems section, you might be asked to use the result of a previous part of a problem in a later part. If you decide (incorrectly) that an endothermic reaction in part (a) is exothermic, you can still get full credit in part (c) for your wrong answer about the reaction's spontaneity, as long as your answer in (c) is correct based on an exothermic reaction.

## ABOUT THE TOPICS COVERED ON THE TEST

These are the topics covered on the AP Chemistry Exam, as described by the College Board.

**I. Structure of Matter (20%)****A. Atomic theory and atomic structure**

1. Evidence for atomic theory
2. Atomic masses and how to determine them experimentally
3. Atomic number and mass number; isotopes
4. Electron energy levels: atomic spectra, quantum numbers, atomic orbitals
5. Periodic trends (atomic radii, ionization energies, electron affinities, oxidation states)

- B. Bonding
  - 1. Forces
    - a. Types: ionic, covalent, metallic, hydrogen bonding, van der Waals (including London dispersion forces)
    - b. Relationships to states, structure, and properties of matter
    - c. Polarity, electronegativity
  - 2. Molecular models
    - a. Lewis structures
    - b. Valence electrons, hybridization of orbitals, resonance, sigma and pi bonds
    - c. VSEPR
  - 3. Geometry of molecules and ions, structural isomerism of simple organic molecules and coordination complexes, dipole moments, relation of properties to structure
- C. Nuclear chemistry: nuclear equations, half-lives, and radioactivity; chemical applications

## II. States of Matter (20%)

- A. Gases
  - 1. Ideal gas laws
    - a. Equation of state for an ideal gas
    - b. Partial pressures, Dalton's law
  - 2. Kinetic-molecular theory
    - a. Interpretation of ideal gas laws on the basis of this theory
    - b. Avogadro's hypothesis and the mole concept
    - c. Dependence of kinetic energy of molecules on temperature; Graham's law
    - d. Deviations from ideal gas laws
- B. Liquids and solids
  - 1. Liquids and solids and kinetic-molecular theory
  - 2. Phase diagrams
  - 3. Changes of state, including critical points and triple points
  - 4. Structure of solids, lattice energies
- C. Solutions
  - 1. Types of solutions and factors affecting solubility
  - 2. Molarity, molality, mole fraction, density
  - 3. Raoult's law, colligative properties, osmosis
  - 4. Nonideal behavior

## III. Reactions (35–40%)

- A. Reaction types
  - 1. Acid-base reactions; Arrhenius, Brønsted-Lowry, and Lewis theories; coordination complexes; amphoterism
  - 2. Precipitation reactions
  - 3. Oxidation-reduction reactions
    - a. Oxidation state
    - b. The role of the electron in oxidation-reduction
    - c. Electrochemistry: electrolytic and galvanic cells; Faraday's laws; standard half-cell potentials; Nernst equation; spontaneity of redox reactions

## B. Stoichiometry

1. Ionic and molecular species present in chemical systems: net ionic equations
2. Balancing of equations, including redox reactions
3. Mass and volume relations, using the mole concept in finding empirical formulas and limiting reactants

## C. Equilibrium

1. Dynamic equilibrium, physical and chemical; Le Châtelier's law; equilibrium constants
2. Quantitative treatment
  - a. Equilibrium constants for gaseous reactions:  $K_p$ ,  $K_c$
  - b. Equilibrium constants for reactions in solution
    - (1) Constants for acids and bases,  $pK$ ,  $pH$
    - (2) Solubility product constants and their application to precipitation and the dissolution of slightly soluble compounds
    - (3) Common ion effect, buffers, hydrolysis

## D. Kinetics

1. Reaction rate
2. Use of rate laws to determine order of reaction and rate constant from experimental data
3. Effect of temperature change on rates
4. Activation energy, catalysts
5. Reaction mechanisms and rate determining steps

## E. Thermodynamics

1. State functions
2. First law: enthalpy change; heat of formation; heat of reaction; Hess's law; heats of vaporization and fusion; calorimetry
3. Second law: entropy; free energy of formation; free energy of reaction; dependence of change in free energy on enthalpy and entropy changes
4. Relationship of change in free energy to equilibrium constants and electrode potentials

## IV. Descriptive Chemistry (10–15%)

- A. Chemical reactivity and products of chemical reactions
- B. Relationships in the periodic table: horizontal, vertical, and diagonal with examples from alkali metals, alkaline earth metals, halogens, and the first series of transition elements
- C. Introduction to organic chemistry: hydrocarbons and functional groups (structure, nomenclature, chemical properties)

## V. Laboratory (5–10%)

Questions based on experiences and skills students acquire in the laboratory: making observations of chemical reactions and substances, recording data, calculating and interpreting results based on the quantitative data obtained, lab safety, experimental errors

The following list summarizes types of specific chemical calculation problems that may appear on the test:

1. Percentage composition
2. Empirical and molecular formulas from experimental data
3. Molar masses from gas density, freezing-point, and boiling-point measurements
4. Gas laws, including the ideal gas law, Dalton's law, and Graham's law
5. Stoichiometric relations using the concept of the mole; titration calculations
6. Mole fractions; molar and molal solutions
7. Faraday's law of electrolysis
8. Equilibrium constants and their applications, including their use for simultaneous equilibria
9. Standard electrode potentials and their use; Nernst equation
10. Thermodynamic and thermochemical calculations
11. Kinetics calculations





# 2

## Preparing for the AP Chemistry Exam

### **THE MONTHS BEFORE THE TEST**

#### **START YOUR REVIEW EARLY**

Try to spend from a half hour to an hour reviewing chemistry three or four times a week. Leave your chemistry books around so you can leaf through them when there's a really bad sitcom on TV between two shows that you like. If you study consistently, even for very short sessions over a period of a few months, you'll find that by the time test week arrives, you'll know the material and you won't have to study for six hours a day for the last six days—that doesn't work very well anyway.

#### **READ THIS BOOK AND DO ALL OF THE QUESTIONS IN IT**

This book covers all of the important information required for the AP Chemistry Exam, and the questions in the book test AP Chemistry material in AP Chemistry style. If you do well on the questions at the end of each chapter and on the practice tests at the end of the book, you will do well on the AP Chemistry Exam.

## GET SOME REAL AP CHEMISTRY EXAMS

The College Board releases some test material after the test has been given. It releases a multiple-choice section every five years or so and the free-response section every year, along with the guidelines that were used to grade it. This is the most valuable study resource you have. Remember, you're not just studying chemistry; you're studying the AP Chemistry Exam.

Ask your teacher or guidance counselor if he or she has copies of released exams. Many teachers keep them on file and use them every year for in-class tests and practice material. The free-response sections with grading guidelines are especially useful; if you know what the graders are looking for, it's much easier to give it to them.

If real AP material is not available at your school, you can buy it directly from the College Board and ETS. Check out their website at [www.collegeboard.com](http://www.collegeboard.com), or call them at 609-771-7300 and ask them to send you a catalog of what's most currently available.

## USE THE INTERNET

If you have a computer or you know someone who does, get on the Internet and try typing "Advanced Placement Chemistry" (or some variation) into a couple of different search engines. Here's what you should find:

- **The College Board home page:** This site gives general information about the test and some test-taking tips. This is one place to go to find out if there have been any last-minute changes to the test.
- **AP students and teachers:** Some AP Chemistry classes have home pages. It might be worth a look to see what other AP classes around the country are up to.

## GET A SECOND TEXTBOOK

Don't get a new one. New science textbooks are way too expensive, and you've probably had to buy one already, not to mention what you shelled out for this book.

Go to one of those slightly stale-smelling used book stores that has books piled from floor to ceiling. Somewhere in there, they should have a first-year chemistry textbook that was printed within the last 20 years. It will probably cost less than ten bucks. You should buy it. Don't worry if it's old; first-year chemistry hasn't changed all that much since you were born.

The reason that it's good to have a second book is that all textbook writers have strengths and weaknesses. An author who can make you understand thermodynamics may leave you totally confused when it comes to kinetics. You don't have to read everything in both books; just use the index to see what the second author has to say about any topic that the first author can't help you understand. Sometimes a second point of view is all you need.

## TEACH SOMEBODY ELSE

The best way to really learn something is to explain it to someone else. Work with the other people in your class whenever you can. When someone else explains something to you, you're learning. When you explain something to someone else, you're learning even more.

## **THE WEEK BEFORE THE TEST**

### **MAINTAIN YOUR USUAL ROUTINE**

Go to sleep at your usual time. Don't start a strange new diet. You can step up your studying a bit, but if you've been studying with any consistency in the last few months, you probably won't have to. Don't try to cram the night before the test; it's a waste of time and effort.

### **REVIEW THIS BOOK**

In assembling the information presented in this book, everything was pared away that was not absolutely necessary to cover for you to do well on the AP Chemistry Exam. So if it's in this book, then you need to know it. If it's not in this book, you can get a 5 without it.

### **REVIEW OLD AP CHEMISTRY EXAMS**

By now you should know the science pretty well. Practice the test. Read the directions on the test carefully so you will already know them on the day of the test. You should know exactly what you're supposed to do on each section long before you sit for the test. Look for the themes and topics that come up on every test; the more familiar the AP test seems to you when you take it, the easier it will be.

## **THE DAY OF THE TEST**

### **EAT BREAKFAST**

Food gives you energy, and you'll need it for the test.

### **BRING EVERYTHING YOU NEED**

You need number-two pencils for the multiple-choice section because that's what the grading machines read. You can use either pen or pencil for the free-response section. You need an eraser.

### **YOU WILL NEED A WATCH**

Without getting obsessive, you should keep track of the time as you do both sections. Never trust a proctor to do this for you.

### **WEAR COMFORTABLE CLOTHING**

You don't want anything to distract you from the business at hand.

### **BRING A SNACK**

A piece of fruit or an energy bar during the break provides a handy energy boost.

### **RELAX**

If you're well prepared, the test is simply an opportunity to show it.



# 3

## Atomic Structure and the Periodic Table

### **HOW OFTEN DOES ATOMIC STRUCTURE APPEAR ON THE EXAM?**

In the multiple-choice section, this topic appears in about 7 out of 75 questions. In the free-response section, this topic appears almost every year.

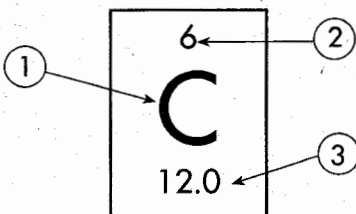
# THE PERIODIC TABLE

The most important tool you will use on this test is the Periodic Table of the Elements.

Periodic Table of the Elements

1 H 1.0																	2 He 4.0	
3 Li 6.9	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2	
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9	
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8	
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3	
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra 226.0	89 Ac 227.0	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Uue (267)										
*Lanthanide Series:			58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0		
†Actinide Series:			90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)		

The periodic table gives you very basic but very important information about each element.



1. This is the **symbol** for the element; carbon, in this case. On the test, the symbol for an element is used interchangeably with the name of the element.
2. This is the **atomic number** of the element. The atomic number is the same as the number of protons in the nucleus of an element; it is also the same as the number of electrons surrounding the nucleus of an element in its neutral state.
3. This is the **molar mass** of the element. It's also called the **atomic weight**.

The identity of an atom is determined by the number of protons contained in its nucleus. The nucleus of an atom also contains neutrons. The mass number of an atom is the sum of its neutrons and protons. Atoms of an element with different numbers of neutrons are called isotopes; for instance, carbon-12, which contains 6 protons and 6 neutrons, and carbon-14, which contains 6 protons and 8 neutrons, are isotopes of carbon. The molar mass given on the periodic table is the average of the mass numbers of all known isotopes weighted by their percent abundance.

The molar mass of an element will give you a pretty good idea of the most common isotope of that element. For instance, the molar mass of carbon is 12.0 and about 99 percent of the carbon in existence is carbon-12.

The horizontal rows of the periodic table are called **periods**.

The vertical columns of the periodic table are called **groups**.

## ELECTRONS

### QUANTUM NUMBERS

The positions of the electrons in relation to the nucleus are described by their **quantum numbers**. Each electron has four quantum numbers that apply to its **shell, subshell, orbital, and spin**.

#### Shells: $n = 1, 2, 3...$

In a hydrogen atom, the principal quantum number, or shell, of an electron determines its average distance from the nucleus as well as its energy. So electrons in shells with higher values are farther away on average from the nucleus and will have more energy and less stability than electrons in shells with lower values.

#### Subshells: $l = 0, 1, 2...$

The angular momentum quantum number, or subshell, describes the shape of an electron's orbital.

- The first shell ( $n = 1$ ) has one subshell:  $s$ , or  $l = 0$ .
- The second shell ( $n = 2$ ) has two subshells:  $s$  ( $l = 0$ ), and  $p$  ( $l = 1$ ).
- The third shell ( $n = 3$ ) has three subshells:  $s$  ( $l = 0$ ),  $p$  ( $l = 1$ ), and  $d$  ( $l = 2$ ).

The orbitals of  $s$  subshells are spherical, while the orbitals of  $p$  subshells are dumbbell shaped.

#### Orbitals: $m_l = ...-1, 0, +1...$

The magnetic quantum number, or orbital, describes the orientation of the orbital in space. Roughly, that means it describes whether the path of the electron lies mostly on the  $x$ ,  $y$ , or  $z$  axis of a three-dimensional grid.

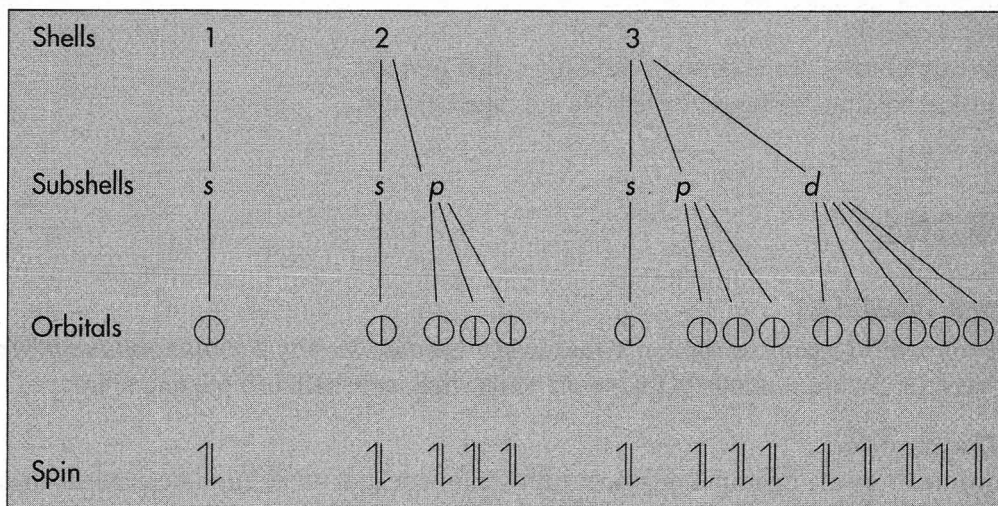
- The  $s$  subshell ( $l = 0$ ) has one orbital:  $m_l = 0$ .
- The  $p$  subshell ( $l = 1$ ) has three orbitals:  $m_l = -1$ ,  $m_l = 0$ , and  $m_l = +1$ .
- The  $d$  subshell ( $l = 2$ ) has five orbitals:  $m_l = -2$ ,  $-1$ ,  $0$ ,  $1$ , and  $2$ .

#### Spin: $m_s = +\frac{1}{2}, -\frac{1}{2}$

Each orbital can contain two electrons: one with a positive spin and one with a negative spin.



Here are a couple of graphical ways of looking at quantum numbers.



The Quantum Numbers for levels 1–4			The number of electrons in the states	
$n$	$l$	$m$	In the subshell	In the level
1	0 (s)	0	2	2
2	0 (s)	0	2	8
	1 (p)	-1, 0, +1	6	
3	0 (s)	0	2	18
	1 (p)	-1, 0, +1	6	
	2 (d)	-2, -1, 0, +1, +2	10	
4	0 (s)	0	2	32
	1 (p)	-1, 0, +1	6	
	2 (d)	-2, -1, 0, +1, +2	10	
	3 (f)	-3, -2, -1, 0, +1, +2, +3	14	

## THE AUFBAU PRINCIPLE

The Aufbau principle states that when building up the electron configuration of an atom, electrons are placed in orbitals, subshells, and shells in order of increasing energy.

## THE PAULI EXCLUSION PRINCIPLE

The Pauli exclusion principle states that within an atom, no two electrons can have the same set of quantum numbers. So, each electron in any atom has its own distinct set of four quantum numbers.

## QUANTUM NUMBERS AND THE PERIODIC TABLE

You can use the periodic table to tell the first two quantum numbers of the valence electrons of any element. Note that  $n$  = principal quantum number.

$n$								$n$		
1s								1s		
2s								2p		
3s				$n - 1$				3p		
4s				3d				4p		
5s				4d				5p		
6s	4f			5d				6p		
7s	5f			6d				$n - 2$		
	4f									
	5f									

You can also tell the order in which shells and subshells are filled by following the table from left to right across each period.

You should note that after the third period, the filling of subshells becomes more complicated. Notice, for instance, that the 4s subshell fills before the 3d subshell.

## HUND'S RULE

**Hund's rule** says that when an electron is added to a subshell, it will always occupy an empty orbital if one is available. Electrons always occupy orbitals singly if possible and pair up only if no empty orbitals are available.

Watch how the  $2p$  subshell fills as we go from boron to neon.

	<u>1s</u>	<u>2s</u>	<u>2p</u>
Boron	↑↓	↑↓	↑
Carbon	↑↓	↑↓	↑ ↑
Nitrogen	↑↓	↑↓	↑ ↑ ↑
Oxygen	↑↓	↑↓	↑↓ ↑ ↑
Fluorine	↑↓	↑↓	↑↓ ↑↓ ↑
Neon	↑↓	↑↓	↑↓ ↑↓ ↑↓

## DIAMAGNETISM AND PARAMAGNETISM

**Diamagnetism** and **paramagnetism** are types of magnetism. **Diamagnetic** elements have all of their electrons spin paired. So, diamagnetic elements are elements with all of their subshells completed.

Some diamagnetic elements are

Helium	$1s^2$
Beryllium	$1s^2 2s^2$
Neon	$1s^2 2s^2 2p^6$

Most of the elements do not have all of their electrons spin paired and are called **paramagnetic** elements.

Paramagnetic elements are strongly affected by magnetic fields, whereas diamagnetic elements are not very strongly affected.

Molecules can also be diamagnetic or paramagnetic, depending on the pairing of electrons in their molecular orbitals, but the same basic rule holds: Paramagnetic molecules are affected by magnetic fields, and diamagnetic molecules are not.

## ELECTRONS AND ENERGY

The positively charged nucleus is always pulling at the negatively charged electrons around it, and the electrons have potential energy that increases with their distance from the nucleus. It works the same way that the gravitational potential energy of a brick on the third floor of a building is greater than the gravitational potential energy of a brick nearer to ground level.

The energy of electrons, however, is **quantized**. That's important. It means that electrons can only exist at specific energy levels, separated by specific intervals. It's kind of like if the brick in the building could be placed only on the first, second, or third floor of the building, but not in-between.

The quantized energy of an electron in a hydrogen atom can be found if you know its principal quantum number or shell.

### Energy of an Electron

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ joules}$$

$E_n$  = the energy of the electron

$n$  = the principal quantum number of the electron

When atoms absorb energy in the form of **electromagnetic radiation**, electrons jump to higher energy levels. When electrons drop from higher to lower energy levels, atoms give off energy in the form of electromagnetic radiation.

The relationship between the change in energy level of an electron and the electromagnetic radiation absorbed or emitted is given below.

### Energy and Electromagnetic Radiation

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$\Delta E$  = energy change

$h$  = Planck's constant,  $6.63 \times 10^{-34}$  joule-sec

$\nu$  = frequency of the radiation

$\lambda$  = wavelength of the radiation

$c$  = the speed of light,  $3.00 \times 10^8$  m/sec ( $c = \lambda f$ )

The energy level changes for the electrons of a particular atom are always the same, so atoms can be identified by their emission and absorption spectra.

## NAMES AND THEORIES

### Dalton's Elements

In the early 1800s, John Dalton presented some basic ideas about atoms that we still use today. He was the first to say that there are many different kinds of atoms, which he called elements. He said that these elements combine to form compounds and that these compounds always contain the same ratios of elements. Water ( $\text{H}_2\text{O}$ ), for instance, always has two hydrogen atoms for every oxygen atom. He also said that atoms are never created or destroyed in chemical reactions.

### Development of the Periodic Table

In 1869, Dmitri Mendeleev and Lothar Meyer independently proposed arranging the elements into early versions of the periodic table, based on the trends of the known elements.

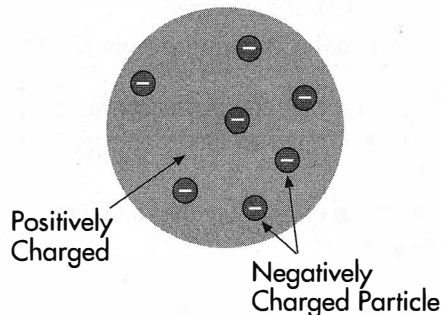
### Thomson's Experiment

In the late 1800s, J. J. Thomson watched the deflection of charges in a cathode ray tube and put forth the idea that atoms are composed of positive and negative charges. The negative charges were called electrons, and Thomson guessed that they were sprinkled throughout the positively charged atom like chocolate chips sprinkled throughout a blob of cookie dough.

## Millikan's Experiment

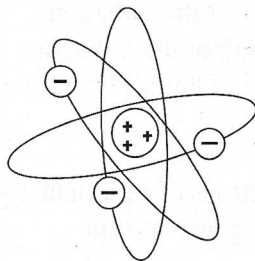
Robert Millikan was able to calculate the charge on an electron by examining the behavior of charged oil drops in an electric field.

The Plum Pudding Model of an Atom



## Rutherford's Experiment

In the early 1900s, Ernest Rutherford fired alpha particles at gold foil and observed how they were scattered. This experiment led him to conclude that all of the positive charge in an atom was concentrated in the center and that an atom is mostly empty space. This led to the idea that an atom has a positively charged nucleus, which contains most of the atom's mass, and that the tiny, negatively charged electrons travel around this nucleus.

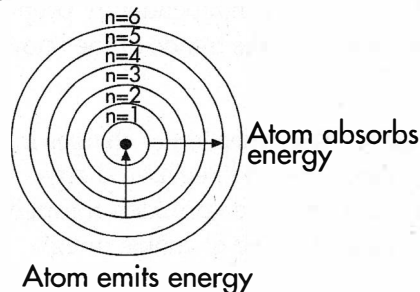


## Quantum Theory

Max Planck figured out that electromagnetic energy is quantized. That is, for a given frequency of radiation (or light), all possible energies are multiples of a certain unit of energy, called a quantum (mathematically, that's  $E = h\nu$ ). So, energy changes do not occur smoothly but rather in small but specific steps.

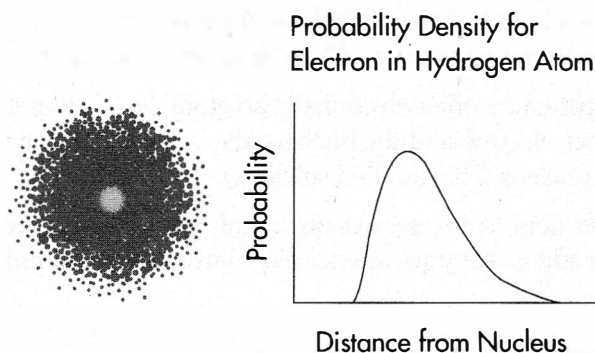
## The Bohr Model

Neils Bohr took the quantum theory and used it to predict that electrons orbit the nucleus at specific, fixed radii, like planets orbiting the Sun. The Bohr model worked for atoms and ions with one electron but not for more complex atoms.



## The Heisenberg Uncertainty Principle

Werner Heisenberg said that it is impossible to know both the position and momentum of an electron at a particular instant. In terms of atomic structure, this means that electron orbitals do not represent specific orbits like those of planets. Instead, an electron orbital is a probability function describing the possibility that an electron will be found in a region of space.



## The de Broglie Hypothesis

Louis de Broglie said that all matter has wave characteristics. This is important because sometimes the behavior of electrons is better described in terms of waves than particles.

There is a simple relationship between an electron's wave and particle characteristics.

### The de Broglie Equation

$$\lambda = \frac{h}{mv}$$

$\lambda$  = wavelength associated with a particle

$m$  = mass of the particle

$v$  = speed of the particle

$mv = p$  = momentum of the particle

$h$  = Planck's constant,  $6.63 \times 10^{-34}$  joule-sec

De Broglie's hypothesis is useful for very small particles, such as electrons. For larger particles, the wavelength becomes too small to be of interest.

## PERIODIC TRENDS

You can make predictions about certain behavior patterns of an atom and its electrons based on the position of the atom in the periodic table. All the periodic trends can be understood in terms of three basic rules.

1. Electrons are attracted to the protons in the nucleus of an atom.
  - a. The closer an electron is to the nucleus, the more strongly it is attracted.
  - b. The more protons in a nucleus, the more strongly an electron is attracted.
2. Electrons are repelled by other electrons in an atom. So, if other electrons are between a valence electron and the nucleus, the valence electron will be less attracted to the nucleus. That's called shielding.
3. Completed shells (and to a lesser extent, completed subshells) are very stable. Atoms prefer to add or subtract valence electrons to create complete shells if possible.

The atoms in the left-hand side of the periodic table are called metals. Metals give up electrons when forming bonds. Most of the elements in the table are metals. The elements in the upper right-hand portion of the table are called nonmetals. Nonmetals generally gain electrons when forming bonds. The metallic character of the elements decreases as you move from left to right across the periodic table. The elements in the borderline between metal and nonmetal, such as silicon and arsenic, are called metalloids.

### ATOMIC RADIUS

The atomic radius is the approximate distance from the nucleus of an atom to its valence electrons.

#### Moving from Left to Right Across a Period (Li to Ne, for Instance), Atomic Radius Decreases

Moving from left to right across a period, protons are added to the nucleus, so the valence electrons are more strongly attracted to the nucleus; this decreases the atomic radius. Electrons are also being added, but they are all in the same shell at about the same distance from the nucleus, so there is not much of a shielding effect.

#### Moving Down a Group (Li to Cs, for Instance), Atomic Radius Increases

Moving down a group, shells of electrons are added to the nucleus. Each shell shields the more distant shells from the nucleus and the valence electrons get farther away from the nucleus. Protons are also being added, but the shielding effect of the negatively charged electron shells cancels out the added positive charge.

#### Cations (Positively Charged Ions) Are Smaller than Atoms

Generally, when electrons are removed from an atom to form a cation, the outer shell is lost, making the cation smaller than the atom. Also, when electrons are removed, electron-electron repulsions are reduced, allowing all of the remaining valence electrons to move closer to the nucleus.

#### Anions (Negatively Charged Ions) Are Larger than Atoms

When an electron is added to an atom, forming an anion, electron-electron repulsions increase, causing the valence electrons to move farther apart, which increases the radius.

## **IONIZATION ENERGY**

Electrons are attracted to the nucleus of an atom, so it takes energy to remove an electron. The energy required to remove an electron from an atom is called the first ionization energy. Once an electron has been removed, the atom becomes a positively charged ion. The energy required to remove the next electron from the ion is called the second ionization energy, and so on.

### **Moving from Left to Right Across a Period, Ionization Energy Increases**

Moving from left to right across a period, protons are added to the nucleus, which increases its positive charge. For this reason, the negatively charged valence electrons are more strongly attracted to the nucleus, which increases the energy required to remove them. Electrons are also being added, and the shielding effect provided by the filling of the *s* subshell causes a slight deviation in the trend in moving from Group 2A to Group 3A. There is also a slight deviation when the electrons in the *p* subshell start to pair up, so oxygen has a slightly lower first ionization energy than nitrogen does.

### **Moving Down a Group, Ionization Energy Decreases**

Moving down a group, shells of electrons are added to the nucleus. Each inner shell shields the more distant shells from the nucleus, reducing the pull of the nucleus on the valence electrons and making them easier to remove. Protons are also being added, but the shielding effect of the negatively charged electron shells cancels out the added positive charge.

### **The Second Ionization Energy Is Greater than the First Ionization Energy**

When an electron has been removed from an atom, electron-electron repulsion decreases and the remaining valence electrons move closer to the nucleus. This increases the attractive force between the electrons and the nucleus, increasing the ionization energy.

### **As Electrons Are Removed, Ionization Energy Increases Gradually Until a Shell Is Empty, Then Makes a Big Jump**

- For each element, when the valence shell is empty, the next electron must come from a shell that is much closer to the nucleus, making the ionization energy for that electron much larger than for the previous ones.
- For Na, the second ionization energy is much larger than the first.
- For Mg, the first and second ionization energies are comparable, but the third is much larger than the second.
- For Al, the first three ionization energies are comparable, but the fourth is much larger than the third.



## ELECTRON AFFINITY

Electron affinity is a measure of the change in energy of an atom when an electron is added to it. When the addition of an electron makes the atom more stable, energy is given off. This is true for most of the elements. When the addition of an electron makes the atom less stable, energy must be put in; that's because the added electron must be placed in a higher energy level, making the element less stable. This is the case for elements with full subshells, like the alkaline earths and the noble gases.

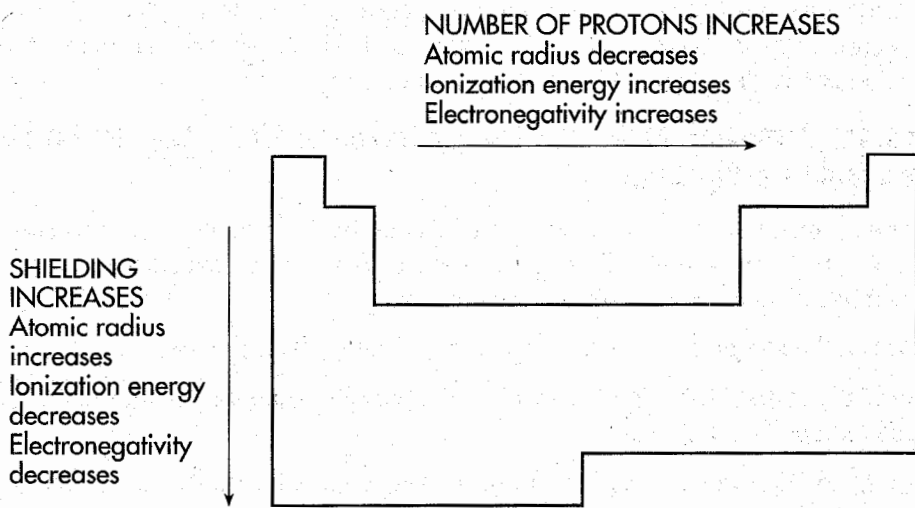
When moving from left to right across a period, the energy given off when an electron is added increases. Electron affinities don't change very much moving down a group.

## ELECTRONEGATIVITY

Electronegativity refers to how strongly the nucleus of an atom attracts the electrons of other atoms in a bond. Electronegativities of elements are estimated based on ionization energies and electron affinities, and they basically follow the same trends.

- Moving from left to right across a period, electronegativity increases.
- Moving down a group, electronegativity decreases.

The various periodic trends, which don't include the noble gases, are summarized in the diagram below.



## CHAPTER 3 QUESTIONS

### MULTIPLE-CHOICE QUESTIONS

#### Questions 1–4

- (A) C
  - (B) N
  - (C) O
  - (D) F
  - (E) Ne
1. This is the most electronegative element.
  2. The nuclear decay of an isotope of this element is used to measure the age of archaeological artifacts.
  3. All of the electrons in this element are spin-paired.
  4. This element, present as a diatomic gas, makes up most of the earth's atmosphere.

#### Questions 5–7

- (A) Hg
  - (B) Si
  - (C) Cu
  - (D) Zn
  - (E) Ag
5. This element is commonly used in the manufacture of semiconductors.
  6. This element is a liquid at room temperature.
  7. After oxygen, this is by far the most common element in the earth's crust.

8. What is the most likely electron configuration for a sodium ion in its ground state?
  - (A)  $1s^2 2s^2 2p^5$
  - (B)  $1s^2 2s^2 2p^6$
  - (C)  $1s^2 2s^2 2p^6 3s^1$
  - (D)  $1s^2 2s^2 2p^5 3s^2$
  - (E)  $1s^2 2s^2 2p^6 3s^2$
9. Which of the following statements is true regarding sodium and chlorine?
  - (A) Sodium has greater electronegativity and a larger first ionization energy.
  - (B) Sodium has a larger first ionization energy and a larger atomic radius.
  - (C) Chlorine has a larger atomic radius and a greater electronegativity.
  - (D) Chlorine has greater electronegativity and a larger first ionization energy.
  - (E) Chlorine has a larger atomic radius and a larger first ionization energy.

10. Which of the following could be the quantum numbers ( $n, l, m_l, m_s$ ) for the valence electron in a potassium atom in its ground state?

- (A)  $3, 0, 0, \frac{1}{2}$
- (B)  $3, 1, 1, \frac{1}{2}$
- (C)  $4, 0, 0, \frac{1}{2}$
- (D)  $4, 1, 1, \frac{1}{2}$
- (E)  $4, 2, 1, \frac{1}{2}$

11. Which of the following elements is diamagnetic?
- (A) H  
(B) Li  
(C) Be  
(D) B  
(E) C
12. Which of the following rules states that no two electrons in an atom can have the same set of quantum numbers?
- (A) Hund's rule  
(B) The Heisenberg uncertainty principle  
(C) The Pauli exclusion principle  
(D) The de Broglie hypothesis  
(E) The Bohr model
13. Which of the following is true of the alkali metal elements?
- (A) They usually take the +2 oxidation state.  
(B) They have oxides that act as acid anhydrides.  
(C) They form covalent bonds with oxygen.  
(D) They are generally found in nature in compounds.  
(E) They have relatively large first ionization energies.
14. Which of the following nuclei has 3 more neutrons than protons? (Remember: the number before the symbol indicates atomic mass.)
- (A)  $^{11}\text{B}$   
(B)  $^{37}\text{Cl}$   
(C)  $^{24}\text{Mg}$   
(D)  $^{70}\text{Ga}$   
(E)  $^{19}\text{F}$
15. Which of the following ions has the smallest ionic radius?
- (A)  $\text{O}^{2-}$   
(B)  $\text{F}^-$   
(C)  $\text{Na}^+$   
(D)  $\text{Mg}^{2+}$   
(E)  $\text{Al}^{3+}$
16. Which of the following is an impossible set of quantum numbers ( $n, l, m_l, m_s$ )?
- (A)  $4, 0, 0, \frac{1}{2}$   
(B)  $4, 0, 1, \frac{1}{2}$   
(C)  $4, 1, 0, \frac{1}{2}$   
(D)  $4, 1, 1, \frac{1}{2}$   
(E)  $4, 2, 1, \frac{1}{2}$
17. Which of the following represents the energy of the single electron in a hydrogen atom when it is in the  $n = 4$  state?
- (A)  $\left(\frac{-2.178 \times 10^{-18}}{2}\right)$  joules  
(B)  $\left(\frac{-2.178 \times 10^{-18}}{4}\right)$  joules  
(C)  $\left(\frac{-2.178 \times 10^{-18}}{8}\right)$  joules  
(D)  $\left(\frac{-2.178 \times 10^{-18}}{16}\right)$  joules  
(E)  $\left(\frac{-2.178 \times 10^{-18}}{64}\right)$  joules

18. When an electron in a hydrogen atom makes the transition from the  $n = 4$  state to the  $n = 2$  state, blue light with a wavelength of 434 nm is emitted. Which of the following expressions gives the energy released by the transition?

(A)  $\frac{(6.63 \times 10^{-34})(3.00 \times 10^8)}{(4.34 \times 10^{-7})}$  joules

(B)  $\frac{(6.63 \times 10^{-34})(4.34 \times 10^{-7})}{(3.00 \times 10^8)}$  joules

(C)  $\frac{(6.63 \times 10^{-34})}{(4.34 \times 10^{-7})(3.00 \times 10^8)}$  joules

(D)  $\frac{(4.34 \times 10^{-7})}{(6.63 \times 10^{-34})(3.00 \times 10^8)}$  joules

(E)  $(6.63 \times 10^{-34})(4.34 \times 10^{-7})$  joules

19. The ionization energies for an element are listed in the table below.

First	Second	Third	Fourth	Fifth
8 eV	15 eV	80 eV	109 eV	141 eV

Based on the ionization energy table, the element is most likely to be

- (A) sodium.  
 (B) magnesium.  
 (C) aluminum.  
 (D) silicon.  
 (E) phosphorous.

20. A researcher listed the first five ionization energies for a silicon atom in order from first to fifth. Which of the following lists corresponds to the ionization energies for silicon?

- (A) 780 kJ, 13,675 kJ, 14,110 kJ, 15,650 kJ, 16,100 kJ  
 (B) 780 kJ, 1,575 kJ, 14,110 kJ, 15,650 kJ, 16,100 kJ  
 (C) 780 kJ, 1,575 kJ, 3,220 kJ, 15,650 kJ, 16,100 kJ  
 (D) 780 kJ, 1,575 kJ, 3,220 kJ, 4,350 kJ, 16,100 kJ  
 (E) 780 kJ, 1,575 kJ, 3,220 kJ, 4,350 kJ, 5,340 kJ

## ESSAYS

- Explain each of the following in terms of atomic and molecular structures and/or forces.
  - The first ionization energy for magnesium is greater than the first ionization energy for calcium.
  - The first and second ionization energies for calcium are comparable, but the third ionization energy is much greater.
  - Solid sodium conducts electricity, but solid sodium chloride does not.
  - The first ionization energy for aluminum is lower than the first ionization energy for magnesium.
- Silicon is a nonmetal with four valence electrons.
  - Write the ground state electron configuration for silicon.
  - Which fundamental atomic theory is violated by the following list of quantum numbers representing silicon's valence electrons?

$n$	$l$	$m_l$	$m_s$
3	0	0	$-\frac{1}{2}$
3	0	0	$-\frac{1}{2}$
3	1	1	$-\frac{1}{2}$
3	1	1	$-\frac{1}{2}$

- Which fundamental atomic theory is violated by the following list of quantum numbers representing silicon's valence electrons?

$n$	$l$	$m_l$	$m_s$
3	0	0	$-\frac{1}{2}$
3	0	0	$+\frac{1}{2}$
3	1	-1	$-\frac{1}{2}$
3	1	-1	$+\frac{1}{2}$

- Will a lone silicon atom be diamagnetic or paramagnetic? Justify your answer.

3. Use your knowledge of the periodic table of the elements to answer the following questions.
- Explain the trend in electronegativity from P to S to Cl.
  - Explain the trend in electronegativity from Cl to Br to I.
  - Explain the trend in atomic radius from Li to Na to K.
  - Explain the trend in atomic radius from Al to Mg to Na.
4. Use your knowledge of atomic theory to answer the following questions.
- State the Heisenberg uncertainty principle.
  - The absorption spectrum of a hydrogen atom contains dark bands at specific wavelengths. The emission spectrum of a hydrogen atom contains bright bands at the same wavelengths. Explain what causes these bright and dark bands at specific wavelengths.
  - Explain why the addition of an electron to a chlorine atom is an exothermic process and the addition of an electron to a magnesium atom is an endothermic process.
  - Explain how the valence electron configuration of sulfur is consistent with the existence of  $\text{Na}_2\text{S}$  and  $\text{SF}_6$ .

## CHAPTER 3 ANSWERS AND EXPLANATIONS

### MULTIPLE-CHOICE QUESTIONS

1. D Fluorine, which needs one electron to complete its outer shell, is the most electronegative element, with an electronegativity of 4.0.
2. A In carbon dating, the ratio of carbon-14 to carbon-12 in an organic artifact is used to determine the age of the artifact.
3. E Neon's second shell is complete, so all of its electrons are spin-paired.
4. B Nitrogen gas ( $N_2$ ) makes up 78 percent of the earth's atmosphere. Oxygen is next at 21 percent.
5. B Silicon (Si) is used in semiconductor technology because it has properties that lie in-between metals and nonmetals.
6. A Mercury (Hg) is unusual among metals in that it is a liquid at room temperature. Its melting point is  $-39$  degrees Celsius.
7. B Silicon makes up 26 percent of the earth's crust by weight (oxygen makes up 50 percent). In fact, compounds including silicon and oxygen make up nearly all rocks and soils.
8. B Neutral sodium in its ground state has the electron configuration shown in choice (C). Sodium forms a bond by giving up its one valence electron and becoming a positively charged ion with the same electron configuration as neon.
9. D As we move from left to right across the periodic table within a single period (from sodium to chlorine), we add protons to the nuclei, which progressively increases the pull of each nucleus on its electrons. So chlorine will have a higher first ionization energy, greater electronegativity, and a smaller atomic radius.
10. C Potassium's valence electron is in the  $4s$  subshell. That means that  $n = 4$ ,  $l = 0$ ,  $m_l = 0$ , and  $m_s = \frac{1}{2}$  or  $-\frac{1}{2}$ .
11. C Beryllium's electrons are paired up in the completed orbitals of the  $1s$  and  $2s$  subshells. Choice (E) is wrong because, according to Hund's rule, carbon's two  $2p$  electrons must be placed in different orbitals.
12. C The Pauli exclusion principle states that no two electrons in an atom can have the same set of quantum numbers.

About the other answers:

- (A) Hund's rule states that within a subshell, electrons will be placed in empty orbitals while they are available and will start to pair up in orbitals only when no more empty orbitals are available.
- (B) The Heisenberg uncertainty principle states that it is impossible to know with certainty both the position and momentum of a particle at the same moment.
- (D) The de Broglie hypothesis relates the wave and particle properties of matter, using the following equation:

$$\text{Wavelength} = \frac{h}{\text{momentum}}$$

$h$  is Planck's constant,  $6.63 \times 10^{-34}$  joule-sec

- (E) The Bohr model of the hydrogen atom (which was disproved by the Heisenberg uncertainty principle) states that electrons orbit the nucleus in fixed, quantized circular orbits.

13. D The alkali metals (Li, Na, K...) are extremely reactive and are found in nature almost exclusively in compounds.  
As for the other answers:  
Choice (A) is wrong because the alkali metals take the +1 oxidation state. Choice (B) is wrong because alkali metal oxides are basic anhydrides; that is, they form basic solutions in water. Choice (C) is wrong because they form ionic bonds with oxygen. Choice (E) is wrong because they have only one valence electron, so they have relatively small first ionization energies.
14. B The atomic mass is the sum of the neutrons and protons in any atom's nucleus. Since atomic number, which indicates the number of protons, is unique to each element we can subtract this from the weight to find the number of neutrons. The atomic number of B is 5, hence the  $^{11}\text{B}$  has 6 neutrons, only 1 in excess. The atomic number of Cl is 17, so  $^{37}\text{Cl}$  has 20 neutrons, 3 in excess. The atomic number of Mg is 12, so  $^{24}\text{Mg}$  has the same number of neutrons as protons. The element Ga has an atomic number of 31, meaning there are 39 neutrons in the given nucleus and the atomic number for F is 9, meaning 10 neutrons in  $^{19}\text{F}$ .
15. E All of the ions listed have the same electron configuration as neutral neon.  $\text{Al}^{3+}$  has the most protons, so its electrons will experience greater attractive force from the nucleus, resulting in the smallest ions.
16. B The  $m_l$  quantum number (orbital) can't be larger than the  $l$  quantum number (subshell), so 4, 0, 1,  $\frac{1}{2}$  is impossible because 1 is greater than 0.
17. D When you know the principal quantum number, you must use the formula for the energy of an electron, which is shown below.
- $$E_n = \left( \frac{-2.178 \times 10^{-18}}{n^2} \right)$$
- The variable  $n$  stands for the principal quantum number; in this case,  $n = 4$ .
18. A When you know the wavelength emitted, you must use the formula for the energy of an electron transition, which is shown below. Remember, a nanometer is equal to  $10^{-9}$  meters.
- $$E_n = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34})(3.00 \times 10^8)}{(4.34 \times 10^{-7})}$$
19. B The ionization energy will show a large jump when enough electrons have been removed to leave a stable shell. In this case, the jump occurs between the second and third electrons removed, so the element is stable after two electrons are removed. Magnesium (Mg) is the only element on the list with exactly two valence electrons.
20. D The ionization energy will show a large jump when enough electrons have been removed to leave a stable shell. Silicon has four valence electrons, so we would expect to see a large jump in ionization energy after the fourth electron has been removed. That's choice (D).

## ESSAYS

- (a) Ionization energy is the energy required to remove an electron from an atom. The outermost electron in Ca is at the 4s energy level. The outermost electron in Mg is at the 3s level. The outermost electron in Ca is at a higher energy level and is more shielded from the nucleus, making it easier to remove.  
  
(b) Calcium has two electrons in its outer shell. The second ionization energy will be larger than the first but still comparable because both electrons are being removed from the same energy level. The third electron is much more difficult to remove because it is being removed from a lower energy level, so it will have a much higher ionization energy than the other two.



(c) Solid sodium exhibits metallic bonding, in which the positively charged sodium ions are held together by a sea of mobile, delocalized electrons. These electrons move freely from nucleus to nucleus, making solid sodium a good conductor.

Sodium chloride exhibits ionic bonding, in which positively charged sodium ions and negatively charged chlorine ions hold fixed places in a crystal lattice. The electrons are localized around particular nuclei and are not free to move about the lattice. This makes solid sodium chloride a bad conductor of electricity.

(d) The valence electron to be removed from magnesium is located in the completed 3s subshell, while the electron to be removed from aluminum is the lone electron in the 3p subshell. It is easier to remove the electron from the higher-energy 3p subshell than from the lower energy (completed) 3s subshell, so the first ionization energy is lower for aluminum.

2. (a)  $1s^2 2s^2 2p^6 3s^2 3p^2$

(b) The Pauli exclusion principle is violated. The Pauli exclusion principle states that no two electrons can have the same set of quantum numbers.

(c) Hund's rule is violated. Hund's rule states that within an energy level, electrons will be placed in empty orbitals while they are available and will only start to pair up in orbitals when no more empty orbitals are available.

(d) A lone silicon atom will be paramagnetic and will be affected by a magnetic field. If all the electrons in an atom are spin-paired, the atom is diamagnetic. If any of the electrons are not spin-paired, the atom is paramagnetic. Silicon has two electrons in the 3p subshell. They will be placed in different orbitals, so they will not be spin-paired.

3. (a) Electronegativity is the pull of the nucleus of one atom on the electrons of other atoms; it increases from P to S to Cl because nuclear charge increases. This is because as you move left to right across the periodic table, atomic radii decrease in size. Increasing nuclear charge means that Cl has the most positively charged nucleus of the three and will exert the greatest pull on the electrons of other atoms.

(b) Electronegativity is the pull of the nucleus of one atom on the electrons of other atoms; it decreases from Cl to Br to I because electron shells are added. The added electron shells shield the nucleus, causing it to have less of an effect on the electrons of other atoms. Therefore, iodine will exert the least pull on the electrons of other atoms.

(c) Atomic radius increases from Li to Na to K because electrons are being added in higher energy levels, which are farther away from the nucleus; therefore, the K atom is the largest of the three.

(d) Atomic radius increases from Al to Mg to Na because protons are being removed from the nucleus while the energy levels of the valence electrons remains unchanged. If there are fewer positive charges in the nucleus, the electrons of Na will be less attracted to the nucleus and will remain farther away.

4. (a) A straightforward statement of the Heisenberg uncertainty principle is as follows: It is impossible to know with certainty both the position and momentum of a particle at one moment.

(b) When a hydrogen atom absorbs energy, its electrons jump to higher energy levels. The absorbed energy shows up as a dark area on the absorption spectrum.

A hydrogen atom gives off energy when its electrons jump back down to lower energy levels. Electromagnetic waves, which are emitted at these jumps, show up as bright areas on the emission spectrum.

In an atom, energy is quantized, which means that electrons can exist only at specific energy levels. When an electron jumps from one energy level to another, it will always emit or absorb exactly the same amount of energy, and because  $\Delta E = hv$ , for a particular energy change, radiation of the same frequency will always be emitted or absorbed.

(c) When an electron is added to chlorine, the chlorine ion created has a complete valence shell, which is an extremely stable, low energy configuration. When something becomes more stable, energy is given off, making the process exothermic.

When an electron is added to a magnesium atom, it must be placed by itself in the  $3p$  energy level. Adding an electron in a higher energy level makes the magnesium ion created more energetic and less stable, which means that the process is endothermic.

(d) Sulfur has six valence electrons in its outer shell. In  $\text{Na}_2\text{S}$ , sulfur gains two electrons to give its outer shell a complete octet. In  $\text{SF}_6$ , sulfur uses  $sp^3d^2$  hybridization to share all six of its valence electrons with fluorine atoms.



# 4

## Bonding

### **HOW OFTEN DOES BONDING APPEAR ON THE EXAM?**

In the multiple-choice section, this topic appears in about 9 out of 75 questions. In the free-response section, this topic appears every year.

### **COULOMB'S LAW**

All bonds occur because of electrostatic attractions. Atoms stick together to form molecules, and atoms and molecules stick together to form liquids or solids because the negatively charged electrons of one atom are attracted to the positively charged nucleus of another atom.

Electrostatic forces are governed by Coulomb's law, and the entire study of bonding comes down to understanding how Coulomb's law applies to different chemical situations.

Let's take a look at Coulomb's law.

Coulomb's Law
Attractive force is proportional to $\frac{(+q)(-q)}{r^2}$
$+q$ = magnitude of the positive charge
$-q$ = magnitude of the negative charge
$r$ = distance between the charges

You should be able to tell two things from the formula above.

- Bigger charges mean stronger bonds; smaller charges mean weaker bonds.
- Charges close together mean stronger bonds; charges far apart mean weaker bonds.

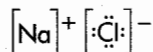
## BONDS

Atoms join to form molecules because atoms like to have a full outer shell of electrons. This usually means having eight electrons in the outer shell. So atoms with too many or too few electrons in their valence shells will find one another and pass the electrons around until all the atoms in the molecule have stable outer shells. Sometimes an atom will give up electrons completely to another atom, forming an ionic bond. Sometimes atoms share electrons, forming covalent bonds.

## IONIC COMPOUNDS

An ionic solid is held together by the electrostatic attractions between ions that are next to one another in a lattice structure. They often occur between metals and nonmetals. In an ionic bond, electrons are not shared. Instead, one atom gives up electrons and becomes a positively charged ion while the other atom accepts electrons and becomes a negatively charged ion.

The two ions in an ionic bond are held together by electrostatic forces. In the diagram below, a sodium atom has given up its single valence electron to a chlorine atom, which has seven valence electrons and uses the electron to complete its outer shell (with eight). The two atoms are then held together by the positive and negative charges on the ions.



The same electrostatic attractions that hold together the ions in a molecule of NaCl hold together a crystal of NaCl, so there is no real distinction between the molecules and the solid. Ionic bonds are strong, and substances held together by ionic bonds have high melting and boiling points.

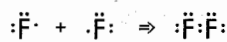
Coulomb's law states that more highly charged ions will form stronger bonds than less highly charged ions and smaller ions will form stronger bonds than larger ions. So an ionic bond composed of ions with +2 and -2 charges will be stronger than a bond composed of ions with +1 and -1 charges. Also from Coulomb's law, we know that the smaller the ions in an ionic bond, the stronger the bond. This is because a small ionic radius allows the charges to get closer together and increases the force between them.

In an ionic solid, each electron is localized around a particular atom, so electrons do not move around the lattice; this makes ionic solids poor conductors of electricity. Ionic liquids, however, do conduct electricity because the ions themselves are free to move about in the liquid phase, although the electrons are still localized on particular atoms. Salts are held together by ionic bonds.

## COVALENT BONDS

In a covalent bond, two atoms share electrons. Each atom counts the shared electrons as part of its valence shell. In this way, both atoms can consider their outer shells complete.

In the diagram below, two fluorine atoms, each of which has seven valence electrons and needs one electron to complete its valence shell, form a covalent bond. Each atom donates an electron to the bond, which is considered to be part of the valence shell of both atoms.



The number of covalent bonds an atom can form is the same as the number of electrons in its valence shell.

The first covalent bond formed between two atoms is called a sigma ( $\sigma$ ) bond. All single bonds are sigma bonds. If additional bonds between the two atoms are formed, they are called pi ( $\pi$ ) bonds. The second bond in a double bond is a pi bond and the second and third bonds in a triple bond are also pi bonds. Double and triple bonds are stronger and shorter than single bonds, but they are not twice or triple the strength.

Summary of Multiple Bonds			
Bond type:	Single	Double	Triple
Bond designation:	One sigma ( $\sigma$ )	One sigma ( $\sigma$ ) and one pi ( $\pi$ )	One sigma ( $\sigma$ ) and two pi ( $\pi$ )
Bond order:	One	Two	Three
Bond length:	Longest	Intermediate	Shortest
Bond energy:	Least	Intermediate	Greatest

Single bonds have a one sigma ( $\sigma$ ) bond and a bond order of one. The single bond has the longest bond length and the least bond energy.

## Polarity

In the  $\text{F}_2$  molecule shown above, the two fluorine atoms share the electrons equally, but that's not usually the case in molecules. Usually, one of the atoms (the more electronegative one) will exert a stronger pull on the electrons in the bond—not enough to make the bond ionic, but enough to keep the electrons on one side of the molecule more than on the other side. This gives the molecule a dipole. That is, the side of the molecule where the electrons spend more time will be negative and the side of the molecule where the electrons spend less time will be positive.

## Dipole Moment

The polarity of a molecule is measured by the dipole moment. The larger the dipole moment, the more polar the molecule. The greater the charge at the ends of the dipole and the greater the distance between the charges, the greater the value of the dipole moment.

## LEWIS DOT STRUCTURES

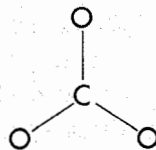
### Drawing Lewis Dot Structures

At some point on the test, you'll be asked to draw the Lewis structure for a molecule or polyatomic ion. Here's how to do it.

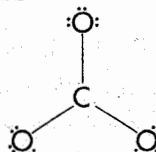
1. Count the valence electrons in the molecule or polyatomic ion; refer to page 18 for a periodic table.
2. If a polyatomic ion has a negative charge, add electrons to the total in (1). If a polyatomic ion has a positive charge, subtract electrons from the total in (1).
3. Draw the skeletal structure of the molecule and place two electrons (or a single bond) between each pair of bonded atoms. If the molecule contains three or more atoms, the least electronegative atom will usually occupy the central position.
4. Add electrons to the surrounding atoms until each has a complete outer shell.
5. Add the remaining electrons to the central atom.
6. Look at the central atom.
  - (a) If the central atom has fewer than eight electrons, remove an electron pair from an outer atom and add another bond between that outer atom and the central atom. Do this until the central atom has a complete octet.
  - (b) If the central atom has a complete octet, you are finished.
  - (c) If the central atom has more than eight electrons, that's okay too.

Let's find the Lewis structure for the  $\text{CO}_3^{2-}$  ion.

1. Carbon has 4 valence electrons; oxygen has 6.  
 $4 + 6 + 6 + 6 = 22$
2. The ion has a charge of  $-2$ .  
 $22 + 2 = 24$
3. Carbon is the central atom.

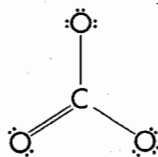


4. Add electrons to the oxygen atoms.



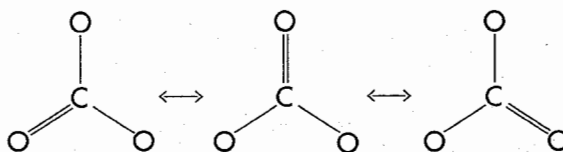
5. We've added all 24 electrons, so there's nothing left to put on the carbon atom.

6. (a) We need to give carbon a complete octet, so we take an electron pair away from one of the oxygens and make a double bond instead.



### Resonance Forms

When we put a double bond into the  $\text{CO}_3^{2-}$  ion, we place it on any one of the oxygen atoms, as shown below.



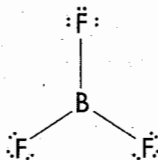
All three resonance forms are considered to exist simultaneously, and the strength and lengths of all three bonds are the same: somewhere between the strength and length of a single bond and a double bond.

### Incomplete Octets

Some atoms can have a complete outer shell with less than eight electrons; for example, hydrogen can have a maximum of two electrons, and beryllium can be stable with only four valence electrons, as in  $\text{BeH}_2$ .



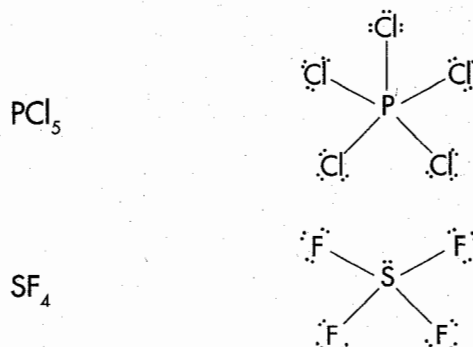
Boron can be stable with only six valence electrons, as in  $\text{BF}_3$ .



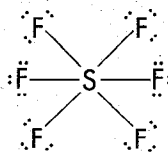
### Expanded Octets

In molecules that have  $d$  subshells available, the central atom can have more than eight valence electrons.

Here are some examples.

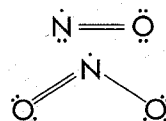






## Odd Numbers of Electrons

Molecules almost always have an even number of electrons, allowing electrons to be paired, but there are exceptions, usually involving nitrogen.



Note that  $\text{NO}_2$  can be shown with either of two resonance forms.

## MOLECULAR GEOMETRY

Electrons repel one another, so when atoms come together to form a molecule, the molecule will assume the shape that keeps its different electron pairs as far apart as possible. When we predict the geometries of molecules using this idea, we are using the **valence shell electron-pair repulsion (VSEPR) model**.

In a molecule with more than two atoms, the shape of the molecule is determined by the number of electron pairs on the central atom. The central atom forms **hybrid orbitals**, each of which has a standard shape. Variations on the standard shape occur depending on the number of bonding pairs and lone pairs of electrons on the central atom.

Here are some things you should remember when dealing with the VSEPR model.

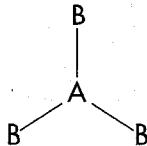
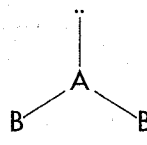
- Double and triple bonds are treated in the same way as single bonds in terms of predicting overall geometry for a molecule; however, multiple bonds have slightly more repulsive strength and will therefore occupy a little more space than single bonds.
- Lone electron pairs have a little more repulsive strength than bonding pairs, so lone pairs will occupy a little more space than bonding pairs.

The tables on the following pages show the different hybridizations and geometries that you might see on the test.

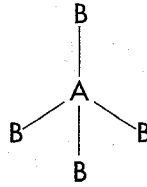
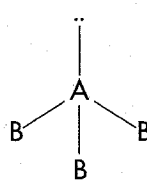
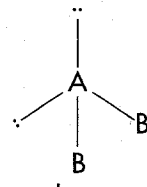
If the central atom has 2 electron pairs, then it has  $sp$  hybridization and its basic shape is **linear**.

<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
0	B—A—B linear	$\text{BeCl}_2$ $\text{CO}_2$

If the central atom has 3 electron pairs, then it has  $sp^2$  hybridization and its basic shape is **trigonal planar**; its bond angles are about  $120^\circ$ .

<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
0	 <p>trigonal planar</p>	$\text{BF}_3$ $\text{SO}_3$ $\text{NO}_3^-$ $\text{CO}_3^{2-}$
1	 <p>bent</p>	$\text{SO}_2$

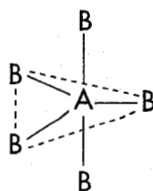
If the central atom has 4 electron pairs, then it has  $sp^3$  hybridization and its basic shape is **tetrahedral**; its bond angles are about  $109.5^\circ$ .

<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
0	 <p>tetrahedral</p>	$\text{CH}_4$ $\text{NH}_4^+$ $\text{ClO}_4^-$ $\text{SO}_4^{2-}$ $\text{PO}_4^{3-}$
1	 <p>trigonal pyramidal</p>	$\text{NH}_3$ $\text{PCl}_3$ $\text{AsH}_3$ $\text{SO}_3^{2-}$
2	 <p>bent</p>	$\text{H}_2\text{O}$ $\text{OF}_2$ $\text{NH}_2^-$

If the central atom has 5 electron pairs, then it has  $sp^3d$  hybridization and its basic shape is trigonal bipyramidal.

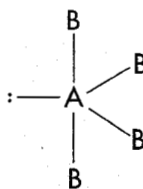
<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
0	 <p>trigonal bipyramidal</p>	$PCl_5$ $PF_5$
1	 <p>folded square, seesaw, distorted tetrahedron</p>	$SF_4$ $IF_4^+$
2	 <p>T-shaped</p>	$ClF_3$ $ICl_3$
3	 <p>linear</p>	$XeF_2$ $I_3^-$

0



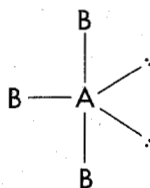
trigonal bipyramidal

1



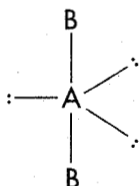
folded square, seesaw,  
distorted tetrahedron

2



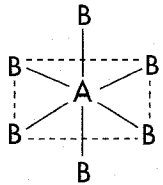
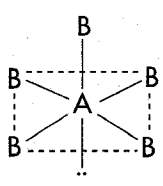
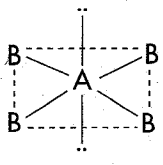
T-shaped

3



linear

If the central atom has 6 electron pairs, then it has  $d^2sp^3$  hybridization and its basic shape is octahedral.

Number of lone pairs	Geometry	Examples
0	 <p>octahedral</p>	$SF_6$
1	 <p>square pyramidal</p>	$BrF_5$ $IF_5$
2	 <p>square planar</p>	$XeF_4$ $ICl_4^-$

In trigonal bipyramidal shapes, place the lone pairs in axial position first. In octahedral shapes, place lone pairs in equatorial position first.

## BONDS BETWEEN MOLECULES — ATTRACTIVE FORCES IN SOLIDS AND LIQUIDS

Sometimes the bonds that hold the atoms or ions in liquids and solids together are the same strong bonds that hold the atoms or ions together in molecules. Intermolecular forces only exist with covalently bonded molecules. We will also discuss metallic and network forces here.

### NETWORK (COVALENT) BONDS

In a network solid, atoms are held together in a lattice of covalent bonds. You can visualize a network solid as one big molecule. Network solids are very hard and have very high melting and boiling points.

The electrons in a network solid are localized in covalent bonds between particular atoms, so they are not free to move about the lattice. This makes network solids poor conductors of electricity.

The most commonly seen network solids are compounds of carbon (diamond) and silicon ( $\text{SiO}_2$ —quartz). The hardness of diamond is due to the tetrahedral network structure formed by carbon atoms whose electrons are configured in  $sp^3$  hybridization. The three-dimensional complexity of the tetrahedral network means that there are no natural seams along which a diamond can be broken.

### METALLIC BONDS

Metallic substances can be compared with a group of nuclei surrounded by a sea of mobile electrons. As with ionic and network substances, a metallic substance can be visualized as one large molecule. Most metals are very hard, although the freedom of movement of electrons in metals makes them malleable and ductile. All metals, except mercury, are solids at room temperature, and most metals have high boiling and melting points.

Metals composed of atoms with smaller nuclei tend to form stronger bonds than metals made up of atoms with larger nuclei. This is because smaller sized nuclei allow the positively charged nuclei to be closer to the negatively charged electrons, increasing the attractive force from Coulomb's law.

The electrons in a metallic substance are delocalized and can move freely throughout the substance. The freedom of the electrons in a metal makes it a very good conductor of heat and electricity.

### VAN DER WAALS FORCES

#### Dipole–Dipole Forces

Dipole–dipole forces occur between neutral, polar molecules: The positive end of one polar molecule is attracted to the negative end of another polar molecule.

Molecules with greater polarity will have greater dipole–dipole attraction, so molecules with larger dipole moments tend to have higher melting and boiling points. Dipole–dipole attractions are relatively weak, however, and these substances melt and boil at very low temperatures. Most substances held together by dipole–dipole attraction are gases or liquids at room temperature.

#### London Dispersion Forces

London dispersion forces occur between neutral, nonpolar molecules. These very weak attractions occur because of the random motions of electrons on atoms within molecules. At a given moment, a nonpolar molecule might have more electrons on one side than on the other, giving it an instantaneous polarity. For that fleeting instant, the molecule will act as a very weak dipole.

Since London dispersion forces depend on the random motions of electrons, molecules with more electrons will experience greater London dispersion forces. So among substances that experience only London dispersion forces, the one with more electrons will generally have higher melting and boiling points. London dispersion forces are even weaker than dipole–dipole forces, so substances that experience only London dispersion forces melt and boil at extremely low temperatures and tend to be gases at room temperature.

## **HYDROGEN BONDS**

Hydrogen bonds are similar to dipole–dipole attractions. In a hydrogen bond, the positively charged hydrogen end of a molecule is attracted to the negatively charged end of another molecule containing an extremely electronegative element (fluorine, oxygen, or nitrogen—F, O, N).

Hydrogen bonds are much stronger than dipole–dipole forces because when a hydrogen atom gives up its lone electron to a bond, its positively charged nucleus is left virtually unshielded. Substances that have hydrogen bonds, like water and ammonia, have higher melting and boiling points than substances that are held together by dipole–dipole forces.

Water is less dense as a solid than as a liquid because its hydrogen bonds force the molecules in ice to form a crystal structure, which keeps them farther apart than they are in liquid form.

## CHAPTER 4 QUESTIONS

### MULTIPLE-CHOICE QUESTIONS

#### Questions 1–4

- (A) Metallic bonding
  - (B) Network covalent bonding
  - (C) Hydrogen bonding
  - (D) Ionic bonding
  - (E) London dispersion forces
1. Solids exhibiting this kind of bonding are excellent conductors of heat.
  2. This kind of bonding is the reason that water is more dense than ice.
  3. This kind of bonding exists between atoms with very different electronegativities.
  4. The stability exhibited by diamonds is due to this kind of bonding.

#### Questions 5–7

- (A)  $\text{CH}_4$
  - (B)  $\text{NH}_3$
  - (C)  $\text{NaCl}$
  - (D)  $\text{N}_2$
  - (E)  $\text{H}_2$
5. This substance undergoes ionic bonding.
  6. This molecule contains two pi ( $\pi$ ) bonds.
  7. This substance undergoes hydrogen bonding.

#### Questions 8–10

- (A)  $\text{BF}_3$
  - (B)  $\text{CO}_2$
  - (C)  $\text{H}_2\text{O}$
  - (D)  $\text{CF}_4$
  - (E)  $\text{PH}_3$
8. The central atom in this molecule forms  $sp^2$  hybrid orbitals.
  9. This molecule has a tetrahedral structure.
  10. This molecule has a linear structure.

11. A liquid whose molecules are held together by which of the following forces would be expected to have the lowest boiling point?
- Ionic bonds
  - London dispersion forces
  - Hydrogen bonds
  - Metallic bonds
  - Network bonds
12. Hydrogen bonding would be seen in a sample of which of the following substances?
- $\text{CH}_4$
  - $\text{H}_2$
  - $\text{H}_2\text{O}$
  - $\text{HI}$
  - All of the above
13. Which of the following species does NOT have a tetrahedral structure?
- $\text{CH}_4$
  - $\text{NH}_4^+$
  - $\text{SF}_4$
  - $\text{AlCl}_4^-$
  - $\text{CBr}_4$
14. Which form of orbital hybridization can form molecules with shapes that are either trigonal pyramidal or tetrahedral?
- $sp$
  - $sp^2$
  - $sp^3$
  - $d^2sp$
  - $dsp^3$
15. The six carbon atoms in a benzene molecule are shown in different resonance forms as three single bonds and three double bonds. If the length of a single carbon-carbon bond is 154 pm and the length of a double carbon-carbon bond is 133 pm, what length would be expected for the carbon-carbon bonds in benzene?
- 126 pm
  - 133 pm
  - 140 pm
  - 154 pm
  - 169 pm
16. Which of the following could be the Lewis structure for sulfur trioxide?
- - 
  - 
  - 
  -
17. In which of the following species does the central atom NOT form  $sp^2$  hybrid orbitals?
- $\text{SO}_2$
  - $\text{BF}_3$
  - $\text{NO}_3^-$
  - $\text{SO}_3$
  - $\text{PCl}_3$
18. A molecule whose central atom has  $d^2sp^3$  hybridization can have which of the following shapes?
- Tetrahedral
  - Square pyramidal
  - Square planar
- I only
  - III only
  - I and II only
  - II and III only
  - I, II, and III



19. Which of the following molecules will have a Lewis dot structure with exactly one unshared electron pair on the central atom?
- (A)  $\text{H}_2\text{O}$   
(B)  $\text{PH}_3$   
(C)  $\text{PCl}_5$   
(D)  $\text{CH}_2\text{Cl}_2$   
(E)  $\text{BeCl}_2$
20. Which of the following lists of species is in order of increasing boiling points?
- (A)  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$   
(B)  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2$   
(C)  $\text{NH}_3$ ,  $\text{H}_2$ ,  $\text{N}_2$   
(D)  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{H}_2$   
(E)  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2$
21. Solid  $\text{NaCl}$  melts at a temperature of  $800^\circ\text{C}$ , while solid  $\text{NaBr}$  melts at  $750^\circ\text{C}$ . Which of the following is an explanation for the higher melting point of  $\text{NaCl}$ ?
- (A) A chlorine ion has less mass than a bromine ion.  
(B) A chlorine ion has a greater negative charge than a bromine ion.  
(C) A chlorine ion has a lesser negative charge than a bromine ion.  
(D) A chlorine ion is smaller than a bromine ion.  
(E) A chlorine ion is larger than a bromine ion.
22. Which of the compounds listed below would require the greatest energy to separate it into ions in the gaseous state?
- (A)  $\text{NaCl}$   
(B)  $\text{NaI}$   
(C)  $\text{MgO}$   
(D)  $\text{Na}_2\text{O}$   
(E)  $\text{MgCl}_2$
23. Which sample of the following compounds contains both ionic and covalent bonds?
- (A)  $\text{H}_2\text{O}_2$   
(B)  $\text{CH}_3\text{Cl}$   
(C)  $\text{C}_2\text{H}_5\text{OH}$   
(D)  $\text{NaNO}_3$   
(E)  $\text{NH}_2\text{OH}$
24. Which of the molecules listed below has the largest dipole moment?
- (A)  $\text{Cl}_2$   
(B)  $\text{HCl}$   
(C)  $\text{SO}_3$   
(D)  $\text{NO}$   
(E)  $\text{N}_2$
25. Which of the following statements about boiling points is (are) correct?
- I.  $\text{H}_2\text{O}$  boils at a higher temperature than  $\text{CO}_2$ .  
II.  $\text{Ar}$  boils at a higher temperature than  $\text{He}$ .  
III.  $\text{Rb}$  boils at a higher temperature than  $\text{Na}$ .
- (A) I only  
(B) I and II only  
(C) I and III only  
(D) II and III only  
(E) I, II, and III

## ESSAYS

- Use the principles of bonding and molecular structure to explain the following statements.
  - The boiling point of argon is  $-186^{\circ}\text{C}$ , whereas the boiling point of neon is  $-246^{\circ}\text{C}$ .
  - Solid sodium melts at  $98^{\circ}\text{C}$ , but solid potassium melts at  $64^{\circ}\text{C}$ .
  - More energy is required to break up a  $\text{CaO(s)}$  crystal into ions than to break up a  $\text{KF(s)}$  crystal into ions.
  - Molten  $\text{KF}$  conducts electricity, but solid  $\text{KF}$  does not.
- The carbonate ion  $\text{CO}_3^{2-}$  is formed when carbon dioxide,  $\text{CO}_2$ , reacts with slightly basic cold water.
  - Draw the Lewis electron dot structure for the carbonate ion. Include resonance forms if they apply.
    - Draw the Lewis electron dot structure for carbon dioxide.
  - Describe the hybridization of carbon in the carbonate ion.
  - Describe the relative lengths of the three  $\text{C-O}$  bonds in the carbonate ion.
    - Compare the average length of the  $\text{C-O}$  bonds in the carbonate ion to the average length of the  $\text{C-O}$  bonds in carbon dioxide.

3.

Substance	Boiling Point ( $^{\circ}\text{C}$ )	Bond Length ( $\text{\AA}$ )	Bond Strength (kcal/mol)
$\text{H}_2$	-253	0.75	104.2
$\text{N}_2$	-196	1.10	226.8
$\text{O}_2$	-182	1.21	118.9
$\text{Cl}_2$	-34	1.99	58.0

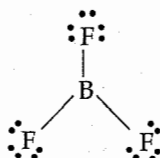
- Explain the differences in the properties given in the table above for each of the following pairs.
    - The bond strengths of  $\text{N}_2$  and  $\text{O}_2$
    - The bond lengths of  $\text{H}_2$  and  $\text{Cl}_2$
    - The boiling points of  $\text{O}_2$  and  $\text{Cl}_2$
  - Use the principles of molecular bonding to explain why  $\text{H}_2$  and  $\text{O}_2$  are gases at room temperature, while  $\text{H}_2\text{O}$  is a liquid at room temperature.
- $\text{H}_2\text{S}$ ,  $\text{SO}_4^{2-}$ ,  $\text{XeF}_2$ ,  $\text{ICl}_4^-$ 
    - Draw a Lewis electron dot diagram for each of the molecules listed above.
    - Use the valence shell electron-pair repulsion (VSEPR) model to predict the geometry of each of the molecules.

5. Use the principles of bonding and molecular structure to explain the following statements.
- The angle between the N–F bonds in  $\text{NF}_3$  is smaller than the angle between the B–F bonds in  $\text{BF}_3$ .
  - $\text{I}_2(\text{s})$  is insoluble in water, but it is soluble in carbon tetrachloride.
  - Diamond is one of the hardest substances on Earth.
  - HCl has a lower boiling point than either HF or HBr.

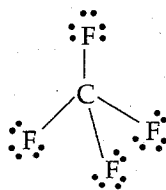
## CHAPTER 4 ANSWERS AND EXPLANATIONS

### MULTIPLE-CHOICE QUESTIONS

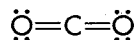
- A** In metallic bonding, nuclei are surrounded by a sea of mobile electrons. The electrons' freedom to move allows them to conduct heat and electricity.
- C** When ice forms, the hydrogen bonds join the molecules in a lattice structure, which forces them to remain farther apart than they were in the liquid form. Because the molecules are farther apart in the solid than in the liquid, the solid (ice) is less dense than the liquid.
- D** Electronegativity is a measure of how much pull an atom exerts on another atom's electrons. If the difference in electronegativities is large enough (greater than 1.7) then the more electronegative atom will simply take an electron away from the other atom. The two atoms will then be held together by electrostatic attraction (the atom that has gained an electron becomes negative and the atom that has lost an electron becomes positive). That's an ionic bond.
- B** The carbon atoms in diamond are held together by a network of covalent bonds. The carbon atoms form  $sp^3$  hybrid orbitals, resulting in a tetrahedral structure, which is very stable and has no simple breaking points.
- C** NaCl is composed of two elements that have very different electronegativities than each other, so Na gives up an electron to Cl and the two are held together by electrostatic attraction in an ionic bond.
- D**  $\text{N}_2$  contains a triple bond, so it has one sigma ( $\sigma$ ) bond and two pi ( $\pi$ ) bonds.
- B** Hydrogen bonding occurs between hydrogen atoms of one molecule and electronegative elements (F, O, or N) of another molecule. So in ammonia, hydrogens from one ammonia molecule will form bonds with nitrogens from another ammonia molecule.
- A** In  $\text{BF}_3$ , boron forms three bonds with fluorine atoms and has no unbonded valence electrons, so it must form  $sp^2$  hybrid orbitals.



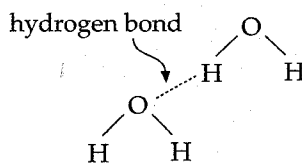
9. **D**  $\text{CF}_4$  forms a tetrahedral structure as shown in the diagram below. The central carbon atom is hybridized  $sp^3$ .



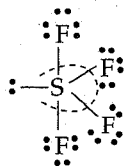
10. **B**  $\text{CO}_2$  forms a linear structure as shown in the diagram below. The central carbon atom is  $sp$  hybridized.



11. **B** A liquid with a low boiling point must be held together by weak bonds. London dispersion forces are the weakest kind of intermolecular forces.
12. **C** Hydrogen bonding specifically describes the attraction experienced by a hydrogen atom in one molecule to an extremely electronegative element (F, O, or N) in another molecule. So in water, a hydrogen atom in one water molecule will be attracted to an oxygen atom in another water molecule.

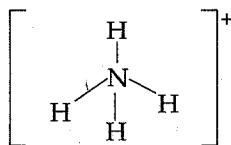


13. **C**  $\text{SF}_4$  has 34 valence electrons distributed in the Lewis dot structure and shape shown below.



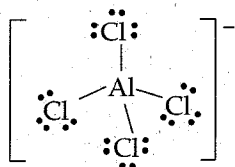
In this molecule, sulfur forms  $dsp^3$  hybrid orbitals, which have a trigonal bipyramid structure. Because  $\text{SF}_4$  has one unshared electron pair, the molecule takes the "seesaw" or "folded square" shape.

Choices (A) and (B),  $\text{CH}_4$  and  $\text{NH}_4^+$ , each have 8 valence electrons distributed in the same Lewis dot structure and shape, shown below for  $\text{NH}_4^+$ .



In these molecules, the central atom forms  $sp^3$  hybrid orbitals, which have a tetrahedral structure. There are no unshared electron pairs on the central atom, so the molecules are tetrahedral.

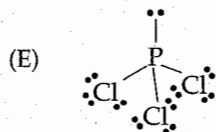
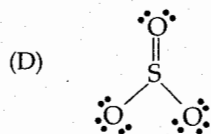
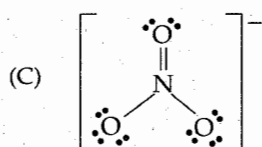
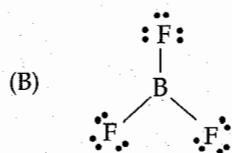
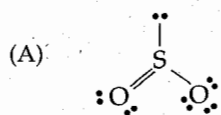
Choices (D) and (E),  $\text{AlCl}_4^-$  and  $\text{CBr}_4$ , each have 32 valence electrons distributed in the same Lewis dot structure and shape, shown below for  $\text{AlCl}_4^-$ .



In these molecules, the central atom forms  $sp^3$  hybrid orbitals, which have a tetrahedral structure. There are no unshared electron pairs on the central atom, so the molecules are tetrahedral.

14. **C** The  $sp^3$  hybrid orbitals take a tetrahedral shape if the central atom has no unshared electron pairs ( $\text{CH}_4$ , for instance). If the central atom has one unshared electron pair, the molecule takes the trigonal pyramid shape ( $\text{NH}_3$ , for instance).
15. **C** Resonance is used to describe a situation that lies between single and double bonds, so the bond length would also be expected to be in between that of single and double bonds.
16. **A** Choice (A) has the correct number of valence electrons ( $6 + 6 + 6 + 4 + 2 = 24$ ), and 8 valence electrons on each atom.
- About the other choices:
- (B) There are only 6 valence electrons on the sulfur atom.
- (C) There are too many valence electrons (10) on the sulfur atom.
- (D) There are too many valence electrons (26).
- (E) There are too many valence electrons (10) on the sulfur atom and not enough (6) on one of the oxygen atoms.

17. E  $\text{PCl}_3$  is the only one that doesn't form  $sp^2$  hybrid orbitals, forming  $sp^3$  orbitals instead. The Lewis dot structures for all of the choices are shown below (note that boron does not need an octet).



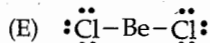
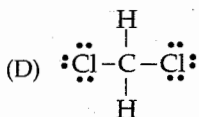
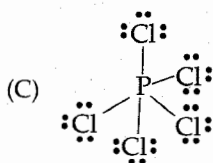
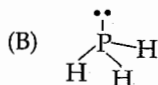
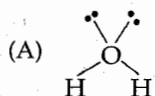
18. D A molecule with  $d^2sp^3$  hybridization has octahedral structure if the central atom has no unbonded electrons ( $\text{SF}_6$ , for instance).

If the central atom has one unbonded electron pair, the molecule is square pyramidal ( $\text{IF}_5$ , for instance).

If the central atom has two unbonded electron pairs, the molecule is square planar ( $\text{XeF}_4$ , for instance).

A molecule with  $d^2sp^3$  hybridization can never be tetrahedral.

19. **B** The Lewis dot structures for the answer choices are shown below. Only  $\text{PH}_3$  has a single unshared electron pair on its central atom.



20. **A**  $\text{H}_2$  experiences only van der Waals forces and has the lowest boiling point.  $\text{N}_2$  also experiences only van der Waals forces, but it is larger than  $\text{H}_2$  and has more electrons, so it has stronger van der Waals interactions with other molecules.  $\text{NH}_3$  is polar and undergoes hydrogen bonding, so it has the strongest intermolecular interactions and the highest boiling point.
21. **D** The greater the bond strength, the higher the melting point. Both  $\text{NaCl}$  and  $\text{NaBr}$  are held together by ionic bonds, and the strength of ionic bonds depends on the strength of the charges and the sizes of the ions. The strength of the charges doesn't matter in this case because both chlorine and bromine ions have charges of  $-1$ . The reason for  $\text{NaCl}$ 's higher melting point is that chlorine ions are smaller than bromine ions, so the ions can get closer together.
22. **C** The energy required to separate an ionic compound into gaseous ions is called the lattice energy. The most important factor in determining the lattice energy is the strength of the charges on the two ions. In  $\text{MgO}$ , the  $\text{Mg}$  ion is  $+2$  and the  $\text{O}$  ion is  $-2$ . All of the other choices listed contain  $+1$  or  $-1$  ions, so their lattice energies will not be as large.
23. **D** A sample of  $\text{NaNO}_3$  contains an  $\text{Na}^+$  ion and an  $\text{NO}_3^-$  polyatomic ion, which are held together with ionic bonds. The atoms in the  $\text{NO}_3^-$  ion are held together by covalent bonds. All of the bonds in the other choices are covalent bonds.

24. **B** The bond that holds HCl together is a covalent bond with a large polarity. The bond that holds NO together is also polar covalent, but its polarity is very small because N and O are so close together on the periodic table. Cl<sub>2</sub> and N<sub>2</sub> are nonpolar because they share electrons equally, and SO<sub>3</sub> is nonpolar because it is symmetrical (trigonal planar). Nonpolar molecules have dipole moments of zero.
25. **B** Groups I and II are listed in order of increasing melting points. Remember, stronger bonds or intermolecular forces mean higher melting points.

I. H<sub>2</sub>O has hydrogen bonding, which makes its intermolecular forces much stronger than those of CO<sub>2</sub>, which is nonpolar and exhibits only London dispersion forces. So water has a higher boiling point than CO<sub>2</sub>.

II. These are nonpolar atoms, so they are held together by weak London dispersion forces. Because London dispersion forces depend on the random movement of electrons, the more electrons in a compound the stronger the London dispersion forces. Ar has more electrons than He, so it has stronger London dispersion forces and a higher boiling point.

III. These are held together by metallic bonding. In general, the smaller the nucleus of a metal, the stronger the metallic bonds. Rb has a larger nucleus than Na, so it has weaker metallic bonds and a lower boiling point, so this statement is not correct.

## ESSAYS

1. (a) Molecules of noble gases in the liquid phase are held together by London dispersion forces, which are weak interactions brought about by instantaneous polarities in nonpolar atoms and molecules.

Atoms with more electrons are more easily polarized and experience stronger London dispersion forces. Argon has more electrons than neon, so it experiences stronger London dispersion forces and boils at a higher temperature.

(b) Sodium and potassium are held together by metallic bonds and positively charged ions in a delocalized sea of electrons.

Potassium is larger than sodium, so the electrostatic attractions that hold the atoms together act at a greater distance, reducing the attractive force and resulting in its lower melting point.

(c) Both CaO(s) and KF(s) are held together by ionic bonds in crystal lattices.

Ionic bonds are held together by an electrostatic force, which can be determined by using Coulomb's law.

$$F = k \frac{Q_1 Q_2}{r^2}$$

CaO is more highly charged, with Ca<sup>2+</sup> bonded to O<sup>2-</sup>. So for CaO, Q<sub>1</sub> and Q<sub>2</sub> are +2 and -2.

KF is not as highly charged, with K<sup>+</sup> bonded to F<sup>-</sup>. So for KF, Q<sub>1</sub> and Q<sub>2</sub> are +1 and -1.

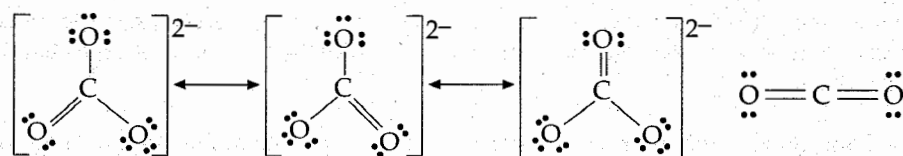
CaO is held together by stronger forces and is more difficult to break apart.

(d) KF is composed of K<sup>+</sup> and F<sup>-</sup> ions. In the liquid (molten) state, these ions are free to move and can thus conduct electricity.

In the solid state, the K<sup>+</sup> and F<sup>-</sup> ions are fixed in a crystal lattice and their electrons are localized around them, so there is no charge that is free to move and thus no conduction of electricity.



2. (a) (i)



(ii)

(b) The central carbon atom forms three sigma bonds with oxygen atoms and has no free electron pairs, so its hybridization must be  $sp^2$ .

(c) (i) All three bonds will be the same length because no particular resonance form is preferred over the others. The actual structure is an average of the resonance structures.

(ii) The C–O bonds in the carbonate ion have resonance forms between single and double bonds, while the C–O bonds in carbon dioxide are both double bonds.

The bonds in the carbonate ion will be shorter than single bonds and longer than double bonds, so the carbonate bonds will be longer than the carbon dioxide bonds.

3. (a) (i) The bond strength of  $N_2$  is larger than the bond strength of  $O_2$  because  $N_2$  molecules have triple bonds and  $O_2$  molecules have double bonds. Triple bonds are stronger and shorter than double bonds.

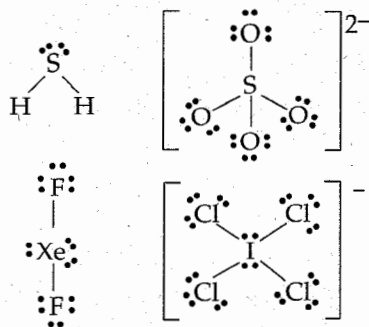
(ii) The bond length of  $H_2$  is smaller than the bond length of  $Cl_2$  because hydrogen is a smaller atom than chlorine, allowing the hydrogen nuclei to be closer together.

(iii) Liquid oxygen and liquid chlorine are both nonpolar substances that experience only London dispersion forces of attraction. These forces are greater for  $Cl_2$  because it has more electrons (which makes it more polarizable), so  $Cl_2$  has a higher boiling point than  $O_2$ .

(b)  $H_2$  and  $O_2$  are both nonpolar molecules that experience only London dispersion forces, which are too weak to form the bonds required for a substance to be liquid at room temperature.

$H_2O$  is a polar substance whose molecules form hydrogen bonds with each other. Hydrogen bonds are strong enough to form the bonds required in a liquid at room temperature.

4. (a)



(b)  $H_2S$  has two bonds and two free electron pairs on the central S atom. The greatest distance between the electron pairs is achieved by tetrahedral arrangement. The electron pairs at two of the four corners will cause the molecule to have a bent shape, like water.

$SO_4^{2-}$  has four bonds around the central S atom and no free electron pairs. The four bonded pairs will be farthest apart when they are arranged in a tetrahedral shape, so the molecule is tetrahedral.

$XeF_2$  has two bonds and three free electron pairs on the central Xe atom. The greatest distance between the electron pairs can be achieved by a trigonal bipyramidal arrangement. The three

free electron pairs will occupy the equatorial positions, which are 120 degrees apart, to minimize repulsion. The two F atoms are at the poles, so the molecule is linear.

$\text{ICl}_4^-$  has four bonds and two free electron pairs on the central I atom. The greatest distance between the electron pairs can be achieved by an octahedral arrangement. The two free electron pairs will be opposite each other to minimize repulsion. The four Cl atoms are in the equatorial positions, so the molecule is square planar.

5. (a)  $\text{BF}_3$  has three bonds on the central B atom and no free electron pairs, so the structure of  $\text{BF}_3$  is trigonal planar, with each of the bonds 120 degrees apart.

$\text{NF}_3$  has three bonds and one free electron pair on the central N atom. The four electron pairs are pointed toward the corners of a tetrahedron, 109.5 degrees apart. The added repulsion from the free electron pair causes the N-F bonds to be even closer together, and the angle between them is more like 107°.

(b) Polar solvents are best at dissolving polar solutes. Nonpolar solvents are best at dissolving nonpolar solutes.

$\text{I}_2(\text{s})$  is nonpolar, so it dissolves better in carbon tetrachloride,  $\text{CCl}_4$ , which is nonpolar, than in water,  $\text{H}_2\text{O}$ , which is polar.

(c) The carbon atoms in diamond are bonded together in a tetrahedral network, with each carbon atom bonded to three other carbon atoms. The tetrahedral structure of the network bonds does not leave any seams along which the diamond can be broken, so a diamond behaves as one big molecule with no weaknesses.

(d) HBr and HCl are polar molecules. In liquid form, both substances are held together by dipole-dipole interactions. These interactions are stronger for molecules with more electrons, so HBr has stronger intermolecular bonds and a higher boiling point.

HF has a higher boiling point than HCl because HF undergoes hydrogen bonding, while HCl does not; this causes HF to remain a liquid at higher temperatures than HCl, although HF is a polar molecule with fewer electrons than HCl.



# 5

## Stoichiometry and Chemical Equations

### **HOW OFTEN DO STOICHIOMETRY AND CHEMICAL EQUATIONS APPEAR ON THE EXAM?**

In the multiple-choice section, this topic appears in about 7 out of 75 questions.

In the free-response section, this topic appears almost every year.

## SOME MATH

### SIGNIFICANT FIGURES

When you do calculations on the AP Chemistry Exam, you'll be expected to present your answers with the proper number of significant figures, so let's review the rules.

- Nonzero digits and zeros between nonzero digits *are* significant.  
245      3 significant figures  
7.907    4 significant figures  
907.08   5 significant figures
- Zeros to the *left* of the first nonzero digit in a number are *not* significant.  
0.005    1 significant figure  
0.0709   3 significant figures
- Zeros at the *end of a number* to the *right* of the decimal point *are* significant.  
12.000   5 significant figures  
0.080    2 significant figures  
1.0      2 significant figures
- Zeros at the *end of a number greater than 1* are *not* significant, unless their significance is indicated by the presence of a decimal point.  
1,200    2 significant figures  
1,200.   4 significant figures  
10       1 significant figure  
10.      2 significant figures
- The coefficients of a balanced equation and numbers obtained by counting objects are infinitely significant. So if a balanced equation calls for 3 moles of carbon, we can think of it as 3.00 moles of carbon.
- When multiplying and dividing, the result should have the same number of significant figures as the number in the calculation with the smallest number of significant figures.  
 $0.352 \times 0.90876 = 0.320$   
 $864 \times 12 = 1.0 \times 10^4$   
 $7 \div 0.567 = 10$
- When adding and subtracting, the result should have the same number of decimal places as the number in the calculation with the smallest number of decimal places.  
 $26 + 45.88 + 0.09534 = 72$   
 $780 + 35 + 4 = 819$

The whole point is that the result of a calculation cannot be more accurate than the least accurate number in the calculation.

## LOGARITHMS

Let's review some basic facts about logarithms.

$$\text{If } 10^x = y, \text{ then } \log y = x$$

$$\text{If } e^x = y, \text{ then } \ln y = x$$

$$e = 2.7183$$

$$\ln y = 2.303 \log y$$

$$\log(ab) = \log a + \log b$$

$$\log\left(\frac{a}{b}\right) = \log a - \log b$$

## MOLES

The mole (**Avogadro's number**) is the most important number in chemistry, serving as a bridge that connects all the different quantities that you'll come across in chemical calculations. The coefficients in chemical reactions tell you about the reactants and products in terms of moles, so most of the stoichiometry questions you'll see on the test will be exercises in converting between moles and grams, liters, molarities, and other units.

### MOLES AND MOLECULES

The definition of Avogadro's number gives you the information you need to convert between moles and individual molecules and atoms.

$$1 \text{ mole} = 6.022 \times 10^{23} \text{ molecules}$$

$$\text{Moles} = \frac{\text{molecules}}{(6.022 \times 10^{23})}$$

### MOLES AND GRAMS

Moles and grams can be related by using the atomic weights given in the periodic table. Atomic weights on the periodic table are given in terms of atomic mass units (amu), but an amu is the same as a gram per mole, so if 1 carbon atom weighs 12 amu, then 1 mole of carbon atoms weighs 12 grams.

You can use the relationship between amu and g/mol to convert between grams and moles by using the following equation:

$$\text{Moles} = \frac{\text{grams}}{\text{molar mass}}$$

## MOLES AND GASES

We'll talk more about the ideal gas equation in Chapter 6, but for now, you should know that you can use it to calculate the number of moles of a gas if you know some of the gas's physical properties. All you need to remember at this point is that in the equation  $PV = nRT$ ,  $n$  stands for moles of gas.

$$\text{Moles} = \frac{PV}{RT}$$

$P$  = pressure (atm)

$V$  = volume (L)

$T$  = temperature (K)

$R$  = the gas constant, 0.0821 L-atm/mol-K

The equation above gives the general rule for finding the number of moles of a gas. Many gas problems will take place at STP, or standard temperature and pressure, where  $P = 1$  atmosphere and  $T = 273$  K. At STP, the situation is much simpler and you can convert directly between the volume of a gas and the number of moles. That's because at STP, one mole of gas always occupies 22.4 liters.

$$\text{Moles} = \frac{\text{liters}}{(22.4 \text{ L/mol})}$$

## MOLES AND SOLUTIONS

We'll talk more about molarity and molality in Chapter 9, but for now you should realize that you can use the equations that define these common measures of concentration to find the number of moles of solute in a solution. Just rearrange the equations to isolate moles of solute.

$$\text{Moles} = (\text{molarity})(\text{liters of solution})$$

$$\text{Moles} = (\text{molality})(\text{kilograms of solvent})$$

## PERCENT COMPOSITION

To solve many problems on the exam, you will need to use percent composition, or mass percents. Percent composition is the percent by mass of each element that makes up a compound. It is calculated by dividing the mass of each element or component in a compound by the total molar mass for the substance.

## EMPIRICAL AND MOLECULAR FORMULAS

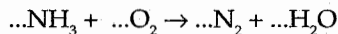
You will also need to know how to determine the empirical and molecular formula of a compound given masses or mass percents of the components of that compound. Remember that the empirical formula represents the simplest ratio of one element to another in a compound (e.g.  $\text{C}_6\text{H}_{12}\text{O}_6$ ), while the molecular formula represents the actual formula for the substance (e.g.  $\text{C}_{12}\text{H}_{24}\text{O}_{12}$ ).

## CHEMICAL EQUATIONS

### BALANCING CHEMICAL EQUATIONS

Normally, balancing a chemical equation is a trial-and-error process. You start with the most complicated-looking compound in the equation and work from there. There is, however, an old Princeton Review SAT trick that you may want to try if you see a balancing equation question on the multiple-choice section. The trick is called **backsolving**.

It works like this: To make a balancing equation question work in a multiple-choice format, one of the answer choices is the correct coefficient for one of the species in the reaction. So instead of starting blind in the trial-and-error process, you can insert the answer choices one by one to see which one works. You probably won't have to try all five, and if you start in the middle and the number doesn't work, it might be obviously too small or large, eliminating other choices before you have to try them. Let's try it.



1. If the equation above were balanced with lowest whole number coefficients, the coefficient for  $\text{NH}_3$  would be
  - (A) 1
  - (B) 2
  - (C) 3
  - (D) 4
  - (E) 5

Start at (C) because it's the middle number. If there are 3  $\text{NH}_3$ 's, then there can't be a whole number coefficient for  $\text{N}_2$ , so (C) is wrong, and so are the other odd number answers, (A) and (E).

Try (D).

If there are 4  $\text{NH}_3$ 's, then there must be 2  $\text{N}_2$ 's and 6  $\text{H}_2\text{O}$ 's.

If there are 6  $\text{H}_2\text{O}$ 's, then there must be 3  $\text{O}_2$ 's, and the equation is balanced with lowest whole number coefficients.

Backsolving is more efficient than the methods that you're accustomed to. If you use the answer choices that you're given, you streamline the trial-and-error process and allow yourself to use POE as you work on the problem.

### CHEMICAL EQUATIONS AND CALCULATIONS

Many of the stoichiometry problems on the test will be formatted in the following way: You will be given a balanced chemical equation and told that you have some number of grams (or liters of gas, or molar concentration, and so on) of reactant. Then you will be asked what number of grams (or liters of gas, or molar concentration, and so on) of products are generated.

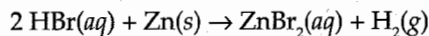
In these cases, follow this simple series of steps.

1. Convert whatever quantity you are given into moles.
2. If you are given information about two reactants, you may have to use the equation coefficients to determine which one is the limiting reagent. Remember, the limiting reagent is not necessarily the reactant that you have the least of; it is the reactant that runs out first.



- Use the balanced equation to determine how many moles of the desired product are generated.
- Convert moles of product to the desired unit.

Let's try one.



- A piece of solid zinc weighing 98 grams was added to a solution containing 324 grams of HBr. What is the volume of  $\text{H}_2$  produced at standard temperature and pressure if the reaction above runs to completion?

- 11 liters
- 22 liters
- 34 liters
- 45 liters
- 67 liters

- Convert whatever quantity you are given into moles.

$$\text{Moles of Zn} = \frac{\text{grams}}{\text{molar mass}} = \frac{(98 \text{ g})}{(65.4 \text{ g/mol})} = 1.5 \text{ mol}$$

$$\text{Moles of HBr} = \frac{\text{grams}}{\text{molar mass}} = \frac{(324 \text{ g})}{(80.9 \text{ g/mol})} = 4.0 \text{ mol}$$

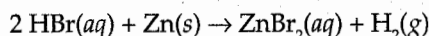
- Use the balanced equation to find the limiting reagent.  
From the balanced equation, 2 moles of HBr are used for every mole of Zn that reacts, so when 1.5 moles of Zn react, 3 moles of HBr are consumed, and there will be HBr left over when all of the Zn is gone. That makes Zn the limiting reagent.
- Use the balanced equation to determine how many moles of the desired product are generated.  
1 mole of  $\text{H}_2$  is produced for every mole of Zn consumed, so if 1.5 moles of Zn are consumed, then 1.5 moles of  $\text{H}_2$  are produced.
- Convert moles of product to the desired unit.

The  $\text{H}_2$  gas is at STP, so we can convert directly from moles to volume.

$$\text{Volume of H}_2 = (\text{moles})(22.4 \text{ L/mol}) = (1.5 \text{ mol})(22.4 \text{ L/mol}) = 33.6 \text{ L} \approx 34 \text{ L}$$

So (C) is correct.

Let's try another one using the same reaction.



3. A piece of solid zinc weighing 13.1 grams was placed in a container. A 0.10-molar solution of HBr was slowly added to the container until the zinc was completely dissolved. What was the volume of HBr solution required to completely dissolve the solid zinc?

- (A) 1.0 L
- (B) 2.0 L
- (C) 3.0 L
- (D) 4.0 L
- (E) 5.0 L

1. Convert whatever quantity you are given into moles.

$$\text{Moles of Zn} = \frac{\text{grams}}{\text{MW}} = \frac{(13.1 \text{ g})}{(65.4 \text{ g/mol})} = 0.200 \text{ mol}$$

2. Use the balanced equation to find the limiting reagent.
3. Use the balanced equation to determine how many moles of the desired product are generated.

In this case, we're using the balanced reaction to find out how much of one reactant is required to consume the other reactant. It's a slight variation on the process described in (2) and (3).

We can see from the balanced equation that it takes 2 moles of HBr to react completely with 1 mole of Zn, so it will take 0.400 moles of HBr to react completely with 0.200 moles of Zn.

4. Convert moles of product to the desired unit.

$$\text{Moles of HBr} = (\text{molarity})(\text{volume})$$

$$\text{Volume of HBr} = \frac{\text{moles}}{\text{molarity}} = \frac{(0.400 \text{ mol})}{(0.10 \text{ mol/L})} = 4.0 \text{ L}$$

So (D) is correct.

When you perform calculations, always include units. Including units in your calculations will help you (and the person scoring your test) keep track of what you are doing. Including units will also get you partial credit points on the free-response section.

# CHAPTER 5 QUESTIONS

## MULTIPLE-CHOICE QUESTIONS

### Questions 1–3

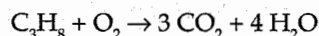
- (A) Moles
- (B) Liters
- (C) Grams
- (D) Atmospheres
- (E) Volts

1. One mole of solid zinc has a mass of 65.39 of these.
2. These units can be calculated by dividing a quantity by  $6.02 \times 10^{23}$ .
3. Four grams of helium gas occupy 22.4 of these at standard temperature and pressure.
4. What is the mass ratio of fluorine to boron in a boron trifluoride molecule?
  - (A) 1.8 to 1
  - (B) 3.0 to 1
  - (C) 3.5 to 1
  - (D) 5.3 to 1
  - (E) 6.0 to 1
5. A hydrocarbon sample with a mass of 6 grams underwent combustion, producing 11 grams of carbon dioxide. If all of the carbon initially present in the compound was converted to carbon dioxide, what was the percent of carbon, by mass, in the hydrocarbon sample?
  - (A) 25%
  - (B) 33%
  - (C) 50%
  - (D) 66%
  - (E) 75%
6. What is the mass of oxygen in 148 grams of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ )?
  - (A) 16 grams
  - (B) 24 grams
  - (C) 32 grams
  - (D) 48 grams
  - (E) 64 grams

7. An ion containing only oxygen and chlorine is 31% oxygen by mass. What is its empirical formula?

- (A)  $\text{ClO}^-$
- (B)  $\text{ClO}_2^-$
- (C)  $\text{ClO}_3^-$
- (D)  $\text{ClO}_4^-$
- (E)  $\text{Cl}_2\text{O}^-$

8. A sample of propane,  $\text{C}_3\text{H}_8$ , was completely burned in air at STP. The reaction occurred as shown below.



If 67.2 liters of  $\text{CO}_2$  were produced and all of the carbon in the  $\text{CO}_2$  came from the propane, what was the mass of the propane sample?

- (A) 11 grams
- (B) 22 grams
- (C) 33 grams
- (D) 44 grams
- (E) 55 grams

9. What is the percent composition by mass of the elements in the compound  $\text{NaNO}_3$ ?

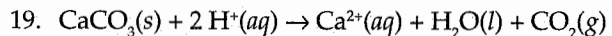
- (A) Na 20%, N 20%, O 60%
- (B) Na 23%, N 14%, O 48%
- (C) Na 23%, N 14%, O 63%
- (D) Na 27%, N 16%, O 57%
- (E) Na 36%, N 28%, O 36%

10.  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

A sample of pure  $\text{CaCO}_3$  was heated and decomposed according to the reaction given above. If 28 grams of  $\text{CaO}$  were produced by the reaction, what was the initial mass of  $\text{CaCO}_3$ ?

- (A) 14 grams
- (B) 25 grams
- (C) 42 grams
- (D) 50 grams
- (E) 84 grams

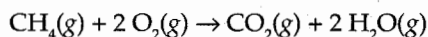
11. The composition of a typical glass used in bottles is 12.0%  $\text{Na}_2\text{O}$ , 12.0%  $\text{CaO}$ , and 76.0%  $\text{SiO}_2$ . Which of the following lists the three compounds in order of greatest to least number of moles present in a typical sample of bottle glass?
- (A)  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$   
 (B)  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$   
 (C)  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{CaO}$   
 (D)  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{SiO}_2$   
 (E)  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$
12. The concentration of sodium chloride in sea water is about 0.5 molar. How many grams of  $\text{NaCl}$  are present in 1 kg of sea water?
- (A) 30 grams  
 (B) 60 grams  
 (C) 100 grams  
 (D) 300 grams  
 (E) 600 grams
13. A sample of a hydrate of  $\text{CuSO}_4$  with a mass of 250 grams was heated until all the water was removed. The sample was then weighed and found to have a mass of 160 grams. What is the formula for the hydrate?
- (A)  $\text{CuSO}_4 \cdot 10 \text{H}_2\text{O}$   
 (B)  $\text{CuSO}_4 \cdot 7 \text{H}_2\text{O}$   
 (C)  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$   
 (D)  $\text{CuSO}_4 \cdot 2 \text{H}_2\text{O}$   
 (E)  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$
14. A compound containing only sulfur and oxygen is 50% sulfur by weight. What is the empirical formula for the compound?
- (A)  $\text{SO}$   
 (B)  $\text{SO}_2$   
 (C)  $\text{SO}_3$   
 (D)  $\text{S}_2\text{O}$   
 (E)  $\text{S}_3\text{O}$
15.  $2 \text{Na}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{NaOH}(aq) + \text{H}_2(g)$
- Elemental sodium reacts with water to form hydrogen gas as shown above. If a sample of sodium reacts completely to form 20 liters of hydrogen gas, measured at standard temperature and pressure, what was the mass of the sodium?
- (A) 5 grams  
 (B) 10 grams  
 (C) 20 grams  
 (D) 30 grams  
 (E) 40 grams
16.  $\text{ZnSO}_3(s) \rightarrow \text{ZnO}(s) + \text{SO}_2(g)$
- What is the STP volume of  $\text{SO}_2$  gas produced by the above reaction when 145 grams of  $\text{ZnSO}_3$  are consumed?
- (A) 23 liters  
 (B) 36 liters  
 (C) 45 liters  
 (D) 56 liters  
 (E) 90 liters
17.  $\dots\text{CN}^- + \dots\text{OH}^- \rightarrow \dots\text{CNO}^- + \dots\text{H}_2\text{O} + \dots e^-$
- When the half reaction above is balanced, what is the coefficient for  $\text{OH}^-$  if all the coefficients are reduced to the lowest whole number?
- (A) 1  
 (B) 2  
 (C) 3  
 (D) 4  
 (E) 5
18.  $\dots\text{MnO}_4^- + \dots\text{I}^- + \dots\text{H}_2\text{O} \rightarrow \dots\text{MnO}_2 + \dots\text{IO}_3^- + \dots\text{OH}^-$
- The oxidation-reduction reaction above is to be balanced with lowest whole number coefficients. What is the coefficient for  $\text{OH}^-$ ?
- (A) 1  
 (B) 2  
 (C) 3  
 (D) 4  
 (E) 5



If the reaction above took place at standard temperature and pressure and 150 grams of  $\text{CaCO}_3(s)$  were consumed, what was the volume of  $\text{CO}_2(g)$  produced at STP?

- (A) 11 L
- (B) 22 L
- (C) 34 L
- (D) 45 L
- (E) 56 L

20. A gaseous mixture at  $25^\circ\text{C}$  contained 1 mole of  $\text{CH}_4$  and 2 moles of  $\text{O}_2$  and the pressure was measured at 2 atm. The gases then underwent the reaction shown below.



What was the pressure in the container after the reaction had gone to completion and the temperature was allowed to return to  $25^\circ\text{C}$ ?

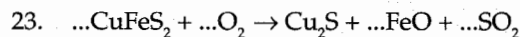
- (A) 1 atm
- (B) 2 atm
- (C) 3 atm
- (D) 4 atm
- (E) 5 atm

21. A sample of a hydrate of  $\text{BaCl}_2$  with a mass of 61 grams was heated until all the water was removed. The sample was then weighed and found to have a mass of 52 grams. What is the formula for the hydrate?

- (A)  $\text{BaCl}_2 \cdot 5 \text{H}_2\text{O}$
- (B)  $\text{BaCl}_2 \cdot 4 \text{H}_2\text{O}$
- (C)  $\text{BaCl}_2 \cdot 3 \text{H}_2\text{O}$
- (D)  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$
- (E)  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$

22. A hydrocarbon was found to be 20% hydrogen by weight. If 1 mole of the hydrocarbon has a mass of 30 grams, what is its molecular formula?

- (A) CH
- (B)  $\text{CH}_2$
- (C)  $\text{CH}_3$
- (D)  $\text{C}_2\text{H}_4$
- (E)  $\text{C}_2\text{H}_6$



When the half-reaction above is balanced, what is the coefficient for  $\text{O}_2$  if all the coefficients are reduced to the lowest whole number?

- (A) 2
- (B) 3
- (C) 4
- (D) 6
- (E) 8

24. A hydrocarbon contains 75% carbon by mass. What is the empirical formula for the compound?

- (A)  $\text{CH}_2$
- (B)  $\text{CH}_3$
- (C)  $\text{CH}_4$
- (D)  $\text{C}_2\text{H}_5$
- (E)  $\text{C}_3\text{H}_8$

25. When chlorine gas is combined with fluorine gas, a compound is formed that is 38% chlorine and 62% fluorine. What is the empirical formula of the compound?

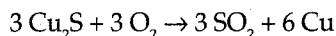
- (A) ClF
- (B)  $\text{ClF}_2$
- (C)  $\text{ClF}_3$
- (D)  $\text{ClF}_5$
- (E)  $\text{ClF}_7$

## PROBLEMS

1. A 10.0 gram sample containing calcium carbonate and an inert material was placed in excess hydrochloric acid. A reaction occurred producing calcium chloride, water, and carbon dioxide.
  - (a) Write the balanced equation for the reaction.
  - (b) When the reaction was complete, 900 milliliters of carbon dioxide gas were collected at 740 mmHg and 30°C. How many moles of calcium carbonate were consumed in the reaction?
  - (c) If all of the calcium carbonate initially present in the sample was consumed in the reaction, what percent by mass of the sample was due to calcium carbonate?
  - (d) If the inert material was silicon dioxide, what was the molar ratio of calcium carbonate to silicon dioxide in the original sample?
2. A gaseous hydrocarbon sample is completely burned in air, producing 1.80 liters of carbon dioxide at standard temperature and pressure and 2.16 grams of water.
  - (a) What is the empirical formula for the hydrocarbon?
  - (b) What was the mass of the hydrocarbon consumed?
  - (c) The hydrocarbon was initially contained in a closed 1.00 liter vessel at a temperature of 32°C and a pressure of 760 millimeters of mercury. What is the molecular formula of the hydrocarbon?
  - (d) Write the balanced equation for the combustion of the hydrocarbon.
3. The table below shows three common forms of copper ore.

Ore #	Empirical Formula	Percent by Weight		
		Copper	Sulfur	Iron
1	Cu <sub>2</sub> S	?	?	0
2	?	34.6	34.9	30.5
3	?	55.6	28.1	16.3

- (a) What is the percent by weight of copper in Cu<sub>2</sub>S?
- (b) What is the empirical formula of ore #2?
- (c) If a sample of ore #3 contains 11.0 grams of iron, how many grams of sulfur does it contain?
- (d) Cu can be extracted from Cu<sub>2</sub>S by the following process:



If 3.84 grams of O<sub>2</sub> are consumed in the process, how many grams of Cu are produced?

4.  $2 \text{Mg}(s) + 2 \text{CuSO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow 2 \text{MgSO}_4(aq) + \text{Cu}_2\text{O}(s) + \text{H}_2(g)$
- (a) If 1.46 grams of  $\text{Mg}(s)$  are added to 500 milliliters of a 0.200-molar solution of  $\text{CuSO}_4$ , what is the maximum molar yield of  $\text{H}_2(g)$ ?
- (b) When all of the limiting reagent has been consumed in (a), how many moles of the other reactant (not water) remain?
- (c) What is the mass of the  $\text{Cu}_2\text{O}$  produced in (a)?
- (d) What is the value of  $[\text{Mg}^{2+}]$  in the solution at the end of the experiment? (Assume that the volume of the solution remains unchanged.)

## CHAPTER 5 ANSWERS AND EXPLANATIONS

### MULTIPLE-CHOICE QUESTIONS

- C The units for atomic weight are grams/mole.
- A A mole is equal to  $6.02 \times 10^{23}$ .
- B Four grams of helium is a mole. A mole of gas occupies 22.4 liters at STP.
- D The empirical formula of boron trifluoride is  $\text{BF}_3$ .

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of boron} = (1 \text{ mol})(10.8 \text{ g/mol}) = 10.8 \text{ g}$$

$$\text{Grams of fluorine} = (3 \text{ mol})(19.0 \text{ g/mol}) = 57.0 \text{ g}$$

So the mass ratio is about 57 to 11, which is about 5.3 to 1.

5. C Moles =  $\frac{\text{grams}}{\text{MW}}$

$$\text{Moles of CO}_2 = \frac{(11 \text{ g})}{(44 \text{ g/mol})} = \frac{1}{4} \text{ mol}$$

If  $\frac{1}{4}$  mole of  $\text{CO}_2$  was produced, then  $\frac{1}{4}$  mole of C was consumed.

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of carbon} = \left(\frac{1}{4} \text{ mol}\right)(12 \text{ g/mol}) = 3 \text{ g}$$

$$\text{So the percent by mass of carbon was } \frac{3}{6} = \frac{1}{2} = 50\%$$

6. E Moles =  $\frac{\text{grams}}{\text{MW}}$

Moles of calcium hydroxide =  $\frac{(148 \text{ g})}{(74 \text{ g/mol})} = 2 \text{ moles}$

Every mole of  $\text{Ca(OH)}_2$  contains 2 moles of oxygen.

So there are  $(2)(2) = 4$  moles of oxygen

Grams = (moles)(MW)

So grams of oxygen =  $(4 \text{ mol})(16 \text{ g/mol}) = 64 \text{ grams}$

7. A Assume that we have 100 grams of the compound. That means that we have 31 grams of oxygen and 69 grams of chlorine.

Moles =  $\frac{\text{grams}}{\text{MW}}$

Moles of oxygen =  $\frac{(31 \text{ g})}{(16 \text{ g/mol})} = \text{slightly less than 2 mol}$

Moles of chlorine =  $\frac{(69 \text{ g})}{(35.5 \text{ g/mol})} = \text{slightly less than 2 mol}$

So the ratio of chlorine to oxygen is 1 to 1, and the empirical formula is  $\text{ClO}$ .

8. D Moles =  $\frac{\text{liters}}{(22.4 \text{ L/mol})}$

Moles of  $\text{CO}_2$  =  $\frac{67.2 \text{ L}}{(22.4 \text{ L/mol})} = 3 \text{ mol}$

According to the balanced equation, if 3 moles of  $\text{CO}_2$  were produced, 1 mole of  $\text{C}_3\text{H}_8$  was consumed.

Grams = (moles)(MW)

So grams of  $\text{C}_3\text{H}_8$  =  $(1 \text{ mol})(44 \text{ g/mol}) = 44 \text{ grams}$

9. D The molecular weight of  $\text{NaNO}_3$  is:  $(23) + (14) + (3)(16) = 85 \text{ g/mol}$

We can get the answer using pretty rough estimates.

The percent by mass of Na =  $\frac{(23)}{(85)} = \text{between } 25\% \left(\frac{1}{4}\right) \text{ and } 33\% \left(\frac{1}{3}\right)$

The percent by mass of N =  $\frac{(14)}{(85)} = \text{between } 10\% \left(\frac{1}{10}\right) \text{ and } 20\% \left(\frac{1}{5}\right)$

The percent by mass of O =  $\frac{(48)}{(85)} = \text{between } 50\% \left(\frac{1}{2}\right) \text{ and } 60\% \left(\frac{3}{5}\right)$

You can use POE to get choice (D).



10. D  $\text{Moles} = \frac{\text{grams}}{\text{MW}}$

$$\text{Moles of CaO} = \frac{(28 \text{ g})}{(56 \text{ g/mol})} = 0.50 \text{ mol}$$

From the balanced equation, if 0.50 mol of CaO was produced, then 0.50 mol of  $\text{CaCO}_3$  was consumed.

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of CaCO}_3 = (0.50 \text{ mol})(100 \text{ g/mol}) = 50 \text{ g}$$

11. A The molecular weights of the three compounds are as follows:

$$\text{Na}_2\text{O} - 62 \text{ g/mol}$$

$$\text{CaO} - 56 \text{ g/mol}$$

$$\text{SiO}_2 - 60 \text{ g/mol}$$

Because the molecular weights are close together, we can safely say that  $\text{SiO}_2$ , which makes up a much greater percentage by mass of bottle glass than the other two, will have far and away the most moles in a sample. So the answer must be (A) or (B).

Remember,  $(\text{grams}) = (\text{moles})(\text{MW})$ . Because a sample of bottle glass will have the same number of grams of  $\text{Na}_2\text{O}$  and  $\text{CaO}$ , the one with the smaller molecular weight must have the greater number of moles. So there must be more moles of  $\text{CaO}$  than  $\text{Na}_2\text{O}$ .

12. A First, you have to remember that 1 liter of water has a mass of 1 kg.

$$\text{Moles} = (\text{molarity})(\text{liters})$$

$$\text{Moles of NaCl} = (0.5 \text{ M})(1 \text{ L}) = 0.5 \text{ moles}$$

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of NaCl} = (0.5 \text{ mol})(59 \text{ g/mol}) = 30 \text{ g}$$

13. C The molecular weight of  $\text{CuSO}_4$  is 160 g/mol, so we have only 1 mole of the hydrate. The lost mass was due to water, so 1 mole of the hydrate must have contained 90 grams of  $\text{H}_2\text{O}$ .

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of water} = \frac{(90 \text{ g})}{(18 \text{ g/mol})} = 5 \text{ moles}$$

So if 1 mole of hydrate contains 5 moles of  $\text{H}_2\text{O}$ , then the formula for the hydrate must be  $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ .

14. B You might be able to do this one in your head just from knowing that sulfur's molecular weight is twice as large as oxygen's. If not, let's say you have 100 grams of the compound. So you have 50 grams of sulfur and 50 grams of oxygen.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of sulfur} = \frac{(50 \text{ g})}{(32 \text{ g/mol})} = \text{a little more than } 1.5$$

$$\text{Moles of oxygen} = \frac{(50 \text{ g})}{(16 \text{ g/mol})} = \text{a little more than } 3$$

The molar ratio of O to S is 2 to 1, so the empirical formula must be  $\text{SO}_2$ .

15. E  $\text{Moles} = \frac{\text{liters}}{(22.4 \text{ L/mol})}$

$$\text{Moles of H}_2 = \frac{(20 \text{ L})}{(22.4 \text{ L/mol})} = \text{about } 0.9 \text{ moles}$$

From the balanced equation, for every mole of  $\text{H}_2$  produced, 2 moles of Na are consumed, so 1.8 moles of Na are consumed.

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of Na} = (1.8 \text{ mol})(23 \text{ g/mol}) = \text{about } 40 \text{ grams}$$

You don't really have to do the math, because you can get the answer by using rough estimates.

16. A  $\text{Moles} = \frac{\text{grams}}{\text{MW}}$

$$\text{Moles of ZnSO}_3 = \frac{(145 \text{ g})}{(145 \text{ g/mol})} = 1 \text{ mole}$$

From the balanced equation, when 1 mole of  $\text{ZnSO}_3$  is consumed, 1 mole of  $\text{SO}_2$  will be produced. So about 1 mole of  $\text{SO}_2$  is produced.

$$\text{Liters} = (\text{moles})(22.4 \text{ L/mol})$$

$$\text{Liters of SO}_2 = (\text{about } 1 \text{ mol})(22.4 \text{ L}) = 23 \text{ liters}$$

17. B Use trial and error or backsolve.

Start with (C). If there are 3  $\text{OH}^-$ , there can't be a whole number coefficient for  $\text{H}_2\text{O}$ , so (C) is wrong. You should also be able to see that the answer can't be an odd number, so (A) and (E) are also wrong.

Try (D). If there are 4  $\text{OH}^-$ , then there are 2  $\text{H}_2\text{O}$ .

That leaves 2 more Os on the product side, so there must be 2  $\text{CNO}^-$ .

If there are 2  $\text{CNO}^-$  then there are 2  $\text{CN}^-$ .

These are all whole numbers, but they are not the lowest whole numbers, so (D) is wrong.

If we divide all the coefficients by 2, we get the lowest whole number coefficients. That leaves us with 2  $\text{OH}^-$ , which is choice (B).

By the way,  $\text{N}^{5-}$  (in  $\text{CN}^-$ ) is oxidized to  $\text{N}^{3-}$  (in  $\text{CNO}^-$ ), so there are 2  $e^-$ .

18. B Use trial and error or backsolve.

Start at (C).

If there are 3  $\text{OH}^-$ , there can't be a whole number coefficient for  $\text{H}_2\text{O}$ , so (C) is wrong. Also, the answer can't be an odd number, so (A) and (E) are wrong.

Notice that you don't have to test both of the remaining answers. If the one you pick works, you're done. If the one you pick doesn't work, then the one that's left must be correct. With a choice of only two answers, pick the one that looks easier to work with.

Try (B) because it's smaller. If there are 2  $\text{OH}^-$ , then there is 1  $\text{H}_2\text{O}$ . If you put in 1 for  $\text{I}^-$  and  $\text{IO}_3^-$  and 2 for  $\text{MnO}_4^-$  and  $\text{MnO}_2$ , the equation is balanced. So (B) is correct.

19. C  $\text{Moles} = \frac{\text{grams}}{\text{MW}}$

$$\text{Moles of CaCO}_3 = \frac{(150 \text{ g})}{(100 \text{ g/mol})} = 1.5 \text{ moles}$$

From the balanced equation, for every mole of  $\text{CaCO}_3$  consumed, one mole of  $\text{CO}_2$  is produced.

So 1.5 moles of  $\text{CO}_2$  are produced.

At STP, volume of gas = (moles)(22.4 L)

So volume of  $\text{CO}_2 = (1.5)(22.4) = 34 \text{ L}$

20. B All of the reactants are consumed in the reaction and the temperature doesn't change, so the pressure will only change if the number of moles of gas changes over the course of the reaction. The number of moles of gas (3 moles) doesn't change in the balanced equation, so the pressure will remain the same (2 atm) at the end of the reaction as at the beginning.

21. D The molecular weight of  $\text{BaCl}_2$  is 208 g/mol, so we can figure out how many moles of the hydrate we have.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of hydrate} = \frac{(52 \text{ g})}{(208 \text{ g/mol})} = \frac{1}{4} \text{ mole}$$

The lost mass was due to water, so 1 mole of the hydrate must have contained 9 grams of  $\text{H}_2\text{O}$ .

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of water} = \frac{(9 \text{ g})}{(18 \text{ g/mol})} = \frac{1}{2} \text{ moles}$$

So if  $\frac{1}{4}$  mole of hydrate contains  $\frac{1}{2}$  mole of  $\text{H}_2\text{O}$ , there must be 2 moles of  $\text{H}_2\text{O}$  for every mole of hydrate, and the formula for the hydrate must be  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ .

22. E Let's say we have 100 grams of the compound.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{So moles of carbon} = \frac{(80 \text{ g})}{(12 \text{ g/mol})} = 6.7 \text{ moles}$$

$$\text{and moles of hydrogen} = \frac{(20 \text{ g})}{(1 \text{ g/mol})} = 20 \text{ moles}$$

According to our rough calculation, there are about three times as many moles of hydrogen in the compound as there are moles of carbon, so the empirical formula is  $\text{CH}_3$ .

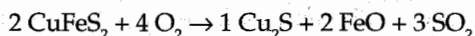
The molar mass for the empirical formula is 15 g/mol, so we need to double the moles of each element to get a compound with a molar mass of 30 g/mol. That makes the molecular formula of the compound  $\text{C}_2\text{H}_6$ .

23. C Backsolving doesn't work so well in this case because there are two different compounds that contain oxygen on the right side of the equation, which makes the process kind of confusing. Instead, let's just try plugging in values for the most complicated compound in the equation,  $\text{CuFeS}_2$ .

What if there's 1  $\text{CuFeS}_2$ ? That's impossible because there are 2 Cu's on the right.

What if there are 2  $\text{CuFeS}_2$ 's? Then the right side has 1  $\text{Cu}_2\text{S}$  to balance the Cu and 2  $\text{FeO}$  to balance the Fe. The right side must also have 3  $\text{SO}_2$  to balance the S.

Now there are 8 O's on the right, so there must be 4  $\text{O}_2$ 's on the left, and the equation is balanced.



24. C Let's say we have 100 grams of the compound.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{So moles of carbon} = \frac{(75 \text{ g})}{(12 \text{ g/mol})} = 6 \text{ moles}$$

$$\text{and moles of hydrogen} = \frac{(25 \text{ g})}{(1 \text{ g/mol})} = 25 \text{ moles}$$

According to our rough calculation, there are about four times as many moles of hydrogen in the compound as there are moles of carbon, so the empirical formula is  $\text{CH}_4$ .

25. C Let's say we have 100 grams of the compound.

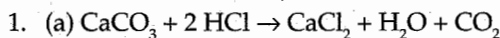
$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of chlorine} = \frac{(38 \text{ g})}{(35.5 \text{ g/mol})} = \text{about 1 mole}$$

$$\text{Moles of fluorine} = \frac{(62 \text{ g})}{(19 \text{ g/mol})} = \text{about 3 moles}$$

According to our rough calculation, there are about three times as many moles of fluorine in the compound as there are moles of chlorine, so the empirical formula is  $\text{ClF}_3$ .

## PROBLEMS



(b) Use the ideal gas equation to find the number of moles of  $\text{CO}_2$  produced. Remember to convert to the proper units.

$$n = \frac{PV}{RT} = \frac{\left(\frac{740}{760} \text{ atm}\right)(0.900 \text{ L})}{(0.0821)(303 \text{ K})} = 0.035 \text{ moles}$$

From the balanced equation, for every mole of  $\text{CO}_2$  produced, 1 mole of  $\text{CaCO}_3$  was consumed.

So 0.035 moles of  $\text{CaCO}_3$  were consumed.

(c) We know the number of moles of  $\text{CaCO}_3$ , so we can find the mass.

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of CaCO}_3 = (0.035 \text{ mol})(100 \text{ g/mol}) = 3.50 \text{ grams}$$

$$\text{Percent by mass} = \frac{\text{mass of CaCO}_3}{\text{mass of sample}} \times 100 = \frac{(3.50 \text{ g})}{(10.0 \text{ g})} \times 100 = 35\%$$

(d) Mass of  $\text{SiO}_2 = 10.0 \text{ g} - 3.5 \text{ g} = 6.5 \text{ g}$

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of SiO}_2 = \frac{(6.5 \text{ g})}{(60 \text{ g/mol})} = 0.11 \text{ mol}$$

$$\text{Molar ratio} = \frac{\text{moles of CaCO}_3}{\text{moles of SiO}_2} = \frac{(0.035)}{(0.11)} = 0.32$$

2. (a) All of the hydrogen in the water and all of the carbon in the carbon dioxide must have come from the hydrocarbon.

$$\text{Moles of H}_2\text{O} = \frac{(2.16 \text{ g})}{(18.0 \text{ g/mol})} = 0.120 \text{ moles}$$

Every mole of water contains 2 moles of hydrogen, so there are 0.240 moles of hydrogen.

$$\text{Moles of CO}_2 = \frac{(1.80 \text{ L})}{(22.4 \text{ L/mol})} = 0.080 \text{ moles}$$

Every mole of  $\text{CO}_2$  contains 1 mole of carbon, so there are 0.080 moles of carbon.

There are three times as many moles of hydrogen as there are moles of carbon, so the empirical formula of the hydrocarbon is  $\text{CH}_3$ .

(b) In (a), we found the number of moles of hydrogen and carbon consumed, so we can find the mass of the hydrocarbon.

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of H} = (0.240 \text{ mol})(1.01 \text{ g/mol}) = 0.242 \text{ g}$$

$$\text{Grams of C} = (0.080 \text{ mol})(12.01 \text{ g/mol}) = 0.961 \text{ g}$$

$$\text{Grams of hydrocarbon} = (0.242) + (0.961) = 1.203 \text{ g}$$

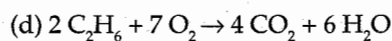
(c) First let's find the number of moles of hydrocarbon from the ideal gas law. Don't forget to convert to the appropriate units (760 mmHg = 1 atm, 32°C = 305 K).

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{(0.0821)(305 \text{ K})} = 0.040 \text{ moles}$$

Now we can use the mass we found in (b) to find the molecular weight of the hydrocarbon.

$$\text{MW} = \frac{\text{grams}}{\text{moles}} = \frac{(1.203 \text{ g})}{(0.040 \text{ mol})} = 30.1 \text{ g/mole}$$

CH<sub>3</sub> would have a molecular weight of 15, so we can just double the empirical formula to get the molecular formula, which is C<sub>2</sub>H<sub>6</sub>.



3. (a) First find the molecular weight of Cu<sub>2</sub>S.

$$\begin{aligned} \text{MW of Cu}_2\text{S} &= (2)(63.6) + (1)(32.1) = 159.3\% \text{ by mass of Cu} = \frac{\text{mass of Cu}}{\text{mass of Cu}_2\text{S}} \times 100 \\ &= \frac{(2)(63.6)}{(159.3)} \times 100 = 79.8\% \end{aligned}$$

(b) Assume that we have 100 grams of ore #2. So we have 34.6 g of Cu, 30.5 g of Fe, and 34.9 g of S. To get the empirical formula, we need to find the number of moles of each element.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of Cu} = \frac{(34.6 \text{ g})}{(63.6 \text{ g/mol})} = 0.544 \text{ moles of Cu}$$

$$\text{Moles of Fe} = \frac{(30.5 \text{ g})}{(55.9 \text{ g/mol})} = 0.546 \text{ moles of Fe}$$

$$\text{Moles of S} = \frac{(34.9 \text{ g})}{(32.1 \text{ g/mol})} = 1.09 \text{ moles of S}$$

So the molar ratio of Cu:Fe:S is 1:1:2 and the empirical formula for ore #2 is CuFeS<sub>2</sub>.

(c) You can use the ratio of the percents by weight.

$$\text{Mass of S} = \frac{\% \text{ by mass of S}}{\% \text{ by mass of Fe}} \times (\text{mass of Fe}) = \frac{(28.1\%)}{(16.3\%)} (11.0 \text{ g}) = 19.0 \text{ g}$$

(d) First find the moles of O<sub>2</sub> consumed.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of O}_2 = \frac{(3.84 \text{ g})}{(32.0 \text{ g/mol})} = 0.120 \text{ moles}$$

From the balanced equation, for every 3 moles of O<sub>2</sub> consumed, 6 moles of Cu are produced, so the number of moles of Cu produced will be twice the number of moles of O<sub>2</sub> consumed. So 0.240 moles of Cu are produced.

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of Cu} = (0.240 \text{ mol})(63.6 \text{ g/mol}) = 15.3 \text{ grams}$$

4. (a) We need to find the limiting reagent. There's plenty of water, so it must be one of the other two reactants.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of Mg} = \frac{(1.46 \text{ g})}{(24.3 \text{ g/mol})} = 0.060 \text{ moles}$$

$$\text{Moles} = (\text{molarity})(\text{volume})$$

$$\text{Moles of CuSO}_4 = (0.200 \text{ M})(0.500 \text{ L}) = 0.100 \text{ moles}$$

From the balanced equation, Mg and CuSO<sub>4</sub> are consumed in a 1:1 ratio, so we'll run out of Mg first. Mg is the limiting reagent, and we'll use it to find the yield of H<sub>2</sub>.

From the balanced equation, 1 mole of H<sub>2</sub> is produced for every 2 moles of Mg consumed, so the number of moles of H<sub>2</sub> produced will be half the number of moles of Mg consumed.

$$\text{Moles of H}_2 = \frac{1}{2} (0.060 \text{ mol}) = 0.030 \text{ moles}$$

(b) Mg is the limiting reagent, so some CuSO<sub>4</sub> will remain. From the balanced equation, Mg and CuSO<sub>4</sub> are consumed in a 1:1 ratio, so when 0.060 moles of Mg are consumed, 0.060 moles of CuSO<sub>4</sub> are also consumed.

$$\text{Moles of CuSO}_4 \text{ remaining} = (0.100 \text{ mol}) - (0.060 \text{ mol}) = 0.040 \text{ moles}$$

(c) From the balanced equation, 1 mole of Cu<sub>2</sub>O is produced for every 2 moles of Mg consumed, so the number of moles of Cu<sub>2</sub>O produced will be half the number of moles of Mg consumed.

$$\text{Moles of Cu}_2\text{O} = \frac{1}{2} (0.060 \text{ mol}) = 0.030 \text{ moles}$$

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of Cu}_2\text{O} = (0.030 \text{ mol})(143 \text{ g/mol}) = 4.29 \text{ grams}$$

(d) All of the Mg consumed ends up as Mg<sup>2+</sup> ions in the solution.

$$\text{Molarity} = \frac{\text{moles}}{\text{liters}}$$

$$[\text{Mg}^{2+}] = \frac{(0.060 \text{ mol})}{(0.500 \text{ L})} = 0.120 \text{ M}$$

# 6

## Gases

### **HOW OFTEN DO GASES APPEAR ON THE EXAM?**

In the multiple-choice section, this topic appears in about 5 out of 75 questions. In the free-response section, this topic appears almost every year.

### **STANDARD TEMPERATURE AND PRESSURE (STP)**

You should be familiar with standard temperature and pressure (STP), which comes up fairly often in problems involving gases.

At STP: Pressure = 1 atmosphere = 760 millimeters of mercury (mmHg)

Temperature =  $0^{\circ}\text{C}$  = 273 K

At STP, 1 mole of gas occupies 22.4 liters



## KINETIC MOLECULAR THEORY

Most of the gas problems you will see on the test will assume that gases behave in what is called an ideal manner. For ideal gases, the following assumptions can be made:

- The kinetic energy of an ideal gas is directly proportional to its absolute temperature:  
The greater the temperature, the greater the average kinetic energy of the gas molecules.

### The Total Kinetic Energy of a Gas Sample

$$KE = \frac{3}{2}nRT$$

$R$  = the gas constant; 8.31 joules/mol-K  
 $T$  = absolute temperature (K)  
 $n$  = number of moles (mol)

### The Average Kinetic Energy of a Single Gas Molecule

$$KE = \frac{1}{2}mv^2$$

$m$  = mass of the molecule (kg)  
 $v$  = speed of the molecule (meters/sec)  
 $KE$  is measured in joules

- If several different gases are present in a sample at a given temperature, all the gases will have the same average kinetic energy. That is, the average kinetic energy of a gas depends only on the absolute temperature, not on the identity of the gas.
- The volume of an ideal gas particle is insignificant when compared with the volume in which the gas is contained.
- There are no forces of attraction between the gas molecules in an ideal gas.
- Gas molecules are in constant motion, colliding with one another and with the walls of their container.

## THE IDEAL GAS EQUATION

You can use the ideal gas equation to calculate any of the four variables relating to the gas, provided that you already know the other three.

### The Ideal Gas Equation

$$PV = nRT$$

$P$  = the pressure of the gas (atm)  
 $V$  = the volume of the gas (L)  
 $n$  = the number of moles of gas  
 $T$  = the absolute temperature of the gas (K)  
 $R$  = the gas constant, 0.0821 L-atm/mol-K

You can also manipulate the ideal gas equation to figure out how changes in each of its variables affect the other variables.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$P$  = the pressure of the gas (atm)

$V$  = the volume of the gas (L)

$T$  = the absolute temperature of the gas (K)

You should be comfortable with the following simple relationships:

- If the volume is constant: As pressure increases, temperature increases; as temperature increases, pressure increases.
- If the temperature is constant: As pressure increases, volume decreases; as volume increases, pressure decreases. That's Boyle's law.
- If the pressure is constant: As temperature increases, volume increases; as volume increases, temperature increases. That's Charles's law.

## DALTON'S LAW

Dalton's law states that the total pressure of a mixture of gases is just the sum of all the partial pressures of the individual gases in the mixture.

### Dalton's Law

$$P_{\text{total}} = P_a + P_b + P_c + \dots$$

You should also note that the partial pressure of a gas is directly proportional to the number of moles of that gas present in the mixture. So if 25 percent of the gas in a mixture is helium, then the partial pressure due to helium will be 25 percent of the total pressure.

### Partial Pressure

$$P_a = (P_{\text{total}})(X_a)$$

$$X_a = \frac{\text{moles of gas A}}{\text{total moles of gas}}$$

## GRAHAM'S LAW

Part of the first assumption of kinetic molecular theory was that all gases at the same temperature have the same average kinetic energy. Knowing this, we can find the average speed of a gas molecule at a given temperature.

$$u_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

$u_{\text{rms}}$  = average speed of a gas molecule (meters/sec)

$T$  = absolute temperature (K)

$m$  = mass of the gas molecule (kg)

$M$  = molecular weight of the gas (kg/mol)

$k$  = Boltzmann's constant,  $1.38 \times 10^{-23}$  joule/K

$R$  = the gas constant, 8.31 joules/mol-K

By the way, you may have noticed that Boltzmann's constant,  $k$ , and the gas constant,  $R$ , differ only by a factor of Avogadro's number,  $N_A$ , the number of molecules in a mole. That is,  $R = kN_A$ .

Knowing that the average kinetic energy of a gas molecule is dependent only on the temperature, we can compare the average speeds (and the rates of effusion) of two different gases in a sample. The equation used to do this is called Graham's law.

### Graham's Law

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$r$  = rate of effusion of a gas or average speed of the molecules of a gas

$M$  = molecular weight

You should note that Graham's law states that at a given temperature, lighter molecules move faster than heavier molecules.

## VAN DER WAALS EQUATION

At low temperature and/or high pressure, gases behave in a less-than-ideal manner. That's because the assumptions made in kinetic molecular theory become invalid under conditions where gas molecules are packed too tightly together.

Two things happen when gas molecules are packed too tightly.

- *The volume of the gas molecules becomes significant.*

The ideal gas equation does not take the volume of gas molecules into account, so the actual volume of a gas under nonideal conditions will be larger than the volume predicted by the ideal gas equation.

- Gas molecules attract one another and stick together.

The ideal gas equation assumes that gas molecules never stick together. When a gas is packed tightly together, van der Waals forces (dipole–dipole attractions and London dispersion forces) become significant, causing some gas molecules to stick together. When gas molecules stick together, there are fewer particles bouncing around and creating pressure, so the real pressure in a nonideal situation will be smaller than the pressure predicted by the ideal gas equation.

The van der Waals equation adjusts the ideal gas equation to take nonideal conditions into account.

#### Van der Waals Equation

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$P$  = the pressure of the gas (atm)

$V$  = the volume of the gas (L)

$n$  = the number of moles of gas (mol)

$T$  = the absolute temperature of the gas (K)

$R$  = the gas constant, 0.0821 L-atm/mol-K

$a$  = a constant, different for each gas, that takes into account the attractive forces between molecules

$b$  = a constant, different for each gas, that takes into account the volume of each molecule

## DENSITY

You may be asked about the density of a gas. The density of a gas is measured in the same way as the density of a liquid or solid: in mass per unit volume.

#### Density of a Gas

$$D = \frac{m}{V}$$

$D$  = density

$m$  = mass of gas, usually in grams

$V$  = volume occupied by a gas, usually in liters

## CHAPTER 6 QUESTIONS

### MULTIPLE-CHOICE QUESTIONS

#### Questions 1–5

- (A)  $\text{H}_2$
- (B) He
- (C)  $\text{O}_2$
- (D)  $\text{N}_2$
- (E)  $\text{CO}_2$

1. This is the most plentiful gas in the earth's atmosphere.
2. A 1 mole sample of this gas occupying 1 liter will have the greatest density.
3. At a given temperature, this gas will have the greatest rate of effusion.
4. The molecules of this nonpolar gas contain polar bonds.
5. The molecules of this gas contain triple bonds.
6. The temperature of a sample of an ideal gas confined in a 2.0 L container was raised from  $27^\circ\text{C}$  to  $77^\circ\text{C}$ . If the initial pressure of the gas was 1,200 mmHg, what was the final pressure of the gas?
  - (A) 300 mmHg
  - (B) 600 mmHg
  - (C) 1,400 mmHg
  - (D) 2,400 mmHg
  - (E) 3,600 mmHg
7. A sealed container containing 8.0 grams of oxygen gas and 7.0 of nitrogen gas is kept at a constant temperature and pressure. Which of the following is true?
  - (A) The volume occupied by oxygen is greater than the volume occupied by nitrogen.
  - (B) The volume occupied by oxygen is equal to the volume occupied by nitrogen.
  - (C) The volume occupied by nitrogen is greater than the volume occupied by oxygen.
  - (D) The density of nitrogen is greater than the density of oxygen.
  - (E) The average molecular speeds of the two gases are the same.
8. A gas sample contains 0.1 mole of oxygen and 0.4 moles of nitrogen. If the sample is at standard temperature and pressure, what is the partial pressure due to nitrogen?
  - (A) 0.1 atm
  - (B) 0.2 atm
  - (C) 0.5 atm
  - (D) 0.8 atm
  - (E) 1.0 atm

9. A mixture of gases contains 1.5 moles of oxygen, 3.0 moles of nitrogen, and 0.5 moles of water vapor. If the total pressure is 700 mmHg, what is the partial pressure of the nitrogen gas?
- (A) 70 mmHg  
(B) 210 mmHg  
(C) 280 mmHg  
(D) 350 mmHg  
(E) 420 mmHg
10. A mixture of helium and neon gases has a total pressure of 1.2 atm. If the mixture contains twice as many moles of helium as neon, what is the partial pressure due to neon?
- (A) 0.2 atm  
(B) 0.3 atm  
(C) 0.4 atm  
(D) 0.8 atm  
(E) 0.9 atm
11. Nitrogen gas was collected over water at 25°C. If the vapor pressure of water at 25°C is 23 mmHg, and the total pressure in the container is measured at 781 mmHg, what is the partial pressure of the nitrogen gas?
- (A) 23 mmHg  
(B) 46 mmHg  
(C) 551 mmHg  
(D) 735 mmHg  
(E) 758 mmHg
12. When 4.0 moles of oxygen are confined in a 24-liter vessel at 176°C, the pressure is 6.0 atm. If the oxygen is allowed to expand isothermally until it occupies 36 liters, what will be the new pressure?
- (A) 2 atm  
(B) 3 atm  
(C) 4 atm  
(D) 8 atm  
(E) 9 atm
13. A gas sample is confined in a 5-liter container. Which of the following will occur if the temperature of the container is increased?
- I. The kinetic energy of the gas will increase.  
II. The pressure of the gas will increase.  
III. The density of the gas will increase.
- (A) I only  
(B) II only  
(C) I and II only  
(D) I and III only  
(E) I, II, and III
14. A 22.0 gram sample of an unknown gas occupies 11.2 liters at standard temperature and pressure. Which of the following could be the identity of the gas?
- (A)  $\text{CO}_2$   
(B)  $\text{SO}_3$   
(C)  $\text{O}_2$   
(D)  $\text{N}_2$   
(E) He
15. A gaseous mixture at a constant temperature contains  $\text{O}_2$ ,  $\text{CO}_2$ , and He. Which of the following lists the three gases in order of increasing average molecular speeds?
- (A)  $\text{O}_2$ ,  $\text{CO}_2$ , He  
(B)  $\text{O}_2$ , He,  $\text{CO}_2$   
(C) He,  $\text{CO}_2$ ,  $\text{O}_2$   
(D) He,  $\text{O}_2$ ,  $\text{CO}_2$   
(E)  $\text{CO}_2$ ,  $\text{O}_2$ , He
16. Which of the following conditions would be most likely to cause the ideal gas laws to fail?
- I. High pressure  
II. High temperature  
III. Large volume
- (A) I only  
(B) II only  
(C) I and II only  
(D) I and III only  
(E) II and III only

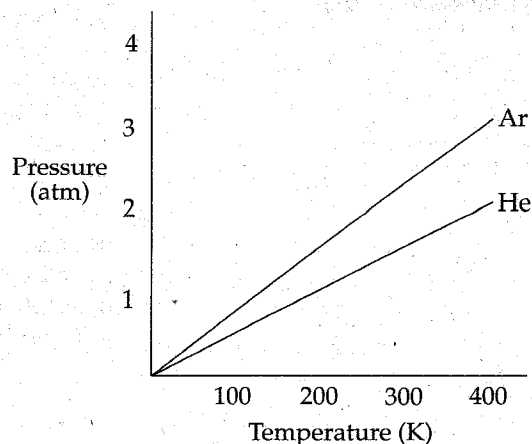
17. Which of the following expressions is equal to the density of helium gas at standard temperature and pressure?
- (A)  $\frac{1}{22.4}$  g/L  
 (B)  $\frac{2}{22.4}$  g/L  
 (C)  $\frac{1}{4}$  g/L  
 (D)  $\frac{4}{22.4}$  g/L  
 (E)  $\frac{4}{4}$  g/L
18. An ideal gas is contained in a 5.0 liter chamber at a temperature of 37°C. If the gas exerts a pressure of 2.0 atm on the walls of the chamber, which of the following expressions is equal to the number of moles of the gas? The gas constant,  $R$ , is 0.08 (L-atm)/(mol-K).
- (A)  $\frac{(2.0)(5.0)}{(0.08)(37)}$  moles  
 (B)  $\frac{(2.0)(0.08)}{(5.0)(37)}$  moles  
 (C)  $\frac{(2.0)(0.08)}{(5.0)(310)}$  moles  
 (D)  $\frac{(2.0)(310)}{(0.08)(5.0)}$  moles  
 (E)  $\frac{(2.0)(5.0)}{(0.08)(310)}$  moles
19. Which of the following gases would be expected to have a rate of effusion that is one-third as large as that of  $H_2$ ?
- (A)  $O_2$   
 (B)  $N_2$   
 (C) He  
 (D)  $H_2O$   
 (E)  $CO_2$
20. In an experiment  $H_2(g)$  and  $O_2(g)$  were completely reacted, above the boiling point of water, according to the following equation in a sealed container of constant volume and temperature:
- $$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$
- If the initial pressure in the container before the reaction is denoted as  $P_i$ , which of the following expressions gives the final pressure, assuming ideal gas behavior?
- (A)  $P_i$   
 (B)  $2 P_i$   
 (C)  $(3/2)P_i$   
 (D)  $(2/3)P_i$   
 (E)  $(1/2)P_i$
21. Nitrogen gas was collected over water at a temperature of 40°C, and the pressure of the sample was measured at 796 mmHg. If the vapor pressure of water at 40°C is 55 mmHg, what is the partial pressure of the nitrogen gas?
- (A) 55 mmHg  
 (B) 741 mmHg  
 (C) 756 mmHg  
 (D) 796 mmHg  
 (E) 851 mmHg
22. A balloon occupies a volume of 1.0 liter when it contains 0.16 grams of helium at 37°C and 1 atm pressure. If helium is added to the balloon until it contains 0.80 grams while pressure and temperature are kept constant, what will be the new volume of the balloon?
- (A) 0.50 liters  
 (B) 1.0 liters  
 (C) 2.0 liters  
 (D) 4.0 liters  
 (E) 5.0 liters

23. An ideal gas fills a balloon at a temperature of  $27^{\circ}\text{C}$  and 1 atm pressure. By what factor will the volume of the balloon change if the gas in the balloon is heated to  $127^{\circ}\text{C}$  at constant pressure?
- (A)  $\frac{27}{127}$   
 (B)  $\frac{3}{4}$   
 (C)  $\frac{4}{3}$   
 (D)  $\frac{2}{1}$   
 (E)  $\frac{127}{27}$
24. A gas sample with a mass of 10 grams occupies 6.0 liters and exerts a pressure of 2.0 atm at a temperature of  $26^{\circ}\text{C}$ . Which of the following expressions is equal to the molecular mass of the gas? The gas constant,  $R$ , is  $0.08 \text{ (L-atm)/(mol-K)}$ .
- (A)  $\frac{(10)(0.08)(299)}{(2.0)(6.0)} \text{ g/mol}$   
 (B)  $\frac{(299)(0.08)}{(10)(2.0)(6.0)} \text{ g/mol}$   
 (C)  $\frac{(2.0)(6.0)(299)}{(10)(0.08)} \text{ g/mol}$   
 (D)  $\frac{(10)(2.0)(6.0)}{(299)(0.08)} \text{ g/mol}$   
 (E)  $\frac{(2.0)(6.0)}{(10)(299)(0.08)} \text{ g/mol}$
25. Which of the following assumptions is (are) valid based on kinetic molecular theory?
- I. Gas molecules have negligible volume.  
 II. Gas molecules exert no attractive forces on one another.  
 III. The temperature of a gas is directly proportional to its kinetic energy.
- (A) I only  
 (B) III only  
 (C) I and III only  
 (D) II and III only  
 (E) I, II, and III



## PROBLEMS

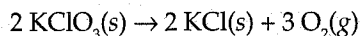
1.



The graph above shows the changes in pressure with changing temperature of gas samples of helium and argon confined in a closed 2-liter vessel.

- What is the total pressure of the two gases in the container at a temperature of 200 K?
- How many moles of helium are contained in the vessel?
- How many molecules of helium are contained in the vessel?
- What is the ratio of the average speeds of the helium atoms to the average speeds of the argon atoms?
- If the volume of the container were reduced to 1 liter at a constant temperature of 300 K, what would be the new pressure of the helium gas?

2.



The reaction above took place, and 1.45 liters of oxygen gas were collected over water at a temperature of 29°C and a pressure of 755 millimeters of mercury. The vapor pressure of water at 29°C is 30.0 millimeters of mercury.

- What is the partial pressure of the oxygen gas collected?
- How many moles of oxygen gas were collected?
- What would be the dry volume of the oxygen gas at a pressure of 760 millimeters of mercury and a temperature of 273 K?
- What was the mass of the  $\text{KClO}_3$  consumed in the reaction?

## ESSAYS

3. Equal molar quantities of two gases,  $O_2$  and  $H_2O$ , are confined in a closed vessel at constant temperature.
  - (a) Which gas, if any, has the greater partial pressure?
  - (b) Which gas, if any, has the greater density?
  - (c) Which gas, if any, has the greater concentration?
  - (d) Which gas, if any, has the greater average kinetic energy?
  - (e) Which gas, if any, will show the greater deviation from ideal behavior?
  - (f) Which gas, if any, has the greater average molecular speed?
  
4.  $SF_6$ ,  $H_2O$ , and  $CO_2$  are all greenhouse gases because they absorb infrared radiation in the atmosphere. As such they are of interest to many researchers.
  - (a) Of the three gases, which deviates the most from ideal gas behavior?
  - (b) If all three ideal gases are held at constant temperature, which gas would have the highest average molecular speed?
  - (c) A container was with equal amounts  $H_2O$  and  $CO_2$  and the pressure was measured. Assuming ideal behavior, if  $SF_6$  was then added such that the final pressure was four times that before its addition, the final number of moles of  $SF_6$  is how many times that of  $H_2O$ ?
  - (d) If a container held equal molar amounts of all three greenhouse gases, but was then compressed decreasing the volume within, which of the gases has the highest, final partial pressure assuming ideal behavior?
  - (e) Gas molecules exert pressure through collisions with the walls of the containers they are in. If a container is filled with equal amounts of each of the greenhouse gases, which gas undergoes the fewest collisions with the wall of the container per unit time?

## CHAPTER 6 ANSWERS AND EXPLANATIONS

### MULTIPLE-CHOICE QUESTIONS

1. **D** Nitrogen gas makes up about 78 percent of the gas in the earth's atmosphere.
2. **E** Density is a measure of grams per liter.  $\text{CO}_2$  has the greatest molecular mass (44), so 1 mole of  $\text{CO}_2$  will have the most mass in 1 liter and, therefore, the greatest density.
3. **A** According to Graham's law, the lighter the gas, the greater the rate of effusion.  $\text{H}_2$  is the lightest gas ( $\text{MW} = 2$ ), so it will have the greatest rate of effusion.
4. **E**  $\text{CO}_2$  is the only gas listed that has bonds between atoms of differing electronegativity. The carbon-oxygen bonds in  $\text{CO}_2$  are polar, although the linear geometry of the molecule makes the molecule nonpolar overall.
5. **D**  $\text{N}_2$  is the only gas listed whose atoms are held together in a triple bond.
6. **C** Remember to convert Celsius to Kelvin ( $^\circ\text{C} + 273 = \text{K}$ ).

$$27^\circ\text{C} = 300 \text{ K and } 77^\circ\text{C} = 350 \text{ K.}$$

From the relationship  $\frac{P_1}{T_1} = \frac{P_2}{T_2}$  we get

$$\frac{(1,200 \text{ mmHg})}{(300 \text{ K})} = \frac{P_2}{(350 \text{ K})}$$

$$\text{So } P_2 = 1,400 \text{ mmHg}$$

7. **B** 8.0 grams of oxygen and 7.0 grams of nitrogen both equal 0.25 moles. Avogadro's law states equal volumes contain equal moles. This makes (A) and (C) wrong.  
  
(D) This is reversed: the density of oxygen gas would be greater than the density of nitrogen.  
  
(E) From Graham's law, if the kinetic energies of the two gases are the same, then the molecules of the less massive gas must be moving faster, on average.
8. **D** If the gases are at STP, then the total pressure must be 1.0 atmosphere.  
If  $\frac{4}{5}$  of the gas in the sample is nitrogen, then from Dalton's law,  $\frac{4}{5}$  of the pressure must be due to the nitrogen.  
  
So the partial pressure due to nitrogen is  $\frac{4}{5} (1.0 \text{ atm}) = 0.8 \text{ atm}$ .
9. **E** From Dalton's law, the partial pressure of a gas depends on the number of moles of the gas that are present.  
The total number of moles of gas present is  
 $1.5 + 3.0 + 0.5 = 5.0$  total moles  
If there are 3 moles of nitrogen, then  $\frac{3}{5}$  of the pressure must be due to nitrogen.  
 $(\frac{3}{5})(700 \text{ mmHg}) = 420 \text{ mmHg}$

10. C From Dalton's law, the partial pressure of a gas depends on the number of moles of the gas that are present. If the mixture has twice as many moles of helium as neon, then the mixture must be  $\frac{1}{3}$  neon. So  $\frac{1}{3}$  of the pressure must be due to neon.

$$\left(\frac{1}{3}\right)(1.2 \text{ atm}) = 0.4 \text{ atm.}$$

11. E From Dalton's law, the partial pressures of nitrogen and water vapor must add up to the total pressure in the container. The partial pressure of water vapor in a closed container will be equal to the vapor pressure of water, so the partial pressure of nitrogen is

$$781 \text{ mmHg} - 23 \text{ mmHg} = 758 \text{ mmHg}$$

12. C From the gas laws, we know that with constant temperature

$$P_1 V_1 = P_2 V_2$$

Solving for  $P_2$ , we get

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{(6.0 \text{ atm})(24 \text{ L})}{(36 \text{ L})} = 4.0 \text{ atm}$$

13. C From kinetic molecular theory, we know that kinetic energy is directly proportional to temperature (think of the expression:  $KE = \frac{3}{2}kT$ ), so (I) is true.

From the gas laws, we know that at constant volume, an increase in temperature will bring about an increase in pressure (think of  $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ ), so (II) is true.

The density of a gas is equal to mass per unit volume, which is not changed by changing temperature, so (III) is not true.

14. A Use the relationship

$$\text{Moles} = \frac{\text{liters}}{22.4 \text{ L/mol}}$$

$$\text{Moles of unknown gas} = \frac{11.2 \text{ L}}{22.4 \text{ L/mol}} = 0.500 \text{ moles}$$

$$\text{MW} = \frac{\text{grams}}{\text{mole}}$$

$$\text{MW of unknown gas} = \frac{22.0 \text{ g}}{0.500 \text{ mole}} = 44.0 \text{ grams/mole}$$

That's the molecular weight of  $\text{CO}_2$ .

15. E According to Graham's law, at a given temperature, heavier molecules will have lower average speeds and lighter molecules will have higher speeds.

Helium is the lightest of the three molecules (MW = 4), oxygen is next (MW = 32), and carbon dioxide is the heaviest (MW = 44).

16. A The ideal gas laws fail under conditions where gas molecules are packed too tightly together. This can happen as a result of high pressure (I), low temperature (not listed as a choice), or small volume (not listed as a choice).

17. **D** Density is measured in grams per liter. One mole of helium gas has a mass of 4 grams and occupies a volume of 22.4 liters at STP, so the density of helium gas at STP is

$$\frac{4}{22.4} \text{ g/L.}$$

18. **E** From the ideal gas equation, we know that  $PV = nRT$ .

Remember to convert  $37^\circ\text{C}$  to 310 K.

Then we just rearrange the equation to solve for  $n$ .

$$n = \frac{PV}{RT} = \frac{(2.0)(5.0)}{(0.08)(310)} \text{ moles}$$

19. **D** Remember Graham's law, which relates the average speeds of different gases (and thus their rates of effusion) to their molecular weights.

$$\frac{v_1}{v_2} = \sqrt{\frac{MW_2}{MW_1}}$$

To get a velocity and rate of effusion that is one-third as large as  $\text{H}_2$ 's, we need a molecule with a molecular weight that is nine times as large. The molecular weight of  $\text{H}_2$  is 2, so we need a molecule with a molecular weight of 18. That's  $\text{H}_2\text{O}$ .

20. **D** As long as the gases act ideally, the total pressure in the container will only be a function of the number of gas moles present so long as volume and temperature are held constant. The relationship between moles and pressure before and after the reaction, from the ideal gas equation ( $PV = nRT$ ), will be  $P_i/n_i = P_f/n_f$  where  $n_i$ ,  $P_f$ ,  $n_f$  are the initial moles, the final pressure, and the final moles respectively. We can rearrange this equation to  $P_f = P_i(n_f/n_i)$ , and since there are 2 moles of gas in the products for every 3 moles in the reactants, we can say that  $P_f = (2/3)P_i$ .

21. **B** From Dalton's law, the partial pressures of nitrogen and water vapor must add up to the total pressure in the container. The partial pressure of water vapor in a closed container will be equal to its vapor pressure, so the partial pressure of nitrogen is

$$796 \text{ mmHg} - 55 \text{ mmHg} = 741 \text{ mmHg}$$

22. **E** According to the ideal gas laws, at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles.

We increased the number of grams by a factor of 5 ( $[0.16][5] = [0.80]$ ). That's the same as increasing the number of moles by a factor of 5. So we must have increased the volume by a factor of 5. Therefore,  $(5)(1 \text{ L}) = 5 \text{ L}$ .

23. **C** From the ideal gas laws, for a gas sample at constant pressure

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\text{Solving for } V_2 \text{ we get } V_2 = V_1 \frac{T_2}{T_1}$$

So  $V_1$  is multiplied by a factor of  $\frac{T_2}{T_1}$

$$\text{Remember to convert Celsius to Kelvin, } \frac{127^\circ\text{C} + 273}{27^\circ\text{C} + 273} = \frac{400 \text{ K}}{300 \text{ K}} = \frac{4}{3}$$

24. A We can find the number of moles of gas from  $PV = nRT$ .

Remember to convert  $26^\circ\text{C}$  to 299 K.

Then solve for  $n$ .

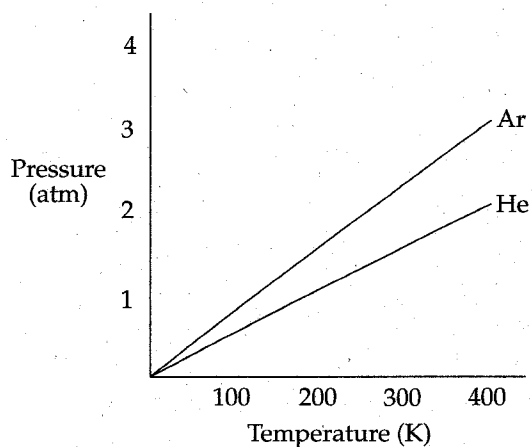
$$n = \frac{PV}{RT} = \frac{(2.0)(6.0)}{(0.08)(299)} \text{ mol}$$

Now, remember

$$\text{MW} = \frac{\text{grams}}{\text{moles}} = \frac{(10 \text{ g})}{\left(\frac{(2.0)(6.0)}{(0.08)(299)} \text{ mol}\right)} = \frac{(10)(0.08)(299)}{(2.0)(6.0)} \text{ g/mol}$$

25. E All three assumptions are included in kinetic molecular theory.

## PROBLEMS



1. (a) Read the graph, and add the two pressures.

$$P_{\text{Total}} = P_{\text{He}} + P_{\text{Ar}}$$

$$P_{\text{Total}} = (1 \text{ atm}) + (1.5 \text{ atm}) = 2.5 \text{ atm}$$

- (b) Read the pressure (1 atm) at 200 K, and use the ideal gas equation.

$$n = \frac{PV}{RT} = \frac{(1.0 \text{ atm})(2.0 \text{ L})}{(0.082 \text{ L-atm/mol-K})(200 \text{ K})} = 0.12 \text{ moles}$$

- (c) Use the definition of a mole.

$$\text{Molecules} = (\text{moles})(6.02 \times 10^{23})$$

$$\text{Molecules (atoms) of helium} = (0.12)(6.02 \times 10^{23}) = 7.2 \times 10^{22}$$

- (d) Use Graham's law.

$$\frac{v_1}{v_2} = \sqrt{\frac{\text{MW}_2}{\text{MW}_1}}$$

$$\frac{v_{\text{He}}}{v_{\text{Ar}}} = \sqrt{\frac{\text{MW}_{\text{Ar}}}{\text{MW}_{\text{He}}}} = \sqrt{\frac{(40)}{(4)}} = 3.2 \text{ to } 1$$

(e) Use the relationship

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

With  $T$  constant

$$P_1 V_1 = P_2 V_2$$

$$(1.5 \text{ atm})(2.0 \text{ L}) = P_2(1.0 \text{ L})$$

$$P_2 = 3.0 \text{ atm}$$

2. (a) Use Dalton's law.

$$P_{\text{Total}} = P_{\text{Oxygen}} + P_{\text{Water}}$$

$$(755 \text{ mmHg}) = (P_{\text{Oxygen}}) + (30.0 \text{ mmHg})$$

$$P_{\text{Oxygen}} = 725 \text{ mmHg}$$

(b) Use the ideal gas law. Don't forget to convert to the proper units.

$$n = \frac{PV}{RT} = \frac{\left(\frac{725}{760} \text{ atm}\right)(1.45 \text{ L})}{(0.082 \text{ L}\cdot\text{atm} / \text{mol}\cdot\text{K})(302 \text{ K})} = 0.056 \text{ moles}$$

(c) At STP, moles of gas and volume are directly related.

$$\text{Volume} = (\text{moles})(22.4 \text{ L/mol})$$

$$\text{Volume of O}_2 = (0.056 \text{ mol})(22.4 \text{ L/mol}) = 1.25 \text{ L}$$

(d) We know that 0.056 moles of  $\text{O}_2$  were produced in the reaction.

From the balanced equation, we know that for every 3 moles of  $\text{O}_2$  produced, 2 moles of  $\text{KClO}_3$  are consumed. So there are  $\frac{2}{3}$  as many moles of  $\text{KClO}_3$  as  $\text{O}_2$ .

$$\text{Moles of KClO}_3 = \left(\frac{2}{3}\right)(\text{moles of O}_2)$$

$$\text{Moles of KClO}_3 = \left(\frac{2}{3}\right)(0.056 \text{ mol}) = 0.037 \text{ moles}$$

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of KClO}_3 = (0.037 \text{ mol})(122 \text{ g/mol}) = 4.51 \text{ g}$$

## ESSAYS

3. (a) The partial pressures depend on the number of moles of gas present. Because the number of moles of the two gases are the same, the partial pressures are the same.
- (b)  $O_2$  has the greater density. Density is mass per unit volume. Both gases have the same number of moles in the same volume, but oxygen has heavier molecules, so it has greater density.
- (c) Concentration is moles per volume. Both gases have the same number of moles in the same volume, so their concentrations are the same.
- (d) According to kinetic-molecular theory, the average kinetic energy of a gas depends only on the temperature. Both gases are at the same temperature, so they have the same average kinetic energy.
- (e)  $H_2O$  will deviate most from ideal behavior. Ideal behavior for gas molecules assumes that there will be no intermolecular interactions.
- $H_2O$  is polar, and  $O_2$  is not.  $H_2O$  undergoes hydrogen bonding while  $O_2$  does not. So  $H_2O$  has stronger intermolecular interactions, which will cause it to deviate more from ideal behavior.
- (f)  $H_2O$  has the greater average molecular speed. From Graham's law, if two gases are at the same temperature, the one with the smaller molecular weight (MW of  $H_2O = 18$ , MW of  $O_2 = 32$ ) will have the greater average molecular speed.
4. (a)  $H_2O$  deviates most drastically from ideal behavior due to very strong hydrogen bonding interactions. A truly ideal gas has no interactions with surrounding molecules. These hydrogen bonding interactions are why  $H_2O$  is a liquid at room temperature and the others are gases.
- (b) As per Graham's law, the species with the lowest molecular weight would have the greatest average molecular speed.  $H_2O$ , MW = 18 g/mol, is the lightest, and hence would be the fastest.
- (c) By Dalton's law of partial pressures, if  $SF_6$  was added until the pressure was 4 times the pressure with just (an equal mixture of)  $H_2O$  and  $CO_2$ , then there must be 3 times as much  $SF_6$  as  $H_2O$  and  $CO_2$  combined. This means that, in the end, there 6 times more  $SF_6$  than  $H_2O$ . For example, imagine starting with 1 atm each of  $CO_2$  and  $H_2O$ . In this case the initial pressure is 2 atm, and to get to 8 atm one must add 6 atm of  $SF_6$  which is 6 times that of the  $H_2O$  present.
- (d) All three gases will have identical partial pressures. The equation for partial pressure of any component a is  $P_a = (P_{total})(X_a)$ . Since we know that each has the same mol fraction the total pressure doesn't matter, and each will have the same partial pressure, relative to one another.
- (e)  $SF_6$  will have the fewest collisions per unit time. Since the kinetic theory assumes that the gas molecules are moving randomly, the one with the most collisions with the walls of the containers will be the one moving the fastest. On the other hand, the slowest molecule will have the fewest collisions. The slowest molecule will be the most massive one, as per Graham's law, which in this case is  $SF_6$ .





# 7

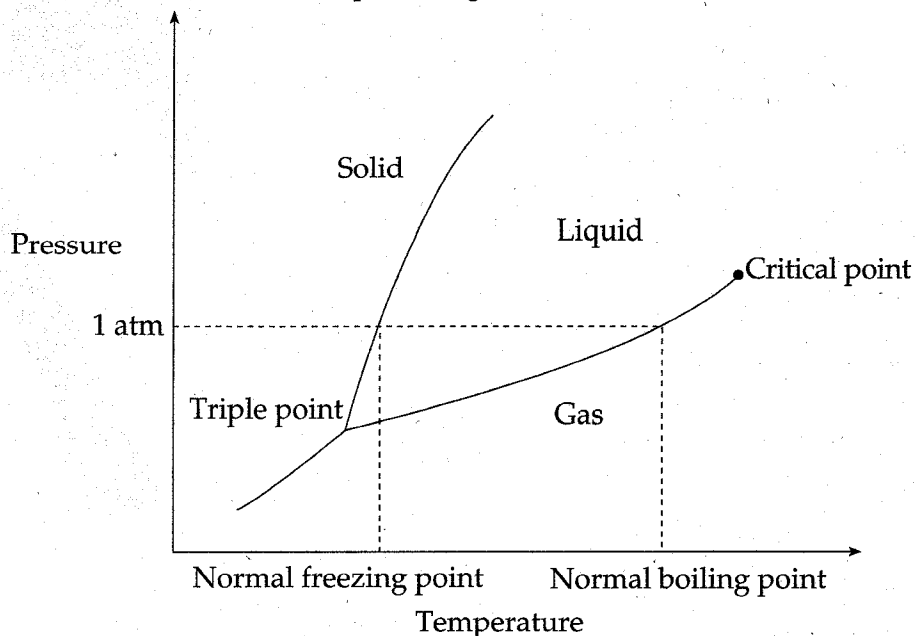
## Phase Changes

### **HOW OFTEN DO PHASE CHANGES APPEAR ON THE EXAM?**

In the multiple-choice section, this topic appears in about 4 out of 75 questions. In the free-response section, this topic appears occasionally.

## THE PHASE DIAGRAM

You should know how to work with the phase diagram below.



At high pressure and low temperature, a substance is in a solid phase. At low pressure and high temperature, a substance is in a gas phase. Liquid phase is in between these two.

The lines that separate the phases correspond to points at which the substance can exist simultaneously in both phases at equilibrium. The normal freezing point is the temperature at which the solid-liquid phase equilibrium line crosses the 1 atmosphere pressure line. The normal boiling point is the temperature at which the liquid-gas equilibrium line crosses the 1 atmosphere pressure line.

The **triple point** is the temperature and pressure at which all three phases can exist simultaneously in equilibrium.

The **critical point** is the temperature beyond which the molecules of a substance have too much kinetic energy to stick together and form a liquid.

## PHASE CHANGES

### NAMING THE PHASE CHANGES

<i>Solid to liquid</i>	—	<b>Melting</b>
<i>Liquid to solid</i>	—	<b>Freezing</b>
<i>Liquid to gas</i>	—	<b>Vaporization</b>
<i>Gas to liquid</i>	—	<b>Condensation</b>
<i>Solid to gas</i>	—	<b>Sublimation</b>
<i>Gas to solid</i>	—	<b>Deposition</b>

Phase changes occur because of changes in temperature and/or pressure. You should be able to read the phase diagram and see how a change in pressure or temperature will affect the phase of a substance.

Some particles in a liquid or solid will have enough energy to break away from the surface and become gaseous. The pressure exerted by these molecules as they escape from the surface is called the **vapor pressure**. When the liquid or solid phase of a substance is in equilibrium with the gas phase, the pressure of the gas will be equal to the vapor pressure of the substance. As temperature increases, the vapor pressure of a liquid will increase. When the vapor pressure of a liquid increases to the point where it is equal to the surrounding atmospheric pressure, the liquid boils.

## HEAT OF FUSION

The **heat of fusion** is the energy that must be put into a solid to melt it. This energy is needed to overcome the forces holding the solid together. Alternatively, the heat of fusion is the heat given off by a substance when it freezes. The intermolecular forces within a solid are more stable and, therefore, have lower energy than the forces within a liquid, so energy is released in the freezing process.

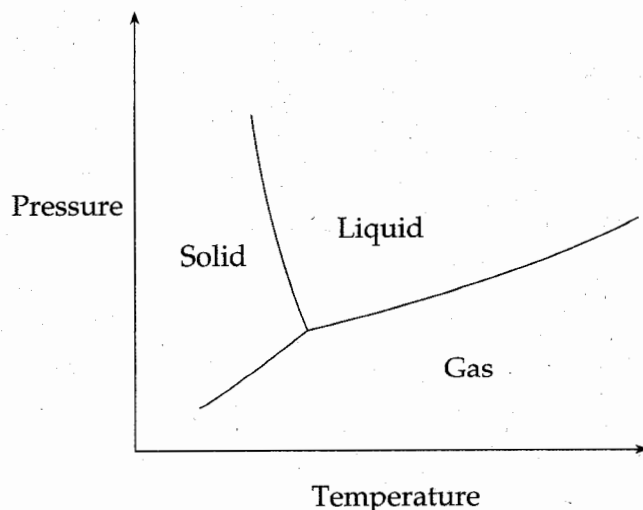
## HEAT OF VAPORIZATION

The **heat of vaporization** is the energy that must be put into a liquid to vaporize it. This energy is needed to overcome the forces holding the liquid together. Alternatively, the heat of vaporization is the heat given off by a substance when it condenses. Intermolecular forces become stronger when a gas condenses; the gas becomes a liquid, which is more stable, and energy is released.

As heat is added to a substance in equilibrium, the temperature of the substance can increase or the substance can change phases, but both changes cannot occur simultaneously.

## THE PHASE DIAGRAM FOR WATER

You should recognize how the phase diagram for water differs from the phase diagram for most other substances.

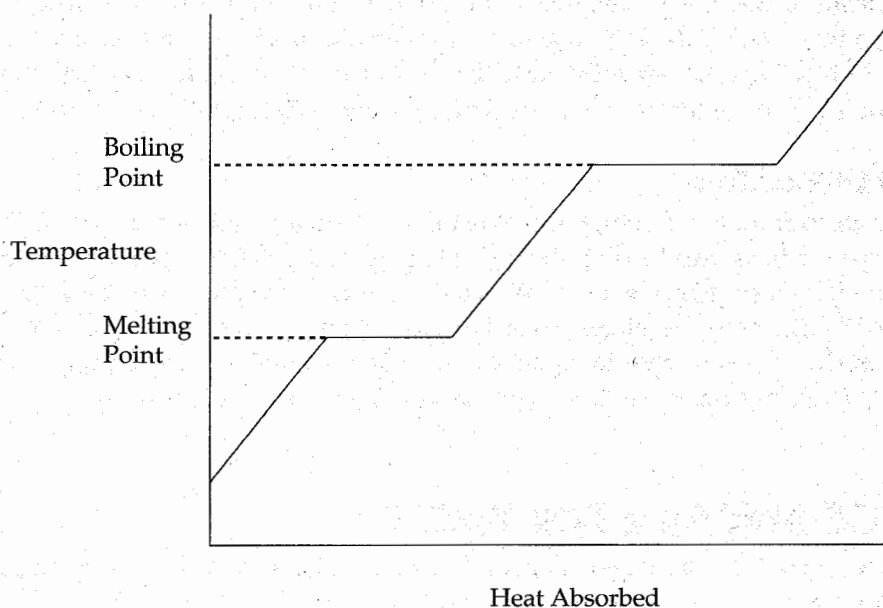


In the phase diagram for substances other than water, the solid-liquid equilibrium line slopes upward. In the phase diagram for water, the solid-liquid equilibrium line slopes downward. What this means is that when pressure is increased, a normal substance will change from liquid to solid, but water will change from solid to liquid.

Water has this odd property because its hydrogen bonds form a lattice structure when it freezes. This forces the molecules to remain farther apart in ice than in water, making the solid phase less dense than the liquid phase. That's why ice floats on water.

## THE HEATING CURVE

You should be familiar with the heating curve below, which shows how the temperature of a substance changes as it is heated. In the diagram shown, the substance starts as a solid. As heat is added, the kinetic energy of the substance increases and the temperature increases. When the temperature reaches the melting point, the line flattens out. At this point, during the phase change from solid to liquid, all added heat goes toward overcoming the intermolecular forces in the solid; therefore, there is no increase in kinetic energy during the phase change, and the temperature stays the same. The same thing occurs at the boiling point (during the phase change from liquid to gas).

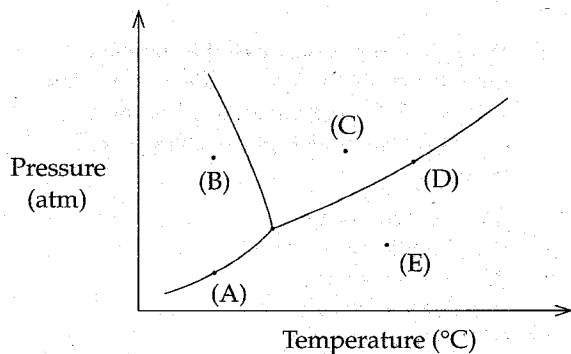


The length of the horizontal line at the melting point will be proportional to the heat of fusion, and the length of the line at the boiling point will be proportional to the heat of vaporization. Notice that the heat of vaporization is larger than the heat of fusion. That's because many more intermolecular forces must be overcome in vaporization than in melting. Also, because it's easier to change the temperature of substance with a low specific heat, a graph whose temperature curve has a steep slope will indicate a substance that has a low specific heat.

## CHAPTER 7 QUESTIONS

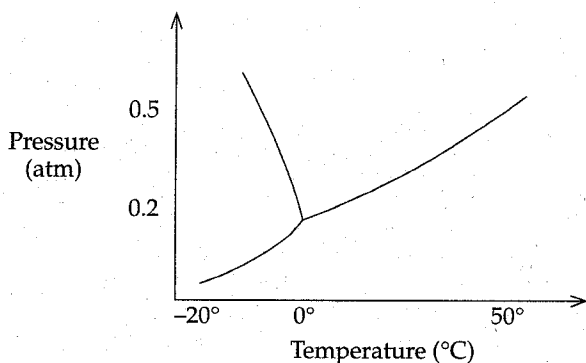
### MULTIPLE-CHOICE QUESTIONS

Questions 1–4 refer to the phase diagram below.



1. At this point, the substance represented by the phase diagram will be solely in the solid phase at equilibrium.
2. This point represents a boiling point of the substance.
3. At this point, the substance represented by the phase diagram will be undergoing sublimation.
4. At this point, the substance represented by the phase diagram will be solely in the liquid phase at equilibrium.
5. When a substance undergoes a phase change from liquid to solid, which of the following will occur?
  - (A) Energy will be released by the substance because intermolecular forces are being weakened.
  - (B) Energy will be released by the substance because intermolecular forces are being strengthened.
  - (C) Energy will be absorbed by the substance because intermolecular forces are being weakened.
  - (D) Energy will be absorbed by the substance because intermolecular forces are being strengthened.
  - (E) The energy of the substance will not be changed.
6. During which of the following phase changes must heat be added to overcome intermolecular forces?
  - I. Vaporization
  - II. Sublimation
  - III. Deposition
  - (A) I only
  - (B) II only
  - (C) I and II only
  - (D) I and III only
  - (E) I and III only

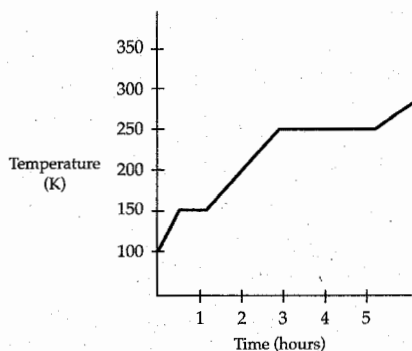
Questions 7–10 are based on the phase diagram below.



7. As pressure on the substance depicted in the diagram is increased at constant temperature, which of the following phase changes CANNOT occur?
- I. Condensation
  - II. Melting
  - III. Freezing
- (A) I only  
(B) II only  
(C) III only  
(D) I and II only  
(E) I and III only
8. At a temperature of 50°C and a pressure of 0.2 atmospheres, the substance depicted in the diagram is
- (A) in the gas phase.  
(B) in the liquid phase.  
(C) in the solid phase.  
(D) at its triple point.  
(E) at its critical point.
9. Which of the following lists the three phases of the substance shown in the diagram in order of increasing density at -5°C?
- (A) Solid, gas, liquid  
(B) Solid, liquid, gas  
(C) Gas, liquid, solid  
(D) Gas, solid, liquid  
(E) Liquid, solid, gas
10. When the temperature of the substance depicted in the diagram is decreased from 10°C to -10°C at a constant pressure of 0.3 atmospheres, which phase change will occur?
- (A) Gas to liquid  
(B) Liquid to solid  
(C) Gas to solid  
(D) Liquid to gas  
(E) Solid to liquid
11. Which of the following processes can occur when the temperature of a substance is increased at constant pressure?
- I. Sublimation
  - II. Melting
  - III. Boiling
- (A) I only  
(B) II only  
(C) I and II only  
(D) II and III only  
(E) I, II, and III
12. The temperature above which gas molecules become too energetic to form a true liquid, no matter what the pressure, is called the
- (A) melting point.  
(B) critical point.  
(C) boiling point.  
(D) triple point.  
(E) freezing point.

Questions 13–15 are based on the information given below.

In an experiment, a solid 1 molar sample of Substance *A* was gradually heated by a source of constant energy for several hours and the temperature was measured periodically. At the end of the heating period, Substance *A* had been converted to the gas phase. The heating curve produced by this experiment is shown below.



13. During the course of the experiment, there was a period of time when the solid phase of Substance *A* was in equilibrium with the liquid phase. At what temperature did this occur?

- (A) Between 100 K and 150 K
- (B) At 150 K
- (C) Between 150 K and 250 K
- (D) At 250 K
- (E) Between 250 K and 350 K

14. Based on the data given in the heating curve, which of the following statements is NOT true regarding Substance *A*?

- (A) The boiling point of Substance *A* is 250 K.
- (B) The freezing point of Substance *A* is 150 K.
- (C) The heat of vaporization of Substance *A* is greater than the heat of fusion.
- (D) Substance *A* is a liquid at room temperature.
- (E) The intermolecular forces exhibited by Substance *A* are weaker than those of water.

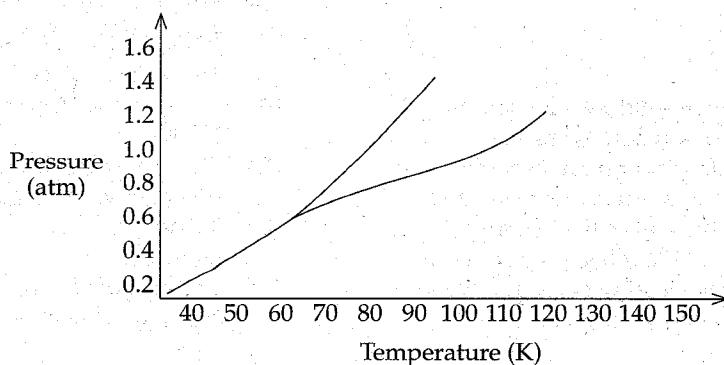
15. During the course of the experiment, Substance *A* was gradually heated from 100 K to 350 K. When the temperature reached 250 K, the energy absorbed by Substance *A*

- (A) was used to change from liquid to gas phase.
- (B) was used to change from gas to liquid phase.
- (C) was used to change from solid to liquid phase.
- (D) was used to change from liquid to solid phase.
- (E) was reduced to zero.



## ESSAYS

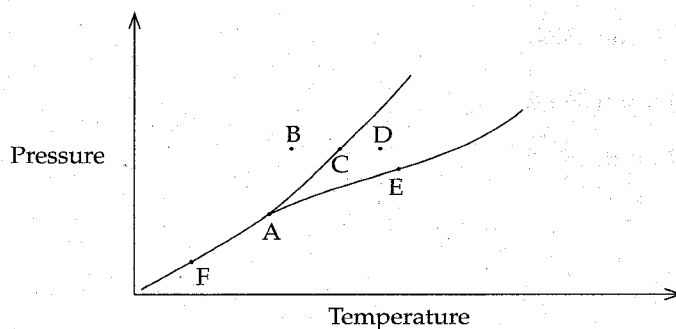
1.



The phase diagram for a substance is shown above. Use the diagram and your knowledge of phase changes to answer the following questions.

- When the substance is at a pressure of 0.8 atmospheres and a temperature of 50 K, what is its phase?
- Describe the change in phase that the substance undergoes when the pressure is decreased from 1.2 atmospheres to 0.6 atmospheres at a constant temperature of 110 K.
- A constant source of heat was applied to the substance at a constant pressure of 0.8 atmospheres. The substance was initially at a temperature of 50 K. The temperature of the substance increased at a constant rate until 70 K was reached. At this point, the temperature remained constant for a period of time, then continued to climb at a constant rate. Explain what has happened.
- What is the normal boiling point for this substance?

2.



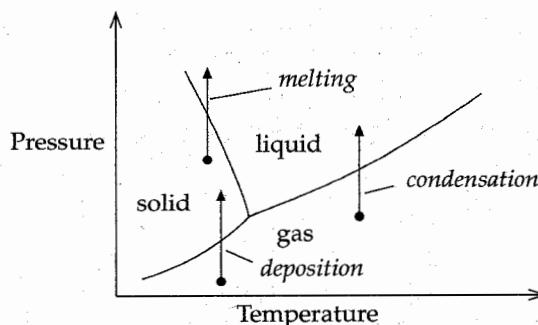
The phase diagram for a substance is shown above. Use the diagram and your knowledge of phase changes to answer the following questions.

- Describe the phase change that the substance undergoes as the temperature is increased from points B to C to D at constant pressure.
- Which of the phases are in equilibrium at point F? Give a name for one of the phase changes between these two phases.
- Could this phase diagram represent water? Explain why or why not.
- What is the name given to point A, and what is the situation particular to this point?

## CHAPTER 7 ANSWERS AND EXPLANATIONS

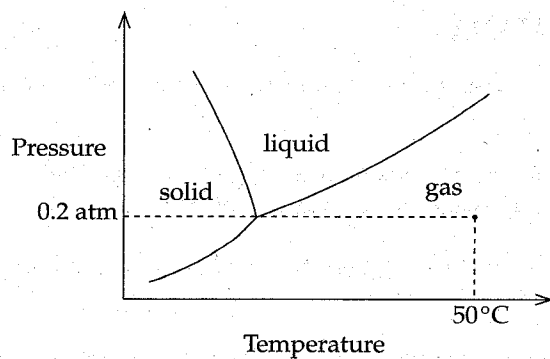
### MULTIPLE-CHOICE QUESTIONS

1. **B** Point (B) is in a region of high pressure and low temperature. That corresponds to the solid phase.
2. **D** Point (D) is on the phase change line between liquid and gas. The temperature at point (D) is the boiling point of the substance at the pressure at point (D).
3. **A** Point (A) is on the phase change line between solid and gas. Sublimation is the phase change from solid directly to gas.
4. **C** Point (C) is in the liquid region, which is the middle region between solid and gas.
5. **B** The intermolecular forces in the solid phase of any substance are stronger than the intermolecular forces in the liquid phase. Whenever intermolecular forces are strengthened, energy is given off.
6. **C** Intermolecular forces must be overcome to convert a liquid to a gas (vaporization). Likewise, in sublimation (the conversion of a solid to a gas), intermolecular forces must be overcome. However, in deposition (as a gas changes to a solid), intermolecular forces are strengthened.
7. **C** This diagram has the downward slope between the solid and liquid phases that is typical of water, so you've got to be careful in dealing with solid-liquid phase changes. The possible phase changes for increasing pressure and constant temperature are given in the diagram below.

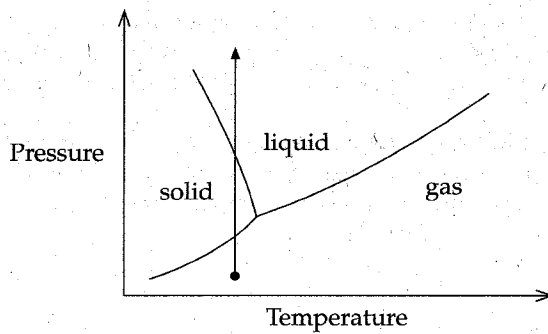


This substance will melt under increased pressure instead of freezing, so while choices (I) and (II) can occur, choice (III) cannot.

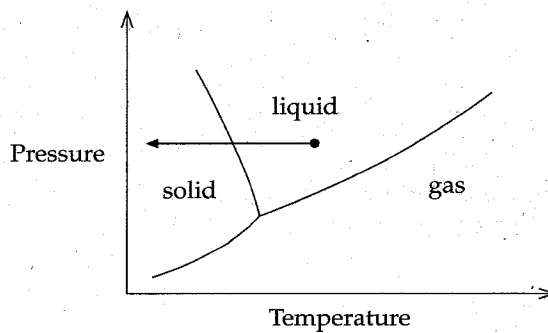
8. A At 50°C and 0.2 atm the substance is a gas.



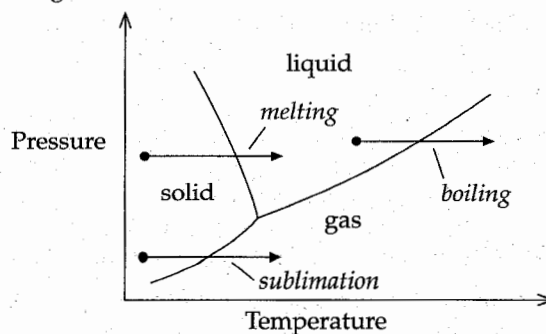
9. D As pressure is increased, density will increase; so increasing density is shown by the arrow in the diagram below.



10. B The phase change will occur as shown in the diagram below.



11. E All three phase changes listed can occur when temperature is increased at constant pressure. This is shown in the diagram below.



12. B At temperatures above the critical point, gases can become dense, but liquids do not form.
13. B The first flat part of the heating curve corresponds to the phase change from solid to liquid. During the phase change, an equilibrium exists between the two phases.
14. D Choice (D) is the only choice that's not true. Room temperature is about 298 K. At 298 K, Substance A is in the gas phase, not the liquid phase. As for the other answers, Choices (A) and (B) accurately give the boiling and freezing points. Choice (C) is accurate because the vaporization line is much longer than the fusion line. Heat of vaporization is usually much higher than heat of fusion. Choice (E) is accurate because the boiling and freezing points of Substance A are lower than those of water, so Substance A must be held together by weaker intermolecular forces.
15. A At 250 K, Substance A boiled. That means that the temperature remained constant while the energy absorbed was used to break up the forces holding the liquid together and convert the substance to a gas.

## ESSAYS

- (a) The phase is solid, which corresponds to high pressure and low temperature.

(b) The substance starts as a liquid and changes to a gas (vaporizes) when the pressure has dropped to about 0.9 atm.

(c) At 70 K, the substance melted. While the substance was melting, the heat from the constant source went toward overcoming the strong intermolecular forces of the solid instead of increasing the temperature. The heat that must be put into a solid to melt it is called the heat of fusion. When the heat of fusion was overcome and the substance was entirely in the liquid phase, the temperature of the liquid began to increase at a constant rate.

(d) The normal boiling point is the boiling point at a pressure of 1 atmosphere. We can find the normal boiling point by looking for the spot at which the gas-liquid equilibrium line crosses the 1 atm line. This happens at 115 K.
- (a) At point B, the substance is a solid.  
At point C, the substance is in equilibrium between solid and liquid phase; that is, it's melting.  
At point D, the substance is entirely in liquid phase.

(b) At point F, the substance is in equilibrium between the gas and solid phases.  
When a substance changes from solid to gas phase, it's called sublimation.  
When a substance changes from gas to solid phase, it's called deposition.

(c) The diagram CANNOT represent water.  
For water, the slope of the solid-liquid equilibrium line must be negative, indicating that the liquid phase of water is denser than the solid phase.

(d) Point A is called the triple point.  
At the triple point, all three phases can exist simultaneously in equilibrium.

# 8

## Thermodynamics

### HOW OFTEN DOES THERMODYNAMICS APPEAR ON THE EXAM?

In the multiple-choice section, this topic appears in about 5 out of 75 questions. In the free-response section, this topic appears every year.

### THE FIRST AND SECOND LAWS OF THERMODYNAMICS

The **first law of thermodynamics** says that the energy of the universe is constant. Energy can be neither created nor destroyed, so while energy can be *converted* in a chemical process, the total energy remains constant.

The **second law of thermodynamics** says that if a process is spontaneous in one direction, then it can't be spontaneous in the reverse direction, and that the entropy of the universe always increases during spontaneous reactions.

## STATE FUNCTIONS

Enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ), and free-energy change ( $\Delta G$ ) are **state functions**. That means they all depend only on the change between the initial and final states of a system, not on the process by which the change occurs. For a chemical reaction, this means that the thermodynamic state functions are independent of reaction pathway; for instance, the addition of a catalyst to a reaction will have no effect on the overall energy or entropy change of the reaction.

## STANDARD STATE CONDITIONS

When the values of thermodynamic quantities are given on the test, they are almost always given for standard state conditions. A thermodynamic quantity under standard state conditions is indicated by the little superscript circle, so the following is true under standard state conditions:

$$\Delta H = \Delta H^\circ$$

$$\Delta S = \Delta S^\circ$$

$$\Delta G = \Delta G^\circ$$

### Standard State Conditions

- All gases are at 1 atmosphere pressure.
- All liquids are pure.
- All solids are pure.
- All solutions are at 1-molar (1 M) concentration.
- The energy of formation of an element in its normal state is defined as zero.
- The temperature used for standard state values is almost invariably room temperature: 25°C (298 K). Standard state values can be calculated for other temperatures, however.

## ENTHALPY

### ENTHALPY CHANGE, $\Delta H$

The enthalpy of a substance is a measure of the energy that is released or absorbed by the substance when bonds are broken and formed during a reaction.

#### The Basic Rules of Enthalpy

When bonds are *formed*, energy is *released*.

When bonds are *broken*, energy is *absorbed*.

The change in enthalpy,  $\Delta H$ , that takes place over the course of a reaction can be calculated by subtracting the enthalpy of the reactants from the enthalpy of the products.

#### Enthalpy Change

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

If the products have stronger bonds than the reactants, then the products have lower enthalpy than the reactants and are more stable; in this case, energy is released by the reaction, which is **exothermic**.

If the products have weaker bonds than the reactants, then the products have higher enthalpy than the reactants and are less stable; in this case, energy is absorbed by the reaction, which is **endothermic**.

All substances like to be in the lowest possible energy state, which gives them the greatest stability. This means that, in general, exothermic processes are more likely to occur spontaneously than endothermic processes.

## HEAT OF FORMATION, $\Delta H_f^\circ$

Heat of formation is the change in energy that takes place when one mole of a compound is formed from its component pure elements under standard state conditions. Heat of formation is almost always calculated at a temperature of 25°C (298 K).

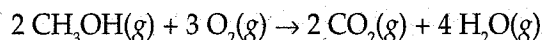
Remember,  $\Delta H_f^\circ$  for a pure element is defined as zero.

- If  $\Delta H_f^\circ$  for a compound is negative, energy is released when the compound is formed from pure elements, and the product is *more* stable than its constituent elements. That is, the process is exothermic.
- If  $\Delta H_f^\circ$  for a compound is positive, energy is absorbed when the compound is formed from pure elements, and the product is *less* stable than its constituent elements. That is, the process is endothermic.

If the  $\Delta H_f^\circ$  values of the products and reactants are known,  $\Delta H$  for a reaction can be calculated.

$$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants}$$

Let's find  $\Delta H^\circ$  for the reaction below.



Compound	$\Delta H_f^\circ$ (kJ/mol)
$\text{CH}_3\text{OH}(g)$	-201
$\text{O}_2(g)$	0
$\text{CO}_2(g)$	-394
$\text{H}_2\text{O}(g)$	-242

$$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants}$$

$$\Delta H^\circ = [(2)(\Delta H_f^\circ \text{CO}_2) + (4)(\Delta H_f^\circ \text{H}_2\text{O})] - [(2)(\Delta H_f^\circ \text{CH}_3\text{OH}) + (3)(\Delta H_f^\circ \text{O}_2)]$$

$$\Delta H^\circ = [(2)(-394 \text{ kJ}) + (4)(-242 \text{ kJ})] - [(2)(-201 \text{ kJ}) + (3)(0 \text{ kJ})]$$

$$\Delta H^\circ = (-1,756 \text{ kJ}) - (-402 \text{ kJ})$$

$$\Delta H^\circ = -1,354 \text{ kJ}$$

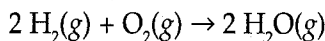


## BOND ENERGY

Bond energy is the energy required to break a bond. Because the breaking of a bond is an endothermic process, bond energy is always a positive number. When a bond is formed, energy equal to the bond energy is released.

$$\Delta H^\circ = \Sigma \text{ Bond energies of bonds broken} - \Sigma \text{ Bond energies of bonds formed}$$

The bonds broken will be the reactant bonds, and the bonds formed will be the product bonds. Let's find  $\Delta H^\circ$  for the reaction below.



Bond	Bond Energy (kJ/mol)
H-H	436
O=O	499
O-H	463

$$\Delta H^\circ = \Sigma \text{ Bond energies of bonds broken} - \Sigma \text{ Bond energies of bonds formed}$$

$$\Delta H^\circ = [(2)(\text{H-H}) + (1)(\text{O=O})] - [(4)(\text{O-H})]$$

$$\Delta H^\circ = [(2)(436 \text{ kJ}) + (1)(499 \text{ kJ})] - [(4)(463 \text{ kJ})]$$

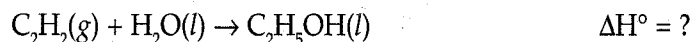
$$\Delta H^\circ = (1,371 \text{ kJ}) - (1,852 \text{ kJ})$$

$$\Delta H^\circ = -481 \text{ kJ}$$

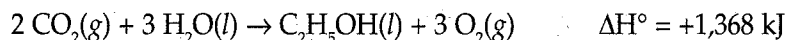
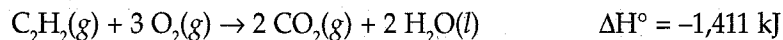
## HESS'S LAW

Hess's law says that if a reaction can be described as a series of steps, then  $\Delta H$  for the overall reaction is simply the sum of the  $\Delta H$  values for all the steps.

For example, let's say you wanted to calculate the enthalpy change for the following reaction:



And let's say that you know the enthalpy changes for the following two reactions:



If you add the two reactions whose enthalpy changes you know (as though they were simultaneous equations) and cancel the substances that appear on both sides, you'll get the reaction that you're looking for. This means that you can add the enthalpy changes for the reactions that you know to get the enthalpy change that you're looking for.

$$-1,411 \text{ kJ} + 1,368 \text{ kJ} = -43 \text{ kJ}$$

## HEAT CAPACITY AND SPECIFIC HEAT

Heat capacity,  $C_p$ , is a measure of how much the temperature of an object is raised when it absorbs heat.

Heat Capacity
$C_p = \frac{\Delta H}{\Delta T}$ <p><math>C_p</math> = heat capacity <math>\Delta H</math> = heat added (J or cal) <math>\Delta T</math> = temperature change (K or °C)</p>

An object with a large heat capacity can absorb a lot of heat without undergoing much of a change in temperature, whereas an object with a small heat capacity shows a large increase in temperature even if only a small amount of heat is absorbed.

**Specific heat** is the amount of heat required to raise the temperature of one gram of a substance one degree Celsius.

Specific Heat
$q = mc\Delta T$ <p><math>q</math> = heat added (J or cal) <math>m</math> = mass of the substance (g or kg) <math>c</math> = specific heat <math>\Delta T</math> = temperature change (K or °C)</p>

## ENTROPY

The entropy,  $S$ , of a system is a measure of the randomness or disorder of the system; the greater the disorder of a system, the greater its entropy. Because zero entropy is defined as a solid crystal at 0 K, all substances that we encounter will have some positive value for entropy. Standard entropies,  $S^\circ$ , are calculated at 25°C (298 K).

You should be familiar with several simple rules concerning entropies.

- Liquids have higher entropy values than solids.
- Gases have higher entropy values than liquids.
- Particles in solution have higher entropy values than solids.
- Two moles of a substance have higher entropy value than one mole.

## ENTROPY CHANGE, $\Delta S^\circ$

The standard entropy change,  $\Delta S^\circ$ , that has taken place at the completion of a reaction is the difference between the standard entropies of the products and the standard entropies of the reactants.

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

## GIBBS FREE ENERGY

The Gibbs free energy, or simply free energy,  $G$ , of a process is a measure of the spontaneity of the process.

For a given reaction

- if  $\Delta G$  is negative, the reaction is spontaneous
- if  $\Delta G$  is positive, the reaction is not spontaneous
- if  $\Delta G = 0$ , the reaction is at equilibrium

## FREE ENERGY CHANGE, $\Delta G$

The standard free energy change,  $\Delta G$ , for a reaction can be calculated from the standard free energies of formation,  $\Delta G_f^\circ$ , of its products and reactants in the same way that  $\Delta S^\circ$  was calculated.

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

## $\Delta G$ , $\Delta H$ , AND $\Delta S$

In general, nature likes to move toward two different and seemingly contradictory states—low energy and high disorder, so spontaneous processes must result in decreasing enthalpy or increasing entropy or both.

There is an important equation that relates spontaneity ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) to one another.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$T = \text{absolute temperature (K)}$

The chart below shows how different values of enthalpy and entropy affect spontaneity.

$\Delta H$	$\Delta S$	$T$	$\Delta G$	
-	+	Low	-	Always spontaneous
		High	-	
+	-	Low	+	Never spontaneous
		High	+	
+	+	Low	+	Not spontaneous at low temperature
		High	-	Spontaneous at high temperature
-	-	Low	-	Spontaneous at low temperature
		High	+	Not spontaneous at high temperature

You should note that at low temperature, enthalpy is dominant, while at high temperature, entropy is dominant.

## $\Delta G$ AND $\Delta G^\circ$

The standard free energy change,  $\Delta G^\circ$ , gives the spontaneity of a reaction when all the concentrations of reactants and products are in their standard state concentrations (at 1 molar). The free energy change, and thus the spontaneity, of a reaction will be different from the standard free energy change if the initial concentrations of reactants and products are not 1 molar.

The standard free energy change,  $\Delta G^\circ$ , can be related to  $\Delta G$  for other conditions by the following equations:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

or

$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

$\Delta G^\circ$  = standard free energy change (J)

$\Delta G$  = free energy change under given initial conditions (J)

$R$  = the gas constant, 8.31 J/mol-K

$T$  = absolute temperature (K)

$Q$  = the reaction quotient for the given initial conditions

## STANDARD FREE ENERGY CHANGE AND THE EQUILIBRIUM CONSTANT

Let's look at the equation relating  $\Delta G$  and  $\Delta G^\circ$ .

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium,  $\Delta G = 0$  and  $Q = K$ .

Knowing this, we can derive an equation relating the standard free energy change,  $\Delta G^\circ$ , and the equilibrium constant,  $K$ .

$$\Delta G^\circ = -RT \ln K$$

or

$$\Delta G^\circ = -2.303RT \log K$$

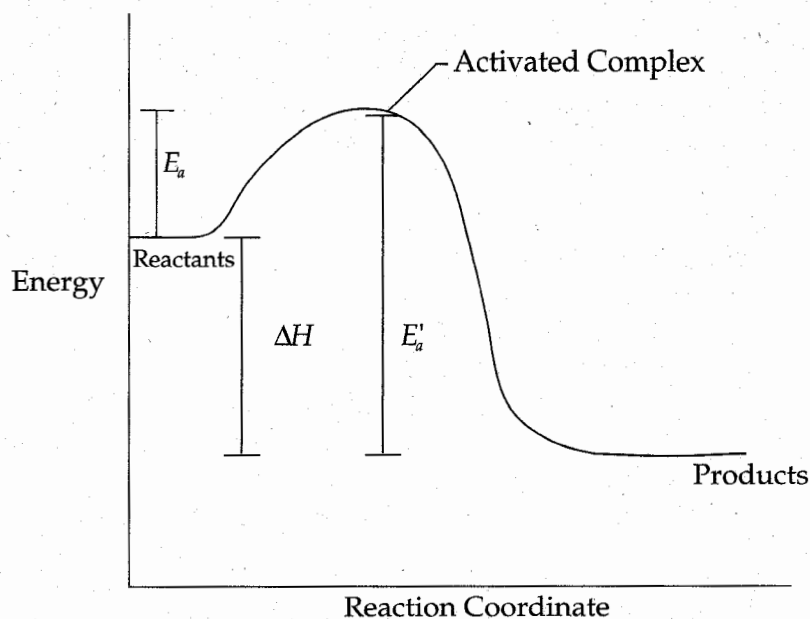
$\Delta G^\circ$  = the gas constant, 8.31 J/mol-K

$T$  = absolute temperature (K)

$K$  = the equilibrium constant

Notice that if  $\Delta G^\circ$  is negative,  $K$  must be greater than 1, and products will be favored at equilibrium. Alternatively, if  $\Delta G^\circ$  is positive,  $K$  must be less than 1, and reactants will be favored at equilibrium.

## ENERGY DIAGRAMS



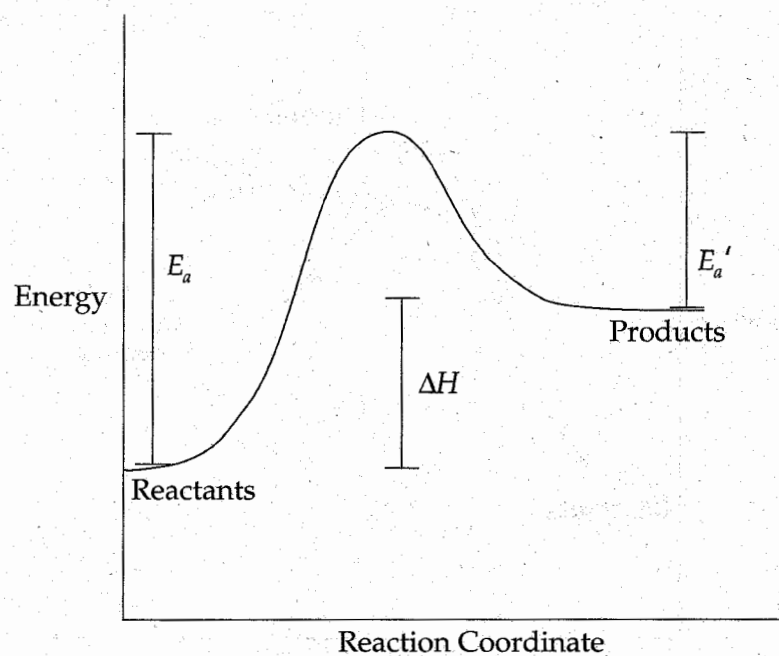
### EXOTHERMIC REACTION

The diagram above shows the energy change that takes place during an exothermic reaction. The reactants start with a certain amount of energy (read the graph from left to right). For the reaction to proceed, the reactants must have enough energy to reach the transition state, where they are part of an activated complex. This is the highest point on the graph above. The amount of energy needed to reach this point is called the **activation energy**,  $E_a$ . At this point, all reactant bonds have been broken, but no product bonds have been formed, so this is the point in the reaction with the highest energy and lowest stability. The energy needed for the reverse reaction is shown as line  $E'_a$ .

Moving to the right past the activated complex, product bonds start to form, and we eventually reach the energy level of the products.

This diagram represents an exothermic reaction, so the products are at a lower energy level than the reactants and  $\Delta H$  is negative.

The diagram below shows an endothermic reaction.

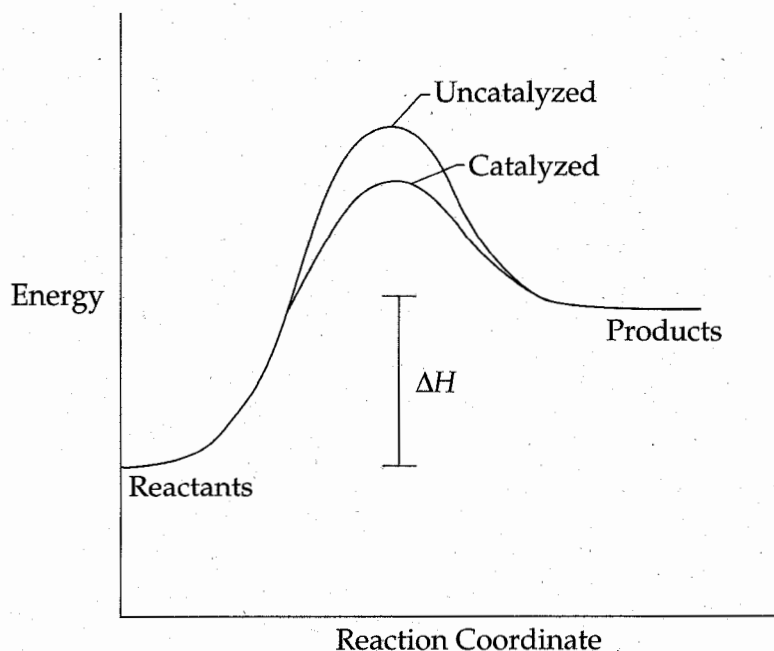


### ENDOTHERMIC REACTION

In this diagram, the energy of the products is greater than the energy of the reactants, so  $\Delta H$  is positive.

Reaction diagrams can be read in both directions, so the reverse reaction for an exothermic reaction is endothermic and vice versa.

## CATALYSTS AND ENERGY DIAGRAMS



A catalyst speeds up a reaction by providing the reactants with an alternate pathway that has a lower activation energy, as shown in the diagram above.

Notice that the only difference between the catalyzed reaction and the uncatalyzed reaction is that the energy of the activated complex is lower for the catalyzed reaction. A catalyst lowers the activation energy, but it has no effect on the energy of the reactants, the energy of the products, or  $\Delta H$  for the reaction.

Also note that a catalyst lowers the activation energy for both the forward and the reverse reaction, so it has no effect on the equilibrium conditions.

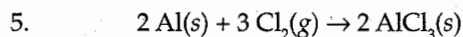
## CHAPTER 8 QUESTIONS

### MULTIPLE-CHOICE QUESTIONS

#### Questions 1–4

- (A) Free energy change ( $\Delta G$ )
- (B) Entropy change ( $\Delta S$ )
- (C) Heat of vaporization
- (D) Heat of fusion
- (E) Heat capacity

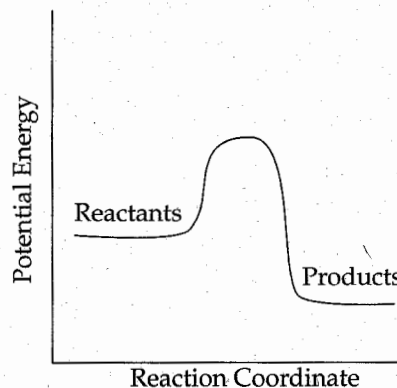
1. If this has a negative value for a process, then the process occurs spontaneously.
2. This is a measure of how the disorder of a system is changing.
3. This is the energy given off when a substance condenses.
4. This is the energy taken in by a substance when it melts.



The reaction above is not spontaneous under standard conditions, but becomes spontaneous as the temperature decreases toward absolute zero. Which of the following is true at standard conditions?

- (A)  $\Delta S$  and  $\Delta H$  are both negative.
- (B)  $\Delta S$  and  $\Delta H$  are both positive.
- (C)  $\Delta S$  is negative, and  $\Delta H$  is positive.
- (D)  $\Delta S$  is positive, and  $\Delta H$  is negative.
- (E)  $\Delta S$  and  $\Delta H$  are both equal to zero.

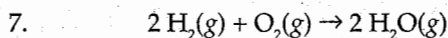
6.



Which of the following is true of the reaction shown in the diagram above?

- (A) The reaction is endothermic because the reactants are at a higher energy level than the products.
- (B) The reaction is endothermic because the reactants are at a lower energy level than the products.
- (C) The reaction is exothermic because the reactants are at a higher energy level than the products.
- (D) The reaction is exothermic because the reactants are at a lower energy level than the products.
- (E) The reaction is endothermic because the reactants are at the same energy level as the products.





Based on the information given in the table below, what is  $\Delta H^\circ$  for the above reaction?

Bond	Average bond energy (kJ/mol)
H-H	500
O=O	500
O-H	500

- (A) -2,000 kJ  
 (B) -1,500 kJ  
 (C) -500 kJ  
 (D) +1,000 kJ  
 (E) +2,000 kJ

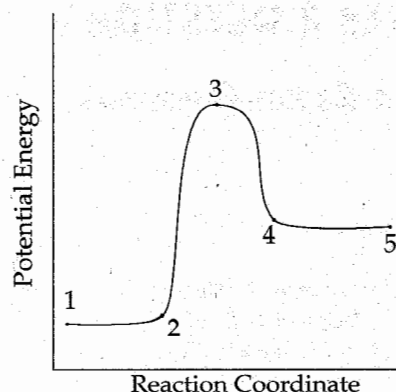
8. Which of the following is true of a reaction that is spontaneous at 298 K but becomes nonspontaneous at a higher temperature?

- (A)  $\Delta S^\circ$  and  $\Delta H^\circ$  are both negative.  
 (B)  $\Delta S^\circ$  and  $\Delta H^\circ$  are both positive.  
 (C)  $\Delta S^\circ$  is negative, and  $\Delta H^\circ$  is positive.  
 (D)  $\Delta S^\circ$  is positive, and  $\Delta H^\circ$  is negative.  
 (E)  $\Delta S^\circ$  and  $\Delta H^\circ$  are both equal to zero.

9. Which of the following will be true when a pure substance in liquid phase freezes spontaneously?

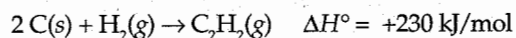
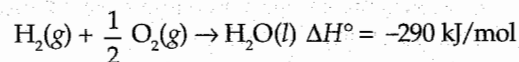
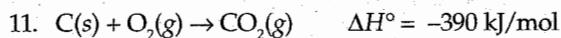
- (A)  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  are all positive.  
 (B)  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  are all negative.  
 (C)  $\Delta G$  and  $\Delta H$  are negative, but  $\Delta S$  is positive.  
 (D)  $\Delta G$  and  $\Delta S$  are negative, but  $\Delta H$  is positive.  
 (E)  $\Delta S$  and  $\Delta H$  are negative, but  $\Delta G$  is positive.

10.

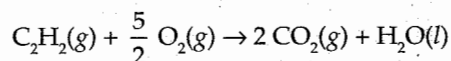


Which point on the graph shown above corresponds to activated complex or transition state?

- (A) 1  
 (B) 2  
 (C) 3  
 (D) 4  
 (E) 5

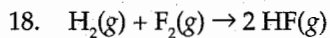


Based on the information given above, what is  $\Delta H^\circ$  for the following reaction?



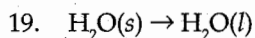
- (A) -1,300 kJ  
 (B) -1,070 kJ  
 (C) -840 kJ  
 (D) -780 kJ  
 (E) -680 kJ

12. If an endothermic reaction is spontaneous at 298 K, which of the following must be true for the reaction?
- $\Delta G$  is greater than zero.
  - $\Delta H$  is greater than zero.
  - $\Delta S$  is greater than zero.
- (A) I only  
 (B) II only  
 (C) I and II only  
 (D) II and III only  
 (E) I, II, and III
13. The addition of a catalyst will have which of the following effects on a chemical reaction?
- The enthalpy change will decrease.
  - The entropy change will decrease.
  - The activation energy will decrease.
- (A) I only  
 (B) II only  
 (C) III only  
 (D) I and II only  
 (E) II and III only
14.  $C(s) + 2 H_2(g) \rightarrow CH_4(g) \quad \Delta H^\circ = x$   
 $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = y$   
 $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \quad \Delta H^\circ = z$
- Based on the information given above, what is  $\Delta H^\circ$  for the following reaction?
- $$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$$
- (A)  $x + y + z$   
 (B)  $x + y - z$   
 (C)  $z + y - 2x$   
 (D)  $2z + y - x$   
 (E)  $2z + y - 2x$
15. For which of the following processes will  $\Delta S$  be positive?
- $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
  - $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$
  - $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- (A) I only  
 (B) II only  
 (C) I and II only  
 (D) I and III only  
 (E) I, II, and III
16. In which of the following reactions is entropy increasing?
- $2 SO_2(g) + O_2(g) \rightarrow 2 SO_3(g)$
  - $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$
  - $H_2(g) + Cl_2(g) \rightarrow 2 HCl(g)$
  - $2 NO_2(g) \rightarrow 2 NO(g) + O_2(g)$
  - $2 H_2S(g) + 3 O_2(g) \rightarrow 2 H_2O(g) + 2 SO_2(g)$
17. When pure sodium is placed in an atmosphere of chlorine gas, the following spontaneous reaction occurs.
- $$2 Na(s) + Cl_2(g) \rightarrow 2 NaCl(s)$$
- Which of the following statements is true about the reaction?
- $\Delta S > 0$
  - $\Delta H < 0$
  - $\Delta G > 0$
- (A) I only  
 (B) II only  
 (C) I and II only  
 (D) II and III only  
 (E) I, II, and III



Gaseous hydrogen and fluorine combine in the reaction above to form hydrogen fluoride with an enthalpy change of  $-540 \text{ kJ}$ . What is the value of the heat of formation of  $\text{HF}(\text{g})$ ?

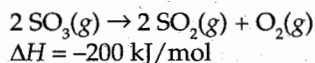
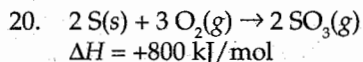
- (A)  $-1,080 \text{ kJ/mol}$
- (B)  $-540 \text{ kJ/mol}$
- (C)  $-270 \text{ kJ/mol}$
- (D)  $270 \text{ kJ/mol}$
- (E)  $540 \text{ kJ/mol}$



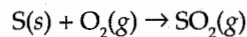
Which of the following is true of the reaction shown above at room temperature?

- I.  $\Delta G$  is greater than zero.
- II.  $\Delta H$  is greater than zero.
- III.  $\Delta S$  is greater than zero.

- (A) II only
- (B) III only
- (C) I and II only
- (D) I and III only
- (E) II and III only



Based on the information given above, what is  $\Delta H$  for the following reaction?



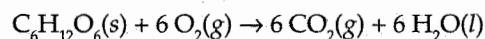
- (A)  $300 \text{ kJ}$
- (B)  $500 \text{ kJ}$
- (C)  $600 \text{ kJ}$
- (D)  $1,000 \text{ kJ}$
- (E)  $1,200 \text{ kJ}$

## PROBLEMS

1.

Substance	Absolute Entropy, $S^\circ$ (J/mol-K)	Molecular Weight
$C_6H_{12}O_6(s)$	212.13	180
$O_2(g)$	205	32
$CO_2(g)$	213.6	44
$H_2O(l)$	69.9	18

Energy is released when glucose is oxidized in the following reaction, which is a metabolism reaction that takes place in the body.

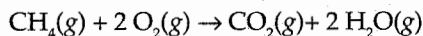


The standard enthalpy change,  $\Delta H^\circ$ , for the reaction is  $-2,801$  kJ at 298 K.

- Calculate the standard entropy change,  $\Delta S^\circ$ , for the oxidation of glucose.
- Calculate the standard free energy change,  $\Delta G^\circ$ , for the reaction at 298 K.
- What is the value of  $K_{eq}$  for the reaction?
- How much energy is given off by the oxidation of 1.00 gram of glucose?

2.

Bond	Average Bond Dissociation Energy (kJ/mol)
C-H	415
O=O	495
C=O	799
O-H	463



The standard free energy change,  $\Delta G^\circ$ , for the reaction above is  $-801$  kJ at 298 K.

- Use the table of bond dissociation energies to find  $\Delta H^\circ$  for the reaction above.
- What is the value of  $K_{eq}$  for the reaction?
- What is the value of  $\Delta S^\circ$  for the reaction at 298 K?
- Give an explanation for the size of the entropy change found in (c).



The heat of formation,  $\Delta H_f^\circ$ , of  $\text{NH}_3(\text{g})$  is  $-46.2 \text{ kJ/mol}$ . The free energy of formation,  $\Delta G_f^\circ$ , of  $\text{NH}_3(\text{g})$  is  $-16.7 \text{ kJ/mol}$ .

- What are the values of  $\Delta H^\circ$  and  $\Delta G^\circ$  for the reaction?
- What is the value of the entropy change,  $\Delta S^\circ$ , for the reaction above at 298 K?
- As the temperature is increased, what is the effect on  $\Delta G$  for the reaction? How does this affect the spontaneity of the reaction?
- At what temperature can  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  gases be maintained together in equilibrium, each with a partial pressure of 1 atm?

## ESSAYS



The reaction above proceeds spontaneously from standard conditions at 298 K.

- Predict the sign of the entropy change,  $\Delta S^\circ$ , for the reaction. Explain.
- How would the value of  $\Delta S^\circ$  for the reaction change if the product of the reaction was  $\text{H}_2\text{O}(\text{g})$ ?
- What is the sign of  $\Delta G^\circ$  at 298 K? Explain.
- What is the sign of  $\Delta H^\circ$  at 298 K? Explain.



The reaction above is spontaneous at 298 K, and the heat of reaction,  $\Delta H^\circ$ , is  $-178 \text{ kJ}$ .

- Predict the sign of the entropy change,  $\Delta S^\circ$ , for the reaction. Explain.
- What is the sign of  $\Delta G^\circ$  at 298 K? Explain.
- What change, if any, occurs to the value of  $\Delta G^\circ$  as the temperature is increased from 298 K?
- As the reaction takes place in a closed container, what changes will occur in the concentration of  $\text{CO}_2$  and the temperature?



At 298 K, the value of the equilibrium constant,  $K$ , for the reaction above is 0.036.

- What is the sign of  $\Delta S^\circ$  for the reaction above at 298 K?
- What is the sign of  $\Delta H^\circ$  for the reaction above at 298 K?
- What is the sign of  $\Delta G^\circ$  for the reaction above at 298 K?
- At approximately what temperature will  $\Delta G$  for the reaction be equal to zero?

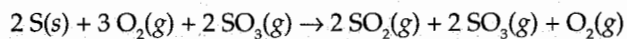
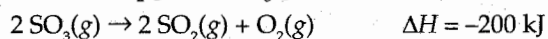
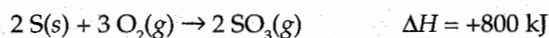
# CHAPTER 8 ANSWERS AND EXPLANATIONS

## MULTIPLE-CHOICE QUESTIONS

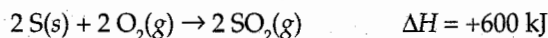
- A** A negative value for  $\Delta G$  means that the process is spontaneous. A positive value for  $\Delta G$  means that the process is nonspontaneous.
- B** Entropy is a measure of the disorder of a system. A positive value for  $\Delta S$  means that a system has become more disordered. A negative value for  $\Delta S$  means that a system has become more orderly.
- C** The heat of vaporization is the heat given off when a substance condenses. It is also the heat that must be put into a substance to make it vaporize.
- D** The heat of fusion is the heat that must be put into a substance to melt it. It is also the heat given off when a substance freezes.  
By the way, choice (E), heat capacity, is a measure of how much heat must be added to a given object to raise its temperature  $1^\circ\text{C}$ .
- A** Remember  $\Delta G = \Delta H - T\Delta S$ .  
If the reaction is spontaneous only when the temperature is very low, then  $\Delta G$  is only negative when  $T$  is very small. This can only happen when  $\Delta H$  is negative (which favors spontaneity) and  $\Delta S$  is negative (which favors nonspontaneity). A very small value for  $T$  will eliminate the influence of  $\Delta S$ .
- C** In an exothermic reaction, energy is given off as the products are created because the products have less potential energy than the reactants.
- C** The bond energy is the energy that must be put into a bond to break it. First let's figure out how much energy must be put into the reactants to break their bonds.  
To break 2 moles of H–H bonds, it takes  $(2)(500) \text{ kJ} = 1,000 \text{ kJ}$   
To break 1 mole of O=O bonds, it takes 500 kJ.  
So to break up the reactants, it takes +1,500 kJ.  
Energy is given off when a bond is formed; that's the negative of the bond energy. Now let's see how much energy is given off when 2 moles of  $\text{H}_2\text{O}$  are formed.  
2 moles of  $\text{H}_2\text{O}$  molecules contain 4 moles of O–H bonds, so  $(4)(-500) \text{ kJ} = -2,000 \text{ kJ}$  are given off.  
So the value of  $\Delta H^\circ$  for the reaction is  
 $(-2,000 \text{ kJ, the energy given off}) + (1,500 \text{ kJ, the energy put in}) = -500 \text{ kJ}$ .
- A** Remember,  $\Delta G = \Delta H - T\Delta S$ . If the reaction is spontaneous at standard temperature but becomes nonspontaneous at higher temperatures, then  $\Delta G$  is negative only at lower temperatures. This can only happen when  $\Delta H$  is negative (which favors spontaneity) and  $\Delta S$  is negative (which favors nonspontaneity). As the value of  $T$  increases, the influence of  $\Delta S$  increases, eventually making the reaction nonspontaneous.
- B** The process is spontaneous, so  $\Delta G$  must be negative. The intermolecular forces become stronger and the substance moves to a lower energy level when it freezes, so  $\Delta H$  must be negative. The substance becomes more orderly when it freezes, so  $\Delta S$  must be negative.

10. C Point 3 represents the activated complex, which is the point of highest energy. This point is the transition state between the reactants and the products.
11. A The equations given on top give the heats of formation of all the reactants and products (remember, the heat of formation of  $O_2$ , an element in its most stable form, is zero).  
 $\Delta H^\circ$  for a reaction = ( $\Delta H^\circ$  for the products) - ( $\Delta H^\circ$  for the reactants).  
 First, the products:  
 From  $CO_2$ , we get  $(2)(-390 \text{ kJ}) = -780 \text{ kJ}$   
 From  $H_2O$ , we get  $-290 \text{ kJ}$   
 So  $\Delta H^\circ$  for the products =  $(-780 \text{ kJ}) + (-290 \text{ kJ}) = -1,070 \text{ kJ}$   
 Now the reactants:  
 From  $C_2H_2$ , we get  $+230 \text{ kJ}$ . The heat of formation of  $O_2$  is defined as zero, so that's it for the reactants.  
 $\Delta H^\circ$  for the reaction =  $(-1,070 \text{ kJ}) - (+230 \text{ kJ}) = -1,300 \text{ kJ}$ .
12. D The reaction is spontaneous, so  $\Delta G$  must be less than zero, so (I) is not true. The reaction is endothermic, so  $\Delta H$  must be greater than zero; therefore, (II) is true.  
 The only way that an endothermic reaction can be spontaneous is if the entropy is increasing, so  $\Delta S$  is greater than zero, and (III) is true.
13. C The addition of a catalyst speeds up a reaction by lowering the activation energy. A catalyst has no effect on the entropy or enthalpy change of a reaction.
14. D The equations given above the question give the heats of formation of all the reactants and products (remember, the heat of formation of  $O_2$ , an element in its most stable form, is zero).  
 $\Delta H^\circ$  for a reaction = ( $\Delta H^\circ$  for the products) - ( $\Delta H^\circ$  for the reactants).  
 First, the products:  
 From  $2 H_2O$ , we get  $2z$   
 From  $CO_2$ , we get  $y$   
 So  $\Delta H^\circ$  for the products =  $2z + y$   
 Now the reactants:  
 From  $CH_4$ , we get  $x$ . The heat of formation of  $O_2$  is defined to be zero, so that's it for the reactants.  
 $\Delta H^\circ$  for the reaction =  $(2z + y) - (x) = 2z + y - x$ .
15. D In (I),  $NaCl$  goes from a solid to aqueous particles. Aqueous particles are more disorderly than a solid, so  $\Delta S$  will be positive.  
 In (II), we go from 3 moles of gas to 2 moles of gas. Fewer moles and less gas means less entropy, so  $\Delta S$  will be negative.  
 In (III), we go from a solid to a solid and a gas. More moles and the production of more gas means increasing entropy, so  $\Delta S$  will be positive.
16. D Choice (D) is the only reaction where the number of moles of gas is increasing, going from 2 moles of gas on the reactant side to 3 moles of gas on the product side. In all the other choices, the number of moles of gas either decreases or remains constant.

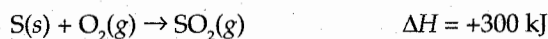
17. **B** In the reaction, a solid combines with a gas to produce fewer moles of solid, so the entropy change is negative and (I) is not true. The reaction is spontaneous, so the free energy change is negative and (III) is not true. For a reaction with decreasing entropy to be spontaneous, it must be exothermic. The enthalpy change is negative for an exothermic reaction and (II) is true.
18. **C** The reaction that forms 2 moles of HF(g) from its constituent elements has an enthalpy change of -540 kJ. The heat of formation is given by the reaction that forms 1 mole from these elements, so you can just divide -540 kJ by 2 to get -270 kJ.
19. **E** Ice melts spontaneously at room temperature, so  $\Delta G$  is less than zero; therefore, (I) is not true. In this reaction, ice melts, so heat is absorbed to break up the intermolecular forces, and  $\Delta H$  is greater than zero; therefore, (II) is true. Liquid water is less orderly than ice, so the entropy change when ice melts is positive; therefore,  $\Delta S$  is greater than zero, and (III) is true.
20. **A** You can use Hess's law. Add the two reactions together, and cancel things that appear on both sides.



This reduces to



Now we can cut everything in half to get the equation we want.





## PROBLEMS

1. (a) Use the entropy values in the table.

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(6)(213.6) + (6)(69.9)] - [(212.13) + (6)(205)] \text{ J/K}$$

$$\Delta S^\circ = 259 \text{ J/K}$$

- (b) Use the equation below. Remember that enthalpy values are given in kJ and entropy values are given in J.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta G^\circ = (-2,801 \text{ kJ}) - (298)(0.259 \text{ kJ}) = -2,880 \text{ kJ}$$

- (c) Use the equation below. Remember that the gas constant is given in terms of J.

$$\log K = \frac{\Delta G^\circ}{-2.303RT}$$

$$\log K = \frac{(-2,880,000)}{(-2.303)(8.31)(298)} = 505$$

$$K = 10^{505}$$

- (d) The enthalpy change of the reaction,  $H^\circ$ , is a measure of the energy given off by 1 mole of glucose.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of glucose} = \frac{(1.00 \text{ g})}{(180 \text{ g/mol})} = 0.00556 \text{ moles}$$

$$(0.00556 \text{ mol})(2,801 \text{ kJ/mol}) = 15.6 \text{ kJ}$$

2. (a) Use the relationship below.

$$\Delta H^\circ = \sum \text{Energies of the bonds broken} - \sum \text{Energies of the bonds formed}$$

$$\Delta H^\circ = [(4)(415) + (2)(495)] - [(2)(799) + (4)(463)] \text{ kJ}$$

$$\Delta H^\circ = -800 \text{ kJ}$$

- (b) Use the following equation. Remember that the gas constant is given in terms of J.

$$\log K = \frac{\Delta G^\circ}{-2.303RT}$$

$$\log K = \frac{(-801,000)}{(-2.303)(8.31)(298)} = 140$$

$$K = 10^{140}$$

(c) Use  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

Remember that enthalpy values are given in kJ and entropy values are given in J.

$$\Delta S^\circ = \frac{\Delta H - \Delta G}{T} = \frac{(-800 \text{ kJ}) - (-801 \text{ kJ})}{(298 \text{ K})}$$

$$\Delta S^\circ = 0.003 \text{ kJ/K} = 3 \text{ J/K}$$

(d)  $\Delta S^\circ$  is very small, which means that the entropy change for the process is very small. This makes sense because the number of moles remains constant, the number of moles of gas remains constant, and the complexity of the molecules remains about the same.

3. (a) By definition,  $\Delta H_f^\circ$  and  $\Delta G_f^\circ$  for  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  are equal to zero.

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta H^\circ = [(2 \text{ mol})(-46.2 \text{ kJ/mol})] - 0 = -92.4 \text{ kJ}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = [(2 \text{ mol})(-16.7 \text{ kJ/mol})] - 0 = -33.4 \text{ kJ}$$

(b) Use  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

Remember that enthalpy values are given in kJ and entropy values are given in J.

$$\Delta S^\circ = \frac{\Delta H - \Delta G}{T} = \frac{(-92.4 \text{ kJ}) - (-33.4 \text{ kJ})}{(298 \text{ K})}$$

$$\Delta S^\circ = -0.198 \text{ kJ/K} = -198 \text{ J/K}$$

(c) Use  $\Delta G = \Delta H^\circ - T \Delta S^\circ$

From (b),  $\Delta S^\circ$  is negative, so increasing the temperature increases the value of  $\Delta G^\circ$ , making the reaction less spontaneous.

(d) Use  $\Delta G = \Delta H^\circ - T \Delta S^\circ$

At equilibrium,  $\Delta G = 0$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-92,400 \text{ J})}{(-198 \text{ J/K})} = 467 \text{ K}$$

## ESSAYS

4. (a)  $\Delta S^\circ$  is negative because the products are less random than the reactants. That's because gas is converted into liquid in the reaction.
- (b) The value of  $\Delta S^\circ$  would increase, becoming less negative because  $\text{H}_2\text{O}(g)$  is more random than water but remaining negative because the entropy would still decrease from reactants to products.
- (c)  $\Delta G^\circ$  is negative because the reaction proceeds spontaneously.
- (d)  $\Delta H^\circ$  must be negative at 298 K. For a reaction to occur spontaneously from standard conditions, either  $\Delta S^\circ$  must be positive or  $\Delta H^\circ$  must be negative. This reaction is spontaneous although  $\Delta S^\circ$  is negative, so  $\Delta H^\circ$  must be negative.
5. (a)  $\Delta S^\circ$  is negative because the products are less random than the reactants. That's because two moles of reactants are converted to one mole of products and gas is converted into solid in the reaction.
- (b)  $\Delta G^\circ$  is negative because the reaction proceeds spontaneously.
- (c) Use  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$   
 $\Delta G^\circ$  will become less negative because as temperature is increased, the entropy change of a reaction becomes more important in determining its spontaneity. The entropy change for this reaction is negative, which discourages spontaneity, so increasing temperature will make the reaction less spontaneous, thus making  $\Delta G^\circ$  less negative.
- (d) The concentration of  $\text{CO}_2$  will decrease as the reaction proceeds in the forward direction and the reactants are consumed. The temperature will increase as heat is given off by the exothermic reaction.
6. (a)  $\Delta S^\circ$  is positive because the product is more random than the reactant. That's because liquid is converted into gas in the reaction.
- (b)  $\Delta H^\circ$  is positive because  $\text{H}_2\text{O}(g)$  is less stable than water. Energy must be put into water to overcome intermolecular forces and create water vapor.
- (c) Use  $\Delta G^\circ = -2.203RT \log K$   
If  $K$  is less than 1,  $\log K$  will be negative, making  $\Delta G^\circ$  positive.
- (d)  $\Delta G$  will be equal to zero at 373 K or  $100^\circ\text{C}$ .  $\Delta G$  will be equal to zero at equilibrium. The point at which water and  $\text{H}_2\text{O}(g)$  are in equilibrium is the boiling point.

# 9

## Solutions

### HOW OFTEN DO SOLUTIONS APPEAR ON THE EXAM?

In the multiple-choice section, this topic appears in about 9 out of 75 questions. In the free-response section, this topic appears almost every year.

### CONCENTRATION MEASUREMENTS

#### MOLARITY

Molarity ( $M$ ) expresses the concentration of a solution in terms of volume. It is the most widely used unit of concentration, turning up in calculations involving equilibrium, acids and bases, and electrochemistry, among others.

When you see a chemical symbol in brackets on the test, that means they are talking about molarity. For instance, “[Na<sup>+</sup>]” is the same as “the molar concentration (molarity) of sodium ions.”

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

## MOLALITY

Molality ( $m$ ) expresses concentration in terms of the mass of a solvent. It is the unit of concentration used for determining the effect of most colligative properties, where the number of moles of solute is more important than the nature of the solute.

$$\text{Molality } (m) = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

Molarity and molality differ in two ways: Molarity tells you about moles of solute per *volume* of the *entire solution* (that is, the solute and the solvent), whereas molality tells you about moles of solute per *mass* of the *solvent*. Keeping in mind that one liter of water weighs one kilogram, and that for a dilute solution, the amount of solution is about the same as the amount of solvent, you should be able to see that for dilute aqueous solutions, molarity and molality are basically the same.

## MOLE FRACTION

Mole fraction ( $X_s$ ) gives the fraction of moles of a given substance (S) out of the total moles present in a sample. It is used in determining how the vapor pressure of a solution is lowered by the addition of a solute.

$$\text{Mole Fraction } (X_s) = \frac{\text{moles of substance S}}{\text{total number of moles in solution}}$$

## SOLUTES AND SOLVENTS

There is a basic rule for remembering which solutes will dissolve in which solvents.

### Like dissolves like

That means that polar or ionic solutes (like salt) will dissolve in polar solvents (like water). That also means that nonpolar solutes (like organic compounds) are best dissolved in nonpolar solvents. When an ionic substance dissolves, it breaks up into ions. That's **dissociation**. Free ions in a solution are called electrolytes because they can conduct electricity.

The **van't Hoff factor ( $i$ )** tells how many ions one unit of a substance will dissociate into in solution. For instance

- $\text{C}_6\text{H}_{12}\text{O}_6$  does not dissociate, so  $i = 1$
- $\text{NaCl}$  dissociates into  $\text{Na}^+$  and  $\text{Cl}^-$ , so  $i = 2$
- $\text{HNO}_3$  dissociates into  $\text{H}^+$  and  $\text{NO}_3^-$ , so  $i = 2$
- $\text{CaCl}_2$  dissociates into  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{Cl}^-$ , so  $i = 3$

## COLLIGATIVE PROPERTIES

Colligative properties are properties of a solution that depend on the number of solute particles in the solution. For colligative properties, the identity of the particles is not important.

### BOILING-POINT ELEVATION

When a solute is added to a solution, the boiling point of the solution increases.

Boiling-Point Elevation
$\Delta T = ik_b m$
$i$ = the van't Hoff factor, the number of particles into which the added solute dissociates
$k_b$ = the boiling-point elevation constant for the solvent
$m$ = molality

### FREEZING-POINT DEPRESSION

When solute is added to a solution, the freezing point of the solution decreases.

Freezing-Point Depression
$\Delta T = ik_f m$
$i$ = the van't Hoff factor, the number of particles into which the added solute dissociates
$k_f$ = the freezing-point depression constant for the solvent
$m$ = molality

### VAPOR PRESSURE LOWERING (RAOULT'S LAW)

When a solute is added to a solution, the vapor pressure of the solution will decrease. You may want to note that a direct result of the lowering of vapor pressure of a solution is the raising of its boiling point.

Vapor Pressure Lowering, Raoult's Law
$P = XP^\circ$
$P$ = vapor pressure of the solution
$P^\circ$ = vapor pressure of the pure solvent
$X$ = the mole fraction of the solvent

## OSMOTIC PRESSURE

When a pure solvent and a solution are separated by a membrane that only allows solvent to pass through, the solvent will try to pass through the membrane to dilute the solution. The pressure that must be applied to stop this process is called the **osmotic pressure**. The greater the concentration of solute in the solution, the greater the osmotic pressure. The equation for osmotic pressure takes a form that is similar to the ideal gas equation, as shown below.

Osmotic Pressure
$\lambda = \frac{nRT}{V} i = MRTi$
$\lambda$ = osmotic pressure (atm)
$n$ = moles of solute
$R$ = the gas constant, 0.0821 (L-atm)/(mol-K)
$T$ = absolute temperature (K)
$V$ = volume of the solution (L)
$i$ = the van't Hoff factor, the number of particles into which the added solute dissociates
$M$ = molarity of the solution ( $M = \frac{n}{V}$ )

## DENSITY

Density is the measure of mass per unit volume. Density can be used to describe liquids, solids, or gases. Because density relates mass and volume, it is useful if you need to convert between molarity, which deals with volume, and molality, which deals with mass.

Density of a Solution
$D = \frac{m}{V}$
$m$ = mass of the solution
$V$ = volume of the solution

## SOLUBILITY

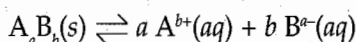
Roughly speaking, a salt can be considered to be “soluble” if more than 1 gram of the salt can be dissolved in 100 milliliters of water. Soluble salts are usually assumed to dissociate completely in aqueous solution. Most, but not all, solids become more soluble in a liquid as the temperature is increased.

## SOLUBILITY PRODUCT ( $K_{sp}$ )

Salts that are “slightly soluble” and “insoluble” still dissociate in solution to some extent. The solubility product ( $K_{sp}$ ) is a measure of the extent of a salt’s dissociation in solution. The  $K_{sp}$  is one of the forms of the equilibrium expression, which we’ll discuss in Chapter 10. The greater the value of the solubility product for a salt, the more soluble the salt.

### Solubility Product

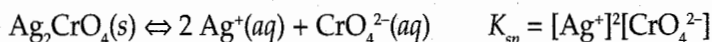
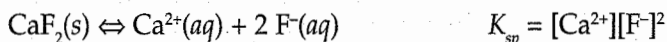
For the reaction



The solubility expression is

$$K_{sp} = [A^{b+}]^a [B^{a-}]^b$$

For example:



## THE COMMON ION EFFECT

Let’s look at the solubility expression for AgCl.

$$K_{sp} = [\text{Ag}^{+}][\text{Cl}^{-}] = 1.6 \times 10^{-10}$$

If we throw a block of solid AgCl into a beaker of water, we can tell from the  $K_{sp}$  what the concentrations of  $\text{Ag}^{+}$  and  $\text{Cl}^{-}$  will be at equilibrium. For every unit of AgCl that dissociates, we get one  $\text{Ag}^{+}$  and one  $\text{Cl}^{-}$ , so we can solve the equation above as follows:

$$[\text{Ag}^{+}][\text{Cl}^{-}] = 1.6 \times 10^{-10}$$

$$(x)(x) = 1.6 \times 10^{-10}$$

$$x^2 = 1.6 \times 10^{-10}$$

$$x = [\text{Ag}^{+}] = [\text{Cl}^{-}] = 1.3 \times 10^{-5} \text{ M}$$

So there are very small amounts of  $\text{Ag}^{+}$  and  $\text{Cl}^{-}$  in the solution.

Let’s say we add 0.10 mole of NaCl to 1 liter of the AgCl solution. NaCl dissociates completely, so that’s the same thing as adding 1 mole of  $\text{Na}^{+}$  ions and 1 mole of  $\text{Cl}^{-}$  ions to the solution. The  $\text{Na}^{+}$  ions will not affect the AgCl equilibrium, so we can ignore them; but the  $\text{Cl}^{-}$  ions must be taken into account. That’s because of the **common ion effect**.



The common ion effect says that the newly added  $\text{Cl}^-$  ions will affect the  $\text{AgCl}$  equilibrium, although the newly added  $\text{Cl}^-$  ions did not come from  $\text{AgCl}$ .

Let's look at the solubility expression again. Now we have 0.10 mole of  $\text{Cl}^-$  ions in 1 liter of the solution, so  $[\text{Cl}^-] = 0.10 \text{ M}$ .

$$[\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

$$[\text{Ag}^+](0.10 \text{ M}) = 1.6 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{(1.6 \times 10^{-10})}{(0.10)} \text{ M}$$

$$[\text{Ag}^+] = 1.6 \times 10^{-9} \text{ M}$$

Now the number of  $\text{Ag}^+$  ions in the solution has decreased drastically because of the  $\text{Cl}^-$  ions introduced to the solution by  $\text{NaCl}$ . So when solutions of  $\text{AgCl}$  and  $\text{NaCl}$ , which share a common  $\text{Cl}^-$  ion, are mixed, the more soluble salt ( $\text{NaCl}$ ) can cause the less soluble salt ( $\text{AgCl}$ ) to precipitate. In general, when two salt solutions that share a common ion are mixed, the salt with the lower value for  $K_{sp}$  will precipitate first.

## SOLUBILITY RULES

You should have a good working knowledge of the solubilities of common salts. This is especially useful for the part in Section II in which you are asked to predict the outcome of chemical reactions.

### Cations

- **Alkali Metals:**  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$   
All salts of the alkali metals are **soluble**.
- **Ammonium:**  $\text{NH}_4^+$   
All ammonium salts are **soluble**.
- **Alkaline Earths and Transition Metals**  
The solubility of these elements varies depending on the identity of the anion.

### Anions

The following are mostly soluble:

- **Nitrate:**  $\text{NO}_3^-$   
All nitrate salts are **soluble**.
- **Chlorate:**  $\text{ClO}_3^-$   
All chlorate salts are **soluble**.
- **Perchlorate:**  $\text{ClO}_4^-$   
All perchlorate salts are **soluble**.
- **Acetate:**  $\text{C}_2\text{H}_3\text{O}_2^-$   
All acetate salts are **soluble**.

- **Chloride, Bromide, Iodide:**  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$   
Salts containing  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  are **soluble**  
EXCEPT for those containing:  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}_2^{2+}$ .
- **Sulfate:**  $\text{SO}_4^{2-}$   
Sulfate salts are **soluble**  
EXCEPT for those containing:  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ .

The following are mostly insoluble:

- **Hydroxide:**  $\text{OH}^-$   
Hydroxide salts are **insoluble**  
EXCEPT for those containing alkali metals, which are soluble  
AND those containing  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ , which fall in the gray area of moderate solubility.
- **Carbonate:**  $\text{CO}_3^{2-}$   
Carbonate salts are **insoluble**  
EXCEPT for those containing alkali metals and ammonium, which are soluble.
- **Phosphate:**  $\text{PO}_4^{3-}$   
Phosphate salts are **insoluble**  
EXCEPT for those containing alkali metals and ammonium, which are soluble.
- **Sulfite:**  $\text{SO}_3^{2-}$   
Sulfite salts are **insoluble**  
EXCEPT for those containing alkali metals and ammonium, which are soluble.
- **Chromate:**  $\text{CrO}_4^{2-}$   
Chromate salts are **insoluble**  
EXCEPT for those containing alkali metals and ammonium, which are soluble.
- **Sulfide:**  $\text{S}^{2-}$   
Sulfide salts are **insoluble**  
EXCEPT for those containing alkali metals, the alkaline earths, and ammonium, which are soluble.

## SOLUBILITY OF GASES

The lower the temperature and the higher the pressure of the gas, the more soluble the gas will be. Think of what happens when you open a bottle of warm seltzer. The gas suddenly escapes from the warm liquid when you release the pressure.

## CHAPTER 9 QUESTIONS

### MULTIPLE-CHOICE QUESTIONS

#### Questions 1–4

- (A) Molarity ( $M$ )  
(B) Molality ( $m$ )  
(C) Density  
(D) pH  
(E) pOH
- Has the units moles/kg.
  - This is the negative logarithm of the hydrogen ion concentration.
  - Can have the units grams/liter.
  - Has the units moles per liter.
- Which of the following is (are) colligative properties?
    - Freezing-point depression
    - Vapor pressure lowering
    - Boiling-point elevation

(A) I only  
(B) I and II only  
(C) I and III only  
(D) II and III only  
(E) I, II, and III
  - Which of the following aqueous solutions has the highest boiling point?

(A)  $0.5\ m\ NaCl$   
(B)  $0.5\ m\ KBr$   
(C)  $0.5\ m\ CaCl_2$   
(D)  $0.5\ m\ C_6H_{12}O_6$   
(E)  $0.5\ m\ NaNO_3$
  - When sodium chloride is added to a saturated aqueous solution of silver chloride, which of the following precipitates would be expected to appear?

(A) Sodium  
(B) Silver  
(C) Chlorine  
(D) Sodium chloride  
(E) Silver chloride
  - A substance is dissolved in water, forming a  $0.50$ -molar solution. If  $4.0$  liters of solution contains  $240$  grams of the substance, what is the molecular mass of the substance?

(A)  $60$  grams/mole  
(B)  $120$  grams/mole  
(C)  $240$  grams/mole  
(D)  $480$  grams/mole  
(E)  $640$  grams/mole

9. The solubility product,  $K_{sp}$ , of AgCl is  $1.8 \times 10^{-10}$ . Which of the following expressions is equal to the solubility of AgCl?
- (A)  $(1.8 \times 10^{-10})^2$  molar  
 (B)  $\frac{1.8 \times 10^{-10}}{2}$  molar  
 (C)  $1.8 \times 10^{-10}$  molar  
 (D)  $(2)(1.8 \times 10^{-10})$  molar  
 (E)  $\sqrt{1.8 \times 10^{-10}}$  molar
10. A 0.1-molar solution of which of the following acids will be the best conductor of electricity?
- (A)  $\text{HC}_2\text{H}_3\text{O}_2$   
 (B)  $\text{H}_2\text{CO}_3$   
 (C)  $\text{H}_2\text{S}$   
 (D) HF  
 (E)  $\text{HNO}_3$
11. When 31.0 grams of a nonionic substance is dissolved in 2.00 kg of water, the observed freezing-point depression of the solution is  $0.93^\circ\text{C}$ . If  $k_f$  for water is  $1.86^\circ\text{C}/m$ , which of the following expressions is equal to the molar mass of the substance?
- (A)  $\frac{(31.0)(0.93)(2.00)}{(1.86)}$  g/mol  
 (B)  $\frac{(31.0)(1.86)}{(0.93)(2.00)}$  g/mol  
 (C)  $\frac{(1.86)(2.00)}{(31.0)(0.93)}$  g/mol  
 (D)  $\frac{(0.93)}{(31.0)(1.86)(2.00)}$  g/mol  
 (E)  $(31.0)(0.93)(1.86)(2.00)$  g/mol
12. What is the boiling point of a 2 m solution of NaCl in water? (The boiling point elevation constant,  $k_b$ , for water is  $0.5^\circ\text{C}/m$ .)
- (A)  $100^\circ\text{C}$   
 (B)  $101^\circ\text{C}$   
 (C)  $102^\circ\text{C}$   
 (D)  $103^\circ\text{C}$   
 (E)  $104^\circ\text{C}$
13. When an aqueous solution of potassium chloride is compared with water, the salt solution will have
- (A) a higher boiling point, a lower freezing point, and a lower vapor pressure.  
 (B) a higher boiling point, a higher freezing point, and a lower vapor pressure.  
 (C) a higher boiling point, a higher freezing point, and a higher vapor pressure.  
 (D) a lower boiling point, a lower freezing point, and a lower vapor pressure.  
 (E) a lower boiling point, a higher freezing point, and a higher vapor pressure.
14. If 46 grams of  $\text{MgBr}_2$  (molar mass 184 grams) are dissolved in water to form 0.50 liters of solution, what is the concentration of bromine ions in the solution?
- (A) 0.25-molar  
 (B) 0.50-molar  
 (C) 1.0-molar  
 (D) 2.0-molar  
 (E) 4.0-molar
15. A solution contains equal masses of glucose (molecular mass 180) and toluene (molecular mass 90). What is the mole fraction of glucose in the solution?
- (A)  $\frac{1}{4}$   
 (B)  $\frac{1}{3}$   
 (C)  $\frac{1}{2}$   
 (D)  $\frac{2}{3}$   
 (E)  $\frac{3}{4}$

16. When benzene and toluene are mixed together, they form an ideal solution. If benzene has a higher vapor pressure than toluene, then the vapor pressure of a solution that contains an equal number of moles of benzene and toluene will be
- higher than the vapor pressure of benzene.
  - equal to the vapor pressure of benzene.
  - lower than the vapor pressure of benzene and higher than the vapor pressure of toluene.
  - equal to the vapor pressure of toluene.
  - lower than the vapor pressure of toluene.
17. How many moles of  $\text{Na}_2\text{SO}_4$  must be added to 500 milliliters of water to create a solution that has a 2-molar concentration of the  $\text{Na}^+$  ion? (Assume the volume of the solution does not change).
- 0.5 moles
  - 1 mole
  - 2 moles
  - 4 moles
  - 5 moles
18. Given that a solution of  $\text{NaCl}$  (molar mass 58.5 g/mole) in water (molar mass 18 g/mole) has a molality of 0.5  $m$ , which of the following can be determined?
- The mass of the  $\text{NaCl}$  in the solution
  - The total mass of the solution
  - The mole fraction of the  $\text{NaCl}$  in the solution
- I only
  - III only
  - I and II only
  - II and III only
  - I, II, and III
19. How many liters of water must be added to 4 liters of a 6-molar  $\text{HNO}_3$  solution to create a solution that is 2-molar?
- 2 liters
  - 4 liters
  - 6 liters
  - 8 liters
  - 12 liters
20. Which of the following expressions is equal to the  $K_{sp}$  of  $\text{Ag}_2\text{CO}_3$ ?
- $K_{sp} = [\text{Ag}^+][\text{CO}_3^{2-}]$
  - $K_{sp} = [\text{Ag}^+][\text{CO}_3^{2-}]^2$
  - $K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$
  - $K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]^2$
  - $K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]^3$
21. If the solubility of  $\text{BaF}_2$  is equal to  $x$ , which of the following expressions is equal to the solubility product,  $K_{sp}$ , for  $\text{BaF}_2$ ?
- $x^2$
  - $2x^2$
  - $x^3$
  - $2x^3$
  - $4x^3$
22. A beaker contains 50.0 ml of a 0.20 M  $\text{Na}_2\text{SO}_4$  solution. If 50.0 ml of a 0.10 M solution of  $\text{Ba}(\text{NO}_3)_2$  is added to the beaker, what will be the final concentration of sulfate ions in the solution?
- 0.20 M
  - 0.10 M
  - 0.050 M
  - 0.025 M
  - 0.012 M
23. The solubility of strontium fluoride in water is  $1 \times 10^{-3} M$  at room temperature. What is the value of the solubility product for  $\text{SrF}_2$ ?
- $2 \times 10^{-3}$
  - $4 \times 10^{-6}$
  - $2 \times 10^{-6}$
  - $4 \times 10^{-9}$
  - $2 \times 10^{-9}$

24. The bottler of a carbonated beverage dissolves carbon dioxide in water by placing carbon dioxide in contact with water at a pressure of 1 atm at room temperature. The best way to increase the amount of dissolved  $\text{CO}_2$  would be to
- increase the temperature and increase the pressure of  $\text{CO}_2$ .
  - decrease the temperature and decrease the pressure of  $\text{CO}_2$ .
  - decrease the temperature and increase the pressure of  $\text{CO}_2$ .
  - increase the temperature without changing the pressure of  $\text{CO}_2$ .
  - increase the pressure of  $\text{CO}_2$  without changing the temperature.
25. When 300. ml of a 0.60 M NaCl solution is combined with 200. ml of a 0.40 M  $\text{MgCl}_2$  solution, what will be the molar concentration of  $\text{Cl}^-$  ions in the solution?
- 0.20 M
  - 0.34 M
  - 0.68 M
  - 0.80 M
  - 1.0 M
26. Silver hydroxide will be LEAST soluble in a solution with a pH of
- 3
  - 5
  - 7
  - 9
  - 11
27. Copper (II) chloride will be LEAST soluble in a 0.02-molar solution of which of the following compounds?
- NaCl
  - $\text{CuNO}_3$
  - $\text{CaCl}_2$
  - $\text{NaCO}_3$
  - KI
28. A student added 0.10 mol of NaBr and 0.20 mol of  $\text{BaBr}_2$  to 2 liters of water to create an aqueous solution. What is the minimum number of moles of  $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$  that the student must add to the solution to precipitate out all of the  $\text{Br}^-$  ions as AgBr?
- 0.20
  - 0.30
  - 0.40
  - 0.50
  - 1.00
29. A student added 1 liter of a 1.0 M KCl solution to 1 liter of a 1.0 M  $\text{Pb}(\text{NO}_3)_2$  solution. A lead chloride precipitate formed, and nearly all of the lead ions disappeared from the solution. Which of the following lists the ions remaining in the solution in order of decreasing concentration?
- $[\text{NO}_3^-] > [\text{K}^+] > [\text{Pb}^{2+}]$
  - $[\text{NO}_3^-] > [\text{Pb}^{2+}] > [\text{K}^+]$
  - $[\text{K}^+] > [\text{Pb}^{2+}] > [\text{NO}_3^-]$
  - $[\text{K}^+] > [\text{NO}_3^-] > [\text{Pb}^{2+}]$
  - $[\text{Pb}^{2+}] > [\text{NO}_3^-] > [\text{K}^+]$
30. The solubility of PbS in water is  $3 \times 10^{-14}$  molar. What is the solubility product constant,  $K_{sp}$ , for PbS?
- $2 \times 10^{-7}$
  - $9 \times 10^{-7}$
  - $3 \times 10^{-14}$
  - $3 \times 10^{-28}$
  - $9 \times 10^{-28}$

## PROBLEMS

- The molecular weight and formula of a hydrocarbon are to be determined through the use of the freezing-point depression method. The hydrocarbon is known to be 86 percent carbon and 14 percent hydrogen by mass. In the experiment, 3.72 grams of the unknown hydrocarbon were placed into 50.0 grams of liquid benzene,  $C_6H_6$ . The freezing point of the solution was measured to be  $0.06^\circ C$ . The normal freezing point of benzene is  $5.50^\circ C$ , and the freezing-point depression constant for benzene is  $5.12^\circ C/m$ .
  - What is the molecular weight of the compound?
  - What is the molecular formula of the hydrocarbon?
  - What is the mole fraction of benzene in the solution?
  - If the density of the solution is 875 grams per liter, what is the molarity of the solution?
- The value of the solubility product,  $K_{sp}$ , for calcium hydroxide,  $Ca(OH)_2$ , is  $5.5 \times 10^{-6}$ , at  $25^\circ C$ .
  - Write the  $K_{sp}$  expression for calcium hydroxide.
  - What is the mass of  $Ca(OH)_2$  in 500 ml of a saturated solution at  $25^\circ C$ ?
  - What is the pH of the solution in (b)?
  - If 1.0 mole of  $OH^-$  is added to the solution in (b), what will be the resulting  $Ca^{2+}$  concentration? Assume that the volume of the solution does not change.

## ESSAYS

- Explain the following statements in terms of the chemical properties of the substances involved.
  - A 1-molal aqueous solution of sodium chloride has a lower freezing point than a 1-molal aqueous solution of ethanol.
  - $NaCl$  is a strong electrolyte, whereas  $PbCl_2$  is a weak electrolyte.
  - Propanol is soluble in water, but propane is not.
  - In a dilute aqueous solution, molarity and molality will have the same value.
- For sodium chloride, the solution process with water is endothermic.
  - Describe the change in entropy when sodium chloride dissociates into aqueous particles.
  - Two saturated aqueous  $NaCl$  solutions, one at  $20^\circ C$  and one at  $50^\circ C$ , are compared. Which one will have higher concentration? Justify your answer.
  - The solubility product of  $Ce_2(SO_4)_3$  decreases as temperature increases. Is the solution process for this salt endothermic or exothermic? Justify your answer.
  - When equal molar quantities of  $HF$  and  $HCl$  are added to separate containers filled with the same amount of water, the  $HCl$  solution will freeze at a lower temperature. Explain.

## CHAPTER 9 ANSWERS AND EXPLANATIONS

### MULTIPLE-CHOICE QUESTIONS

1. **B** Molality is the measure of moles of solute per kilograms of solvent.
2. **D**  $\text{pH} = -\log[\text{H}^+]$
3. **C** Density is a measure of mass per unit volume (e.g., grams per liter).
4. **A** Molarity is the measure of moles of solute per liter of solution.
5. **E** All of the choices are colligative properties, which means they depend only on the number of particles in solution, not on the identity of those particles.
6. **C** Boiling-point elevation is a colligative property. That is, it depends only on the number of particles in solution, not on the specific particles.

Remember the formula:  $\Delta T = kmx$ .

All of the solutions have the same molality, so the one with the greatest boiling-point elevation will be the one that breaks up into the most ions in solution.  $\text{CaCl}_2$  breaks up into 3 ions,  $\text{C}_6\text{H}_{12}\text{O}_6$  doesn't break up into ions, and the other three break up into 2 ions.

7. **E** Sodium chloride is much more soluble than silver chloride. Because of the common ion effect, the chloride ions introduced into the solution by sodium chloride will disrupt the silver chloride equilibrium, causing silver chloride to precipitate from the solution.
8. **B** First find the number of moles.

Moles = (molarity)(volume)

Moles of substance =  $(0.50 \text{ M})(4.0 \text{ L}) = 2 \text{ moles}$

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{So MW} = \frac{240 \text{ g}}{2 \text{ mol}} = 120 \text{ g/mol}$$

9. **E** The solubility of a substance is equal to its maximum concentration in solution.

For every  $\text{AgCl}$  in solution, we get one  $\text{Ag}^+$  and one  $\text{Cl}^-$ , so the solubility of  $\text{AgCl}$ —let's call it  $x$ —will be the same as  $[\text{Ag}^+]$ , which is the same as  $[\text{Cl}^-]$ .

So for  $\text{AgCl}$ ,  $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} = x^2$ .

$$x = \sqrt{1.8 \times 10^{-10}}$$

10. **E** The best conductor of electricity (also called the strongest electrolyte) will be the solution that contains the most charged particles.  $\text{HNO}_3$  is the only strong acid listed in the answer choices, so it is the only choice where the acid has dissociated completely in solution into  $\text{H}^+$  and  $\text{NO}_3^-$  ions. So a 0.1-molar  $\text{HNO}_3$  solution will contain the most charged particles and, therefore, be the best conductor of electricity.



11. **B** We can get the molality from the freezing-point depression with the expression  $\Delta T = k_f m x$ . Because the substance is nonionic, it will not dissociate, and  $x$  will be equal to 1, so we can leave it out of the calculation.

$$m = \frac{\Delta T}{k_f}$$

We know the molality and the mass of the solvent, so we can calculate the number of moles of solute.

$$\text{Moles} = (\text{molality})(\text{kilograms of solvent}) = \frac{\Delta T}{k_f} (\text{kg})$$

Now we use one of our stoichiometry relationships.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{MW} = \frac{\text{grams}}{\text{moles}} = \frac{(\text{grams})}{\left(\frac{(\Delta T)(\text{kg})}{k_f}\right)} = \frac{(\text{grams})(k_f)}{(\Delta T)(\text{kg})} = \frac{(31.0\text{g})(1.86\text{ K}\cdot\text{kg/mol})}{(0.93\text{ K})(2.00\text{kg})} = \frac{(31.0)(1.86)}{(0.93)(2.00)} \text{ grams/mol}$$

12. **C**  $\Delta T = k_b m x$ .

Each NaCl dissociates into two particles, so  $x = 2$ .

$$\Delta T = (0.5^\circ\text{C}/m)(2\text{ }m)(2) = 2^\circ\text{C}$$

So the boiling point of the solution is  $102^\circ\text{C}$ .

13. **A** Particles in solution tend to interfere with phase changes, so the boiling point is raised, the freezing point is lowered, and the vapor pressure is lowered.
14. **C** First we'll find the molarity of the  $\text{MgBr}_2$  solution.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of MgBr}_2 \text{ added} = \frac{(46\text{ g})}{(184\text{ g/mol})} = 0.25 \text{ moles}$$

$$\text{Molarity} = \frac{\text{moles}}{\text{liters}} = \frac{(0.25\text{ mol})}{(0.50\text{ L})} = 0.50\text{-molar}$$

For every  $\text{MgBr}_2$  in solution, 2  $\text{Br}^-$  ions are produced, so a 0.50-molar  $\text{MgBr}_2$  solution will have twice the concentration of  $\text{Br}^-$  ions, so the bromine ion concentration is 1.0-molar.

15. **B** Let's say the solution contains 180 grams of glucose and 180 grams of toluene. That's 1 mole of glucose and 2 moles of toluene. So that's 1 mole of glucose out of a total of 3 moles, for a mole fraction of  $\frac{1}{3}$ .
16. **C** From Raoult's law, the vapor pressure of an ideal solution depends on the mole fractions of the components of the solution. The vapor pressure of a solution with equal amounts of benzene and toluene will look like as follows.

$$(P_{\text{solution}}) = \left(\frac{1}{2}\right)(P_{\text{benzene}}) + \left(\frac{1}{2}\right)(P_{\text{toluene}})$$

That's just the average of the two vapor pressures.

17. **A** Let's find out how many moles of  $\text{Na}^+$  we have to add.  
 Moles = (molarity)(volume)  
 Moles of  $\text{Na}^+$  =  $(2\text{ M})(0.5\text{ L}) = 1\text{ mole}$   
 Because we get 2 moles of  $\text{Na}^+$  ions for every mole of  $\text{Na}_2\text{SO}_4$  we add, we only need to add 0.5 moles of  $\text{Na}_2\text{SO}_4$ .
18. **B** We can't determine (I) and (II) because we don't know how much solution we have. We can figure out (III) because molality tells us the number of moles of  $\text{NaCl}$  found in 1 kilogram of water. We can figure out how many moles of water there are in 1 kilogram. So if we have a ratio of moles of  $\text{NaCl}$  to moles of water, we can figure out the mole fraction of  $\text{NaCl}$ .
19. **D** The number of moles of  $\text{HNO}_3$  remains constant.  
 Moles = (molarity)(volume)  
 Moles of  $\text{HNO}_3 = (6\text{ M})(4\text{ L}) = (2\text{ M})(x)$   
 $x = 12$  liters, but that's not the answer.  
 To get a 2-molar solution we need 12 liters, but the solution already has 4 liters, so we need to add 8 liters of water. That's the answer.
20. **C**  $K_{sp}$  is just the equilibrium constant without a denominator.  
 When  $\text{Ag}_2\text{CO}_3$  dissociates, we get the following reaction:  

$$\text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2\text{Ag}^+ + \text{CO}_3^{2-}$$
 In the equilibrium expression, coefficients become exponents, so we get  

$$K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$
21. **E** For  $\text{BaF}_2$ ,  $K_{sp} = [\text{Ba}^{2+}][\text{F}^-]^2$ .  
 For every  $\text{BaF}_2$  that dissolves, we get one  $\text{Ba}^{2+}$  and two  $\text{F}^-$ .  
 So if the solubility of  $\text{BaF}_2$  is  $x$ , then  $[\text{Ba}^{2+}] = x$ , and  $[\text{F}^-] = 2x$   
 So  $K_{sp} = (x)(2x)^2 = (x)(4x^2) = 4x^3$
22. **C** The  $\text{Ba}^{2+}$  ions and the  $\text{SO}_4^{2-}$  ions will combine and precipitate out of the solution, so let's find out how many of each we have.  
 Moles = (molarity)(volume)  
 Moles of  $\text{SO}_4^{2-} = (0.20\text{ M})(0.050\text{ L}) = 0.010\text{ mole}$   
 Moles of  $\text{Ba}^{2+} = (0.10\text{ M})(0.050\text{ L}) = 0.0050\text{ mole}$   
 To find the number of moles of  $\text{SO}_4^{2-}$  left in the solution, subtract the moles of  $\text{Ba}^{2+}$  from the moles of  $\text{SO}_4^{2-}$ .  
 $0.010\text{ mole} - 0.0050\text{ mole} = 0.0050\text{ mole}$   
 Now use the formula for molarity to find the concentration of  $\text{SO}_4^{2-}$  ions. Don't forget to add the volumes of the two solutions.  

$$\text{Molarity} = \frac{\text{moles}}{\text{liters}} = \frac{(0.0050\text{ mol})}{(0.10\text{ L})} = 0.050\text{ M}$$

23. **D** Use the formula for  $K_{sp}$ . For every  $\text{SrF}_2$  in solution, there will be one strontium ion and two fluoride ions, so  $[\text{Sr}^{2+}]$  will be  $1 \times 10^{-3} \text{ M}$  and  $[\text{F}^-]$  will be  $2 \times 10^{-3} \text{ M}$ .

$$K_{sp} = [\text{Sr}^{2+}][\text{F}^-]^2$$

$$K_{sp} = (1 \times 10^{-3} \text{ M})(2 \times 10^{-3} \text{ M})^2$$

$$K_{sp} = 4 \times 10^{-9}$$

24. **C** The lower the temperature, the more soluble a gas will be in water. The greater the pressure of the gas, the more soluble it will be.
25. **C** The  $\text{Cl}^-$  ions from the two salts will both be present in the solution, so we need to find the number of moles of  $\text{Cl}^-$  contributed by each salt.

$$\text{Moles} = (\text{molarity})(\text{volume})$$

Each  $\text{NaCl}$  produces 1  $\text{Cl}^-$

$$\text{Moles of } \text{Cl}^- \text{ from NaCl} = (0.60 \text{ M})(0.300 \text{ L}) = 0.18 \text{ mole}$$

Each  $\text{MgCl}_2$  produces 2  $\text{Cl}^-$

$$\text{Moles of } \text{Cl}^- \text{ from MgCl}_2 = (2)(0.40 \text{ M})(0.200 \text{ L}) = 0.16 \text{ mole}$$

To find the number of moles of  $\text{Cl}^-$  in the solution, add the two together.

$$0.18 \text{ mole} + 0.16 \text{ mole} = 0.34 \text{ mole}$$

Now use the formula for molarity to find the concentration of  $\text{Cl}^-$  ions. Don't forget to add the volumes of the two solutions.

$$\text{Molarity} = \frac{\text{moles}}{\text{liters}} = \frac{(0.34 \text{ mol})}{(0.500 \text{ L})} = 0.68 \text{ M}$$

26. **E** Silver hydroxide will be least soluble in the solution with the highest hydroxide concentration. That would be the solution with the highest pH.
27. **C** According to the common ion effect, ions already present in a solution will affect the solubility of compounds that also produce those ions. So a solution containing  $\text{Cu}^+$  ions or  $\text{Cl}^-$  ions will inhibit the solubility of  $\text{CuCl}$ .
- A 0.02-molar solution of  $\text{NaCl}$  will have a 0.02-molar concentration of  $\text{Cl}^-$  ions and a 0.02-molar solution of  $\text{CuNO}_3$  will have a 0.02-molar concentration of  $\text{Cu}^+$  ions, so choices (A) and (B) will affect the solubility of  $\text{CuCl}$  to the same extent.
- The correct answer is choice (C),  $\text{CaCl}_2$ , because a 0.02-molar solution of  $\text{CaCl}_2$  will have a 0.04-molar concentration of  $\text{Cl}^-$  ions, so this solution will do the most to inhibit the solubility of  $\text{CuCl}$ . Choices (D) and (E) have no effect on the solubility of  $\text{CuCl}$ .
28. **D** The solution contains 0.50 moles of  $\text{Br}^-$  ions, 0.10 from  $\text{NaBr}$  and 0.40 from  $\text{BaBr}_2$  (each  $\text{BaBr}_2$  provides 2  $\text{Br}^-$  ions). Each  $\text{Ag}^+$  ion will remove 1  $\text{Br}^-$  ion, so the student needs to add 0.50 moles of  $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$ .

29. A At the start, the concentrations of the ions are as follows:

$$[\text{K}^+] = 1 \text{ M}$$

$$[\text{Cl}^-] = 1 \text{ M}$$

$$[\text{Pb}^{2+}] = 1 \text{ M}$$

$$[\text{NO}_3^-] = 2 \text{ M}$$

After  $\text{PbCl}_2$  forms, the concentrations are as follows:

$$[\text{K}^+] = 1 \text{ M}$$

$$[\text{Cl}^-] = 0.5 \text{ M}$$

$$[\text{Pb}^{2+}] = 0 \text{ M}$$

$$[\text{NO}_3^-] = 2 \text{ M}$$

So from greatest to least

$$[\text{NO}_3^-] > [\text{K}^+] > [\text{Pb}^{2+}]$$

30. E The solubility of a substance is equal to its maximum concentration in solution. For every  $\text{PbS}$  in solution, we get one  $\text{Pb}^{2+}$  and one  $\text{S}^{2-}$ , so the concentration of  $\text{PbS}$ ,  $3 \times 10^{-14} \text{ M}$ , will be the same as the concentrations of  $\text{Pb}^{2+}$  and  $\text{S}^{2-}$ .

$$K_{sp} = [\text{Pb}^{2+}][\text{S}^{2-}]$$

$$K_{sp} = (3 \times 10^{-14} \text{ M})(3 \times 10^{-14} \text{ M}) = 9 \times 10^{-28}$$

## PROBLEMS

1. (a) First we'll find the molality of the solution. The freezing point depression,  $\Delta T$ , is  $5.50^\circ\text{C} - 0.06^\circ\text{C} = 5.44^\circ\text{C}$ .

$$\Delta T = km$$

Solve for  $m$

$$m = \frac{\Delta T}{k} = \frac{(5.44^\circ\text{C})}{(5.12^\circ\text{C}/m)} = 1.06m$$

From the molality of the solution, we can find the number of moles of unknown hydrocarbon.

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

Solve for moles.

$$\text{Moles} = (\text{molality})(\text{kg of solvent})$$

$$\text{Moles of hydrocarbon} = (1.06 m)(0.050 \text{ kg}) = 0.053 \text{ moles}$$

Now we can find the molecular weight of the hydrocarbon.

$$\text{MW} = \frac{\text{grams}}{\text{moles}} = \frac{(3.72 \text{ g})}{(0.053 \text{ mol})} = 70.2 \text{ g/mol}$$

(b) You can use the percent by mass and the molecular weight.

For carbon

$$(86\%)(70 \text{ g/mol}) = 60 \text{ g/mol}$$

Carbon has an atomic weight of 12, so there must be  $\frac{60}{12} = 5$  moles of carbon in 1 mole of the hydrocarbon.

For hydrogen

$$(14\%)(70 \text{ g/mol}) = 10 \text{ g/mol}$$

Hydrogen has an atomic weight of 1, so there must be  $\frac{10}{1} = 10$  moles of hydrogen in 1 mole of the hydrocarbon.

So the molecular formula for the hydrocarbon is  $\text{C}_5\text{H}_{10}$ .

(c) We know that there are 0.053 moles of hydrocarbon. We need to find the number of moles of benzene.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of benzene} = \frac{(50.00 \text{ g})}{(78 \text{ g/mol})} = 0.64 \text{ mol}$$

$$\text{Total moles} = 0.64 \text{ mol} + 0.053 \text{ mol} = 0.69 \text{ mol}$$

$$\text{Mole fraction of benzene} = \frac{0.64 \text{ mol}}{0.69 \text{ mol}} = 0.93$$

(d) Remember the definition of molarity.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

We know that the moles of solute is 0.053. We need to find the liters of solution.

The weight of the solution is

$$50.00 \text{ g} + 3.72 \text{ g} = 53.72 \text{ g}$$

$$\text{Density} = \frac{\text{grams}}{\text{liters}}$$

Solve for liters.

$$\text{Liters of solution} = \frac{\text{grams}}{\text{density}} = \frac{(53.72 \text{ g})}{(875 \text{ g/L})} = 0.0614 \text{ L}$$

$$\text{Molarity} = \frac{(0.053 \text{ mol})}{(0.0614 \text{ L})} = 0.863 \text{ M}$$

2. (a) The solubility product is the same as the equilibrium expression, but because the reactant is a solid, there is no denominator.

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

(b) Use the solubility product.

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

$$5.5 \times 10^{-6} = (x)(2x)^2 = 4x^3$$

$$x = 0.01 \text{ M for } \text{Ca}^{2+}$$

One mole of calcium hydroxide produces 1 mole of  $\text{Ca}^{2+}$ , so the concentration of  $\text{Ca}(\text{OH})_2$  must be 0.01 M.

Moles = (molarity)(volume)

Moles of  $\text{Ca}(\text{OH})_2 = (0.01 \text{ M})(0.500 \text{ L}) = 0.005 \text{ moles}$

Grams = (moles)(MW)

Grams of  $\text{Ca}(\text{OH})_2 = (0.005 \text{ mol})(74 \text{ g/mol}) = 0.37 \text{ g}$

(c) We can find  $[\text{OH}^-]$  from (b).

If  $[\text{Ca}^{2+}] = 0.01 \text{ M}$ , then  $[\text{OH}^-]$  must be twice that, so  $[\text{OH}^-] = 0.02 \text{ M}$

$\text{pOH} = -\log[\text{OH}^-] = 1.7$

$\text{pH} = 14 - \text{pOH} = 14 - 1.7 = 12.3$

(d) Find the new  $[\text{OH}^-]$ . The hydroxide already present is small enough to ignore, so we'll use only the hydroxide just added.

Molarity =  $\frac{\text{moles}}{\text{liters}}$

$[\text{OH}^-] = \frac{(1.0 \text{ mol})}{(0.500 \text{ L})} = 2.0 \text{ M}$

Now use the  $K_{sp}$  expression.

$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$

$5.5 \times 10^{-6} = [\text{Ca}^{2+}](2.0 \text{ M})^2$

$[\text{Ca}^{2+}] = 1.4 \times 10^{-6} \text{ M}$

## ESSAYS

3. (a) Freezing-point depression is a colligative property, which means that it depends on the number of particles in solution, not their identity.

Sodium chloride dissociates into  $\text{Na}^+$  and  $\text{Cl}^-$ , so every unit of sodium chloride produces two particles in solution. Ethanol does not dissociate, so sodium chloride will put twice as many particles in solution as ethanol.

(b) An electrolyte is a substance that ionizes in solution, thus causing the solution to conduct electricity.

Both of the salts dissociate into ions, but  $\text{PbCl}_2$  is almost insoluble, so it will produce very few ions in solution, while  $\text{NaCl}$  is extremely soluble and produces many ions.

(c) Water is best at dissolving polar substances.

Propanol ( $\text{C}_3\text{H}_7\text{OH}$ ) has a hydroxide group, which makes it polar, and thus soluble in water. Propane ( $\text{C}_3\text{H}_8$ ) is nonpolar and is best dissolved in nonpolar solvents.

(d) Remember the definitions, and remember that a dilute solution has very little solute.

Molarity =  $\frac{\text{moles of solute}}{\text{liters of solution}}$

Molality =  $\frac{\text{moles of solute}}{\text{kilograms of solvent}}$

For water, 1 liter weighs 1 kilogram, so for a dilute solution this distinction disappears.

If there is very little solute, the mass and volume of the solution will be indistinguishable from the mass and volume of the solvent.

4. (a) Entropy increases when a salt dissociates because aqueous particles have more randomness than a solid.

(b) Most salt solution processes are endothermic, and endothermic processes are favored by an increase in temperature, therefore increasing temperature will increase the solubility of most salts.

(c)  $\text{Ce}_2(\text{SO}_4)_3$  becomes less soluble as temperature increases, so the solution process for this salt must be exothermic.

(d) Freezing-point depression is a colligative property, which means that it depends on the number of particles in solution, not their identity.

HCl is a strong acid, which means that it dissociates completely. This means that 1 mole of HCl in solution will produce 2 moles of particles. HF is a weak acid, which means that it dissociates very little. This means that 1 mole of HF in solution will remain at about 1 mole of particles in solution.

Therefore, the HCl solution will have more particles than the HF solution.

# 10

## Equilibrium

### HOW OFTEN DOES EQUILIBRIUM APPEAR ON THE EXAM?

In the multiple-choice section, this topic appears in about 4 out of 75 questions. In the free-response section, this topic appears every year.

### THE EQUILIBRIUM CONSTANT, $K_{eq}$

Most chemical processes are reversible. That is, reactants react to form products, but those products can also react to form reactants.

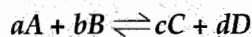
A reaction is at equilibrium when the rate of the forward reaction is equal to the rate of the reverse reaction.

The relationship between the concentrations of reactants and products in a reaction at equilibrium is given by the equilibrium expression, also called the **law of mass action**.



### The Equilibrium Expression

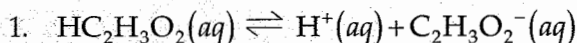
For the reaction



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

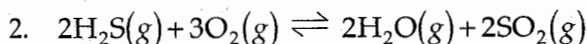
1.  $[A]$ ,  $[B]$ ,  $[C]$ , and  $[D]$  are molar concentrations or partial pressures at equilibrium.
2. Products are in the numerator, and reactants are in the denominator.
3. Coefficients in the balanced equation become exponents in the equilibrium expression.
4. Solids and pure liquids are not included in the equilibrium expression—only aqueous reactants and products are included.
5. Units are not given for  $K_{eq}$ .

Let's look at a few examples:



$$K_{eq} = K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

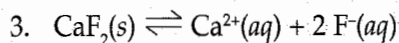
This reaction shows the dissociation of acetic acid in water. All of the reactants and products are aqueous particles, so they are all included in the equilibrium expression. None of the reactants or products have coefficients, so there are no exponents in the equilibrium expression. This is the standard form of  $K_a$ , the acid dissociation constant.



$$K_{eq} = K_c = \frac{[\text{H}_2\text{O}]^2 [\text{SO}_2]^2}{[\text{H}_2\text{S}]^2 [\text{O}_2]^3}$$

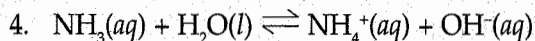
$$K_{eq} = K_p = \frac{P_{\text{H}_2\text{O}}^2 P_{\text{SO}_2}^2}{P_{\text{H}_2\text{S}}^2 P_{\text{O}_2}^3}$$

All of the reactants and products in this reaction are gases, so  $K_{eq}$  can be expressed in terms of concentration ( $K_c$ , moles/liter or molarity) or in terms of partial pressure ( $K_p$ , atmospheres). In the next section, we'll see how these two different ways of looking at the same equilibrium situation are related. All of the reactants and products are included here, and the coefficients in the reaction become exponents in the equilibrium expression.



$$K_{eq} = K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

This reaction shows the dissociation of a slightly soluble salt. There is no denominator in this equilibrium expression because the reactant is a solid. Solids are left out of the equilibrium expression because the concentration of a solid is constant. There must be some solid present for equilibrium to exist, but you do not need to include it in your calculations. This form of  $K_{eq}$  is called the solubility product,  $K_{sp}$ , which we already saw in Chapter 9.



$$K_{eq} = K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

This is the acid-base reaction between ammonia and water. We can leave water out of the equilibrium expression because it is a pure liquid. By pure liquid, we mean that the concentration of water is so large (about 50 molar) that nothing that happens in the reaction is going to change it significantly, so we can consider it to be constant. This is the standard form for  $K_b$ , the base dissociation constant.

Here is a roundup of the equilibrium constants you need to be familiar with for the test.

- $K_c$  is the constant for molar concentrations.
- $K_p$  is the constant for partial pressures.
- $K_{sp}$  is the solubility product, which has no denominator because the reactants are solids.
- $K_a$  is the acid dissociation constant for weak acids.
- $K_b$  is the base dissociation constant for weak bases.
- $K_w$  describes the ionization of water ( $K_w = 1 \times 10^{-14}$ ).

The equilibrium constant has a lot of aliases, but they all take the same form and tell you the same thing. The **equilibrium constant** tells you the relative amounts of products and reactants at equilibrium.

A large value for  $K_{eq}$  means that products are favored over reactants at equilibrium, while a small value for  $K_{eq}$  means that reactants are favored over products at equilibrium.

## $K_{eq}$ AND GASES

As we saw in the example above, the equilibrium constant for a gas phase reaction can be written in terms of molar concentrations,  $K_c$ , or partial pressures,  $K_p$ . These two forms of  $K$  can be related by the following equation, which is derived from the ideal gas law.

$$K_p = K_c (RT)^{\Delta n}$$

$K_p$  = partial pressure constant (using atmospheres as units)

$K_c$  = molar concentration constant (using molarities as units)

$R$  = the ideal gas constant, 0.0821 (L-atm)/(mol-K)

$T$  = absolute temperature (K)

$\Delta n$  = (moles of product gas – moles of reactant gas)

## THE REACTION QUOTIENT, $Q$

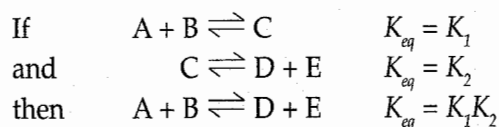
The reaction quotient is determined in exactly the same way as the equilibrium constant, but initial conditions are used in place of equilibrium conditions. The reaction quotient can be used to predict the direction in which a reaction will proceed from a given set of initial conditions.

The Reaction Quotient
For the reaction
$aA + bB \rightleftharpoons cC + dD$
$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
$[A]$ , $[B]$ , $[C]$ , and $[D]$ are initial molar concentrations or partial pressures.
<ul style="list-style-type: none"><li>• If <math>Q</math> is less than the calculated <math>K</math> for the reaction, the reaction proceeds forward, generating products.</li><li>• If <math>Q</math> is greater than <math>K</math>, the reaction proceeds backward, generating reactants.</li><li>• If <math>Q = K</math>, the reaction is already at equilibrium.</li></ul>

## $K_{eq}$ AND MULTISTEP PROCESSES

There is a simple relationship between the equilibrium constants for the steps of a multistep reaction and the equilibrium constant for the overall reaction.

If two reactions can be added together to create a third reaction, then the  $K_{eq}$  for the two reactions can be multiplied together to get the  $K_{eq}$  for the third reaction.



## LE CHÂTELIER'S LAW

Le Châtelier's law says that whenever a stress is placed on a situation at equilibrium, the equilibrium will shift to relieve that stress.

Let's use the **Haber process**, which is used in the industrial preparation of ammonia, as an example.



## CONCENTRATION

- When the concentration of a reactant or product is increased, the reaction will proceed in the direction that will use up the added substance.

If  $N_2$  or  $H_2$  is added, the reaction proceeds in the forward direction. If  $NH_3$  is added, the reaction proceeds in the reverse direction.

- When the concentration of a reactant or product is decreased, the reaction will proceed in the direction that will produce more of the substance that has been removed.

If  $N_2$  or  $H_2$  is removed, the reaction will proceed in the reverse direction. If  $NH_3$  is removed, the reaction will proceed in the forward direction.

## VOLUME

- When the volume in which a reaction takes place is increased, the reaction will proceed in the direction that produces more moles of gas.

When the volume for the Haber process is increased, the reaction proceeds in the reverse direction because the reactants have more moles of gas (4) than the products (2).

- When the volume in which a reaction takes place is decreased, the reaction will proceed in the direction that produces fewer moles of gas.

When the volume for the Haber process is decreased, the reaction proceeds in the forward direction because the products have fewer moles of gas (2) than the reactants (4).

- If there is no gas involved in the reaction, or if the reactants and products have the same number of moles of gas, then volume changes have no effect on the equilibrium.

## TEMPERATURE

- When temperature is increased, the reaction will proceed in the endothermic direction.

When the temperature for the Haber process is increased, the reaction proceeds in the reverse direction because the reverse reaction is endothermic ( $\Delta H^\circ$  is positive).

- When temperature is decreased, the reaction will proceed in the exothermic direction.

When the temperature for the Haber process is decreased, the reaction proceeds in the forward direction because the forward reaction is exothermic ( $\Delta H^\circ$  is negative).

## PRESSURE

- When pressure is increased, the reaction will proceed toward the side with the fewest molecules of gas.
- When pressure is decreased, the reaction will proceed toward the side with the greatest number of molecules of gas.

When an inert gas, like Argon, is added to the system, although the total pressure goes up, the partial pressures of the gases involved in the reaction will remain the same. Therefore, there is no effect on the equilibrium position, because the reaction quotient,  $Q$ , is determined by the individual partial pressures of the gases involved in the reaction.

# CHAPTER 10 QUESTIONS

## MULTIPLE-CHOICE QUESTIONS

### Questions 1–4

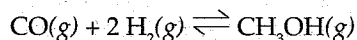
- (A)  $K_c$
- (B)  $K_p$
- (C)  $K_a$
- (D)  $K_w$
- (E)  $K_{sp}$

1. This equilibrium constant uses partial pressures of gases as units.
2. This equilibrium constant always has a value of  $1 \times 10^{-14}$  at  $25^\circ\text{C}$ .
3. This equilibrium constant is used for the dissociation of an acid.
4. The equilibrium expression for this equilibrium constant does not contain a denominator.
5. For a particular salt, the solution process is endothermic. As the temperature at which the salt is dissolved increases, which of the following will occur?
  - (A)  $K_{sp}$  will increase, and the salt will become more soluble.
  - (B)  $K_{sp}$  will decrease, and the salt will become more soluble.
  - (C)  $K_{sp}$  will increase, and the salt will become less soluble.
  - (D)  $K_{sp}$  will decrease, and the salt will become less soluble.
  - (E)  $K_{sp}$  will not change, and the salt will become more soluble.
6.  $2 \text{HI}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{HCl}(g) + \text{I}_2(g) + \text{energy}$ 

A gaseous reaction occurs and comes to equilibrium as shown above. Which of the following changes to the system will serve to increase the number of moles of  $\text{I}_2$  present at equilibrium?

  - (A) Increasing the volume at constant temperature
  - (B) Decreasing the volume at constant temperature
  - (C) Adding a mole of inert gas at constant volume
  - (D) Increasing the temperature at constant volume
  - (E) Decreasing the temperature at constant volume

7. A sealed isothermal container initially contained 2 moles of CO gas and 3 moles of H<sub>2</sub> gas. The following reversible reaction occurred:

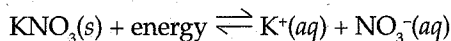


At equilibrium, there was 1 mole of CH<sub>3</sub>OH in the container. What was the total number of moles of gas present in the container at equilibrium?

- (A) 1  
 (B) 2  
 (C) 3  
 (D) 4  
 (E) 5
8.  $4 \text{NH}_3(g) + 3 \text{O}_2(g) \rightleftharpoons 2 \text{N}_2(g) + 6 \text{H}_2\text{O}(g) + \text{energy}$

Which of the following changes to the system at equilibrium shown above would cause the concentration of H<sub>2</sub>O to increase?

- (A) The volume of the system was decreased at constant temperature.  
 (B) The temperature of the system was increased at constant volume.  
 (C) NH<sub>3</sub> was removed from the system.  
 (D) N<sub>2</sub> was removed from the system.  
 (E) O<sub>2</sub> was removed from the system.
9. A sample of solid potassium nitrate is placed in water. The solid potassium nitrate comes to equilibrium with its dissolved ions by the endothermic process shown below.



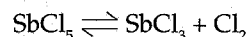
Which of the following changes to the system would increase the concentration of K<sup>+</sup> ions at equilibrium?

- (A) The volume of the solution is increased.  
 (B) The volume of the solution is decreased.  
 (C) Additional solid KNO<sub>3</sub> is added to the solution.  
 (D) The temperature of the solution is increased.  
 (E) The temperature of the solution is decreased.

10. For which of the following gaseous equilibria do K<sub>p</sub> and K<sub>c</sub> differ the most?

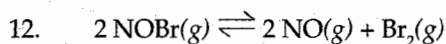
- (A)  $2\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g)$   
 (B)  $\text{NH}_3\text{BH}_3(g) \rightleftharpoons \text{NH}_2\text{BH}_2(g) + \text{H}_2(g)$   
 (C)  $\text{NO}(g) + \text{O}_3(g) \rightleftharpoons \text{NO}_2(g) + \text{O}_2(g)$   
 (D)  $\text{B}_3\text{N}_3\text{H}_6(g) + 3\text{H}_2(g) \rightleftharpoons \text{B}_3\text{N}_3\text{H}_{12}(g)$   
 (E)  $\text{BH}_3(g) + 3\text{HCl}(g) \rightleftharpoons \text{BCl}_3(g) + 3\text{H}_2(g)$

11. A 1M solution of SbCl<sub>5</sub> in organic solvent shows no noticeable reactivity at room temperature. The sample is heated to 200°C and the following equilibrium reaction is found to occur:



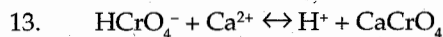
The value of K<sub>eq</sub> at 200°C was measured to be 10<sup>-6</sup>. The reaction was then heated to 350°C, and the equilibrium concentration of Cl<sub>2</sub> was found to be 0.1 M, which of the following best approximated the value of K<sub>eq</sub> at 350°C?

- (A) 1.5  
 (B) 1.0  
 (C) 0.1  
 (D) 0.01  
 (E) 0.001



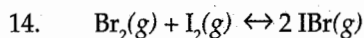
The reaction above came to equilibrium at a temperature of  $100^\circ\text{C}$ . At equilibrium the partial pressure due to  $\text{NOBr}$  was 4 atmospheres, the partial pressure due to  $\text{NO}$  was 4 atmospheres, and the partial pressure due to  $\text{Br}_2$  was 2 atmospheres. What is the equilibrium constant,  $K_p$ , for this reaction at  $100^\circ\text{C}$ ?

- (A)  $\frac{1}{4}$   
 (B)  $\frac{1}{2}$   
 (C) 1  
 (D) 2  
 (E) 4



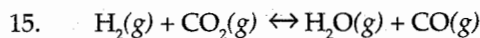
If the acid dissociation constant for  $\text{HCrO}_4^-$  is  $K_a$  and the solubility product for  $\text{CaCrO}_4$  is  $K_{sp}$ , which of the following gives the equilibrium expression for the reaction above?

- (A)  $K_a K_{sp}$   
 (B)  $\frac{K_a}{K_{sp}}$   
 (C)  $\frac{K_{sp}}{K_a}$   
 (D)  $\frac{1}{K_{sp} K_a}$   
 (E)  $\frac{K_a K_{sp}}{2}$



At  $150^\circ\text{C}$ , the equilibrium constant,  $K_c$ , for the reaction shown above has a value of 300. This reaction was allowed to reach equilibrium in a sealed container and the partial pressure due to  $\text{IBr}(g)$  was found to be 3 atm. Which of the following could be the partial pressures due to  $\text{Br}_2(g)$  and  $\text{I}_2(g)$  in the container?

- |     | $\text{Br}_2(g)$ | $\text{I}_2(g)$ |
|-----|------------------|-----------------|
| (A) | 0.1 atm          | 0.3 atm         |
| (B) | 0.3 atm          | 1 atm           |
| (C) | 1 atm            | 1 atm           |
| (D) | 1 atm            | 3 atm           |
| (E) | 3 atm            | 3 atm           |



Initially, a sealed vessel contained only  $\text{H}_2(g)$  with a partial pressure of 6 atm and  $\text{CO}_2(g)$  with a partial pressure of 4 atm. The reaction above was allowed to come to equilibrium at a temperature of 700 K. At equilibrium, the partial pressure due to  $\text{CO}(g)$  was found to be 2 atm. What is the value of the equilibrium constant  $K_p$  for the reaction?

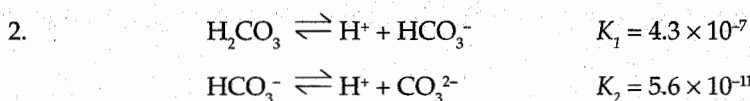
- (A)  $\frac{1}{24}$   
 (B)  $\frac{1}{6}$   
 (C)  $\frac{1}{4}$   
 (D)  $\frac{1}{3}$   
 (E)  $\frac{1}{2}$

## PROBLEMS



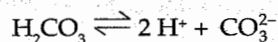
The value of the solubility product,  $K_{sp}$ , for the reaction above is  $1.0 \times 10^{-6}$  at  $25^{\circ}\text{C}$ .

- Write the  $K_{sp}$  expression for  $\text{BaF}_2$ .
- What is the concentration of  $\text{F}^{-}$  ions in a saturated solution of  $\text{BaF}_2$  at  $25^{\circ}\text{C}$ ?
- 500 milliliters of a 0.0060-molar  $\text{NaF}$  solution is added to 400 ml of a 0.0060-molar  $\text{Ba}(\text{NO}_3)_2$  solution. Will there be a precipitate?
- What is the value of  $\Delta G^{\circ}$  for the dissociation of  $\text{BaF}_2$  at  $25^{\circ}\text{C}$ ?



The acid dissociation constants for the reactions above are given at  $25^{\circ}\text{C}$ .

- What is the pH of a 0.050-molar solution of  $\text{H}_2\text{CO}_3$  at  $25^{\circ}\text{C}$ ?
- What is the concentration of  $\text{CO}_3^{2-}$  ions in the solution in (a)?
- How would the addition of each of the following substances affect the pH of the solution in (a)?
  - $\text{HCl}$
  - $\text{NaHCO}_3$
  - $\text{NaOH}$
  - $\text{NaCl}$
- What is the value of  $K_{eq}$  for the following reaction?







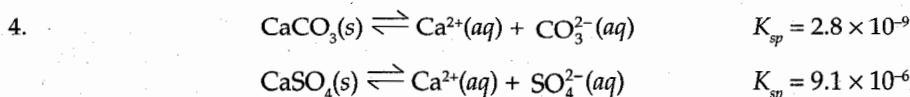
When the reaction above took place at a temperature of 570 K, the following equilibrium concentrations were measured:

$$[\text{NH}_3] = 0.20 \text{ mol/L}$$

$$[\text{N}_2] = 0.50 \text{ mol/L}$$

$$[\text{H}_2] = 0.20 \text{ mol/L}$$

- Write the expression for  $K_c$  and calculate its value.
- What is the value of  $K_p$  for the reaction?
- Describe how the concentration of  $\text{H}_2$  will be affected by each of the following changes to the system at equilibrium:
  - The temperature is increased.
  - The volume of the reaction chamber is increased.
  - $\text{N}_2$  gas is added to the reaction chamber.
  - Helium gas is added to the reaction chamber.



The values for the solubility products for the two reactions above are given at 25°C.

- What is the concentration of  $\text{CO}_3^{2-}$  ions in a saturated 1.00 liter solution of  $\text{CaCO}_3$  at 25°C?
- Excess  $\text{CaSO}_4(\text{s})$  is placed in the solution in (a). Assume that the volume of the solution does not change.
  - What is the concentration of the  $\text{SO}_4^{2-}$  ion?
  - What is the concentration of the  $\text{CO}_3^{2-}$  ion?
- A 0.20 mole sample of  $\text{CaCl}_2$  is placed in the solution in (b). Assume that the volume of the solution does not change.
  - What is the concentration of the  $\text{Ca}^{2+}$  ion?
  - What is the concentration of the  $\text{SO}_4^{2-}$  ion?
  - What is the concentration of the  $\text{CO}_3^{2-}$  ion?

# CHAPTER 10 ANSWERS AND EXPLANATIONS

## MULTIPLE-CHOICE QUESTIONS

- B**  $K_p$  is used for gaseous reactions, and the units used are partial pressures.
- D**  $K_w$  is the dissociation constant for water.  
At 25°C,  $K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$ .
- C**  $K_a$  is known as the acid dissociation constant.
- E**  $K_{sp}$  is the solubility product. It always has a solid as the reactant. Because the reactant is always in the denominator and solids are ignored in the equilibrium expression,  $K_{sp}$  never has a denominator.
- A** From Le Châtelier's law, the equilibrium will shift to counteract any stress that is placed on it. Increasing temperature favors the endothermic direction of a reaction because the endothermic reaction absorbs the added heat. So the salt becomes more soluble, increasing the number of dissociated particles, thus increasing the value of  $K_{sp}$ .
- E** According to Le Châtelier's law, the equilibrium will shift to counteract any stress that is placed on it. If the temperature is decreased, the equilibrium will shift toward the side that produces energy or heat. That's the product side where  $\text{I}_2$  is produced.  
Choices (A) and (B) are wrong because there are equal numbers of moles of gas (3 moles) on each side, so changing the volume will not affect the equilibrium. Choice (C) is wrong because the addition of a substance that does not affect the reaction will not affect the equilibrium conditions.
- C** From the balanced equation:  
If 1 mole of  $\text{CH}_3\text{OH}$  was created, then 1 mole of  $\text{CO}$  was consumed and 1 mole of  $\text{CO}$  remains;  
and if 1 mole of  $\text{CH}_3\text{OH}$  was created, then 2 moles of  $\text{H}_2$  were consumed and 1 mole of  $\text{H}_2$  remains. So at equilibrium, there are  
 $(1 \text{ mol CH}_3\text{OH}) + (1 \text{ mol CO}) + (1 \text{ mol H}_2) = 3 \text{ moles of gas}$
- D** According to Le Châtelier's law, equilibrium will shift to relieve any stress placed on a system. If  $\text{N}_2$  is removed, the equilibrium will shift to the right to produce more  $\text{N}_2$ , with the result that more  $\text{H}_2\text{O}$  will also be produced.  
If the volume is decreased (A), the equilibrium will shift toward the left, where there are fewer moles of gas. If the temperature is increased (B), the equilibrium will shift to the left. That's the endothermic reaction, which absorbs the added energy of the temperature increase. If  $\text{NH}_3$  (C) or  $\text{O}_2$  (E) is removed, the equilibrium will shift to the left to replace the substance removed.
- D** According to Le Châtelier's law, equilibrium will shift to relieve any stress placed on a system. If the temperature is increased, the equilibrium will shift to favor the endothermic reaction because it absorbs the added energy. In this case, the equilibrium will be shifted to the right, increasing the concentration of both  $\text{K}^+$  and  $\text{NO}_3^-$  ions.  
Changing the volume of the solution, (A) and (B), will change the *number* of  $\text{K}^+$  ions in solution, but not the *concentration* of  $\text{K}^+$  ions. Because solids are not considered in the equilibrium expression, adding more solid  $\text{KNO}_3$  to the solution (C) will not change the equilibrium. Decreasing the temperature (E) will favor the exothermic reaction, driving the equilibrium toward the left and decreasing the concentration of  $\text{K}^+$  ions.

10. **D**  $K_p$  and  $K_c$  will differ the most in situations where the moles of gas change drastically from the reactants to the products. This relation is given in the equation

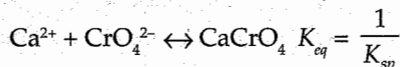
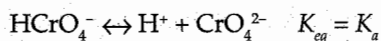
$$K_p = K_c(RT)^{\Delta n}$$

The exponential  $\Delta n$  is the moles of gas in the products minus the moles of gas in the reactants. The biggest change in number of moles of gas is found in the equation in choice D.

11. **D** The information about  $K$  at  $200^\circ\text{C}$  is useless information and can be ignored. Since all the  $\text{Cl}_2$  found in solution must have come from  $\text{SbCl}_5$ , we know that at equilibrium  $[\text{Cl}_2] = [\text{SbCl}_3] = 0.1 \text{ M}$ , and  $[\text{SbCl}_5] = (1.0 - 0.1) \text{ M} = .99 \text{ M}$ . We can then say that  $K = (0.1)(0.1)/.99 = .0101$  which is most closely approximated by choice D.

12. **D** 
$$K_p = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} = \frac{(4)^2(2)}{(4)^2} = 2$$

13. **B** We can think of the reaction given in the question as the sum of two other reactions.



Notice that we are using the reverse reaction for the solvation of  $\text{CaCrO}_4$ , so the reactants and products are reversed and we must take the reciprocal of the solubility product.

When reactions can be added to get another reaction, their equilibrium constants can be multiplied to get the equilibrium constant of the resulting reaction.

$$\text{So } K_{eq} = (K_a)\left(\frac{1}{K_{sp}}\right) = \frac{K_a}{K_{sp}}$$

14. **A** The equilibrium expression for the reaction is as follows:

$$\frac{P_{\text{IBr}}^2}{P_{\text{Br}_2}P_{\text{I}_2}} = 300$$

When all of the values are plugged into the expression, (A) is the only choice that works.

$$\frac{(3)^2}{(0.1)(0.3)} = \frac{9}{0.03} = 300$$

15. **E** Use a table to see how the partial pressures change. Based on the balanced equation, we know that if 2 atm of  $\text{CO}(g)$  were formed, then 2 atm of  $\text{H}_2\text{O}(g)$  must also have formed. We also know that the reactants must have lost 2 atm each.

	$\text{H}_2(g)$	$\text{CO}_2(g)$	$\text{H}_2\text{O}(g)$	$\text{CO}(g)$
Before	6 atm	4 atm	0	0
Change	-2	-2	+2	+2
At Equilibrium	4 atm	2 atm	2 atm	2 atm

Now plug the numbers into the equilibrium expression.

$$K_{eq} = \frac{P_{\text{H}_2\text{O}}P_{\text{CO}}}{P_{\text{H}_2}P_{\text{CO}_2}} = \frac{(2)(2)}{(4)(2)} = \frac{1}{2}$$

## PROBLEMS

1. (a)  $K_{sp} = [\text{Ba}^{2+}][\text{F}^-]^2$

(b) Use the  $K_{sp}$  expression.

$$K_{sp} = [\text{Ba}^{2+}][\text{F}^-]^2$$

Two F<sup>-</sup>s are produced for every Ba<sup>2+</sup>, so [F<sup>-</sup>] will be twice as large as [Ba<sup>2+</sup>].

Let  $x = [\text{F}^-]$

$$1.0 \times 10^{-6} = \left(\frac{x}{2}\right)(x)^2 = \frac{x^3}{2}$$

$$x = [\text{F}^-] = 0.01 \text{ M}$$

(c) First we need to find the concentrations of the Ba<sup>2+</sup> and F<sup>-</sup> ions.

Moles = (molarity)(volume)

$$\text{Moles of Ba}^{2+} = (0.0060 \text{ M})(0.400 \text{ L}) = 0.0024 \text{ mol}$$

$$\text{Moles of F}^- = (0.0060 \text{ M})(0.500 \text{ L}) = 0.0030 \text{ mol}$$

Remember to add the two volumes: (0.400 L) + (0.500 L) = 0.900 L

$$\text{Molarity} = \frac{\text{moles}}{\text{liters}}$$

$$[\text{Ba}^{2+}] = \frac{(0.0024 \text{ mol})}{(0.900 \text{ L})} = 0.0027 \text{ M}$$

$$[\text{F}^-] = \frac{(0.0030 \text{ mol})}{(0.900 \text{ L})} = 0.0033 \text{ M}$$

Now test the solubility expression using the initial values to find the reaction quotient.

$$Q = [\text{Ba}^{2+}][\text{F}^-]^2$$

$$Q = (0.0027)(0.0033)^2 = 2.9 \times 10^{-8}$$

Q is less than  $K_{sp}$ , so no precipitate forms.

(d) Use the standard free energy expression.

$$\Delta G^\circ = -2.303RT \log K$$

$$\Delta G^\circ = (-2.303)(8.31 \text{ J/mol} \cdot \text{K})(298 \text{ K})(\log 1.0 \times 10^{-6}) = 34,000 \text{ J/mol}$$

The positive value of  $\Delta G^\circ$  means that the reaction is not spontaneous under standard conditions.

2. (a) Use the equilibrium expression.

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$[\text{H}^+] = [\text{HCO}_3^-] = x$$

$$[\text{H}_2\text{CO}_3] = (0.050 \text{ M} - x)$$

Assume that  $x$  is small enough that we can use  $[\text{H}_2\text{CO}_3] = (0.050 \text{ M})$ .

$$4.3 \times 10^{-7} = \frac{x^2}{(0.050)}$$

$$x = [\text{H}^+] = 1.5 \times 10^{-4}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.5 \times 10^{-4}) = 3.8$$

- (b) Use the equilibrium expression.

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

From (a) we know:  $[\text{H}^+] = [\text{HCO}_3^-] = 1.5 \times 10^{-4}$ .

$$5.6 \times 10^{-11} = \frac{(1.5 \times 10^{-4})[\text{CO}_3^{2-}]}{(1.5 \times 10^{-4})} = [\text{CO}_3^{2-}]$$

$$[\text{CO}_3^{2-}] = 5.6 \times 10^{-11} \text{ M}$$

- (c) (i) Adding HCl will increase  $[\text{H}^+]$ , lowering the pH.

(ii) From Le Châtelier's law, you can see that adding  $\text{NaHCO}_3$  will cause the first equilibrium to shift to the left to try to use up the excess  $\text{HCO}_3^-$ . This will cause a decrease in  $[\text{H}^+]$ , raising the pH.

You may notice that adding  $\text{NaHCO}_3$  will also cause the second equilibrium to shift toward the right, which should increase  $[\text{H}^+]$ , but because  $K_2$  is much smaller than  $K_1$ , this shift is insignificant.

- (iii) Adding NaOH will neutralize hydrogen ions, decreasing  $[\text{H}^+]$  and raising the pH.

- (iv) Adding NaCl will have no effect on the pH.

(d) The reaction in (d) is just the sum of the two reactions given. When two reactions can be added to give a third reaction, the equilibrium constants for those reactions can be multiplied to give  $K_{eq}$  for the third reaction.

$$K_{eq} = (K_1)(K_2) = (4.3 \times 10^{-7})(5.6 \times 10^{-11}) = 2.4 \times 10^{-17}$$

3. (a)  $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

$$K_c = \frac{(0.20)^2}{(0.50)(0.20)^3} = 10$$

(b) Use the formula that relates the two constants.

$$K_p = K_c(RT)^{\Delta n}$$

$\Delta n$  is the change in the number of moles of gas from reactants to products. So  $\Delta n = -2$ .

$$K_p = (10)[(0.082)(570)]^{-2} = (10)(46.7)^{-2} = 4.7 \times 10^{-3}$$

(c) (i) An increase in temperature favors the endothermic direction. In this case, that's the reverse reaction, so the concentration of  $\text{H}_2$  will increase.

(ii) An increase in volume favors the direction that produces more moles of gas. In this case, that's the reverse direction, so the concentration of  $\text{H}_2$  will increase.

(iii) According to Le Châtelier's law, increasing the concentration of the reactants forces the reaction to proceed in the direction that will use up the added reactants. In this case, adding the reactant  $\text{N}_2$  will shift the reaction to the right and decrease the concentration of  $\text{H}_2$ .

(iv) The addition of He, a gas that takes no part in the reaction, will have no effect on the concentration of  $\text{H}_2$ .

4. (a) Use the solubility product.

$$K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = x$$

$$2.8 \times 10^{-9} = x^2$$

$$x = [\text{CO}_3^{2-}] = 5.3 \times 10^{-5} M$$

- (b) Use the solubility product.

$$(i) K_{sp} = [\text{Ca}^{2+}] [\text{SO}_4^{2-}]$$

$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = x$$

$$K_{sp} = 9.1 \times 10^{-6} = x^2$$

$$x = [\text{SO}_4^{2-}] = 3.0 \times 10^{-3} M$$

$$(ii) K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

Now use the value of  $[\text{Ca}^{2+}]$  that you found in (b)(i).

$$[\text{Ca}^{2+}] = x = 3.0 \times 10^{-3} M$$

$$K_{sp} = 2.8 \times 10^{-9} = (3.0 \times 10^{-3}) [\text{CO}_3^{2-}]$$

$$[\text{CO}_3^{2-}] = 9.3 \times 10^{-7} M$$

- (c) (i) The  $\text{CaCl}_2$  dissociates completely, so the solution can be assumed to contain 0.2 moles of  $\text{Ca}^{2+}$  ions. We can ignore the ions from  $\text{CaCO}_3$  and  $\text{CaSO}_4$  because there are so few of them.

$$\text{Molarity} = \frac{\text{moles}}{\text{volume}}$$

$$[\text{Ca}^{2+}] = \frac{(0.20 \text{ mol})}{(1 \text{ L})} = 0.20 M$$

- (ii) Use  $K_{sp}$  again with the new value of  $[\text{Ca}^{2+}]$ .

$$K_{sp} = [\text{Ca}^{2+}] [\text{SO}_4^{2-}]$$

$$9.1 \times 10^{-6} = (0.20) [\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = 4.6 \times 10^{-5} M$$

- (iii) Use  $K_{sp}$  again with the new value of  $[\text{Ca}^{2+}]$ .

$$K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

$$2.8 \times 10^{-9} = (0.20) [\text{CO}_3^{2-}]$$

$$[\text{CO}_3^{2-}] = 1.4 \times 10^{-8} M$$

# 11

## Acids and Bases

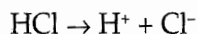
### HOW OFTEN DO ACIDS AND BASES APPEAR ON THE EXAM?

In the multiple-choice section, this topic appears in about 10 out of 75 questions. In the free-response section, this topic appears every year.

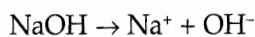
### DEFINITIONS

#### ARRHENIUS

S. A. Arrhenius defined an acid as a substance that ionizes in water and produces hydrogen ions ( $H^+$  ions). For instance, HCl is an acid.



He defined a base as a substance that ionizes in water and produces hydroxide ions ( $OH^-$  ions). For instance, NaOH is a base.

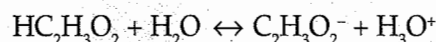




## BRØNSTED-LOWRY

J. N. Brønsted and T. M. Lowry defined an acid as a substance that is capable of donating a proton, which is the same as donating an  $H^+$  ion, and they defined a base as a substance that is capable of accepting a proton.

Look at the reversible reaction below.

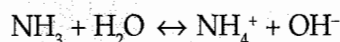


According to Brønsted-Lowry

$HC_2H_3O_2$  and  $H_3O^+$  are acids.

$C_2H_3O_2^-$  and  $H_2O$  are bases.

Now look at this reversible reaction.

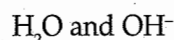
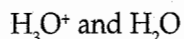
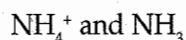
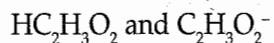


According to Brønsted-Lowry

$NH_3$  and  $OH^-$  are bases.

$H_2O$  and  $NH_4^+$  are acids.

So in each case, the species with the  $H^+$  ion is the acid, and the same species without the  $H^+$  ion is the base; the two species are called a **conjugate pair**. The following are the acid-base conjugate pairs in the reactions above:

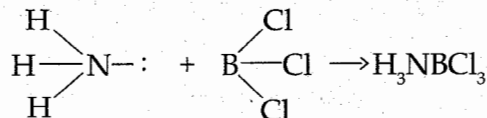


Notice that water can act either as an acid or a base.

## LEWIS

G. N. Lewis focused on electrons, and his definitions are the most broad of the acid-base definitions. Lewis defined a base as an electron pair donor and an acid as an electron pair acceptor; according to Lewis's rule, all of the Brønsted-Lowry bases above are also Lewis bases, and all of the Brønsted-Lowry acids are Lewis acids.

The following reaction is exclusively a Lewis acid-base reaction:



$NH_3$  is the Lewis base, donating its electron pair, and  $BCl_3$  is the Lewis acid, accepting the electron pair.

## pH

Many of the concentration measurements in acid-base problems are given to us in terms of pH and pOH.

$$p(\text{anything}) = -\log(\text{anything})$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{p}K_a = -\log K_a$$

$$\text{p}K_b = -\log K_b$$

In a solution

- when  $[\text{H}^+] = [\text{OH}^-]$ , the solution is neutral, and  $\text{pH} = 7$
- when  $[\text{H}^+]$  is greater than  $[\text{OH}^-]$ , the solution is acidic, and  $\text{pH}$  is less than 7
- when  $[\text{H}^+]$  is less than  $[\text{OH}^-]$ , the solution is basic, and  $\text{pH}$  is greater than 7

It is important to remember that *increasing* pH means *decreasing*  $[\text{H}^+]$ , which means that there are fewer  $\text{H}^+$  ions floating around and the solution is *less acidic*. Alternatively, *decreasing* pH means *increasing*  $[\text{H}^+]$ , which means that there are more  $\text{H}^+$  ions floating around and the solution is *more acidic*.

## WEAK ACIDS

When a weak acid is placed in water, a small fraction of its molecules will dissociate into hydrogen ions ( $\text{H}^+$ ) and conjugate base ions ( $\text{B}^-$ ). Most of the acid molecules will remain in solution as undissociated aqueous particles.

The dissociation constants,  $K_a$  and  $K_b$ , are measures of the strengths of weak acids and bases.  $K_a$  and  $K_b$  are just the equilibrium constants specific to acids and bases.

### Acid Dissociation Constant

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$[\text{H}^+]$  = molar concentration of hydrogen ions ( $M$ )

$[\text{A}^-]$  = molar concentration of conjugate base ions ( $M$ )

$[\text{HA}]$  = molar concentration of undissociated acid molecules ( $M$ )

### Base Dissociation Constant

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

$[\text{HB}^+]$  = protonated base ions ( $M$ )

$[\text{OH}^-]$  = molar concentration of hydroxide ions ( $M$ )

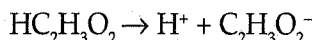
$[\text{B}]$  = unprotonated base molecules ( $M$ )

The greater the value of  $K_a$ , the greater the extent of the dissociation of the acid and the stronger the acid. The same thing goes for  $K_b$ .

## WEAK ACIDS AND CALCULATIONS

If you know the  $K_a$  for an acid and the concentration of the acid, you can find the pH. For instance, let's look at 0.20-molar solution of  $\text{HC}_2\text{H}_3\text{O}_2$ , with  $K_a = 1.8 \times 10^{-5}$ .

First we set up the  $K_a$  equation, plugging in values.



$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Therefore, the ICE (Initial, Change, Equilibrium) table for the above problem is:

	$[\text{HC}_2\text{H}_3\text{O}_2]$	$[\text{H}^+]$	$[\text{C}_2\text{H}_3\text{O}_2^-]$
<b>Initial</b>	0.20	0.0	0.0
<b>Change</b>	$-x$	$+x$	$+x$
<b>Equilibrium</b>	$0.20 - x$	$x$	$x$

Because every acid molecule that dissociates produces one  $\text{H}^+$  and one  $\text{C}_2\text{H}_3\text{O}_2^-$ ,

$$[\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = x$$

and because, strictly speaking, the molecules that dissociate should be subtracted from the initial concentration of  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $[\text{HC}_2\text{H}_3\text{O}_2]$  should be  $(0.20 \text{ M} - x)$ . In practice, however,  $x$  is almost always insignificant compared with the initial concentration of acid, so we just use the initial concentration in the calculation.

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.20 \text{ M}$$

Now we can plug our values and variable into the  $K_a$  expression.

$$1.8 \times 10^{-5} = \frac{x^2}{0.20}$$

Solve for  $x$ .

$$x = [\text{H}^+] = 1.9 \times 10^{-3}$$

Now that we know  $[\text{H}^+]$ , we can calculate the pH.

$$\text{pH} = -\log [\text{H}^+] = -\log (1.9 \times 10^{-3}) = 2.7$$

This is the basic approach to solving many of the weak acid/base problems that will be on the test.

## STRONG ACIDS

Strong acids dissociate completely in water, so the reaction goes to completion and they never reach equilibrium with their conjugate bases. Because there is no equilibrium, there is no equilibrium constant, so there is no dissociation constant for strong acids or bases.

Important Strong Acids
HCl, HBr, HI, HNO <sub>3</sub> , HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub>
Important Strong Bases
LiOH, NaOH, KOH, Ba(OH) <sub>2</sub> , Sr(OH) <sub>2</sub>

Because the dissociation of a strong acid goes to completion, there is no tendency for the reverse reaction to occur, which means that the conjugate base of a strong acid must be extremely weak.

Oxoacids are acids that contain oxygen. The greater the number of oxygen atoms attached to the central atom in an oxoacid, the stronger the acid. For instance, HClO<sub>4</sub> is stronger than HClO<sub>3</sub>, which is stronger than HClO<sub>2</sub>. That's because increasing the number of oxygen atoms that are attached to the central atom weakens the attraction that the central atom has for the H<sup>+</sup> ion.

## STRONG ACIDS AND CALCULATIONS

It's much easier to find the pH of a strong acid solution than it is to find the pH of a weak acid solution. That's because strong acids dissociate completely, so the final concentration of H<sup>+</sup> ions will be the same as the initial concentration of the strong acid.

Let's look at a 0.010-molar solution of HCl.

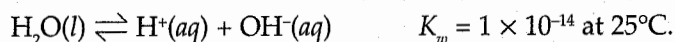
HCl dissociates completely, so [H<sup>+</sup>] = 0.010 M

$$\text{pH} = -\log [\text{H}^+] = -\log (0.010) = -\log (10^{-2}) = 2$$

So you can always find the pH of a strong acid solution directly from its concentration.

## **K<sub>w</sub>**

Water comes to equilibrium with its ions according to the following reaction:



$$K_w = 1 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14$$

The common ion effect tells us that the hydrogen ion and hydroxide ion concentrations for any acid or base solution must be consistent with the equilibrium for the ionization of water. That is, no matter where the H<sup>+</sup> and OH<sup>-</sup> ions came from, when you multiply [H<sup>+</sup>] and [OH<sup>-</sup>], you must get 1 × 10<sup>-14</sup>. So for any aqueous solution, if you know the value of [H<sup>+</sup>], you can find out the value of [OH<sup>-</sup>] and vice versa.

The acid and base dissociation constants for conjugates must also be consistent with the equilibrium for the ionization of water.

$$K_w = 1 \times 10^{-14} = K_a K_b$$

$$\text{p}K_a + \text{p}K_b = 14$$

So if you know K<sub>a</sub> for a weak acid, you can find K<sub>b</sub> for its conjugate base and vice versa.

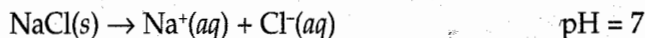
## ACID AND BASE SALTS

A salt solution can be acidic or basic, depending on the identities of the anion and cation in the salt.

- *If a salt is composed of the conjugates of a strong base and a strong acid, its solution will be neutral.*

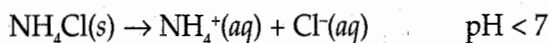
For example, let's look at NaCl.

$\text{Na}^+$  is the conjugate acid of NaOH (a strong base), and  $\text{Cl}^-$  is the conjugate base of HCl (a strong acid).

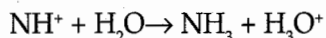


That's because neither ion will react in water because, as you may recall, the conjugates of strong acids and bases are very weak and unreactive.

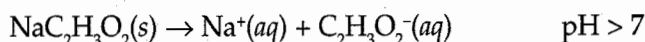
- *If a salt is composed of the conjugates of a weak base and a strong acid, its solution will be acidic.*  
For example, look at  $\text{NH}_4\text{Cl}$ .  
 $\text{NH}_4^+$  is the conjugate acid of  $\text{NH}_3$  (a weak base), and  $\text{Cl}^-$  is the conjugate base of HCl (a strong acid).



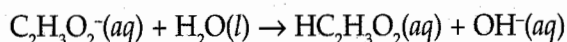
When  $\text{NH}_4\text{Cl}$  ionizes in water, the  $\text{Cl}^-$  ions won't react at all, but the  $\text{NH}_4^+$  will dissociate to some extent to produce some  $\text{H}^+$  ions, as shown in the reaction below, making the solution acidic.



- *If a salt is composed of the conjugates of a strong base and a weak acid, its solution will be basic.*  
For instance, look at  $\text{NaC}_2\text{H}_3\text{O}_2$ .  
 $\text{Na}^+$  is the conjugate acid of NaOH (a strong base), and  $\text{C}_2\text{H}_3\text{O}_2^-$  is the conjugate base of  $\text{HC}_2\text{H}_3\text{O}_2$  (a weak acid).



When  $\text{NaC}_2\text{H}_3\text{O}_2$  ionizes in water, the  $\text{Na}^+$  ions don't react at all, but the  $\text{C}_2\text{H}_3\text{O}_2^-$  ions will react with water according to the following reaction:



This is an acid-base reaction, which produces some  $\text{OH}^-$  ions and increases the pH.

- *If a salt is composed of the conjugates of a weak base and a weak acid, the pH of its solution will depend on the relative strengths of the conjugate acid and base of the specific ions in the salt.*

## ACID-BASE SALTS AND CALCULATIONS

Calculations with salts aren't much different from regular acid-base calculations, except that you may need to convert between  $K_a$  and  $K_b$  and between pH and pOH.

Remember:

$$K_a K_b = 1 \times 10^{-14}, \text{ and } \text{pH} + \text{pOH} = 14$$

Let's find the pH of a 0.10-molar solution of  $\text{NaC}_2\text{H}_3\text{O}_2$ .  $K_a$  for  $\text{HC}_2\text{H}_3\text{O}_2$  is  $1.8 \times 10^{-5}$ . The solution will be basic, so let's find  $K_b$  for  $\text{C}_2\text{H}_3\text{O}_2^-$ .

$$K_b = \frac{(1.0 \times 10^{-14})}{K_a} = \frac{(1.0 \times 10^{-14})}{(1.8 \times 10^{-5})} = 5.6 \times 10^{-10}$$

Therefore, the ICE table for the above equation is:

	$[\text{HC}_2\text{H}_3\text{O}_2]$	$[\text{OH}^-]$	$[\text{C}_2\text{H}_3\text{O}_2^-]$
<b>Initial</b>	0.10	0.0	0.0
<b>Change</b>	$-x$	$+x$	$+x$
<b>Equilibrium</b>	$0.10 - x$	$x$	$x$

Now we can use the base dissociation expression.

$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]}$$

Every  $\text{C}_2\text{H}_3\text{O}_2^-$  polyatomic ion that reacts with a water molecule produces one  $\text{HC}_2\text{H}_3\text{O}_2$  and one  $\text{OH}^-$ , so

$$[\text{HC}_2\text{H}_3\text{O}_2] = [\text{OH}^-] = x$$

Again, we assume that  $x$  is insignificant compared with the initial concentration of  $\text{C}_2\text{H}_3\text{O}_2^-$ ; 0.10 M, so

$$[\text{C}_2\text{H}_3\text{O}_2^-] = (0.10 \text{ M} - x) = 0.10 \text{ M}$$

Now we can plug our values and variable into the  $K_b$  expression.

$$5.6 \times 10^{-10} = \frac{x^2}{0.10}$$

Solve for  $x$ .

$$x = [\text{OH}^-] = 7.5 \times 10^{-6}$$

Once we know the value of  $[\text{OH}^-]$ , we can calculate the pOH.

$$\text{pOH} = -\log [\text{OH}^-] = -\log (7.5 \times 10^{-6}) = 5.1$$

Now we use pOH to find pH.

$$\text{pH} = 14 - \text{pOH} = 14 - 5.1 = 8.9$$

## BUFFERS

A **buffer** is a solution with a very stable pH. You can add acid or base to a buffer solution without greatly affecting the pH of the solution. The pH of a buffer will also remain unchanged if the solution is diluted with water or if water is lost through evaporation.

A buffer is created by placing a large amount of a weak acid or base into a solution along with its conjugate, in the form of salt. A weak acid and its conjugate base can remain in solution together without neutralizing each other. This is called the **common ion effect**.

When both the acid and the conjugate base are together in the solution, any hydrogen ions that are added will be neutralized by the base, while any hydroxide ions that are added will be neutralized by the acid, without this having much of an effect on the solution's pH.

When dealing with buffers, it is useful to rearrange the equilibrium constant to create the **Henderson-Hasselbalch equation**.

The Henderson-Hasselbalch Equation	
$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$	
[HA]	= molar concentration of undissociated weak acid (M)
[A <sup>-</sup> ]	= molar concentration of conjugate base (M)
$\text{pOH} = \text{p}K_b + \log \frac{[HB^+]}{[B]}$	
[B]	= molar concentration of weak base (M)
[HB <sup>+</sup> ]	= molar concentration of conjugate acid (M)

Let's say we have a buffer solution with concentrations of 0.20 M  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.50 M  $\text{C}_2\text{H}_3\text{O}_2^-$ . The acid dissociation constant for  $\text{HC}_2\text{H}_3\text{O}_2$  is  $1.8 \times 10^{-5}$ . Let's find the pH of the solution.

We can just plug the values we have into the Henderson-Hasselbalch equation for acids.

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \\ \text{pH} &= -\log(1.8 \times 10^{-5}) + \log \frac{(0.50\text{M})}{(0.20)} \\ \text{pH} &= -\log(1.8 \times 10^{-5}) + \log(2.5) \\ \text{pH} &= (4.7) + (0.40) = 5.1\end{aligned}$$

Now let's see what happens when  $[\text{HC}_2\text{H}_3\text{O}_2]$  and  $[\text{C}_2\text{H}_3\text{O}_2^-]$  are both equal to 0.20 M.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log \frac{(0.20M)}{(0.20M)}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log(1)$$

$$\text{pH} = (4.7) + (0) = 4.7$$

Notice that when the concentrations of acid and conjugate base in a solution are the same,  $\text{pH} = \text{p}K_a$  (and  $\text{pOH} = \text{p}K_b$ ). When you choose an acid for a buffer solution, it is best to pick an acid with a  $\text{p}K_a$  that is close to the desired pH. That way you can have almost equal amounts of acid and conjugate base in the solution, which will make the buffer as flexible as possible in neutralizing both added  $\text{H}^+$  and  $\text{OH}^-$ .

## POLYPROTIC ACIDS AND AMPHOTERIC SUBSTANCES

Some acids, such as  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ , can give up more than one hydrogen ion in solution. These are called **polyprotic acids**.

Polyprotic acids are always more willing to give up their first protons than later protons. For example,  $\text{H}_3\text{PO}_4$  gives up an  $\text{H}^+$  ion (proton) more easily than does  $\text{H}_2\text{PO}_4^-$ , so  $\text{H}_3\text{PO}_4$  is a stronger acid. In the same way,  $\text{H}_2\text{PO}_4^-$  is a stronger acid than  $\text{HPO}_4^{2-}$ .

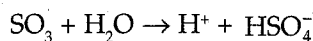
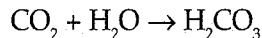
Substances that can act as either acids or bases are called **amphoteric substances**.

For instance

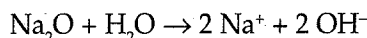
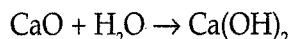
- $\text{H}_2\text{PO}_4^-$  can act as an acid, giving up a proton to become  $\text{HPO}_4^{2-}$ , or it can act as a base, accepting a proton to become  $\text{H}_3\text{PO}_4$
- $\text{HSO}_4^-$  can act as an acid, giving up a proton to become  $\text{SO}_4^{2-}$ , or it can act as a base, accepting a proton to become  $\text{H}_2\text{SO}_4$
- $\text{H}_2\text{O}$  can act as an acid, giving up a proton to become  $\text{OH}^-$ , or it can act as a base, accepting a proton to become  $\text{H}_3\text{O}^+$

## ANHYDRIDES

An **acid anhydride** is a substance that combines with water to form an acid. Generally, oxides of nonmetals are acid anhydrides.



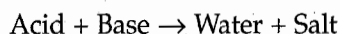
A **basic anhydride** is a substance that combines with water to form a base. Generally, oxides of metals are basic anhydrides.



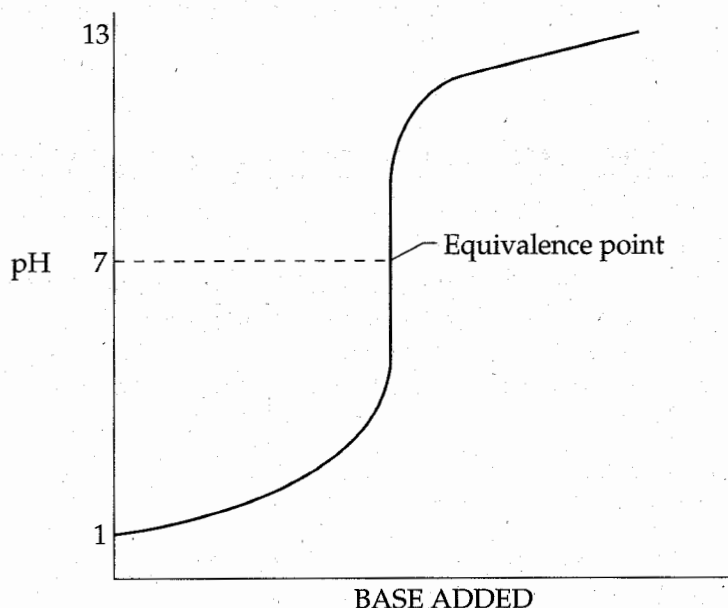


## TITRATION

When an acid and a base are mixed, a **neutralization reaction** occurs. Neutralization reactions can be written in the following form:



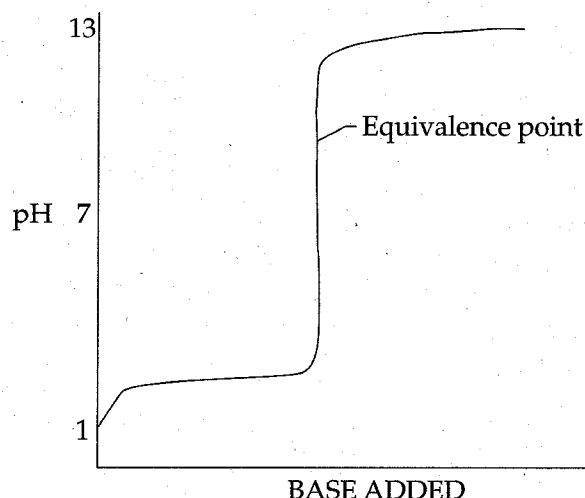
Neutralization reactions are generally performed by titration, where a base of known concentration is slowly added to an acid (or vice versa). The progress of a neutralization reaction can be shown in a titration curve. The diagram below shows the titration of a strong acid by a strong base.



In the diagram above, the pH increases slowly but steadily from the beginning of the titration until just before the equivalence point. The **equivalence point** is the point in the titration when exactly enough base has been added to neutralize all the acid that was initially present. Just before the equivalence point, the pH increases sharply as the last of the acid is neutralized. The equivalence point of a titration can be recognized through the use of an indicator. An indicator is a substance that changes color over a specific pH range. When choosing an indicator, it's important to make sure the equivalence point falls within the pH range for the color change.

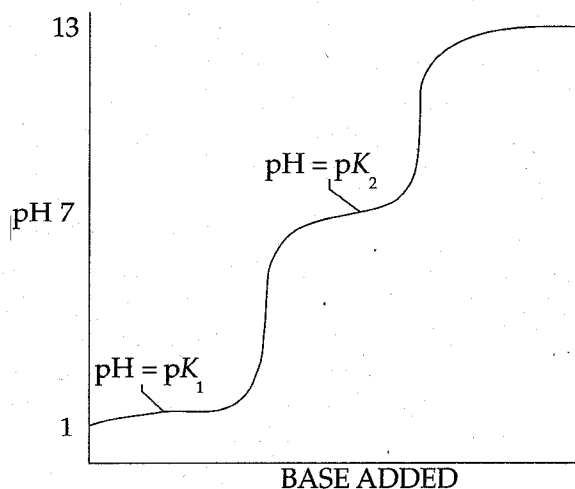
For this titration, the pH at the equivalence point is exactly 7 because the titration of a strong acid by a strong base produces a neutral salt solution.

The following diagram shows the titration of a weak acid by a strong base:



In this diagram, the pH increases more quickly at first, then levels out into a buffer region. At the center of the buffer region is the **half-equivalence point**. At this point, enough base has been added to convert exactly half of the acid into conjugate base; here the concentration of acid is equal to the concentration of conjugate base ( $\text{pH} = \text{p}K_a$ ). The curve remains fairly flat until just before the equivalence point, when the pH increases sharply. For this titration, the pH at the equivalence point is greater than 7 because the titration of a weak acid by a strong base produces a basic salt solution.

The following diagram shows the titration curve of a polyprotic acid:



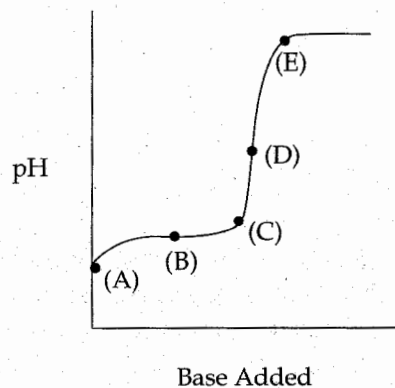
For a polyprotic acid, the titration curve will have as many bumps as there are hydrogen ions to give up. The curve above has two bumps, so it represents the titration of a diprotic acid.

# CHAPTER 11 QUESTIONS

## MULTIPLE-CHOICE QUESTIONS

### Questions 1–4

The diagram below shows the titration of a weak monoprotic acid by a strong base.



1. At this point in the titration, the pH of the solution is equal to the  $pK_a$  of the acid.
2. This is the equivalence point of the titration.
3. Of the points shown on the graph, this is the point when the solution is most basic.
4. At this point the solution is buffered.

### Questions 5–8

- (A) 1
- (B) 3
- (C) 7
- (D) 11
- (E) 13

5. The pH of a solution with a pOH of 11
6. The pH of a 0.1-molar solution of HCl
7. The pH of a 0.001-molar solution of  $\text{HNO}_3$
8. The pH of a 0.1-molar solution of NaOH

### Questions 9–12

- (A)  $\text{HNO}_3$
- (B) HCN
- (C)  $\text{H}_2\text{CO}_3$
- (D) HF
- (E)  $\text{H}_2\text{O}$

9. This is a strong electrolyte.
10. This substance can act as a Lewis base.
11. A 0.1-molar solution of this substance will have the lowest pH of the substances listed.
12. This substance is formed when carbon dioxide is dissolved in water.

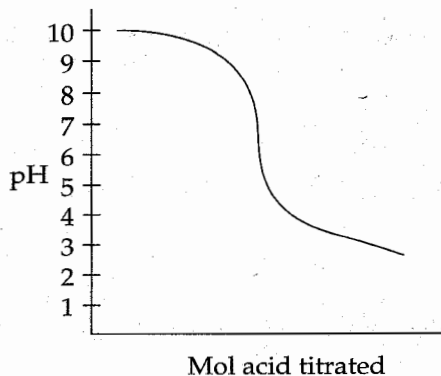
13. What is the pH of a 0.01-molar solution of NaOH?
- (A) 1  
(B) 2  
(C) 8  
(D) 10  
(E) 12
14. What is the volume of 0.05-molar HCl that is required to neutralize 50 ml of a 0.10-molar  $\text{Mg}(\text{OH})_2$  solution?
- (A) 100 ml  
(B) 200 ml  
(C) 300 ml  
(D) 400 ml  
(E) 500 ml
15. Which of the following best describes the pH of a 0.01-molar solution of HBrO? (For HBrO,  $K_a = 2 \times 10^{-9}$ )
- (A) Less than or equal to 2  
(B) Between 2 and 7  
(C) 7  
(D) Between 7 and 11  
(E) Greater than or equal to 11
16. A 0.5-molar solution of which of the following salts will have the lowest pH?
- (A) KCl  
(B)  $\text{NaC}_2\text{H}_3\text{O}_2$   
(C) NaI  
(D)  $\text{KNO}_3$   
(E)  $\text{NH}_4\text{Cl}$
17. Which of the following salts will produce a solution with a pH of greater than 7 when placed in distilled water?
- (A) NaCN  
(B) KCl  
(C)  $\text{NaNO}_3$   
(D)  $\text{NH}_4\text{NO}_3$   
(E) KI
18. A laboratory technician wishes to create a buffered solution with a pH of 5. Which of the following acids would be the best choice for the buffer?
- (A)  $\text{H}_2\text{C}_2\text{O}_4$ ,  $K_a = 5.9 \times 10^{-2}$   
(B)  $\text{H}_3\text{AsO}_4$ ,  $K_a = 5.6 \times 10^{-3}$   
(C)  $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ ,  $K_a = 1.8 \times 10^{-5}$   
(D) HOCl,  $K_a = 3.0 \times 10^{-8}$   
(E) HCN,  $K_a = 4.9 \times 10^{-10}$
19. Which of the following species is amphoteric?
- (A)  $\text{H}^+$   
(B)  $\text{CO}_3^{2-}$   
(C)  $\text{HCO}_3^-$   
(D)  $\text{H}_2\text{CO}_3$   
(E)  $\text{H}_2$
20. How many liters of distilled water must be added to 1 liter of an aqueous solution of HCl with a pH of 1 to create a solution with a pH of 2?
- (A) 0.1 L  
(B) 0.9 L  
(C) 2 L  
(D) 9 L  
(E) 100 L
21. A 1-molar solution of a very weak monoprotic acid has a pH of 5. What is the value of  $K_a$  for the acid?
- (A)  $K_a = 1 \times 10^{-10}$   
(B)  $K_a = 1 \times 10^{-7}$   
(C)  $K_a = 1 \times 10^{-5}$   
(D)  $K_a = 1 \times 10^{-2}$   
(E)  $K_a = 1 \times 10^{-1}$

22. The value of  $K_a$  for  $\text{HSO}_4^-$  is  $1 \times 10^{-2}$ . What is the value of  $K_b$  for  $\text{SO}_4^{2-}$ ?
- (A)  $K_b = 1 \times 10^{-12}$   
(B)  $K_b = 1 \times 10^{-8}$   
(C)  $K_b = 1 \times 10^{-2}$   
(D)  $K_b = 1 \times 10^2$   
(E)  $K_b = 1 \times 10^5$
23. How much 0.1-molar NaOH solution must be added to 100 milliliters of a 0.2-molar  $\text{H}_2\text{SO}_3$  solution to neutralize all of the hydrogen ions in  $\text{H}_2\text{SO}_3$ ?
- (A) 100 ml  
(B) 200 ml  
(C) 300 ml  
(D) 400 ml  
(E) 500 ml
24. The concentrations of which of the following species will be increased when HCl is added to a solution of  $\text{HC}_2\text{H}_3\text{O}_2$  in water?
- I.  $\text{H}^+$   
II.  $\text{C}_2\text{H}_3\text{O}_2^-$   
III.  $\text{HC}_2\text{H}_3\text{O}_2$
- (A) I only  
(B) I and II only  
(C) I and III only  
(D) II and III only  
(E) I, II, and III
25. Which of the following species is amphoteric?
- (A)  $\text{HNO}_3$   
(B)  $\text{HC}_2\text{H}_3\text{O}_2$   
(C)  $\text{HSO}_4^-$   
(D)  $\text{H}_3\text{PO}_4$   
(E)  $\text{ClO}_4^-$
26. If 0.630 grams of  $\text{HNO}_3$  (molecular weight 63.0) are placed in 1 liter of distilled water at  $25^\circ\text{C}$ , what will be the pH of the solution? (Assume that the volume of the solution is unchanged by the addition of the  $\text{HNO}_3$ .)
- (A) 0.01  
(B) 0.1  
(C) 1  
(D) 2  
(E) 3
27. Which of the following procedures will produce a buffered solution?
- I. Equal volumes of 0.5 M NaOH and 1 M HCl solutions are mixed.  
II. Equal volumes of 0.5 M NaOH and 1 M  $\text{HC}_2\text{H}_3\text{O}_2$  solutions are mixed.  
III. Equal volumes of 1 M  $\text{NaC}_2\text{H}_3\text{O}_2$  and 1 M  $\text{HC}_2\text{H}_3\text{O}_2$  solutions are mixed.
- (A) I only  
(B) III only  
(C) I and II only  
(D) II and III only  
(E) I, II, and III

28. Which of the following compounds will most likely act as a *Lewis* acid?

- (A)  $\text{AlBr}_3$
- (B)  $\text{CH}_4$
- (C)  $\text{NH}_3$
- (D)  $\text{PCl}_3$
- (E)  $\text{Xe}$

29. The following titration curve shows the titration of a weak base with a strong acid:



Which of the following values most accurately approximates the  $\text{p}K_b$  of the weak base?

- (A) 9.8
- (B) 8.4
- (C) 7
- (D) 3.3
- (E) 4.2

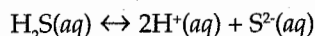
30. Which of the following expressions is equal to the hydrogen ion concentration of a 1-molar solution of a very weak monoprotic acid,  $\text{HA}$ , with an ionization constant  $K_a$ ?

- (A)  $K_a$
- (B)  $K_a^2$
- (C)  $2K_a$
- (D)  $2K_a^2$
- (E)  $\sqrt{K_a}$

## PROBLEMS

1. A beaker contains 100 milliliters of a solution of hypochlorous acid, HOCl, of unknown concentration.
  - (a) The solution was titrated with 0.100 molar NaOH solution, and the equivalence point was reached when 40.0 milliliters of NaOH solution was added. What was the original concentration of the HOCl solution?
  - (b) If the original HOCl solution had a pH of 4.46, what is the value of  $K_a$  for HOCl?
  - (c) What percent of the HOCl molecules were ionized in the original solution?
  - (d) What is the concentration of  $\text{OCl}^-$  ions in the solution at the equivalence point reached in (a)?
  - (e) What is the pH of the solution at the equivalence point?

2. A vessel contains 500 milliliters of a 0.100-molar  $\text{H}_2\text{S}$  solution. For  $\text{H}_2\text{S}$ ,  $K_1 = 1.0 \times 10^{-7}$  and  $K_2 = 1.3 \times 10^{-13}$ .
  - (a) What is the pH of the solution?
  - (b) How many milliliters of 0.100-molar NaOH solution must be added to the solution to create a solution with a pH of 7?
  - (c) What will be the pH when 800 milliliters of 0.100-molar NaOH has been added?
  - (d) What is the value of  $K_{eq}$  for the following reaction?



3. A 100 milliliter sample of 0.100-molar  $\text{NH}_4\text{Cl}$  solution was added to 80 milliliters of a 0.200-molar solution of  $\text{NH}_3$ . The value of  $K_b$  for ammonia is  $1.79 \times 10^{-5}$ .
  - (a) What is the value of  $\text{p}K_b$  for ammonia?
  - (b) What is the pH of the solution described in the question?
  - (c) If 0.200 grams of NaOH were added to the solution, what would be the new pH of the solution? (Assume that the volume of the solution does not change.)
  - (d) If equal molar quantities of  $\text{NH}_3$  and  $\text{NH}_4^+$  were mixed in solution, what would be the pH of the solution?

## ESSAYS

- 4.
- $$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^- \quad K_1 = 7.5 \times 10^{-3}$$
- $$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} \quad K_2 = 6.2 \times 10^{-8}$$
- $$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-} \quad K_3 = 2.2 \times 10^{-13}$$
- (a) Choose an amphoteric species from the reactions listed above, and give its conjugate acid and its conjugate base.
- (b) Explain why the dissociation constant decreases with each hydrogen ion lost.
- (c) Of the acids listed above, which would be most useful in creating a buffer solution with a pH of 7.5?
- (d) Sketch the titration curve that results when  $\text{H}_3\text{PO}_4$  is titrated with excess NaOH and label the two axes.
5. Use the principles of acid-base theory to answer the following questions:
- (a) Predict whether a 0.1-molar solution of sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2$ , will be acidic or basic, and give a reaction occurring with water that supports your conclusion.
- (b) Predict whether a 0.1-molar solution of ammonium chloride,  $\text{NH}_4\text{Cl}$ , will be acidic or basic, and give a reaction occurring with water that supports your conclusion.
- (c) Explain why buffer solutions are made with weak acids instead of strong acids.
- (d) Explain why, although oxygen occupies the same position in both KOH and HBrO, KOH is a base and HBrO is an acid.
6. Identify which one of the acids listed in pairs below is the stronger of the two, and explain why.
- (a) HF and HCl
- (b)  $\text{H}_2\text{SO}_3$  and  $\text{HSO}_3^-$
- (c)  $\text{HNO}_3$  and  $\text{HNO}_2$
- (d)  $\text{HClO}_4$  and  $\text{HBrO}_4$



# CHAPTER 11 ANSWERS AND EXPLANATIONS

## MULTIPLE-CHOICE QUESTIONS

1. **B** At this point, sometimes called the half-equivalence point, enough base has been added to neutralize half of the weak acid. That means that at this point, the concentration of the acid—let's call it HA—will be equal to the concentration of the conjugate base,  $A^-$ .

Now let's look at the equilibrium expression.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

If  $[HA] = [A^-]$ , then they cancel and  $K_a = [H^+]$ .

So  $pH = pK_a$ .

2. **D** The point in the middle of the steep rise in a titration curve is the equivalence point. That's the point when exactly enough base has been added to neutralize all of the acid that was originally in the solution.
3. **E** This is the point with the highest pH, so at this point, the solution is most basic.
4. **B** A buffered solution resists changes to its pH, so the flat part of the titration curve is the buffer region because the pH of the solution is changing very little even when base is being added. At (B), the solution contains a large quantity of both the acid HA, which absorbs added base, and its conjugate base,  $A^-$ , which absorbs added acid.
5. **B** In any aqueous solution at  $25^\circ\text{C}$ ,  $pH + pOH = 14$ .  
So  $pH + 3 = 14$  and  $pH = 11$ .
6. **A** HCl is a strong acid and dissociates completely, so the hydrogen ion concentration is equal to the molarity.  
So  $[H^+] = 0.1\text{ M}$   
 $pH = -\log[H^+] = -\log(0.1) = 1$
7. **B**  $\text{HNO}_3$  is a strong acid and dissociates completely, so the hydrogen ion concentration is equal to the molarity.  
So  $[H^+] = 0.001\text{ M}$   
 $pH = -\log[H^+] = -\log(0.001) = 3$
8. **E** NaOH is a strong acid and dissociates completely, so the hydroxide ion concentration  $[OH^-]$  is equal to the molarity.  
So  $[OH^-] = 0.1\text{ M}$   
 $pOH = -\log[OH^-] = -\log(0.1) = 1$   
Now,  $pH + pOH = 14$   
So  $pH + 1 = 14$  and  $pH = 13$
9. **A** A strong electrolyte is a substance that dissociates to form a lot of ions.  $\text{HNO}_3$  is the only substance listed that ionizes completely in solution.

10. **E** Water can act as a Lewis base by donating an electron pair to a hydrogen ion to form  $\text{H}_3\text{O}^+$ .
11. **A**  $\text{HNO}_3$  is the only strong acid listed, meaning that it is the only acid listed that ionizes completely, so it will have the lowest pH. By the way, in a 0.1 M solution of a strong acid, the hydrogen ion concentration will be 0.1 M, so the pH will be equal to 1.
12. **C**  $\text{H}_2\text{CO}_3$ , carbonic acid, is formed in the reaction between  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .
13. **E** NaOH is a strong base, so it can be assumed to dissociate completely. That means that the  $\text{OH}^-$  concentration will also be 0.01 M.  
 $\text{pOH} = -\log[\text{OH}^-]$ , so  $\text{pOH} = 2$ , but we're looking for the pH.  
 In an aqueous solution,  $\text{pH} + \text{pOH} = 14$ , so  $\text{pH} = 12$ .
14. **B** Every mole of  $\text{Mg}(\text{OH})_2$  molecules dissociates to produce 2 moles of  $\text{OH}^-$  ions, so a 0.10 M  $\text{Mg}(\text{OH})_2$  solution will be a 0.20 M  $\text{OH}^-$  solution.  
 The solution will be neutralized when the number of moles of  $\text{H}^+$  ions added is equal to the number of  $\text{OH}^-$  ions originally in the solution.  
 $\text{Moles} = (\text{molarity})(\text{volume})$   
 $\text{Moles of OH}^- = (0.20 \text{ M})(50 \text{ ml}) = 10 \text{ millimoles} = \text{moles of H}^+ \text{ added}$   

$$\text{Volume} = \frac{\text{moles}}{\text{molarity}}$$
  

$$\text{Volume of HCl} = \frac{(10 \text{ millimoles})}{(0.05 \text{ M})} = 200 \text{ ml}$$
15. **B** You can eliminate (C), (D), and (E) by using common sense.  $\text{HBrO}$  is a weak acid, so an  $\text{HBrO}$  solution will be acidic, with a pH of less than 7.  
 To choose between (A) and (B) you have to remember that  $\text{HBrO}$  is a weak acid. If  $\text{HBrO}$  were a strong acid, it would dissociate completely and  $[\text{H}^+]$  would be equal to 0.01-molar, for a pH of exactly 2. Because  $\text{HBrO}$  is a weak acid, it will not dissociate completely and  $[\text{H}^+]$  will be less than 0.01-molar, which means that the pH will be greater than 2. So by POE, (B) is the answer.
16. **E** To find the lowest pH, we should look for the salt that produces an acidic solution.  
 The salt composed of the conjugate of a weak base ( $\text{NH}_4^+$  is the conjugate of  $\text{NH}_3$ ) and the conjugate of a strong acid ( $\text{Cl}^-$  is the conjugate of  $\text{HCl}$ ) will produce an acidic solution.  
 As for the other choices, (A), (C), and (D) are composed of conjugates of strong acids and bases and will produce neutral solutions.  
 (B) is composed of the conjugate of a strong base ( $\text{Na}^+$ ) and the conjugate of a weak acid ( $\text{C}_2\text{H}_3\text{O}_2^-$ ) and will produce a basic solution.
17. **A** A pH of greater than 7 means that the solution is basic.  
 The salt composed of the conjugate of a strong base ( $\text{Na}^+$  is the conjugate of  $\text{NaOH}$ ) and the conjugate of a weak acid ( $\text{CN}^-$  is the conjugate of  $\text{HCN}$ ) will produce a basic solution.  
 As for the other choices, (B), (C), and (E) are composed of conjugates of strong acids and bases and will produce neutral solutions.  
 (D) is composed of the conjugate of a weak base ( $\text{NH}_4^+$ ) and the conjugate of a strong acid ( $\text{NO}_3^-$ ) and will produce an acidic solution.

18. C The best buffered solution occurs when  $\text{pH} = \text{p}K_a$ . That happens when the solution contains equal amounts of acid and conjugate base. If you want to create a buffer with a pH of 5, the best choice would be an acid with a  $\text{p}K_a$  that is as close to 5 as possible. You shouldn't have to do a calculation to see that the  $\text{p}K_a$  for choice (C) is much closer to 5 than that of any of the others.

19. C An amphoteric species can act either as an acid or a base, gaining or losing a proton.

$\text{HCO}_3^-$  can act as an acid, losing a proton to become  $\text{CO}_3^{2-}$ , or it can act as a base, gaining a proton to become  $\text{H}_2\text{CO}_3$ .

20. D We want to change the hydrogen ion concentration from 0.1 M (pH of 1) to 0.01 M (pH of 2).

The HCl is completely dissociated, so the number of moles of  $\text{H}^+$  will remain constant as we dilute the solution.

Moles = (molarity)(volume) = Constant

$$(M_1)(V_1) = (M_2)(V_2)$$

$$(0.1 \text{ M})(1 \text{ L}) = (0.01 \text{ M})(V_2)$$

So,  $V_2 = 10 \text{ L}$ , which means that 9 L must be added.

21. A A pH of 5 means that  $[\text{H}^+] = 1 \times 10^{-5}$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

For every HA that dissociates, we get one  $\text{H}^+$  and one  $\text{A}^-$ , so  $[\text{H}^+] = [\text{A}^-] = 1 \times 10^{-5}$ .

The acid is weak, so we can assume that very little HA dissociates and that the concentration of HA remains 1-molar.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(1 \times 10^{-5})(1 \times 10^{-5})}{(1)} = 1 \times 10^{-10}$$

22. A For conjugates,  $(K_a)(K_b) = K_w = 1 \times 10^{-14}$

$$K_b = \frac{K_w}{K_a} = \frac{(1 \times 10^{-14})}{(1 \times 10^{-2})} = 1 \times 10^{-12}$$

23. D First let's find out how many moles of  $\text{H}^+$  ions we need to neutralize.

Every  $\text{H}_2\text{SO}_3$  will produce 2  $\text{H}^+$  ions, so for our purposes, we can think of the solution as a 0.4-molar  $\text{H}^+$  solution.

Moles = (molarity)(volume)

Moles of  $\text{H}^+$  = (molarity)(volume) = (0.4 M)(100 ml) = 40 millimoles = moles of  $\text{OH}^-$  required

$$\text{Volume of NaOH} = \frac{\text{moles}}{\text{molarity}} = \frac{(40 \text{ millimoles})}{(0.1 \text{ M})} = 400 \text{ ml}$$

24. C Let's look at the equilibrium expression for the dissociation of  $\text{HC}_2\text{H}_3\text{O}_2$ .

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

When HCl is added to the solution,  $\text{H}^+$  ions are added and  $[\text{H}^+]$  will increase, so (I) is correct.

Because of Le Châtelier's law, the equilibrium will shift to consume some of the added  $\text{H}^+$  ions, so some of the  $\text{H}^+$  ions will combine with  $\text{C}_2\text{H}_3\text{O}_2^-$  ions to form more  $\text{HC}_2\text{H}_3\text{O}_2$ .

So  $[\text{C}_2\text{H}_3\text{O}_2^-]$  will decrease, making (II) wrong, and  $[\text{HC}_2\text{H}_3\text{O}_2]$  will increase, making (III) correct.

25. C An amphoteric species can act either as a base and gain an  $H^+$  or as an acid and lose an  $H^+$ .  
 $HSO_4^-$  can lose an  $H^+$  to become  $SO_4^{2-}$  or it can gain an  $H^+$  to become  $H_2SO_4$ .  
 $HNO_3$  (A),  $HC_2H_3O_2$  (B), and  $H_3PO_4$  (D) can only lose an  $H^+$ .  
 $ClO_4^-$  (E) can only gain an  $H^+$ .
26. D Every unit of  $HNO_3$  added to the solution will place 1 unit of  $H^+$  ions in the solution. So first find the moles of  $HNO_3$  added.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of } H^+ = \frac{0.630 \text{ grams}}{63.0 \text{ g / mole}} = 0.01 \text{ moles}$$

Now it's easy to find the  $H^+$  concentration.

$$\text{Molarity} = \frac{\text{moles}}{\text{liters}}$$

$$[H^+] = \frac{0.01 \text{ moles}}{1 \text{ L}} = 0.01 \text{ M}$$

$$\text{pH} = -\log [H^+] = -\log(0.01) = 2$$

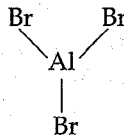
27. D A buffered solution can be prepared by mixing a weak acid with an equal amount of its conjugate or by adding enough strong base to neutralize half of the weak acid present in a solution.

In (I), equal amounts of a strong acid and base are mixed. They'll neutralize each other completely to produce salt water, which is not a buffer.

In (II), enough strong base is added to neutralize half of the weak acid. This will leave equal amounts of weak acid and its conjugate base, producing a buffered solution.

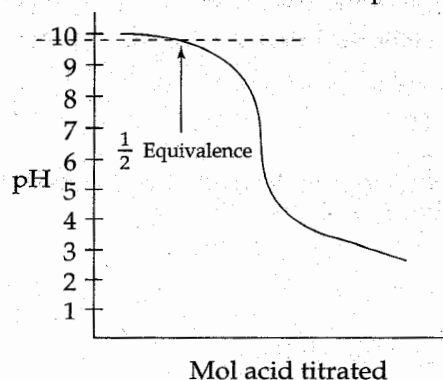
In (III), equal amounts of a weak acid and its conjugate base are mixed. This will produce a buffered solution.

28. A A Lewis acid must be able to accept a pair of electrons. By drawing the Lewis structure of  $AlBr_3$ , shown below, one can see that Al lacks a full octet and therefore is a very strong Lewis acid.



$NH_3$  is a good Lewis base, since it has a lone pair of electrons to donate. Both  $CH_4$  and Xe have full octets, and will not accept more electrons. The compound  $PCl_3$  looks a lot like  $NH_3$ , and has a lone pair of electrons and acts as a Lewis base.

29. E The half equivalence point of this titration, shown in the plot below, is around pH = 9.8.



However, this is not the  $pK_b$  of the weak base. Remember that the Henderson-Hasselbalch equation relates pH with  $pK_a$ , not  $pK_b$ . At the half equivalence point shown, the amount of base (which we can call  $[A^-]$  as we do when talking about acids and pH values) is equal to the neutralized base  $[HA]$ . When these two quantities are equal, the H-H equation tells us that the pH = the  $pK_a$  of the acid form, which when subtracted from 14 gives the  $pK_b$  of the base. So, the  $pK_a$  of the acid form is 9.8, so the  $pK_b$  of the base is 4.2.

30. E Use the equilibrium expression

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{y^2}{(1)}$$

For every HA that dissociates, we get one  $H^+$  and one  $A^-$ , so  $[H^+] = [A^-] = y$ .

The acid is weak, so we can assume that very little HA dissociates and that the concentration of HA remains 1-molar.

$$\text{So } [H^+] = y = \sqrt{K_a}$$

## PROBLEMS

1. (a) First let's find out how many moles of NaOH were added.

$$\text{Moles} = (\text{molarity})(\text{volume})$$

$$\text{Moles of NaOH} = (0.100 \text{ M})(.040 \text{ L}) = 0.004 \text{ moles}$$

Every  $OH^-$  ion neutralizes one  $H^+$  ion, so at the equivalence point, the number of moles of NaOH added is equal to the number of moles of HOCl originally present.

$$(\text{moles of NaOH}) = (\text{moles of HOCl}) = 0.004 \text{ moles}$$

Now we can find the original concentration of the HOCl solution.

$$\text{Molarity} = \frac{\text{moles}}{\text{volume}}$$

$$[HOCl] = \frac{(0.004 \text{ mol})}{(0.100 \text{ L})} = 0.040 \text{ M}$$

(b) Use the equilibrium expression.

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]}$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.46} = 3.47 \times 10^{-5} \text{ M}$$

$$[\text{H}^+] = [\text{OCl}^-] = 3.47 \times 10^{-5} \text{ M}$$

$$[\text{HOCl}] = 0.040 \text{ M}$$

$$K_a = \frac{(3.47 \times 10^{-5} \text{ M})^2}{(0.040 \text{ M} - 3.47 \times 10^{-5} \text{ M})}$$

0.040 is much larger than  $3.47 \times 10^{-5}$ , so we can simplify the expression.

$$K_a = \frac{(3.47 \times 10^{-5} \text{ M})^2}{(0.040 \text{ M})} = \frac{(1.20 \times 10^{-9})}{(0.040 \text{ M})} \text{ M} = 3.00 \times 10^{-8} \text{ M}$$

(c) The percent of molecules ionized is given by the following expression:

$$\% \text{ ionized} = \frac{[\text{H}^+]}{[\text{HOCl}]} \times 100\% = \frac{(3.47 \times 10^{-5} \text{ M})}{(0.040 \text{ M})} \times 100\% = 0.087\%$$

(d) At the equivalence point, all of the HOCl initially present has been converted into OCl<sup>-</sup> ions.

From (a), we know that there were initially 0.004 moles of HOCl, so at equivalence, there are 0.004 moles of OCl<sup>-</sup>.

At equivalence, we have added 40 ml to the 100 ml of solution originally present, so we must take this into account in our concentration calculation.

$$\text{Molarity} = \frac{\text{moles}}{\text{volume}}$$

$$[\text{OCl}^-] = \frac{(0.004 \text{ mol})}{(0.100 \text{ L} + 0.040 \text{ L})} = \frac{(0.004 \text{ mol})}{(0.140 \text{ L})} = 0.029 \text{ M}$$

(e) We know the  $K_a$  for HOCl, so we can use it to find the  $K_b$  for OCl<sup>-</sup>.

$$K_b = \frac{1 \times 10^{-14}}{K_a} = \frac{1 \times 10^{-14}}{3 \times 10^{-8}} = 3.33 \times 10^{-7}$$

Now use the  $K_b$  expression.

$$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$$

$$[\text{HOCl}] = [\text{OH}^-] = x$$

$$[\text{OCl}^-] = 0.029 \text{ M}$$

$$3.33 \times 10^{-7} = \frac{x^2}{(0.029 \text{ M} - x)}$$

Let's assume that 0.029 M is much larger than  $x$ . This simplifies the expression.

$$3.33 \times 10^{-7} = \frac{x^2}{0.029 M}$$

$$x^2 = (3.33 \times 10^{-7})(0.029 M) = 9.67 \times 10^{-9}$$

$$x = 9.83 \times 10^{-5} = [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{OH}^-] = 4$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4 = 10$$

2. (a) Use the equilibrium expression for  $\text{H}_2\text{S}$  to find  $[\text{H}^+]$ .

$$K_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$[\text{H}^+] = [\text{HS}^-] = x$$

$$[\text{H}_2\text{S}] = 0.100 M$$

$$K_1 = 1.0 \times 10^{-7}$$

$$1.0 \times 10^{-7} = \frac{x^2}{(0.100 M - x)}$$

Let's assume that 0.100 is much larger than  $x$ . That simplifies the expression.

$$1.0 \times 10^{-7} = \frac{x^2}{(0.100 M)}$$

$$x^2 = (1.0 \times 10^{-7})(0.100) M^2 = 1.0 \times 10^{-8} M^2$$

$$x = 1.0 \times 10^{-4} M = [\text{H}^+]$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.0 \times 10^{-4}) = 4.0$$

- (b) At the midpoint,  $\text{pH} = \text{p}K_1$

Let's look at the Henderson-Hasselbalch expression.

$$\text{pH} = \text{p}K + \log \frac{[\text{HS}^-]}{[\text{H}_2\text{S}]}$$

When  $\text{pH} = \text{p}K$ ,  $[\text{HS}^-]$  must be equal to  $[\text{H}_2\text{S}]$ , making  $\frac{[\text{HS}^-]}{[\text{H}_2\text{S}]}$  equal to one and  $\log \frac{[\text{HS}^-]}{[\text{H}_2\text{S}]}$  equal to zero.

For every molecule of  $\text{H}_2\text{S}$  neutralized, one unit of  $\text{HS}^-$  is generated, so we must add enough  $\text{NaOH}$  to neutralize half of the  $\text{HS}^-$  initially present. (We are assuming that the further dissociation of  $\text{HS}^-$  into  $\text{H}^+$  and  $\text{S}_2^-$  is negligible and can be ignored.)

Let's find out how many moles of  $\text{H}_2\text{S}$  were initially present.

$$\text{Moles} = (\text{molarity})(\text{volume})$$

$$\text{Moles of } \text{H}_2\text{S} = (0.100 M)(0.500 L) = 0.050 \text{ moles}$$

We need to neutralize half of that, or 0.025 moles, so we need 0.025 moles of  $\text{NaOH}$ .

$$\text{Volume} = \frac{\text{moles}}{\text{molarity}}$$

$$\text{Volume of NaOH} = \frac{(0.025 \text{ mol})}{(0.100 \text{ M})} = 0.250 \text{ L} = 250 \text{ ml}$$

(c) The concentrations of the  $\text{H}_2\text{S}$  solution and NaOH solution are both  $0.100 \text{ M}$ , so the first 500 ml of NaOH solution will completely neutralize the  $\text{H}_2\text{S}$ . The final 300 ml of NaOH solution will neutralize  $\text{HS}^-$  molecules.

Initially, there were 0.050 moles of  $\text{H}_2\text{S}$ , so after 500 ml of NaOH solution was added, there were 0.050 moles of  $\text{HS}^-$ .

By adding 300 ml more of NaOH solution, we added  $(0.100 \text{ M})(0.300 \text{ L}) = 0.030$  moles of NaOH. [Moles = (molarity)(volume)]

Every unit of NaOH added neutralizes one unit of  $\text{HS}^-$ , so when all the NaOH has been added, we have 0.030 moles of  $\text{S}^{2-}$  and  $(0.050 \text{ moles}) - (0.030 \text{ moles}) = 0.020$  moles of  $\text{HS}^-$ .

Now we can use the Henderson-Hasselbalch expression to find the pH. We can use the number of moles we just calculated (0.030 for  $\text{S}^{2-}$  and 0.020 for  $\text{HS}^-$ ) instead of concentrations because in a solution the concentrations are proportional to the number of moles.

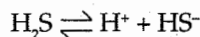
$$\text{pH} = \text{pK} + \log \frac{[\text{S}^{2-}]}{[\text{HS}^-]}$$

$$\text{pK} = -\log(1.3 \times 10^{-13}) = 12.9$$

$$\log \frac{[\text{S}^{2-}]}{[\text{HS}^-]} = \log \frac{(0.030)}{(0.020)} = \log(1.5) = 0.18$$

$$\text{pH} = 12.9 + 0.18 = 13.1.$$

(d) The reaction  $(\text{H}_2\text{S} \rightleftharpoons 2 \text{H}^+ + \text{S}^{2-})$  is the sum of the two acid dissociation reactions below.



If one reaction is the sum of two other reactions, then its equilibrium constant will be the product of the equilibrium constants for the other two reactions.

$$\text{So } K_{eq} = K_1 K_2 = (1.0 \times 10^{-7})(1.3 \times 10^{-13}) = 1.3 \times 10^{-20}$$

3. (a)  $\text{pK}_b = -\log K_b = -\log(1.79 \times 10^{-5}) = 4.75$

(b) This is a buffered solution, so we'll use the Henderson-Hasselbalch expression.

First let's find  $[\text{NH}_4^+]$  and  $[\text{NH}_3]$ .

Moles = (molarity)(volume)

$$\text{Moles of } \text{NH}_4^+ = (0.100 \text{ M})(0.100 \text{ L}) = 0.010 \text{ moles}$$

$$\text{Moles of } \text{NH}_3 = (0.200)(0.080 \text{ L}) = 0.016 \text{ moles}$$

When we mix the solutions, the volume becomes  $(0.100 \text{ L}) + (0.080 \text{ L}) = 0.180 \text{ L}$ .

$$\text{Molarity} = \frac{\text{moles}}{\text{volume}}$$

$$[\text{NH}_4^+] = \frac{(0.010 \text{ mol})}{(0.180 \text{ L})} = 0.056 \text{ M}$$

$$[\text{NH}_3] = \frac{(0.016 \text{ mol})}{(0.180 \text{ mol})} = 0.089 \text{ M}$$



Now we can use the Henderson-Hasselbalch expression for bases.

$$\text{pOH} = \text{p}K + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$\text{p}K = 4.75$$

$$\log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = \log \frac{(0.056 \text{ M})}{(0.089 \text{ M})} = -0.20$$

$$\text{pOH} = 4.75 + (-0.20) = 4.55$$

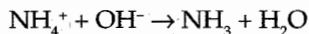
$$\text{pH} = 14 - \text{pOH} = 14 - 4.55 = 9.45$$

(c) First let's find out how many moles of NaOH were added:

$$\text{Moles} = \frac{\text{moles}}{\text{MW}}$$

$$\text{Moles of NaOH} = \frac{(0.200 \text{ g})}{(40.0 \text{ g/m})} = 0.005 \text{ mol}$$

When NaOH is added to the solution, the following reaction occurs:



So for every unit of NaOH added, one ion of  $\text{NH}_4^+$  disappears and one molecule of  $\text{NH}_3$  appears. We can use the results of the molar calculations we did in part (b).

$$\text{Moles of NH}_4^+ = (0.010) - (0.005) = 0.005 \text{ moles}$$

$$\text{Moles of NH}_3 = (0.016) + (0.005) = 0.021 \text{ moles}$$

Now we can use the Henderson-Hasselbalch expression. We can use the number of moles we just calculated (0.005 for  $\text{NH}_4^+$  and 0.021 for  $\text{NH}_3$ ) instead of concentrations because in a solution the concentrations will be proportional to the number of moles.

$$\text{pOH} = \text{p}K + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$\text{p}K = 4.75$$

$$\log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = \log \frac{(0.005 \text{ mol})}{(0.021 \text{ mol})} = -0.62$$

$$\text{pOH} = 4.75 + (-0.62) = 4.13$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.13 = 9.87$$

(d) When equal quantities of a base ( $\text{NH}_3$ ) and its conjugate acid ( $\text{NH}_4^+$ ) are mixed in a solution, the pOH will be equal to the  $\text{p}K_b$ .

$$\text{From (a), pOH} = \text{p}K_b = 4.75$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.75 = 9.25$$

## ESSAYS

4. (a) An amphoteric species can act either as an acid or base.

$\text{H}_2\text{PO}_4^-$  is amphoteric.

Conjugate base:  $\text{HPO}_4^{2-}$

Conjugate acid:  $\text{H}_3\text{PO}_4$

or

$\text{HPO}_4^{2-}$  is amphoteric.

Conjugate base:  $\text{PO}_4^{3-}$

Conjugate acid:  $\text{H}_2\text{PO}_4^-$

- (b) The smaller the dissociation constant, the more tightly the acid holds its hydrogen ions and the weaker the acid becomes.

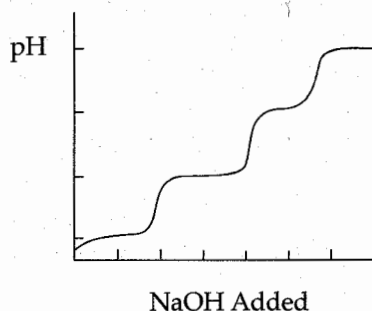
After a hydrogen ion has been removed, the remaining species has a negative charge that attracts the remaining hydrogen ions more strongly.



For  $\text{H}_2\text{PO}_4^-$ ,  $\text{p}K_a = -\log(6.2 \times 10^{-8}) = 7.2$

The best buffer solution is made with an acid whose  $\text{p}K_a$  is approximately equal to the desired pH.

- (d)



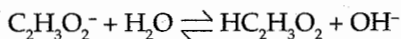
The axes should have the correct labeling (pH and NaOH added).

The curve should show rising pH, and it should have three bumps.

5. (a) The solution will be basic. A salt composed of the conjugate of a strong base ( $\text{Na}^+$ ) and the conjugate of a weak acid ( $\text{C}_2\text{H}_3\text{O}_2^-$ ) will create a basic solution in water.

$\text{NaC}_2\text{H}_3\text{O}_2$  dissociates into  $\text{Na}^+$  and  $\text{C}_2\text{H}_3\text{O}_2^-$ .

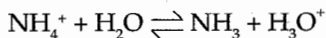
$\text{Na}^+$  does not react with water but  $\text{C}_2\text{H}_3\text{O}_2^-$  does.



- (b) The solution will be acidic. A salt composed of the conjugate of a strong acid ( $\text{Cl}^-$ ) and the conjugate of a weak base ( $\text{NH}_4^+$ ) will create an acidic solution in water.

$\text{NH}_4\text{Cl}$  dissociates into  $\text{NH}_4^+$  and  $\text{Cl}^-$ .

$\text{Cl}^-$  does not react with water but  $\text{NH}_4^+$  does.



(c) For a buffer solution, it is necessary for both an acid (HA) and its conjugate base ( $A^-$ ) to be present in the solution.

By definition, strong acids dissociate completely, so the conjugate base will be too weak to accept any hydrogen atoms that are added to the solution.

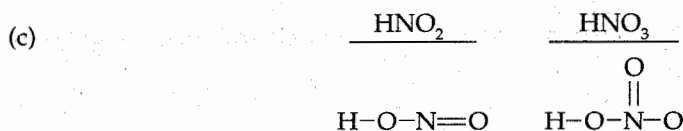
Weak acids do not dissociate completely, so it is possible to have a solution that contains both undissociated acid (HA) and conjugate base ( $A^-$ ). The undissociated acid can react with added hydroxide, and the conjugate base can react with added hydrogen ions.

(d) KOH separates into  $K^+$  and  $OH^-$  in water because the ionic bond between O and K in the unit can be broken by water, which is a polar solvent.

HBrO separates into  $H^+$  and  $BrO^-$  because the covalent O-Br bond pulls electrons away from the O-H bond. This makes the O-H bond more polar and more easily broken by water, a polar solvent.

6. (a) HCl is the stronger acid. The bond between H and Cl is weaker than the bond between H and F, so HCl dissociates more easily.

(b)  $H_2SO_3$  is stronger. As a polyprotic acid gives up hydrogen ions, it becomes negatively charged, causing it to hang onto its remaining hydrogen ions more tightly, which weakens it as an acid.

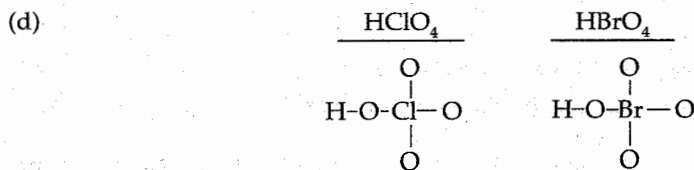


$HNO_3$  is stronger. As more oxygens are added to the central atom of an oxyacid, the oxidation number of the central atom increases.

In  $HNO_2$ , the central atom, N, has an oxidation state of +3.

In  $HNO_3$ , N has an oxidation state of +5.

The increased oxidation state of N makes the N-O bond stronger. This draws electrons away from the O-H bond, making it more polar or weaker. The weakness of the O-H bond makes the acid stronger.



$HClO_4$  is stronger. Cl has greater electronegativity than Br, so Cl draws electrons away from O in the Cl-O bond; this makes the O-H bond more polar or weaker. A weak O-H bond makes for a strong acid.

# 12

## Kinetics

### HOW OFTEN DOES KINETICS APPEAR ON THE EXAM?

In the multiple-choice section, this topic appears in about 3 out of 75 questions. In the free-response section, this topic appears almost every year.

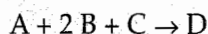
In thermodynamics, you determine whether a reaction will occur spontaneously, based on the relative states of the reactants and products. Kinetics deals with the rate at which a reaction occurs between those states. The rate of a chemical reaction is determined experimentally by measuring the rate at which a reactant disappears or a product appears. So reaction rates are generally measured in moles/time or  $M$ /time.

### THE RATE LAW USING INITIAL CONCENTRATIONS

The rate law for a reaction describes the dependence of the initial rate of a reaction on the concentrations of its reactants. It includes the Arrhenius constant,  $k$ , which takes into account the activation energy for the reaction and the temperature at which the reaction occurs. The rate of a reaction is described in terms of the rate of appearance of a product or the rate of disappearance of a reactant. The rate law for a reaction cannot be determined from a balanced equation; it must be determined from experimental data, which is presented on the test in table form.

### Here's how it's done

The data below were collected for the following hypothetical reaction:



Experiment	Initial Concentration of Reactants (M)			Initial Rate of Formation of D (M/sec)
	[A]	[B]	[C]	
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

The rate law always takes the following form, using the concentrations of the reactants:

$$\text{Rate} = k[A]^x[B]^y[C]^z$$

The greater the value of a reactant's exponent, the more a change in the concentration of that reactant will affect the rate of the reaction. To find the values for the exponents  $x$ ,  $y$ , and  $z$ , we need to examine how changes in the individual reactants affect the rate. The easiest way to find the exponents is to see what happens to the rate when the concentration of an individual reactant is doubled.

#### Let's look at [A]

From experiment 3 to experiment 4, [A] doubles while the other reactant concentrations remain constant. For this reason, it is useful to use the rate values from these two experiments to calculate  $x$  (the order of the reaction with respect to reactant A).

As you can see from the table, the rate quadruples from experiment 3 to experiment 4, going from 0.02 M/sec to 0.08 M/sec.

We need to find a value for the exponent  $x$  that relates the doubling of the concentration to the quadrupling of the rate. The value of  $x$  can be calculated as follows:

$$(2)^x = 4, \text{ so } x = 2$$

Because the value of  $x$  is 2, the reaction is said to be second order with respect to A.

$$\text{Rate} = k[A]^2[B]^y[C]^z$$

#### Let's look at [B]

From experiment 1 to experiment 3, [B] doubles while the other reactant concentrations remain constant. For this reason it is useful to use the rate values from these two experiments to calculate  $y$  (the order of the reaction with respect to reactant B).

As you can see from the table, the rate doubles from experiment 1 to experiment 3, going from 0.01 M/sec to 0.02 M/sec.

We need to find a value for the exponent  $y$  that relates the doubling of the concentration to the doubling of the rate. The value of  $y$  can be calculated as follows:

$$(2)^y = 2, \text{ so } y = 1$$

Because the value of  $y$  is 1, the reaction is said to be first order with respect to B.

$$\text{Rate} = k[A]^2[B][C]^z$$

### Let's look at [C]

From experiment 1 to experiment 2, [C] doubles while the other reactant concentrations remain constant.

The rate remains the same at 0.01 M.

The rate change is  $(2)^z = 1$ , so  $z = 0$ .

Because the value of  $z$  is 0, the reaction is said to be zero order with respect to C.

$$\text{Rate} = k[\text{A}]^2[\text{B}]$$

Because the sum of the exponents is 3, the reaction is said to be third order overall.

Once the rate law has been determined, the value of the rate constant can be calculated using any of the lines of data on the table. The units of the rate constant are dependent on the order of the reaction, so it's important to carry along units throughout all rate constant calculations.

Let's use experiment 3.

$$k = \frac{\text{Rate}}{[\text{A}]^2[\text{B}]} = \frac{(0.02 \text{ M} / \text{sec})}{(0.10 \text{ M})^2(0.20 \text{ M})} = 10 \left( \frac{(M)}{(M)^3(\text{sec})} \right) = 10 \text{ M}^{-2}\text{-sec}^{-1}$$

You should note that we can tell from the coefficients in the original balanced equation that the rate of appearance of D is equal to the rate of disappearance of A and C because the coefficients of all three are the same. The coefficient of D is half as large as the coefficient of B, however, so the rate at which D appears is half the rate at which B disappears.

## THE RATE LAW USING CONCENTRATION AND TIME

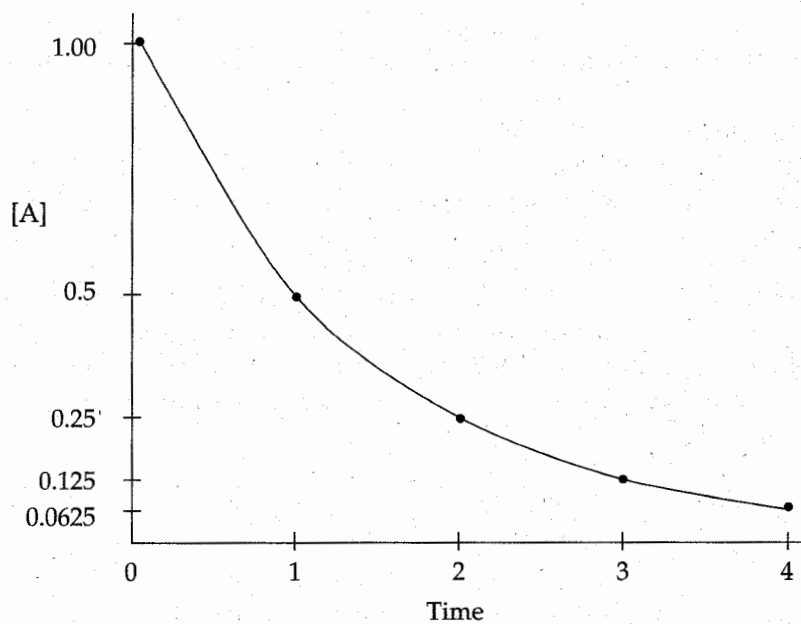
It's also useful to have rate laws that relate the rate constant  $k$  to the way that concentrations change over time. The rate laws will be different depending on whether the reaction is first, second, or zero order, but each rate law can be expressed as a graph that relates the rate constant, the concentration of a reactant, and the elapsed time.

### FIRST-ORDER RATE LAWS

The rate of a first-order reaction depends on the concentration of a single reactant raised to the first power.

$$\text{Rate} = k[\text{A}]$$

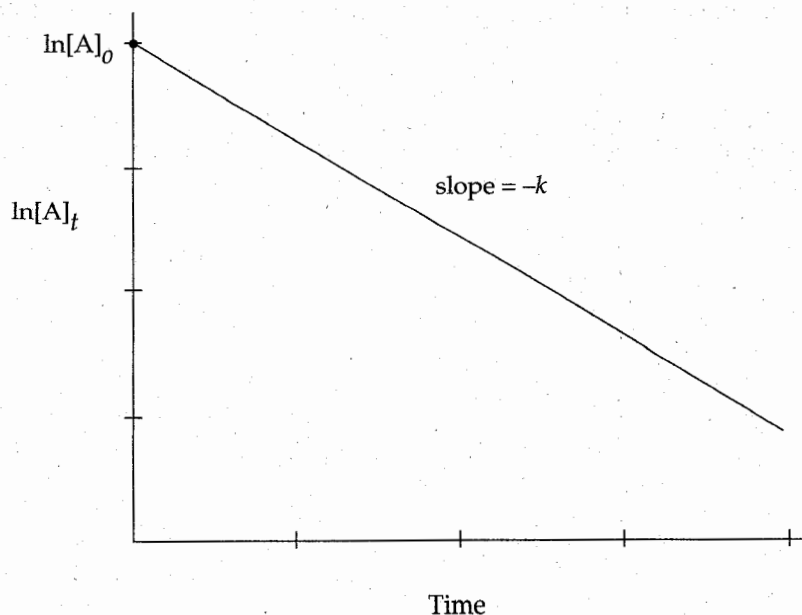
As the concentration of reactant A is depleted over time, the rate of reaction will decrease with a characteristic half-life. This is the same curve you've seen used for nuclear decay, which is also a first-order process.



The rate law for a first-order reaction uses natural logarithms.

First-Order Rate Law
$\ln[A]_t - \ln[A]_0 = -kt$
$[A]_t$ = concentration of reactant A at time $t$
$[A]_0$ = initial concentration of reactant A
$k$ = rate constant
$t$ = time elapsed

The use of natural logarithms in the rate law creates a linear graph comparing concentration and time. The slope of the line is given by  $-k$  and the  $y$ -intercept is given by  $\ln[A]_0$ .



If you are asked to give the half-life of a first-order reaction, you can usually figure it out by looking at the graph or table given in the problem, but it's worth your while to know the equation that gives the half-life in terms of the rate constant.

$$\text{Half-life} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Let's try an example based on the data below.

[A] (M)	Time (min)
2.0	0
1.6	5
1.2	10

(a) Let's find the value of  $k$ . We'll use the first two lines of the table.

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\ln(1.6) - \ln(2.0) = -k(5 \text{ min})$$

$$-0.22 = -(5 \text{ min})k$$

$$k = 0.045 \text{ min}^{-1}$$

(b) Now let's use  $k$  to find  $[A]$  when 20 minutes have elapsed.

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\ln[A]_t - \ln(2.0) = -(0.045 \text{ min}^{-1})(20 \text{ min})$$

$$\ln[A]_t = -0.21$$

$$[A]_t = e^{-0.21} = 0.81 \text{ M}$$

(c) Now let's find the half-life of the reaction.

We can look at the answer (b) to see that the concentration dropped by half (1.6 M to 0.8 M) from 5 minutes to 20 minutes. That makes the half-life about 15 minutes. We can confirm this using the half-life equation.

$$\text{Half-life} = \frac{0.693}{k} = \frac{0.693}{0.045 \text{ min}^{-1}} = 15.4 \text{ minutes}$$



## SECOND-ORDER RATE LAWS

The rate of a second-order reaction depends on the concentration of a single reactant raised to the second power.

$$\text{Rate} = k[A]^2$$

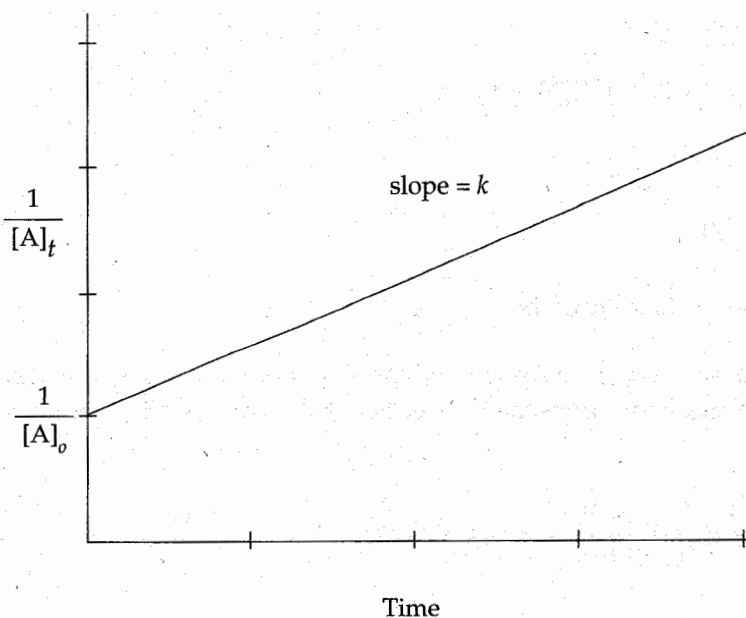
The rate law for a second-order reaction uses the inverses of the concentrations.

Second-Order Rate Law
$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$
$[A]_t$ = concentration of reactant A at time $t$
$[A]_0$ = initial concentration of reactant A
$k$ = rate constant
$t$ = time elapsed

The use of inverses in the rate law creates a linear graph comparing concentration and time.

Notice that the line moves upward as the concentration decreases. The slope of the line is given by  $k$

and the  $y$ -intercept is given by  $\frac{1}{[A]_0}$ .



## ZERO-ORDER RATE LAWS

The rate of a zero-order reaction does not depend on the concentration of reactants at all, so the rate of a zero-order reaction will always be the same at a given temperature.

$$\text{Rate} = k$$

The graph of the change in concentration of a reactant of a zero-order reaction versus time will be a straight line with a slope equal to  $-k$ .

## COLLISION THEORY

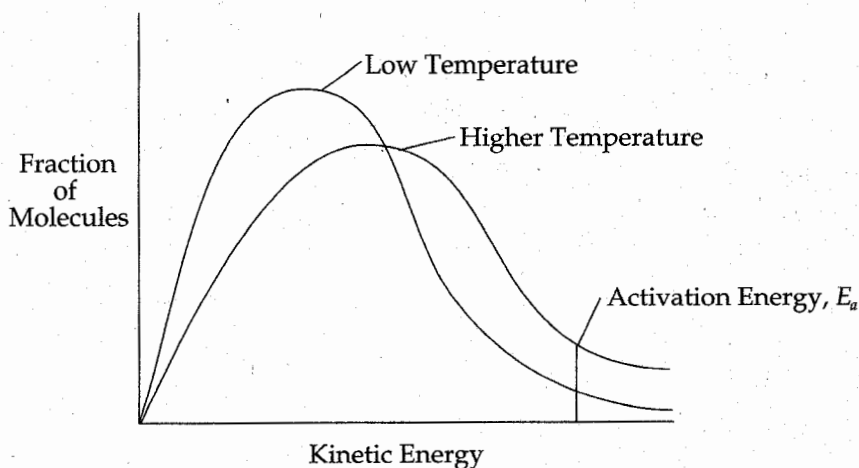
According to collision theory, chemical reactions occur because reactants are constantly moving around and colliding with one another.

When reactants collide with sufficient energy (**activation energy,  $E_a$** ), a reaction occurs. At any given time during a reaction, a certain fraction of the reactant molecules will collide with sufficient energy to cause a reaction between them.

*Reaction rate increases with increasing concentration of reactants* because if there are more reactant molecules moving around in a given volume, then more collisions will occur.

*Reaction rate increases with increasing temperature* because increasing temperature means that the molecules are moving faster, which means that the molecules have greater average kinetic energy. The higher the temperature, the greater the number of reactant molecules colliding with each other with enough energy ( $E_a$ ) to cause a reaction.

The Boltzmann distribution diagram below is often used to show that increasing temperature increases the fraction of reactant molecules above the activation energy.

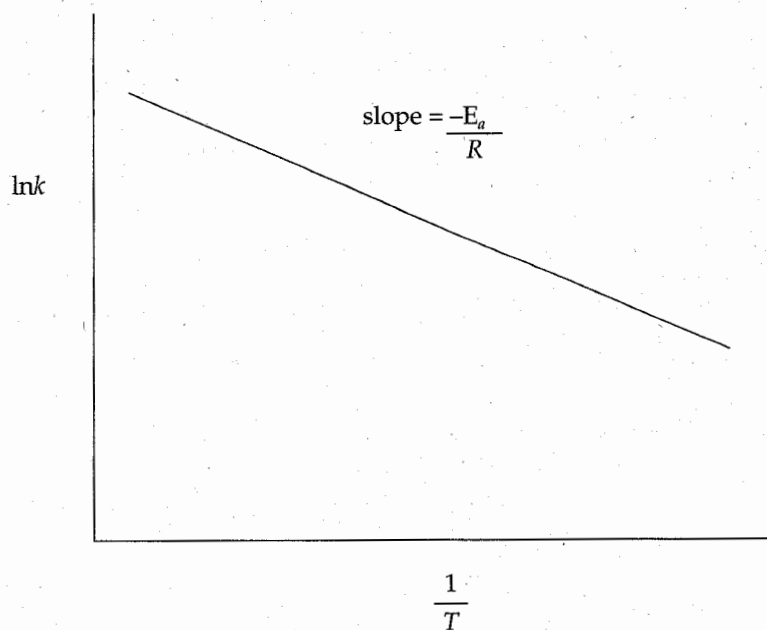


## THE RATE CONSTANT AND TEMPERATURE

The rate constant will increase when temperature is increased. The relationship between temperature and the rate constant is given by the Arrhenius equation,  $k = Ae^{\frac{-E_a}{RT}}$ . This equation is generally rewritten using natural logarithms.

The Arrhenius Equation	
$\ln k = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A$	
$k$	= rate constant
$E_a$	= activation energy
$R$	= gas constant, 8.31 J/k-mol
$T$	= absolute temperature (K)
$A$	= a constant that takes into account collision frequency and orientation

When  $\ln k$  is graphed versus  $\frac{1}{T}$ , it makes a straight line with a slope of  $-\frac{E_a}{R}$ . It's a little difficult to see, but the graph below shows that  $k$  is increasing as the temperature increases.



## REACTION MECHANISMS

Many chemical reactions are not one-step processes. Rather, the balanced equation is the sum of a series of simple steps. Three molecules will not collide simultaneously very often, so steps of a reaction mechanism involve only one or two reactants at a time.

For instance, the following hypothetical reaction:



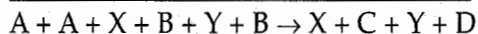
could take place by the following three-step mechanism:

- I.  $A + A \rightleftharpoons X$  (fast)
- II.  $X + B \rightarrow C + Y$  (slow)
- III.  $Y + B \rightarrow D$  (fast)

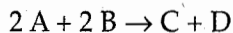
Species X and Y are called **intermediates** because they appear in the mechanism, but they cancel out of the balanced equation. The steps of a reaction mechanism must add up to equal the balanced equation, with all intermediates cancelling out.

Let's show that the mechanism above is consistent with the balanced equation by adding up all the steps.

- I.  $A + A \rightleftharpoons X$
- II.  $X + B \rightarrow C + Y$
- III.  $Y + B \rightarrow D$



Cancel species that appear on both sides.



By adding up all the steps, we get the balanced equation for the overall reaction, so this mechanism is consistent with the balanced equation.

As in any process where many steps are involved, the speed of the whole process can't be faster than the speed of the slowest step in the process, so the slowest step of a reaction is called the **rate-determining step**. Because the slowest step is the most important step in determining the rate of a reaction, the slowest step and the steps leading up to it are used to see if the mechanism is consistent with the rate law for the overall reaction.

Let's look at the reaction and the three-step mechanism again.



The reaction above takes place by the following three-step mechanism.

- I.  $A + A \rightleftharpoons X$  (fast)
- II.  $X + B \rightarrow C + Y$  (slow)
- III.  $Y + B \rightarrow D$  (fast)

Let's show that the reaction mechanism is consistent with the rate law ( $\text{Rate} = k[A]^2[B]$ ).

The slowest step is the rate-determining step, so we should start with the rate law for step II:

$$\text{Rate} = k_2[X][B]$$

But X is an intermediate, which means that it can't appear in the overall rate law. To eliminate X from the rate law, we need to look at the equilibrium reaction in step I. We can assume that the reaction in step I comes to equilibrium quickly. At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction, so we get

$$k_f[A][A] = k_r[X]$$

Now we can solve for [X].

$$[X] = \frac{k_f}{k_r}[A]^2$$

Once we have solved our equilibrium rate expression for [X] in terms of [A], we can substitute for [X] in our step II rate law.

$$\text{Rate} = k_2 \frac{k_f}{k_r} [A]^2 [B] = k [A]^2 [B]$$

Now we have a rate law that contains only reactants from the overall equation and that's consistent with the experimentally derived rate law that we were given. You can always eliminate intermediates from the rate-determining step by this process.

## CATALYSTS

As we mentioned earlier in the book, a catalyst increases the rate of a chemical reaction without being consumed in the process; catalysts do not appear in the balanced equation. In some cases, a catalyst is a necessary part of a reaction because in its absence, the reaction would proceed at too slow a rate to be at all useful.

A catalyst increases the rate of a chemical reaction by providing an alternative reaction pathway with a lower activation energy.

## KINETICS AND EQUILIBRIUM

There is a relationship between the rate constants for the forward and reverse directions of a particular reaction and the equilibrium constant for that reaction.

$$K_{eq} = \frac{k_f}{k_r}$$

$K_{eq}$  = the equilibrium constant

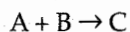
$k_f$  = the rate constant for the forward reaction

$k_r$  = the rate constant for the reverse reaction

## CHAPTER 12 QUESTIONS

### MULTIPLE-CHOICE QUESTIONS

#### Questions 1–3

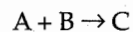


The following are possible rate laws for the hypothetical reaction given above.

- (A) Rate =  $k[A]$
- (B) Rate =  $k[A]^2$
- (C) Rate =  $k[A][B]$
- (D) Rate =  $k[A]^2[B]$
- (E) Rate =  $k[A]^2[B]^2$

1. This is the rate law for a first order reaction.
2. This is the rate law for a reaction that is second order with respect to B.
3. This is the rate law for a third order reaction.

#### Questions 4–6

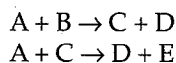


The following are possible rate laws for the hypothetical reaction given above.

- (A) Rate =  $k[A]$
- (B) Rate =  $k[B]^2$
- (C) Rate =  $k[A][B]$
- (D) Rate =  $k[A]^2[B]$
- (E) Rate =  $k[A]^2[B]^2$

4. When [A] and [B] are doubled, the initial rate of reaction will increase by a factor of eight.
5. When [A] and [B] are doubled, the initial rate of reaction will increase by a factor of two.
6. When [A] is doubled and [B] is held constant, the initial rate of reaction will not change.

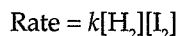
7. A multistep reaction takes place by the following mechanism:



Which of the species shown above is an intermediate in the reaction?

- (A) A  
(B) B  
(C) C  
(D) D  
(E) E
8.  $2 \text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2$
- The reaction above takes place with all of the reactants and products in the gaseous phase. Which of the following is true of the relative rates of disappearance of the reactants and appearance of the products?
- (A) NO appears at twice the rate that NOCl disappears.  
(B) NO appears at the same rate that NOCl disappears.  
(C) NO appears at half the rate that NOCl disappears.  
(D)  $\text{Cl}_2$  appears at the same rate that NOCl disappears.  
(E)  $\text{Cl}_2$  appears at twice the rate that NOCl disappears.
9.  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{g})$

When the reaction given above takes place in a sealed isothermal container, the rate law is

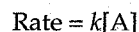


If a mole of  $\text{H}_2$  gas is added to the reaction chamber, which of the following will be true?

- (A) The rate of reaction and the rate constant will increase.  
(B) The rate of reaction and the rate constant will not change.  
(C) The rate of reaction will increase and the rate constant will decrease.  
(D) The rate of reaction will increase and the rate constant will not change.  
(E) The rate of reaction will not change and the rate constant will increase.

10.  $A + B \rightarrow C$

When the reaction given above takes place, the rate law is



If the temperature of the reaction chamber were increased, which of the following would be true?

- (A) The rate of reaction and the rate constant will increase.  
(B) The rate of reaction and the rate constant will not change.  
(C) The rate of reaction will increase and the rate constant will decrease.  
(D) The rate of reaction will increase and the rate constant will not change.  
(E) The rate of reaction will not change and the rate constant will increase.
11.  $A + B \rightarrow C$

Based on the following experimental data, what is the rate law for the hypothetical reaction given above?

Experiment	[A] (M)	[B] (M)	Initial Rate of Formation of C (mol/L-sec)
1	0.20	0.10	$3 \times 10^{-2}$
2	0.20	0.20	$6 \times 10^{-2}$
3	0.40	0.20	$6 \times 10^{-2}$

- (A)  $\text{Rate} = k[\text{A}]$   
(B)  $\text{Rate} = k[\text{A}]^2$   
(C)  $\text{Rate} = k[\text{B}]$   
(D)  $\text{Rate} = k[\text{B}]^2$   
(E)  $\text{Rate} = k[\text{A}][\text{B}]$



The rate law for the hypothetical reaction shown above is as follows:

$$\text{Rate} = k[A]$$

Which of the following changes to the system will increase the rate of the reaction?

- I. An increase in the concentration of A
- II. An increase in the concentration of B
- III. An increase in the temperature

- (A) I only
- (B) I and II only
- (C) I and III only
- (D) II and III only
- (E) I, II, and III



Based on the following experimental data, what is the rate law for the hypothetical reaction given above?

Experiment	[A] (M)	[B] (M)	Initial Rate of Formation of C (M/sec)
1	0.20	0.10	$2.0 \times 10^{-6}$
2	0.20	0.20	$4.0 \times 10^{-6}$
3	0.40	0.40	$1.6 \times 10^{-5}$

- (A) Rate =  $k[A]$
- (B) Rate =  $k[A]^2$
- (C) Rate =  $k[B]$
- (D) Rate =  $k[B]^2$
- (E) Rate =  $k[A][B]$



Based on the following experimental data, what is the rate law for the hypothetical reaction given above?

Experiment	[A] (M)	[B] (M)	Initial Rate of Formation of C (M/sec)
1	0.10	0.10	$1.5 \times 10^{-3}$
2	0.40	0.10	$6.0 \times 10^{-3}$
3	0.40	0.20	$2.4 \times 10^{-2}$

- (A) Rate =  $k[A]$
- (B) Rate =  $k[A]^2$
- (C) Rate =  $k[A][B]^2$
- (D) Rate =  $k[B]^2$
- (E) Rate =  $k[A]^2[B]^2$



Time (Hours)	[A] M
0	0.40
1	0.20
2	0.10
3	0.05

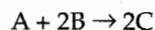
Reactant A underwent a decomposition reaction. The concentration of A was measured periodically and recorded in the chart above. Based on the data in the chart, which of the following is the rate law for the reaction?

- (A) Rate =  $k[A]$
- (B) Rate =  $k[A]^2$
- (C) Rate =  $2k[A]$
- (D) Rate =  $\frac{1}{2}k[A]$
- (E) Rate =  $k$



## PROBLEMS

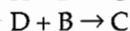
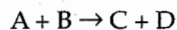
1.



The following results were obtained in experiments designed to study the rate of the reaction above:

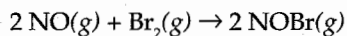
Experiment	Initial Concentration (mol/L)		Initial Rate of Disappearance of A (M/sec)
	[A]	[B]	
1	0.05	0.05	$3.0 \times 10^{-3}$
2	0.05	0.10	$6.0 \times 10^{-3}$
3	0.10	0.10	$1.2 \times 10^{-2}$
4	0.20	0.10	$2.4 \times 10^{-2}$

- Determine the order of the reaction with respect to each of the reactants, and write the rate law for the reaction.
- Calculate the value of the rate constant,  $k$ , for the reaction. Include the units.
- If another experiment is attempted with [A] and [B], both 0.02-molar, what would be the initial rate of disappearance of A?
- The following reaction mechanism was proposed for the reaction above:



- Show that the mechanism is consistent with the balanced reaction.
- Show which step is the rate-determining step, and explain your choice.

2.

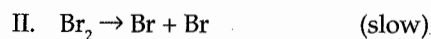
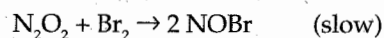
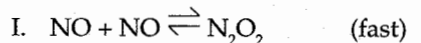


The following results were obtained in experiments designed to study the rate of the reaction above:

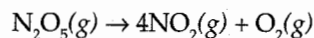
Experiment	Initial Concentration (mol/L)		Initial Rate of Appearance of NOBr (M/sec)
	[NO]	[Br <sub>2</sub> ]	
1	0.02	0.02	$9.6 \times 10^{-2}$
2	0.04	0.02	$3.8 \times 10^{-1}$
3	0.02	0.04	$1.9 \times 10^{-1}$

- Write the rate law for the reaction.
- Calculate the value of the rate constant,  $k$ , for the reaction. Include the units.
- In experiment 2, what was the concentration of NO remaining when half of the original amount of Br<sub>2</sub> was consumed?

- (d) Which of the following reaction mechanisms is consistent with the rate law established in (a)? Explain your choice.



3.

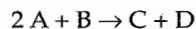


Dinitrogen pentoxide gas decomposes according to the equation above. The first-order reaction was allowed to proceed at 40°C and the data below were collected.

$[\text{N}_2\text{O}_5]$ (M)	Time (min)
0.400	0.0
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

- (a) Calculate the rate constant for the reaction using the values for concentration and time given in the table. Include units with your answer.
- (b) After how many minutes will  $[\text{N}_2\text{O}_5]$  be equal to 0.350 M?
- (c) What will be the concentration of  $\text{N}_2\text{O}_3$  after 100 minutes have elapsed?
- (d) Calculate the initial rate of the reaction. Include units with your answer.
- (e) What is the half-life of the reaction?

4.

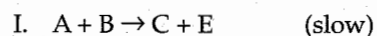


The following results were obtained in experiments designed to study the rate of the reaction above:

Experiment	Initial Concentration (moles/L)		Initial Rate of Formation of D (M/min)
	[A]	[B]	
1	0.10	0.10	$1.5 \times 10^{-3}$
2	0.20	0.20	$3.0 \times 10^{-3}$
3	0.20	0.40	$6.0 \times 10^{-3}$

- (a) Write the rate law for the reaction.
- (b) Calculate the value of the rate constant,  $k$ , for the reaction. Include the units.
- (c) If experiment 2 goes to completion, what will be the final concentration of D? Assume that the volume is unchanged over the course of the reaction and that no D was present at the start of the experiment.

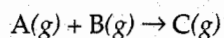
(d) Which of the following possible reaction mechanisms is consistent with the rate law found in (a)?



(e) Calculate the half-life of reactant B.

## ESSAYS

5.



The reaction above is second order with respect to A and zero order with respect to B. Reactants A and B are present in a closed container. Predict how each of the following changes to the reaction system will affect the rate and rate constant and explain why.

(a) More gas A is added to the container.

(b) More gas B is added to the container.

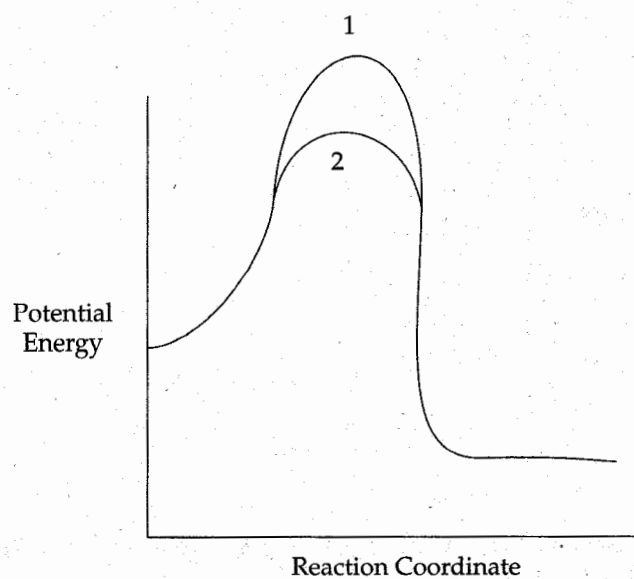
(c) The temperature is increased.

(d) An inert gas D is added to the container.

(e) The volume of the container is decreased.

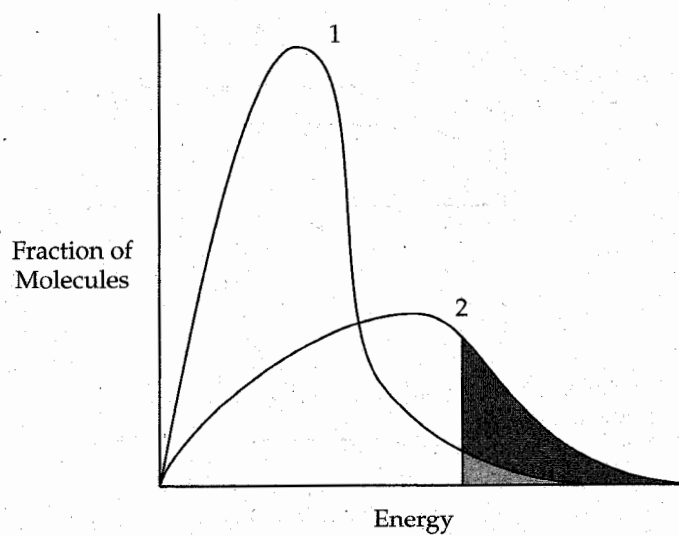
6. Use your knowledge of kinetics to answer the following questions. Justify your answers.

(a)



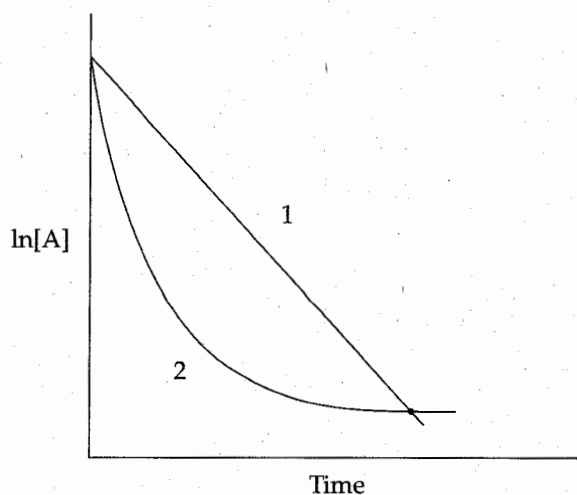
The two lines in the diagram above show different reaction pathways for the same reaction. Which of the two lines shows the reaction when a catalyst has been added?

(b)

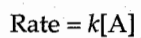


Which of the two lines in the energy distribution diagram shows the conditions at a higher temperature?

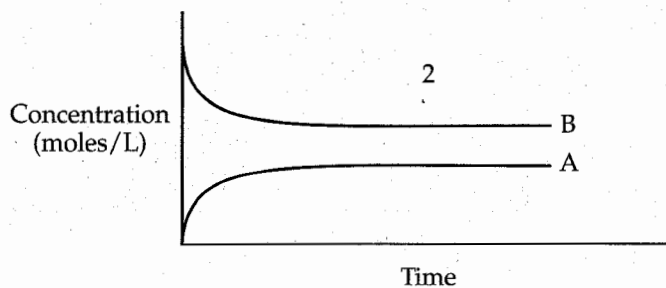
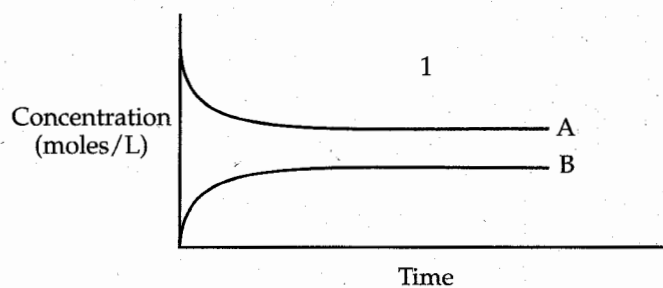
(c)



Which of the two lines in the diagram above shows the relationship of  $\ln[A]$  to time for a first order reaction with the following rate law?



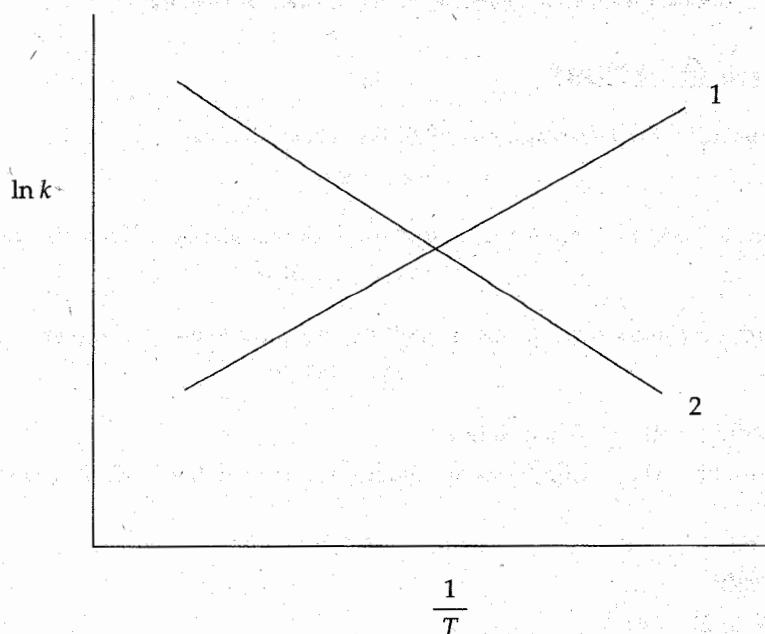
(d)



Which of the two graphs above shows the changes in concentration over time for the following reaction?



(e)



Which of the two lines in the diagram above shows the relationship of  $\ln k$  to  $\frac{1}{T}$  for a reaction?  
How is the slope of the line related to the activation energy for the reaction?

7. Use your knowledge of kinetics to explain each of the following statements:
- (a) An increase in the temperature at which a reaction takes place causes an increase in reaction rate.
  - (b) The addition of a catalyst increases the rate at which a reaction will take place.
  - (c) A catalyst that has been ground into powder will be more effective than a solid block of the same catalyst.
  - (d) Increasing the concentration of reactants increases the rate of a reaction.

## CHAPTER 12 ANSWERS AND EXPLANATIONS

### MULTIPLE-CHOICE QUESTIONS

1. **A** In a first-order reaction, the exponents of all the reactants present in the rate law add up to 1.

$$\text{Rate} = k[A]^1$$

2. **E** The exponent for B in this rate law is 2, so the reaction is second order with respect to B.

$$\text{Rate} = k[A]^2[B]^2$$

3. **D** In a third-order reaction, the exponents of all the reactants present in the rate law add up to 3.

$$\text{Rate} = k[A]^2[B]^1$$

4. **D** Let's say that  $[A] = [B] = 1$ . Then  $\text{Rate} = k$ .

Now if we double  $[A]$  and  $[B]$ , that is, we make  $[A] = [B] = 2$ , here's what we get for each of the answer choices.

$$\text{(A) Rate} = k(2) = 2k$$

$$\text{(B) Rate} = k(2)^2 = 4k$$

$$\text{(C) Rate} = k(2)(2) = 4k$$

$$\text{(D) Rate} = k(2)^2(2) = 8k$$

$$\text{(E) Rate} = k(2)^2(2)^2 = 16k$$

So in (D), the rate increases by a factor of 8.

5. **A** Let's say that  $[A] = [B] = 1$ . Then  $\text{Rate} = k$ .

Now if we double  $[A]$  and  $[B]$ , that is, we make  $[A] = [B] = 2$ , here's what we get for each of the answer choices.

$$\text{(A) Rate} = k(2) = 2k$$

$$\text{(B) Rate} = k(2)^2 = 4k$$

$$\text{(C) Rate} = k(2)(2) = 4k$$

$$\text{(D) Rate} = k(2)^2(2) = 8k$$

$$\text{(E) Rate} = k(2)^2(2)^2 = 16k$$

So in (A), the rate increases by a factor of 2.

6. **B** We need to find the rate law that is independent of changes in  $[A]$ .

The only choice listed that does not include  $[A]$  is choice (B),  $\text{Rate} = k[B]^2$ .

7. **C** C is created and used up in the reaction, so it will not be present in the balanced equation.

8. **B** For every two NO molecules that form, two NOCl molecules must disappear, so NO is appearing at the same rate that NOCl is disappearing. Choices (D) and (E) are wrong because for every mole of  $\text{Cl}_2$  that forms, two moles of NOCl are disappearing, so  $\text{Cl}_2$  is appearing at *half* the rate that NOCl is disappearing.

9. **D** From the rate law given in the question ( $\text{Rate} = k[\text{H}_2][\text{I}_2]$ ), we can see that increasing the concentration of  $\text{H}_2$  will increase the rate of reaction. The rate constant,  $k$ , is not affected by changes in the concentration of the reactants.

10. **A** When temperature increases, the rate constant increases to reflect the fact that more reactant molecules are likely to have enough energy to react at any given time. So both the rate constant and the rate of reaction will increase.
11. **C** From a comparison of experiments 1 and 2, when [B] is doubled while [A] is held constant, the rate doubles. That means that the reaction is first order with respect to B.  
From a comparison of experiments 2 and 3, when [A] is doubled while [B] is held constant, the rate doesn't change. That means that the reaction is zero order with respect to A and that A will not appear in the rate law.  
So the rate law is  $\text{Rate} = k[\text{B}]$ .
12. **C** An increase in the concentration of A will increase the rate, as shown in the rate law for the reaction, so (I) is correct. Reactant B is not included in the rate law, so an increase in the concentration of B will not affect the rate; therefore, (II) is wrong. An increase in temperature causes more collisions with greater energy among reactants and always increases the rate of a reaction, so (III) is correct.
13. **E** From a comparison of experiments 1 and 2, when [B] is doubled while [A] is held constant, the rate doubles. That means that the reaction is first order with respect to B.  
From a comparison of experiments 2 and 3, when both [A] and [B] are doubled, the rate increases by a factor of 4. We would expect the rate to double based on the change in B; because the rate is in fact multiplied by 4, the doubling of A must also change the rate by a factor of 2, so the reaction is also first order with respect to A.  
So the rate law is  $\text{Rate} = k[\text{A}][\text{B}]$ .
14. **C** From a comparison of experiments 1 and 2, when [A] is quadrupled while [B] is held constant, the rate quadruples. That means that the reaction is first order with respect to A.  
From a comparison of experiments 2 and 3, when [B] is doubled while [A] is held constant, the rate quadruples. That means that the reaction is second order with respect to B.  
So the rate law is  $\text{Rate} = k[\text{A}][\text{B}]^2$ .
15. **A** The key to this question is to recognize that reactant A is disappearing with a characteristic half-life. This is a signal that the reaction is first order with respect to A. So the rate law must be  $\text{Rate} = k[\text{A}]$ .

## PROBLEMS

1. (a) When we compare the results of experiments 3 and 4, we see that when [A] doubles, the rate doubles, so the reaction is first order with respect to A.  
When we compare the results of experiments 1 and 2, we see that when [B] doubles, the rate doubles, so the reaction is first order with respect to B.  
 $\text{Rate} = k[\text{A}][\text{B}]$
- (b) Use the values from experiment 3, just because they look the simplest.

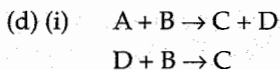
$$k = \frac{\text{Rate}}{[\text{A}][\text{B}]} = \frac{(1.2 \times 10^{-2} \text{ M / sec})}{(0.10 \text{ M})(0.10 \text{ M})} = 1.2 \text{ M}^{-1}\text{sec}^{-1} = 1.2 \text{ L/mol-sec}$$

- (c) Use the rate law.

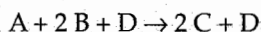
$$\text{Rate} = k[\text{A}][\text{B}]$$

$$\text{Rate} = (1.2 \text{ M}^{-1}\text{sec}^{-1})(0.02 \text{ M})(0.02 \text{ M}) = 4.8 \times 10^{-4} \text{ M/sec}$$

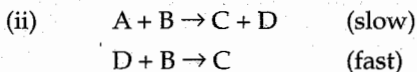
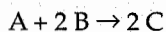




The two reactions add up to



D's cancel, and we're left with the balanced equation.



The first part of the mechanism is the slow, rate-determining step because its rate law is the same as the experimentally determined rate law.

2. (a) When we compare the results of experiments 1 and 2, we see that when [NO] doubles, the rate quadruples, so the reaction is second order with respect to NO.

When we compare the results of experiments 1 and 3, we see that when [Br<sub>2</sub>] doubles, the rate doubles, so the reaction is first order with respect to Br<sub>2</sub>.

$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$

- (b) Use the values from experiment 1, just because they look the simplest.

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{Br}_2]} = \frac{(9.6 \times 10^{-2} \text{ M / sec})}{(0.02 \text{ M})^2(0.02 \text{ M})} = 1.2 \times 10^4 \text{ M}^{-2}\text{sec}^{-1} = 1.2 \times 10^4 \text{ L}^2/\text{mol}^2\text{-sec}$$

- (c) In experiment 2, we started with [Br<sub>2</sub>] = 0.02 M, so 0.01 M was consumed.

From the balanced equation, 2 moles of NO are consumed for every mole of Br<sub>2</sub> consumed. So 0.02 M of NO are consumed.

$$[\text{NO}] \text{ remaining} = 0.04 \text{ M} - 0.02 \text{ M} = 0.02 \text{ M}$$

- (d) Choice (I) agrees with the rate law.



The slow step is the rate-determining step, with the following rate law:

$$\text{Rate} = k[\text{N}_2\text{O}_2][\text{Br}_2]$$

We can replace the intermediate (N<sub>2</sub>O<sub>2</sub>) by assuming that the first step reaches equilibrium instantaneously and remembering that at equilibrium, the rates of the forward and reverse reactions are equal.

$$k_f[\text{NO}]^2 = k_r[\text{N}_2\text{O}_2]$$

Now solve for [N<sub>2</sub>O<sub>2</sub>].

$$[\text{N}_2\text{O}_2] = \frac{k_f}{k_r} [\text{NO}]^2$$

Now we can substitute the rate law for the rate determining step.

$$\text{Rate} = k \frac{k_f}{k_r} [\text{NO}]^2 [\text{Br}_2]$$

This matches the experimentally determined rate law. By the way, the mechanism in choice (II) would have a rate law of Rate = k[Br<sub>2</sub>].