

Hazmat Chemistry Study Guide

— Second Edition —



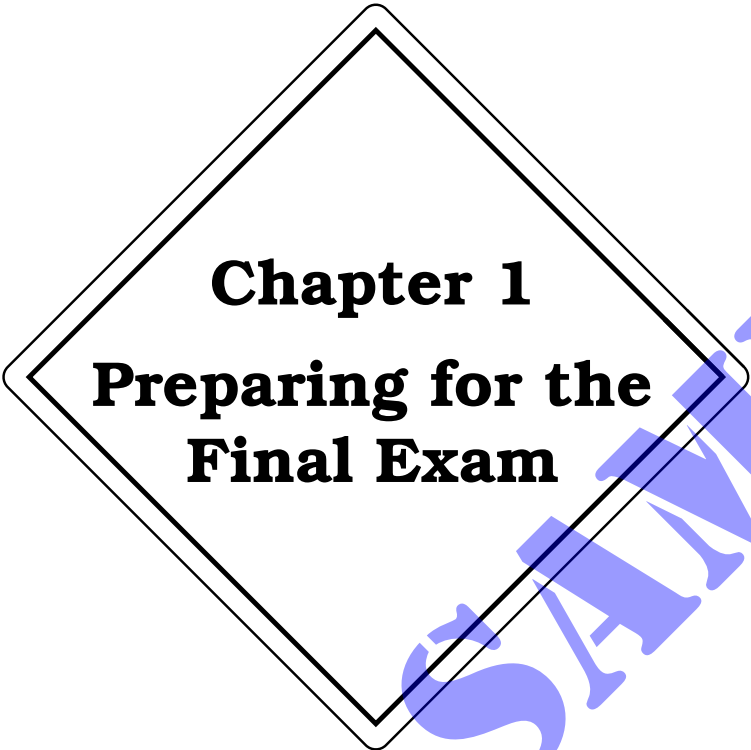
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Table of Contents

Topic	Page
Table of Contents	3
How Much Chemistry Do You Need to Know?	5
Acknowledgments	7
Dedication	8
Chapter 1 - Preparing for the Final Exam	9
Dispelling Test Anxiety	10
Recognizing the Concepts Behind the Questions	15
Chapter 2 - Terms and Definitions	19
Vapor Pressure and Vapor Density	20
Flammability Factors	24
Water Behavior	29
Physical and Chemical Change	32
Toxicity and Risk	37
Toxicological Values and Exposure Limits	40
Chapter 2 Review	46
Chapter 3 - Elements and Compounds	49
Matter	50
The Periodic Table	54
Atomic Structure	62
Chemical Bonding	66
Isomers	73
Chapter 3 Review	75
Chapter 4 - Salts	79
Introduction to Salts	80
Types of Salts	84
Polyatomic Ions and Multiple Oxidation States	89
Chapter 4 Review	92
Chapter 5 - Hydrocarbons and Related Compounds	95
The Four Types of Hydrocarbons	96
Hydrocarbon Names and Formulas	99
The Effect of Molecular Size	105
Hydrocarbon Radicals	108
Overview of Hydrocarbon Derivatives	110
Part 1 Hydrocarbon Derivatives - Carbonyls	114
Other Part 1 Hydrocarbon Derivatives	120
Part 2 Hydrocarbon Derivatives - Nitrogen Based	125
Other Part 2 Hydrocarbon Derivatives	130
Chapter 5 Review	135
Chapter 6 - Hazmat Chemistry and the DOT Hazard Classes	139
Class 1 - Explosives	140
Class 2 - Gases	144
Class 3 - Flammable and Combustible Liquids	148
Class 4 - Flammable Solids, Spontaneously Combustible Materials, Dangerous When Wet Materials	152
Class 5 - Oxidizers and Organic Peroxides	155
Class 6 - Poisonous and Infectious Substances	159
Class 7 - Radioactive Materials	163
Class 8 - Corrosive Materials	170
Class 9 - Miscellaneous Hazardous Materials	175
Chapter 6 Review	176

Table of Contents (continued)

Chapter 7 - Hazmat Chemistry in Some Real World Applications	181
Fire Chemistry	182
Chemical Reactions/Incompatibility	186
Chapter 7 Review	191
Chapter 8 - Answers to Review Questions	193
Appendix	199
Abbreviations and Acronyms	200
Bibliography	202
Index	203
About the Author	208



Chapter 1

Preparing for the Final Exam

This chapter was inspired by a Hazmat Chemistry Prep Course that I developed to help alleviate the anxiety many people feel prior to taking a hazmat chemistry class. The chapter is divided into two sections:

- Dispelling Test Anxiety
- Recognizing the Concepts Behind the Chemistry

The first section first identifies what drives test questions, then provides some important tips to make studying for the exam easier. The second section cites several examples of how focusing on *concepts* more so than *chemicals* can help you do well on final exam. You may be surprised at how easy it is to correctly answer many of the test questions even when you can't always put names to formulas or vice versa.

Dispelling Test Anxiety

Hazmat chemistry classes don't need to be as intimidating as they frequently are. True, students are often hit with an overwhelming amount of information in a very short period, and studying for any final exam can be stressful. However, no one should have nightmares about failing hazmat chemistry.

This second edition of the *Hazmat Chemistry Study Guide* begins with a chapter on preparing for the final exam. This may be the most important chapter in the book because it helps students understand how to study the material in order to do well on the test. You may be tempted to skip this chapter and go directly to the “meat” of hazmat chemistry. However, if you take the time to read this short chapter, it will benefit you greatly through the rest of the book.

Know What Drives the Test Questions

It helps to understand a little bit about the test writing process and what test writers contend with. Several factors influence what questions are used in the final exam:

- Regulations (federal, state, local, tribal). Various regulations dictate what training responders must receive and how they must perform in the field. If you've reviewed the regulations that apply to your area or agency, it can help you anticipate the material you'll be tested on.
- Standards and recommended practices. Two very valuable documents are NFPA 472 and 473. Even better is the *NFPA Hazardous Materials Response Handbook*, which contains the entire texts of 472 and 473, along with explanations and background material. One of the best things you can do to prepare for any hazmat class is to review applicable sections of this book before and during class. (The material in this book is based on the hazmat technician competencies outlined in NFPA 472.)
- Special concerns. Test writers sometimes emphasize special concerns reflective of a given area or industry. For example, in an area with heavy rail transportation of hazardous materials, there are likely to be more test questions related to managing rail incidents and the products commonly shipped by rail than there would be in other parts of the country. As another example, classes taught specifically for the petroleum industry may be given tests that emphasize petroleum products more so than other chemicals.
- Test writer's own focus. Test writers may include questions relating to specific problems they've seen or experienced in the field. For example, they may write questions that drive home key points missed by responders killed in a tragic incident where things went terribly wrong.

Let's look at a couple of examples to illustrate how the factors above can drive test questions. NFPA 472 identifies the competencies expected of hazmat responders. For instance, it lists a number of terms and indicates that the hazardous materials technician shall describe the terms and explain their significance in the risk assessment process. Let's take one of those terms and look at how it can be turned into a test question.

The *NFPA Hazardous Materials Response Handbook* describes *expansion ratio* as the amount of gas produced by a given volume of liquid at a given temperature. For example, liquid propane has an expansion ratio of 270 to 1, while liquefied natural gas has an expansion ratio of 635 to 1. What makes this significant is that the greater the expansion ratio, the more gas is produced and the larger the endangered area becomes.

If NFPA 472 says hazmat technicians should be able to describe such terms, it's reasonable to expect a question that asks you to identify which of several definitions describes expansion ratio...your basic vocabulary question. However, a better question is one that tests if you recognize how expansion ratio affects risk. The example below lists four liquefied gases and their expansion ratios. If you remember that the higher the expansion ratio, the greater the risk, you can easily pick liquid hydrogen (a) as the correct answer.

Which of the following will produce the most gas and endanger the largest area?

- | | |
|--------------------------|----------------------------|
| a. Liquid Hydrogen | (expansion ratio 848 to 1) |
| b. Liquefied Natural Gas | (expansion ratio 635 to 1) |
| c. Liquid Nitrogen | (expansion ratio 694 to 1) |
| d. Liquid Propane | (expansion ratio 270 to 1) |

Dispelling Test Anxiety (continued)

Let's take a different example now, one reflecting a test writer's desire to protect responders from suffering the same tragic fate experienced by firefighters who died battling fires involving ANFO (ammonium nitrate and fuel oil mixture). While not strictly a chemistry question, a question like this is very effective for reinforcing key concepts that matter most in the field. The correct answer is that no attempt should be made to fight a fire involving explosives (a).

According to the NFPA:

- No attempt should be made to fight a fire involving explosives
- Fires involving explosives should be handled from a distance of at least 1000 feet
- Fires involving explosives should be handled from a distance of at least 2000 feet
- Firefighters should wait for the initial explosion, then move in to extinguish a fire involving explosive materials

Pay Attention to Errors, Mistakes, and Misconceptions that Arise in Class

Some of the best test questions use common errors, mistakes, and misconceptions as distracters (wrong answers) because they differentiate between students who know the material and those who don't. If there's something students seem to be struggling with in class or something the instructor identifies as being a difficult concept for students to grasp, that ought to be a blip on your radar screen. Let's look at one example:

What is generally the greatest risk associated with organic peroxides?

- They are very toxic
- They are strong oxidizers that will fuel a fire
- They are flammable and unstable, similar to explosives
- They are highly unpredictable

The correct answer is that organic peroxides are flammable and unstable, similar to explosives (answer c) because they contain both a fuel component and an oxidizer component in the same structure, just as explosives do. They are very sensitive to heat and friction. They're often very sensitive to contamination too.

Students who don't understand the significance of this frequently identify organic peroxides as strong oxidizers (answer b) in part because they're thinking about the Department of Transportation classification system in which oxidizers (Division 5.1) and organic peroxides (Division 5.2) have very similar placards. However, the explosive potential represents a greater risk than the oxidizing potential with these materials. Can organic peroxides be very toxic (answer a)? Yes. Can they be unpredictable (answer d)? Yes...although it's probably more common that emergency responders fail to anticipate what should be very predictable behavior. So with these very plausible distracters, it's easy to see how students could choose a wrong answer.

(The new Division 5.2 placards and labels, which are half red and half yellow, with a flame on top, are designed to more accurately reflect the hazards of organic peroxides. However, the existing placards/labels may be used until January 1, 2011 [rail, vessel, or aircraft] and January 1, 2013 [highway].)

Use the Resources in Your Student Manual

Every student manual or textbook is different, but most contain tools to enhance learning:

- Sample test questions. Student manuals may contain multiple choice test questions similar to what you'll see on the final exam (similar to questions contained in this book). If not, ask your instructor to present some in class.
- Chapter review questions. Chapter review questions are often fill-in or short answer format. For example, you might find a question that asks you to identify which type of hydrocarbon derivative is known for its toxicity and wide flammable range. Or it may ask you to list the hazards generally associated with several hydrocarbon derivatives. This is more difficult than a multiple choice question, but it's very effective for helping students learn.

Dispelling Test Anxiety (continued)

- Exercises and worksheets. A variety of things are possible with exercises and worksheets. You might be asked to do something relatively simple, like draw the structure of a compound. While this isn't something you're likely to have to do on your final exam, it's a great exercise to help you see how the atoms are bonded and help you count the individual elements. Another great activity is one that requires you to apply the information in a way that reflects what you would have to do in the real world, for instance, to look up the chemical and physical properties of a substance in at least three reference sources.

Ask the Instructor

Good instructors are diligent about helping students do well on the test...without giving away the questions or otherwise compromising the integrity of the exam process. However, students should never hesitate to ask instructors for guidance.

What do you need to know to succeed in class? Instructors should be able to identify the topics to concentrate on when studying for the exam. They should also quiz you with sample test questions similar to what you'll see on the final. This book contains almost 400 examples, but they're written by one author who hasn't reviewed every hazmat chemistry exam nationwide. So ask your instructor.

What do you need to know to function safely and effectively in the real world? This is not always the same as what you need to know to pass the test. A 100-question multiple choice test is a far cry from the field test of a real incident.

Are there any test questions known to be problematic? If questions are badly written or difficult to understand, contain outdated (or wrong) information, are frequently misinterpreted by students, or cover trivia students won't normally think to study, it's not compromising the integrity of the test for instructors to give students some additional guidance. The goal, after all, should be to make sure students learn these important concepts, not to frustrate students with bad questions.

Focus on Concepts More than Chemicals

While every test is different and there's no way for this author to know what questions you'll have on your final exam, it's not uncommon to get questions that focus more on *concepts* than *chemicals*. Let's look at one example.

Among the things you'll learn in a hazmat chemistry class is that some gases exist as molecules of two identical atoms. We call those *diatomic gases*. You should be familiar with one of them already...oxygen (O_2). Oxygen as an element (O) cannot exist by itself. It must bond with something to be stable. (Chemical bonding is covered in Chapter 3.) Oxygen can, and does, bond with many elements, including other oxygen atoms. If you understand the definition of a diatomic gas and you've seen an example (O_2), you should be able to recognize other diatomic gases by looking at a chemical formula.

Which of the following is a diatomic gas?

- CO
- CO_2
- Cl_2
- CH_4

In the question above, there's only one answer (c) comprised of two identical atoms...chlorine (Cl_2). While the others are common gases you should be able to recognize—carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4)—you can easily answer the question without knowing what the compounds are.

Many questions are like this. If you understand the concept, you can correctly answer the question without naming the compounds. This idea is important enough that we'll look at it in more depth shortly, with additional examples that should help you as you read through the rest of the book.

Dispelling Test Anxiety (continued)

Aim High When You Study

Expect some vocabulary questions, but plan for questions that require you to apply the information. Let's look at three sample questions with different degrees of difficulty.

A polymerization reaction is best described as one that:

- a. Is highly toxic
- b. Generates heat
- c. Involves rapid expansion as a hazardous material reacts with itself
- d. Results in fire when a hazardous material oxidizes on exposure to air

Which of the following materials are most prone to runaway polymerization?

- a. Oxidizers
- b. Organic peroxides
- c. Cryogenic liquids
- d. Dangerous when wet materials

Which of the following measures is an example of how to prevent polymerization reactions?

- a. Preventing water from coming in contact with salts
- b. Avoiding filling a compressed gas cylinder too quickly
- c. Avoiding applying a water stream to the hot surface of burning oil
- d. Protecting organic peroxides from heat, friction, and contamination

The first question is a simple vocabulary question. It does little more than test that you can define the term polymerization (answer c). The second question also requires you to know what polymerization means, but it takes a step further in asking you to identify substances most prone to runaway polymerization (answer b). The third question is the best of the bunch because it accomplishes everything the first two questions do plus reflects how you might use the information at a hazmat incident (answer d). It's the kind of question this author prefers when writing tests.

Test questions can be categorized based on their level of difficulty and what they require of students:

- Level 1 - Basic Knowledge Requires students to recall, recognize, or identify.
- Level 2 - Competent Requires students to apply information learned to prescribed problems.
- Level 3 - Highly Proficient Requires students to apply information learned to a new set of circumstances. Students need to think beyond what was taught in class.

It's not uncommon for tests to have an abundance of Level 1 and Level 2 questions because they're the easiest to write. However, real life is often more demanding. So students should aim for a higher level of proficiency when studying. Let's look at three more questions to illustrate this concept.

A normal atmosphere contains approximately ____ oxygen.

- a. 19%
- b. 20%
- c. 21%
- d. 22%

The normal atmosphere contains approximately 20.9% oxygen, so answer c is the closest match. This question requires nothing more than simple recall (Level 1). It's important information, but what will you do with it?

Dispelling Test Anxiety (continued)

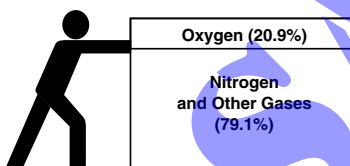
Your meter displays a reading of 19.9% oxygen (a 1% drop from normal). How much of a displacing gas (contaminant) is likely to be present?

- a. 1%
- b. 3%
- c. 5%
- d. 7%

The question above requires you to apply information taught in class to a simple job-related scenario (Level 2). Simple, but very important. And often a source of confusion for students.

Oxygen comprises roughly one fifth (20.9%) the normal atmosphere. When your meter shows an oxygen level of 19.9%, you need to recognize that it reflects only oxygen displacement. When a contaminant gas or vapor displaces oxygen, it also proportionately displaces nitrogen and other gases that make up the total atmosphere (one part oxygen, four parts everything else). So the amount of contaminant likely to be present is close to 5%, not 1%. The illustration below helps clarify this concept.

Atmospheric Displacement (1 Part Oxygen, 4 Parts Nitrogen and Other Gases)



Now let's look at a Level 3 example. It's more than may be expected of you in a hazmat chemistry class, but certainly something you should understand as you get further in your training.

You get a reading of 20.5% oxygen in an atmosphere suspected to contain acetone vapors. Acetone has a lower explosive limit (LEL) of 2.5% and an upper explosive limit (UEL) of 12.8%. What do these initial oxygen readings suggest?

- a. The acetone concentration may be below the LEL
- b. The acetone concentration may be within the flammable range
- c. The acetone concentration may be above the UEL
- d. The initial readings do not provide any information that can be used to predict flammability

This scenario assumes you haven't yet monitored for acetone itself; you're merely looking at oxygen levels. So let's work through the math. A 0.4% drop in oxygen level ($20.9\% - 20.5\% = 0.4\%$) represents a 2.0% displacement of the normal atmosphere ($0.4\% \times 5 = 2.0\%$). Thus the acetone concentration is likely to be below the LEL of 2.5%. Further monitoring is obviously required, but initial readings do provide some useful information.

Most of us don't like to study this hard when preparing for a final exam. But once again, real life is far more demanding than any written test you'll ever take, so it's to your benefit to aim for a higher level of proficiency when studying in any class.

Recognizing the Concepts Behind the Questions

One recommendation made in the preceding pages was to focus on *concepts* more than *chemicals*. If you understand the concepts, you can often correctly answer the test questions without putting names to the formulas or knowing more about the compounds.

Does this mean you shouldn't diligently study the material? Certainly not. What it does mean, however, is that you can reduce your test anxiety a little. More importantly, it helps you in the real world because it enables you to streamline your identification and hazard analysis process. So we'll look at some examples over the next few pages.

Concept: Molecular size affects the behavior of many materials. For instance, smaller hydrocarbon molecules are more active, produce more vapor, and have a higher vapor pressure than do larger hydrocarbon compounds similar in structure at the same temperature and pressure. (Other physical and chemical properties are affected too, but we'll focus just on vapor pressure here.)

The two questions below are identical, and the answers are the same in each, except that one contains formulas and the other contains names. Each question tests whether you recognize the relation between molecular size and vapor pressure. Again, the smaller the compound, the higher the vapor pressure.

Which of the following has the highest vapor pressure?

- a. C_3H_8
- b. C_4H_{10}
- c. C_5H_{12}
- d. C_6H_{14}

Which of the following has the highest vapor pressure?

- a. Propane
- b. Butane
- c. Pentane
- d. Hexane

You don't have to name the compounds in the first question if you recognize that C_3H_8 (answer a) is the smallest compound listed. (Hint: It has the fewest atoms.) Likewise, you don't need to know the formulas to successfully answer the second question. Each compound ends in *-ane*, so they're all alkanes, meaning they all have similar structures. All you need to know at this point is the relation between the prefixes and the number of carbon atoms (*prop* means 3, *but* means 4, *pent* means 5, and *hex* means 6). Propane (answer a) has the fewest carbon atoms (and consequently the fewest total atoms), so it's the smallest compound. (Hydrocarbon types, names, and formulas are covered in Chapter 5.)

Concept: Compounds are categorized as either salts or nonsalts. Most *salt* compounds are comprised of a metal element plus one or more nonmetal elements. (Metal and nonmetal elements can be distinguished by looking at the periodic table of elements. You can look ahead to pages 54 and 55 to see an example.) *Nonsalt* compounds are comprised of two or more nonmetal elements.

There are very few salts that don't contain metal elements. Examples include ammonium chloride (NH_4Cl) and ammonium nitrate (NH_4NO_3). But for now, we'll ignore those exceptions.

Understanding the distinction between salts and nonsalts should make it very easy to answer the questions that follow. Does the name or formula contain a metal element? If so, the compound is a salt. If not, it's a nonsalt. (You should be able to spot the metal elements used in the questions below on a periodic table.)

Which of the following compounds is a salt?

- a. Methyl Chloride
- b. Sodium Cyanide
- c. Vinyl Acetate
- d. Hydrogen Peroxide

Recognizing the Concepts Behind the Questions (continued)

Which of the following compounds is a nonsalt?

- Sodium Hypochlorite
- Potassium Permanganate
- Lithium Bromate
- Methyl Cyanide

These first two questions require you to recognize the names of metal elements (or be able to find them on a periodic table). Sodium is a metal element, so sodium cyanide (b) is the correct answer to the first question. The second question has only one name that doesn't contain a metal element (methyl cyanide), so the answer is d. Now see what you can do with symbols, also found on a periodic table.

Which of the following compounds is a salt?

- H_2O_2
- $\text{CH}_3\text{OC}_2\text{H}_5$
- CaSO_4
- CH_3CN

Which of the following compounds is a nonsalt?

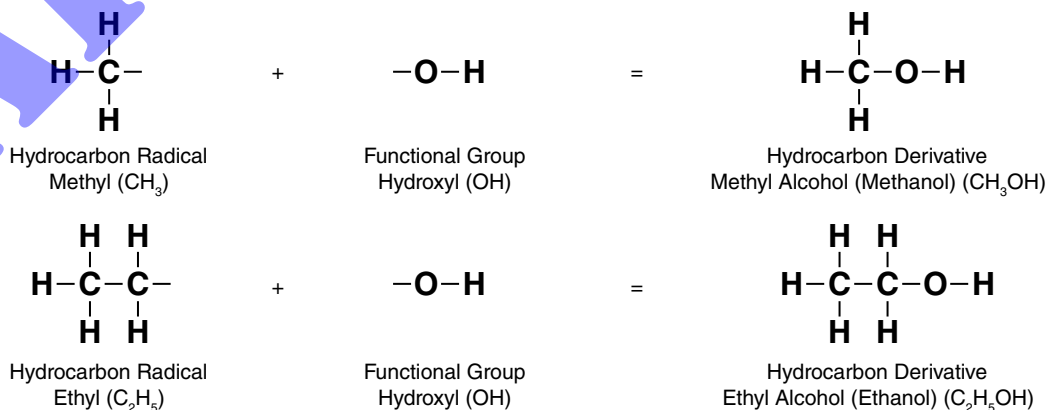
- CaC_2
- KCN
- $\text{C}_2\text{H}_5\text{OH}$
- NaClO

The last two questions are very similar except that you're given formulas instead of names. Calcium (Ca) is a metal element, so CaSO_4 (answer c) is correct for the third question. And only $\text{C}_2\text{H}_5\text{OH}$ (answer c) in the last question has no metal in the formula, making it the one nonsalt.

Notice that all four of the preceding questions can be answered without putting a formula to a name or vice versa. Should you be able to match names and formulas? Absolutely. It's likely that some questions on your final exam will even require you to do so. But understanding the concepts behind the chemistry can help you pick the correct answers with far less anxiety.

Concept: Hydrocarbon derivatives are comprised of one or more hydrocarbon radicals attached to a functional group. (This material is covered in detail in Chapter 5, but a quick introduction should show you that the topic is not as intimidating as it appears.) The graphic below illustrates two examples. In the first column are the hydrocarbon radicals methyl and ethyl. The second column shows the functional group, a hydroxyl (OH) group in both cases. Finally, when the radicals are added to the functional group, the result is methyl alcohol (top) and ethyl alcohol (bottom). Both are in the greater hydrocarbon derivative family known as alcohols and can be recognized by the hydroxyl (OH) group in the formula.

The Making of Hydrocarbon Derivatives



Recognizing the Concepts Behind the Questions (continued)

Later you'll learn about many other hydrocarbon derivatives. However, the key to recognizing each type of hydrocarbon derivative is to isolate the functional group within the formula. Below are a few examples. The table lists five hydrocarbon derivative categories along with the functional groups that comprise them. Those functional groups are underlined in the examples provided to help you recognize them. This is significant because instead of recognizing entire formulas, you can concentrate on picking out the functional groups and identifying what type of hydrocarbon derivatives they're associated with.

Hydrocarbon Derivative	Functional Group	Example	Name
Ketones	CO	CH_3COCH_3	Dimethyl Ketone (Acetone)
Aldehydes	CHO	HCHO	Formaldehyde (Methanal)
Organic Acids	COOH	CH_3COOH	Acetic Acid (Ethanoic Acid)
Esters	COO	$\text{CH}_3\text{COOC}_2\text{H}_5$	Vinyl Acetate
Alcohols	OH	$\text{C}_2\text{H}_5\text{OH}$	Ethyl Alcohol (Ethanol)

Before you look at the following questions, take a moment to study the table above and memorize the first two columns. When you've done so, try the first two questions.

CH_3COCH_3 is a/an:

- Ketone
- Aldehyde
- Ester
- Organic acid

Which of the following is an aldehyde?

- CH_3COCH_3
- $\text{CH}_3\text{COOCH}_3$
- CH_3COOH
- CH_3CHO

Answering the two questions above should be easy if you understand the relation between functional group and type of hydrocarbon derivative. In the first question, CO is the functional group surrounded by two hydrocarbon radicals (CH_3). That signifies a ketone (answer a). Aldehydes contain the function group CHO, so CH_3CHO (answer d) is correct for the second question. Notice that you can answer both questions without putting names to the formulas.

Warning: Despite the repeated emphasis on *concepts* versus *chemicals*, don't be lulled into thinking that you won't have to put names to formulas (or vice versa) on your final exam. It's quite possible you may have several questions that require you do to just that. And you'll certainly need to do it in the real world. However, your knowledge of the basic concepts will help you immensely. Consider the following question.

Which of the following formulas represents methyl ethyl ketone (MEK)?

- CH_3COCH_3
- CH_3COOH
- $\text{CH}_3\text{COC}_2\text{H}_5$
- $\text{CH}_3\text{O}_2\text{C}_2\text{H}_5$

If you haven't memorized the formula for MEK, you'll need to look for two clues. Look for the functional group associated with ketones (CO). Answers a and c both contain that. Then look for the hydrocarbon radicals methyl (CH_3) and ethyl (C_2H_5), which are found in answers c and d. (Hydrocarbon radicals were mentioned briefly on the previous page.) The one formula that meets both requirements is $\text{CH}_3\text{COC}_2\text{H}_5$ (answer c).

Is it necessary to name all four compounds to correctly answer the question above? No. Should you be able to name them. Yes. Again, it may be vital in the real world. However, you can pass the test without doing so. Once you've recognized the value of focusing on *concepts* more than *chemicals*, it makes studying for the final exam infinitely easier. Keep this in mind as you read through the rest of the book.

Chapter 2

Terms and Definitions

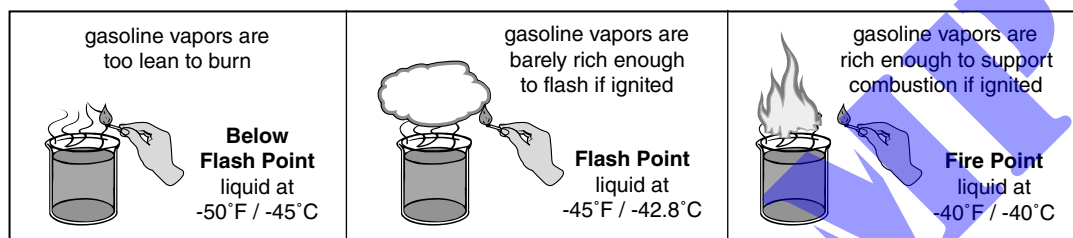
This chapter provides terms and definitions you should be familiar with before proceeding to the other chapters. Other terms will be introduced in subsequent chapters as appropriate. This chapter covers the following:

- Acute Exposure
- Acute Exposure Guideline Level (AEGL)
- Air Reactivity
- Boiling Point
- Carcinogens
- Catalyst
- Ceiling Exposure Limit
- Chemical Reactivity
- Chronic Exposure
- Condensation
- Contamination
- Deposition
- Dose-Response Curve
- Emergency Response Planning Guideline (ERPG)
- Exothermic Reactions
- Exposure
- Flammable (Explosive) Range (LEL & UEL)
- Fire Point
- Flash Point
- Floater
- Freezing / Freezing Point
- Ignition (Autoignition) Temperature
- Immediately Dangerous to Life and Health (IDLH)
- Inhibitor
- Lethal Concentration (LC)
- Lethal Dose (LD)
- Level of Concern (LOC)
- Local Effects
- Melting / Melting Point
- Milligrams per Cubic Meter (mg/m₃)
- Milligrams per Kilogram (mg/kg)
- Miscibility
- Monomer
- Mutagens
- Recommended Exposure Limit (REL)
- Routes of Entry/Exposure
- Odor Threshold
- Parts per Million/Billion (ppm/ppb)
- Permissible Exposure Limit (PEL)
- Physical State (solid, liquid, gas)
- Plasma
- Polarity
- Polymer
- Polymerization
- Protective Action Criteria (PAC)
- Pyrophoric
- Short-Term Exposure Limit (STEL)
- Sinker
- Solubility
- Solute
- Solvent
- Specific Gravity
- Spontaneous Combustion
- Sublimation
- Swimmer
- Synergistic Effect
- Systemic Effects
- Temporary Emergency Exposure Limit (TEEL)
- Teratogens
- Threshold Limit Value (TLV-TWA)
- Vapor Density
- Vapor Pressure
- Vaporization
- Viscosity
- Volatility
- Water Reactivity
- Water Solubility
- Workplace Environmental Exposure Limits (WEEL)

Flammability Factors

Flash point is the minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air. The vapors may ignite if an ignition source is present. However, the flame does not continue to burn when the source of ignition is removed; rather, the vapors flash and are consumed by the flame. **Fire point** is the temperature at which enough vapors are given off to support continuous burning even after the source of ignition has been removed. The fire point is generally just a few degrees above flash point. The following illustration uses gasoline to demonstrate these properties.

Flash Point and Fire Point of Gasoline



Generally, the lower the flash point or fire point, the greater the hazard. (When different reference sources list different temperatures, assume the worst and err on the side of safety.) While other properties, such as flammable range and ignition temperature, play a significant role in flammability, flash point is usually considered to be the most important property in assessing the hazards of flammable and combustible liquids.

Flash point and fire point refer to the temperature of the liquids rather than to the vapors they produce. The flash point of mixtures, such as kerosene and diesel fuel, may be listed as a range of temperatures instead of a single temperature because the flash point can vary depending on composition. Reference sources will sometimes also list flash points for volatile solids—solids that evolve enough flammable vapors under ambient conditions to pose a flammability risk. Flash point and fire point don't apply to gases.

Ambient temperature plays an important role when assessing hazards. A combustible liquid will be below its flash point at normal temperatures. The liquid is normally safe from a flammability standpoint because it does not generate enough vapors to form an ignitable mixture. However, on a hot day or in a hot environment, a combustible liquid may easily reach its flash point. The vapors of both flammable and combustible liquids will be much easier to ignite when the temperature is elevated. (See page 148 for a breakdown on how different agencies distinguish between a flammable liquid and a combustible liquid.)

The **ignition (autoignition) temperature** of a substance is the minimum temperature required to cause self-sustained combustion, independent of an ignition source. Simply put, it's the temperature a material must reach before it will ignite. It is also the temperature the ignition source must be. (See also pages 105 and 106 for the relation between molecular size, flash point, and ignition temperature.) Ignition temperature is sometimes difficult to measure and should be considered an approximation. Ignition comes in two forms:

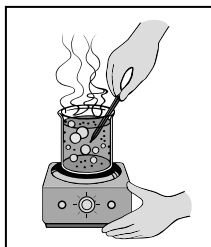
- **Pilot ignition** involves an external ignition source (e.g., a water heater pilot light or a lit cigarette igniting gasoline vapors).
- **Autoignition** is caused by elevated temperatures. In a fire, for example, convection carries hot air and gases to other parts of a building. When the atmosphere becomes hot enough that these gases reach their ignition temperatures, they will ignite without the introduction of any other ignition source. This is called *flashover*.

A few substances are subject to **spontaneous combustion**. Animal and vegetable oils (e.g., mink oil or linseed oil) are good examples. The oil will slowly oxidize when exposed to air, generating heat in the process. If the heat cannot dissipate fast enough, it will accelerate the production of flammable vapors, then spontaneously ignite those vapors. To prevent spontaneous combustion, rags soaked with animal or vegetable oils should be either kept in tightly closed metal containers that exclude air or hung outdoors (e.g., on a clothesline) where air movement would prevent the buildup of heat. They must not be left lying in a pile.

Flammability Factors (continued)

Boiling point is the temperature at which the vapor pressure at the surface of the liquid is equal to or slightly greater than atmospheric pressure, meaning that individual molecules are able to easily break through the surface of the liquid in vapor form, escaping into the atmosphere. Boiling point is the point of maximum vapor production. The lower the boiling point, the greater the hazard potential because it takes less heat to get that liquid to the point of maximum vapor production.

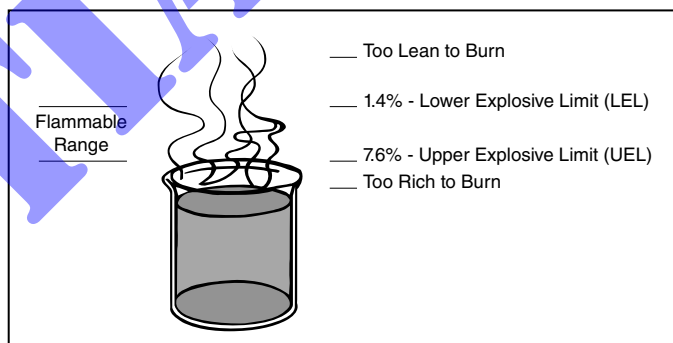
Boiling Point



Flammable (explosive) range is the percentage of vapor in air within which ignition is possible. Below the **lower explosive limit (LEL)**, the vapors are too lean to burn, whereas above the **upper explosive limit (UEL)**, the vapors are too rich to burn. The lower the LEL, the quicker a chemical will enter its flammable range. (Sometimes you will see the terms *lower flammable limit [LFL]* and *upper flammable limit [UFL]* instead. They mean the same thing as lower and upper explosive limits.)

The wider the flammable range, the greater the span at which ignition is possible and the greater the potential risk. Conversely, products with narrower flammable ranges will present less of a fire hazard. Gasoline, for instance, has a relatively narrow flammable range (1.4% to 7.6%). Compare that, for example, to methyl alcohol (6% to 36%) or acetylene (2.5% to 100%). Other factors, like flash point and vapor pressure, also affect the overall flammability risk. However, all things being equal, the greater the flammable range, the greater the fire danger. (When different sources list different LEL and UEL values, assume the worst and err on the side of safety.)

The Flammable Range of Gasoline



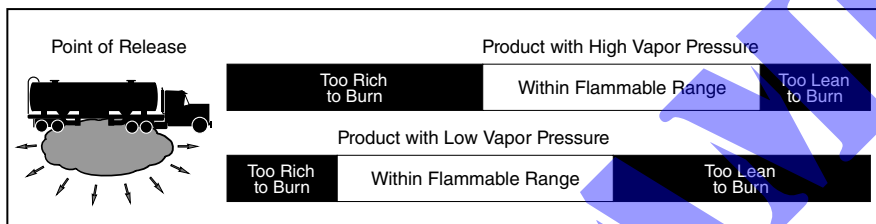
Caution: The word **inflammable** is a confusing term, because the prefix *in-* is often used to mean “not.” However, *inflammable* means *flammable*. It does *not* mean nonflammable.

Flammability Factors (continued)

There is also a direct relation between flammable range and vapor pressure. The higher the vapor pressure, the further vapors will travel and the greater the area that will be affected by the product within its flammable range. The illustration below provides a pictorial representation of this concept, but we can also make it clearer with a couple of examples.

A flammable liquid with a high vapor pressure will give off a large amount of vapor. Near the surface of the liquid, the concentration of vapors will be high enough that it is above the upper explosive limit (UEL); it is too rich to burn. However, the high vapor pressure will continue to push the vapors outward, where they will mix with air and eventually fall within the flammable range.

The Effect of Vapor Pressure on the Distance at Which the Flammable Range Is Found



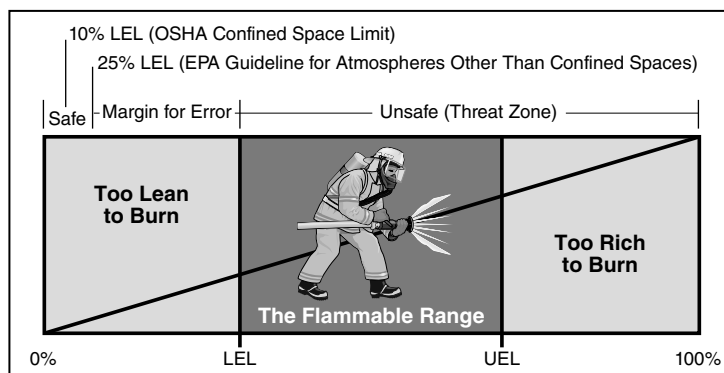
A flammable liquid with a low vapor pressure, on the other hand, will give off less vapor, so the vapors will enter the flammable range closer to the surface of the liquid and become too lean to burn much closer as well. Therefore, flammable liquids with low vapor pressures present a greater risk close to the source, whereas those with higher vapor pressures present a risk of ignition at greater distances from the release.

Keep in mind that this is a very simplified representation of risk. It assumes that both products have equally wide flammable ranges, which may not be the case. Also, the product with the lower vapor pressure will not spread as far as the one with the higher vapor pressure and therefore won't be detectable as far.

Only atmospheres that are well below the LEL are safe to enter. Consequently, many response agencies have SOPs or SOGs that prohibit working in an atmosphere greater than 10% of the LEL. (That's 10% of the LEL, not a 10% contaminant concentration in the atmosphere.) In part, this comes from OSHA regulations that prohibit working in *confined spaces* with more than 10% of the LEL. However, when the environment does not meet the definition of a confined space, the Environmental Protection Agency's guidelines suggest that hazardous materials technicians can keep working up to 25% of the LEL if they're cautious and use continuous monitoring. Both limits (10% and 25%) still leave a good margin of error to guard against everything from fluctuations in the chemical concentration to defective monitors or errors in interpreting the meter readings.

Even though the vapors are too rich to burn *above* the UEL, never consider that to be a safe atmosphere because the vapor concentration may drop to within the flammable range during emergency operations.

Flammable Range



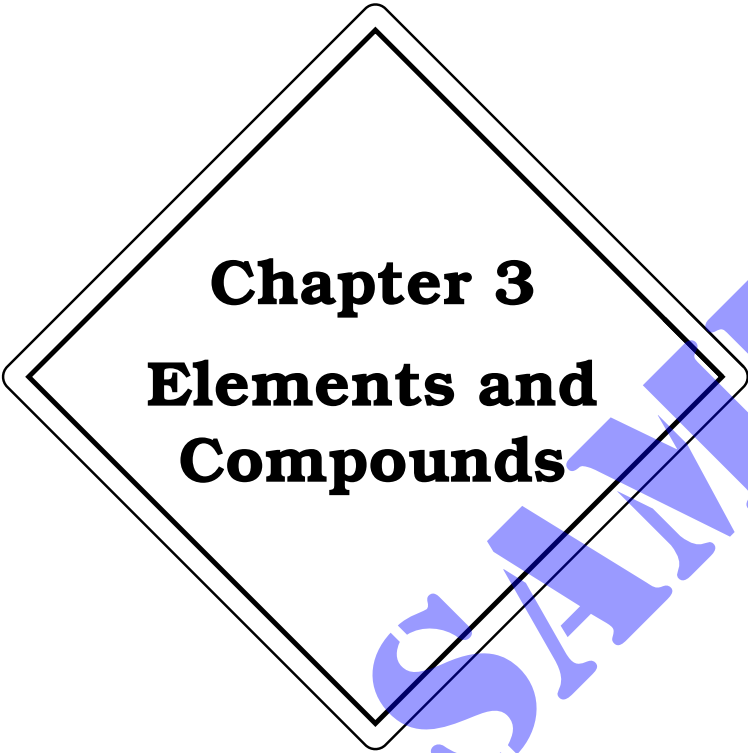
Flammability Factors (continued)

Review Questions (answers on page 194)

1. Ignition (autoignition) temperature is the:
 - a. Minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air.
 - b. Temperature at which enough vapors are given off to support continuous burning even after the source of ignition has been removed.
 - c. Minimum temperature required to cause self-sustained combustion independent of an ignition source.
 - d. Temperature at which vapor pressure of the substance is equal to or slightly greater than atmospheric pressure.
2. Flash point is the:
 - a. Minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air.
 - b. Temperature at which enough vapors are given off to support continuous burning even after the source of ignition has been removed.
 - c. Minimum temperature required to cause self-sustained combustion independent of an ignition source.
 - d. Temperature at which vapor pressure of the substance is equal to or slightly greater than atmospheric pressure.
3. Boiling point is the:
 - a. Minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air.
 - b. Temperature at which enough vapors are given off to support continuous burning even after the source of ignition has been removed.
 - c. Minimum temperature required to cause self-sustained combustion independent of an ignition source.
 - d. Temperature at which vapor pressure of the substance is equal to or slightly greater than atmospheric pressure.
4. Which property is generally considered to be the most important property when assessing the hazards of flammable and combustible liquids?
 - a. Flash point
 - b. Flammable range
 - c. Ignition temperature
 - d. Vapor pressure
5. What is the point of maximum vapor production?
 - a. Vapor point
 - b. Fire point
 - c. Boiling point
 - d. Critical pressure
6. Which of the following substances are subject to spontaneous combustion?
 - a. Catalysts and inhibitors
 - b. Animal and vegetable oils
 - c. Fuel oils
 - d. Ethylene monomers
7. Products with higher vapor pressures generally present a greater risk:
 - a. Closer to the release
 - b. At greater distances from the release

Flammability Factors (continued)

8. The lower the boiling point, the greater the hazard potential.
- a. True
 - b. False
9. The higher the flash point, the more vapors will be produced and the greater the flammability hazard.
- a. True
 - b. False
10. The higher the ambient temperature, the more easily a flammable or combustible liquid will vaporize.
- a. True
 - b. False
11. The wider the flammable range, the greater the risk of ignition.
- a. True
 - b. False
12. Atmospheres above the upper explosive limit are safe to enter because the vapors are too rich to burn.
- a. True
 - b. False
13. OSHA confined space regulations identify ____ of the LEL as the cutoff prohibiting work in flammable atmospheres.
- a. 10%
 - b. 15%
 - c. 20%
 - d. 25%
14. The word *inflammable* means "not flammable."
- a. True
 - b. False



Chapter 3

Elements and Compounds

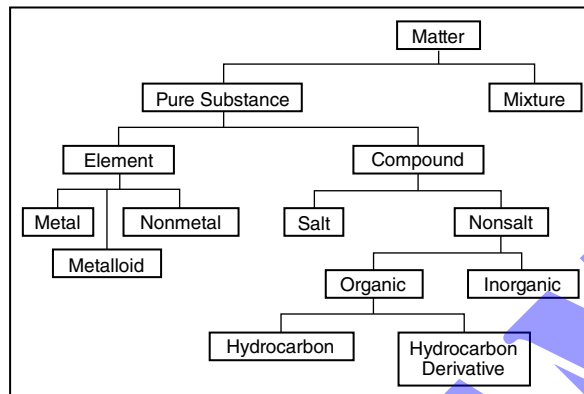
Hazardous materials (and in fact, all matter) consist of elements and compounds. So understanding how elements bond to create compounds is fundamental to understanding hazardous materials in general. This chapter covers the following:

- Matter
- The Periodic Table
- Atomic Structure
- Chemical Bonding
- Isomers

Matter

Matter is anything that occupies space and has mass. It is often classified as shown below.

The Classification of Matter



Matter is first divided into pure substances or mixtures. A **pure substance** is a homogenous one—one in which every sample of the same substance is identical in composition. Examples include sodium chloride (NaCl), benzene (C₆H₆), propane (C₃H₈), and ethanol (C₂H₅OH).

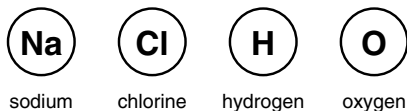
A **mixture** consists of two or more elements or compounds that are physically mixed, but not chemically bonded. For example, sodium chloride (NaCl) and water (H₂O) mix to form salt water, but neither compound is chemically altered during the mixing process. Gasoline, kerosene, and fuel oil are common examples of other mixtures. Unlike pure substances, mixtures can vary from one sample to another. For instance, gasoline purchased from two different service stations may contain ingredients and additives in different percentages.

Although the largest percentage of hazardous materials that exist in the world today are mixtures, this study guide, like most hazmat chemistry classes, concentrates on pure substances. Mixtures is too big of a topic to tackle successfully in a one-week class, and it's much harder to make generalizations about them. However, when a pure substance is the major component of a particular mixture, you are well on your way to understanding its hazards and characteristics.

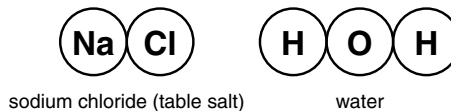
A pure substance may be either a single **element** (such as sodium, chlorine, hydrogen, or oxygen) or a **compound** (such as sodium chloride or water) comprised of two or more elements chemically bonded to form a **molecule**. In other words, compounds can be broken down to release simpler substances (the individual elements), whereas elements cannot be broken down into anything simpler without getting into atomic structure (protons, neutrons, and electrons).

Elements are represented by a single capital letter (for example, H or O) or by a capital letter followed by a lowercase letter (for example, Na or Cl). Compounds are represented by formulas showing multiple elements (for example, NaCl or H₂O). When the formula contains numbers, it indicates that more than one atom of the same element (or group of elements) is present. You'll see more examples of this shortly.

Four Elements



Two Compounds (Molecules)



Matter (continued)

Elements are further divided into metals, nonmetals, and metalloids (or semimetals). The distinction between metals and nonmetals, in particular, will become clearer later when we discuss chemical bonding. For now, however, the following provides a brief overview.

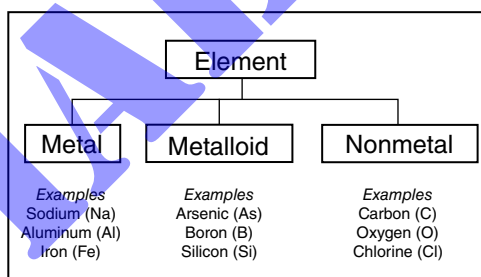
Metals, in general, have a characteristic lustrous (shiny) appearance and are good conductors of heat and electricity. They are malleable (can be hammered into thin sheets) and ductile (can be drawn into wires). Most metals are solids in their natural states. The exceptions are mercury (Hg), cesium (Cs), and francium (Fr), all of which are liquids.

Nonmetals, in general, do not have a lustrous appearance and are not good conductors. They are neither malleable nor ductile. All of the nonmetals are either solids or gases, with the exception of the liquid element bromine (Br).

Metals and nonmetals each bond (react) with other elements in specific ways. Metals bond with nonmetals by donating electrons. Nonmetals usually bond to metals by accepting electrons (to form salts) or to other nonmetals by sharing electrons (to form nonsalts). This will be covered in more detail in the section on chemical bonding.

While periodic tables draw a definite distinction between metals and nonmetals (see pages 54 and 55), the distinction is not as absolute as it appears to be. **Metalloids**, or **semimetals**, are elements immediately surrounding the dividing line between metals and nonmetals. They tend to have properties of each. The metalloids are boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te), and polonium (Po). Further discussion of metalloids is beyond the scope of this study guide. However, you should recognize that some elements will not precisely fit the classic profile you've come to associate with metals or nonmetals. That's one reason it's so important to check reference sources at a hazmat incident rather than rely solely on your chemistry training, training that often contains generalizations which, while they simplify the learning process, can mislead you when dealing with materials that are slightly different.

Elements: Metal, Metalloid, or Nonmetal



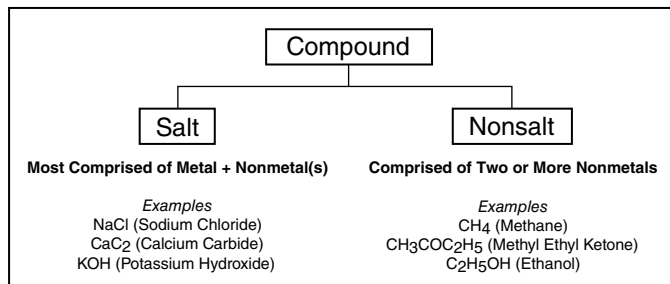
Alloys (or *metal alloys*) are generally described as a mixture of two or more metals, the purpose of which is to create a material that is somehow stronger or better for a particular application than any one metal would be alone. For example, brass is comprised of approximately 70% copper (Cu) and 30% zinc (Zn). The titanium alloy contains 90% titanium (Ti), 5% aluminum (Al), and 5% vanadium (V). There can be slight variations in actual concentration with most alloys.

Alloys sometimes contain a small percentage of nonmetal elements. Steel, for example, is comprised primarily of iron (Fe), but contains 0.1% to 1.5% carbon (C). Stainless steel is roughly 80% iron (Fe), 15% chromium (Cr), 4% nickel (Ni), and 0.5% to 1% carbon (C).

Compounds are further divided into salts and nonsalts, both of which are described in more detail later. In general, however, most **salt compounds** consist of a metal element bonded to one or more nonmetal elements, whereas **nonsalt compounds** consist solely of nonmetal elements.

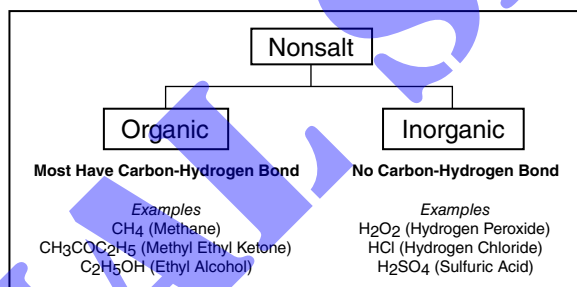
Matter (continued)

Compounds: Salt or Nonsalt



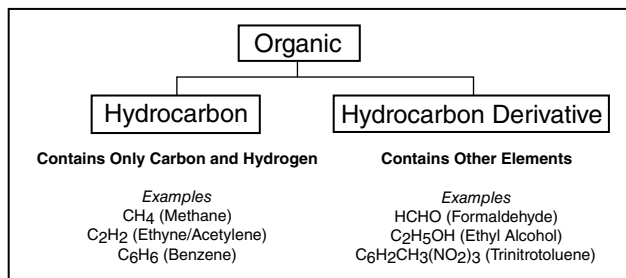
Nonsalt compounds are either organic or inorganic. **Organic compounds** are those derived from living (or once living) organisms; **inorganic compounds** are not. However, this can be confusing for someone trying to decipher a name or formula, so we sometimes see other definitions. It's commonly considered that organic compounds are those containing carbon, whereas inorganic compounds are those without carbon. However, several compounds containing carbon are classified as inorganic. Examples include carbon dioxide (CO₂), sodium cyanide (NaCN), calcium carbonate (CaCO₃), and carbon tetrachloride (CCl₄). It's more accurate to describe organic compounds as those containing carbon-hydrogen bonds; almost all organic compounds fit this definition.

Nonsalts: Organic or Inorganic



Organic compounds are classified as either hydrocarbons or hydrocarbon derivatives. **Hydrocarbons** are those containing only carbon and hydrogen atoms. Most **hydrocarbon derivatives** contain carbon and hydrogen, along with other nonmetal elements, such as nitrogen, oxygen, or chlorine. However, as you'll see in a later chapter, these materials are all derived from the basic hydrocarbons; hence the name hydrocarbon derivatives.

Organic Compounds: Hydrocarbons or Hydrocarbon Derivatives



More is written throughout this book about various elements and compounds that comprise the groups identified in this section. For now, however, it's sufficient that you picture an organizational chart that groups materials according to their chemical makeup. This is a very different way of organizing materials than the more familiar DOT (Department of Transportation) hazard classes.

Matter (continued)

Review Questions (answers on page 194)

1. Which of the following is an element?
 - a. Ca
 - b. CO
 - c. CO₂
 - d. HCl

2. Which of the following is a compound?
 - a. He
 - b. Hf
 - c. HF
 - d. Hg

3. Of the following definitions used to describe organic compounds, which is most accurate and most helpful for enabling hazmat technicians to distinguish organic compounds from inorganic compounds?
 - a. Derived from living (or once living) tissues
 - b. Containing carbon
 - c. Containing carbon-hydrogen bonds

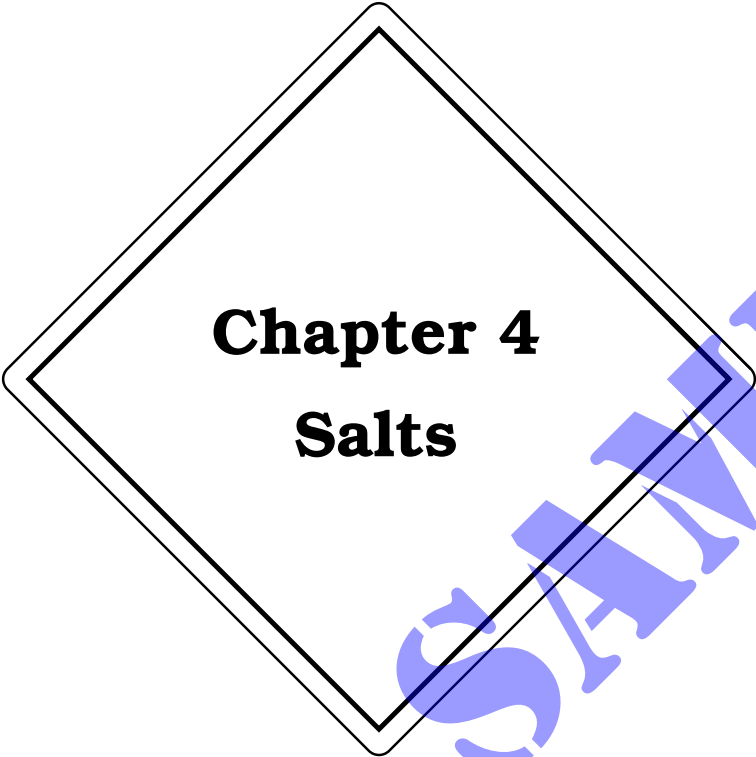
4. Hydrocarbon compounds are those that contain:
 - a. Carbon and oxygen
 - b. Nitrogen and carbon
 - c. Oxygen and hydrogen
 - d. Carbon and hydrogen

5. Which of the following is an organic compound?
 - a. CaO
 - b. CH₄
 - c. H₂O
 - d. NaCl

6. Which of the following is an inorganic compound?
 - a. C₂H₅OH
 - b. CH₃COC₂H₅
 - c. H₂SO₄
 - d. HCHO

7. Which of the following is a plain hydrocarbon (not a hydrocarbon derivative or a salt)?
 - a. CHCl₃
 - b. C₃H₈
 - c. C₃H₅(OH)₃
 - d. KCN

8. Gasoline, kerosene, and fuel oil are examples of:
 - a. Elements
 - b. Pure compounds
 - c. Mixtures
 - d. Salt compounds



Chapter 4

Salts

Salts are compounds typically formed of a bond between a metal element plus one or more nonmetal elements. This chapter first provides an overview of salts, then examines six types of salts in more detail.

Types of Salts

Shown below is another abbreviated version of the chart on the first page of this chapter, this one emphasizing the composition of the various salts. This section provides more detail on each of these salts and their common characteristics. (These generalizations apply primarily to salts containing alkali metals and alkaline earth metals. In general, when salts contain transition metals, toxicity and environmental damage are common concerns; reactivity is usually less of a problem.)

Composition of the Salts

Salt	Composition	Naming	Example
Binary Salt	metal + nonmetal (not otherwise listed below)	metal + nonmetal root (ends in "ide")	CaC ₂ calcium carbide
Metal Oxide (Binary Oxide)	metal + oxygen	metal + "oxide"	Na ₂ O sodium oxide
Metal Cyanide	metal + cyanide	metal + "cyanide"	KCN potassium cyanide
Metal Hydroxide	metal + hydroxide	metal + "hydroxide" (or alkali, caustic, or base)	NaOH sodium hydroxide
Metal Peroxide	metal (Group I or II) + peroxide	metal + "peroxide"	Na ₂ O ₂ sodium peroxide
Metal Oxy salt	metal + element + oxygen	metal + oxyradical (ends in "ate" or "ite") (may include prefix "per" or "hypo")	NaNO ₃ sodium nitrate

Binary Salts

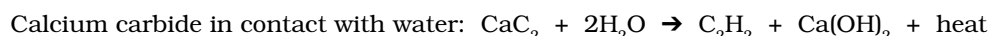
Binary salts consist of only two elements, one metal and one nonmetal (other than oxygen), although there may be more than one atom of either or both elements. The name begins with the metal element, followed by the nonmetal element, modified to provide the *-ide* ending.

Examples of Binary Salts

Names	Formulas
Sodium chloride (table salt)	NaCl
Calcium carbide	CaC ₂
Lithium sulfide	Li ₂ S
Aluminum chloride	AlCl ₃

The toxicity can vary, even among binary salts that are chemically similar. For example, sodium fluoride (NaF) is very toxic, whereas sodium chloride (NaCl) is not. However, when in doubt, assume the binary salts are toxic.

The worst of the binary salts are water-reactive, particularly the nitrides, carbides, some chlorides, hydrides, and phosphides. (Some people remember them with the abbreviation NCHP.) These binary salts in contact with water will produce a flammable and/or toxic gas, a caustic solution, and heat by means of a chemical reaction where some bonds are broken and others are formed. For example, when calcium carbide comes in contact with water, both the calcium carbide (CaC₂) and water (H₂O) are broken down, and the elements combine with others to form flammable acetylene gas (C₂H₂), a mildly caustic solution of calcium hydroxide (Ca(OH)₂), and heat.



Metal sulfides, a subdivision of binary salts, are comprised of a metal element and sulfur. These salts are very reactive with acid, producing highly toxic hydrogen sulfide gas (H₂S).

Types of Salts (continued)

Metal Oxide Salts (Binary Oxide Salts)

Metal oxide salts, also called binary oxide salts, consist of a metal element bonded to oxygen. The name begins with the metal element, followed by *oxide*.

Examples of Metal Oxide Salts

<u>Names</u>	<u>Formulas</u>
Sodium oxide	Na ₂ O
Potassium oxide	K ₂ O
Calcium oxide	CaO
Magnesium oxide	MgO
Aluminum oxide	Al ₂ O ₃
Iron (III) oxide (rust)	Fe ₂ O ₃

The worst of the metal oxides are caustic (corrosive), particularly those containing alkali metals (Group I elements). They are water-reactive. Metal oxides containing alkali metals (e.g., lithium, sodium, and potassium) react violently with water to produce a caustic solution and a lot of heat. However, metal oxides do *not* release a gas when in contact with water, and despite the name, most metal oxides are *not* oxidizers. Many are toxic, however, so you should assume metal oxides are toxic until proven otherwise.

Metal Cyanide Salts

Metal cyanide salts consist of a metal element ionically bonded to a complex ion of carbon and nitrogen (CN). The name begins with the metal element, followed by *cyanide*.

Examples of Metal Cyanide Salts

<u>Names</u>	<u>Formulas</u>
Sodium cyanide	NaCN
Potassium cyanide	KCN

Cyanide salts are highly toxic. They react with acids to produce hydrogen cyanide (HCN), which is a very toxic and flammable gas.

Metal Hydroxide Salts

Metal hydroxide salts consist of a metal element bonded to a complex ion of oxygen and hydrogen (OH). This ion is referred to as a *hydroxide*. Therefore, the name begins with the metal element, followed by *hydroxide*. Like many hazardous materials, however, these compounds can have multiple names. Because some of the most common corrosives come from the metal hydroxide family, it's particularly important to recognize frequently used trivial (slang) names.

Examples of Metal Hydroxide Salts

<u>IUPAC Names</u>	<u>Common Trivial (Slang) Names</u>	<u>Formulas</u>
Sodium hydroxide	Caustic soda, lye	NaOH
Potassium hydroxide	Caustic potash, potash lye	KOH
Calcium hydroxide	Caustic lime, slaked lime	Ca(OH) ₂

The worst of the metal hydroxides are caustic (corrosive), particularly those containing alkali metals (Group I elements). Alkali metal hydroxides are some of the most destructive chemicals you may encounter. Metal hydroxides react with, attack, corrode, and dissolve many substances. They are extremely destructive to skin and other body tissues. They are water-reactive and will even react with moisture on the skin. Many are toxic.

Types of Salts (continued)

Metal Peroxide Salts

Metal peroxide salts consist of a metal element bonded to a peroxide radical (two oxygen atoms covalently bonded to each other). The name begins with the metal element, followed by *peroxide*.

Examples of Metal Peroxide Salts

Names	Formulas
Sodium peroxide	Na_2O_2
Potassium peroxide	K_2O_2
Calcium peroxide	CaO_2

Metal peroxides are very strong oxidizers and can react with fuels. They are water-reactive, producing a caustic solution, heat, and oxygen gas when in contact with water. Some react violently.

Metal Oxysalts

Metal oxysalts consist of a metal element, oxygen, and a third element. That third element is most often a nonmetal, but not always. Notice the example of sodium permanganate below. It contains two metals (sodium and manganese).

Examples of Metal Oxysalts

Names	Formulas
Sodium hypochlorite	NaClO
Sodium permanganate	NaMnO_4
Potassium nitrate	KNO_3
Calcium carbonate	CaCO_3

The worst of the oxysalts are very strong oxidizers and will react readily in contact with fuels. Oxysalts formed with halogens (e.g., chlorates or bromates) or nitrogen (nitrates) are the most hazardous.

Naming oxysalts is more complex than naming any of the other salts. Like the others, oxysalts start with the metal element, followed by the root of the second element. However, they end in either *-ate* or *-ite*, not *-ide* like the others, and may contain the prefixes *per-* or *hypo-*. The chart below gives an example of how oxygen content affects the name of an oxysalt. Why this happens will be explained in more detail shortly. For now, focus simply on how the name changes based on oxygen content.

Naming Oxysalts Containing Sodium, Chlorine, and Oxygen

Oxygen Content	Naming	Oxyradical	Example	Formula
1 extra atom	"per ____ ate"	Perchlorate	Sodium Perchlorate	NaClO_4
base state	"____ ate"	Chlorate	Sodium Chlorate	NaClO_3
1 less atom	"____ ite"	Chlorite	Sodium Chlorite	NaClO_2
2 less atoms	"hypo ____ ite"	Hypochlorite	Sodium Hypochlorite	NaClO

The two nonmetal elements in an oxysalt form what is often called an **oxyradical**. (Oxyradicals are also referred to as *polyatomic* or *complex ions*, a concept explained in the next section.) Oxyradicals can exist in different states, depending on the number of oxygen atoms they contain. The normal (or most stable) state of any oxyradical is known as its **base state**. For example, an oxyradical of chlorine and oxygen is most stable as ClO_3 (one chlorine atom and three oxygen atoms). This oxyradical is known as *chlorate*, *chlor-* to indicate chlorine and *-ate* to identify it as an oxyradical.

The chlorate oxyradical (ClO_3) combines with sodium to form sodium chlorate. If there's an additional atom of oxygen (ClO_4), it forms sodium perchlorate, *per-* to indicate the extra oxygen content. With one less oxygen atom (ClO_2), the compound becomes sodium chlorite, *-ite* to indicate less oxygen. The compound with the lowest oxygen content (ClO), two atoms less than the base state, is sodium hypochlorite. Here the name uses both prefix *hypo-* and suffix *-ite*. (Note that none of these names contains the *-ide* ending. Sodium chloride is a binary salt [NaCl] with no oxygen.)

Types of Salts (continued)

The chart below shows the base states of various oxyradicals. Again, the base state is the most stable configuration.

Base States of Various Oxyradicals

Base State with 3 Oxygen Atoms

Chlorate	ClO_3
Bromate	BrO_3
Iodate	IO_3
Nitrate	NO_3
Manganate	MnO_3
Carbonate	CO_3

Base State with 4 Oxygen Atoms

Sulfate	SO_4
Chromate	CrO_4
Phosphate	PO_4
Arsenate	AsO_4

Types of Salts (continued)

Review Questions (answers on page 195)

1. Which of the following is a binary salt?
 - a. NaCN
 - b. Li_2S
 - c. KOH
 - d. NaClO
2. Which of the following is a metal hydroxide salt?
 - a. NaOH
 - b. CH_3OH
 - c. MgO
 - d. Na_2O_2
3. Which of the following is a metal oxide?
 - a. K_2O_2
 - b. KMnO_3
 - c. Na_2O
 - d. KOH
4. K_2S is a/an:
 - a. Binary salt
 - b. Oxysalt
 - c. Metal cyanide
 - d. Metal oxide
5. KNO_3 is a/an:
 - a. Metal oxide
 - b. Metal peroxide
 - c. Metal hydroxide
 - d. Metal oxysalt
6. Which of the following are generally the most destructive, particularly to skin and body tissues?
 - a. Metal cyanides
 - b. Metal oxysalts
 - c. Metal hydroxides
 - d. Metal peroxides
7. Which of the following react with acids to produce toxic hydrogen cyanide gas?
 - a. Binary salts
 - b. Metal oxides
 - c. Metal hydroxides
 - d. Metal cyanides
8. Oxygen content can vary in which of the following salts?
 - a. Metal oxides
 - b. Metal oxysalts
 - c. Metal hydroxides
 - d. Metal peroxides

Chapter 5 Hydrocarbons and Related Compounds

Many of the hazardous materials we encounter are hydrocarbons or hydrocarbon derivatives (compounds formed when part of the original hydrocarbon bonds with another element or compound). This chapter covers the following:

- The Four Types of Hydrocarbons
- Hydrocarbon Names and Formulas
- The Effect of Molecular Size
- Hydrocarbon Radicals
- Overview of Hydrocarbon Derivatives
- Part 1 Hydrocarbon Derivatives - Carbonyls
- Other Part 1 Hydrocarbon Derivatives
- Part 2 Hydrocarbon Derivatives - Nitrogen Based
- Other Part 2 Hydrocarbon Derivatives
- Chapter 5 Review

Hydrocarbon Names and Formulas

Hydrocarbon types can often be identified by name. For example, the *-ane* ending signifies an alkane, and the *-yne* ending signifies an alkyne. The *-ene* ending may indicate either an alkene or an aromatic, so you have to look at the prefix to make a determination.

As with any other naming system, there are exceptions. For example, despite the *-ene* ending, acetylene (C_2H_2) is an alkyne with a highly unstable triple bond between carbon atoms. (Acetylene is also known as *ethyne*.)

Endings Used to Name Hydrocarbons

Type	Ending	Examples
Alkane	-ane	Methane, Ethane
Alkene	-ene	Ethene, Propene *
Alkyne	-yne	Ethyne, Propyne
Aromatic	-ene	Benzene, Toluene

* The alkenes *ethene*, *propene*, and *butene* are commonly known in the United States as *ethylene*, *propylene*, and *butylene*. However, the shorter names are sometimes used in this book where consistency in the prefixes (*eth-*, *prop-*, and *but-*) helps show the relation between alkanes, alkenes, and alkynes.

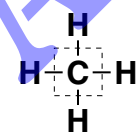
Alkanes, alkenes, and alkynes use common prefixes based on the number of carbon atoms in the formula. Those prefixes are identified below.

Prefixes Used to Name Alkanes, Alkenes, and Alkynes

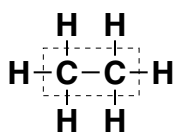
# Carbon Atoms	Prefix	Example
1	Meth-	Methane
2	Eth-	Ethane
3	Prop-	Propane
4	But-	Butane
5	Pent-	Pentane
6	Hex-	Hexane
7	Hept-	Heptane
8	Oct-	Octane
9	Non-	Nonane
10	Dec-	Decane

The following illustration is a graphic representation of the information identified above. Again, the prefixes identify the number of carbon atoms in the compound. The illustration shows only four examples, but the others follow the same pattern.

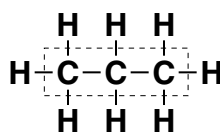
The Relation Between Prefixes and the Number of Carbon Atoms



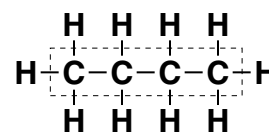
1 carbon atom
methane (CH_4)



2 carbon atoms
ethane (C_2H_6)



3 carbon atoms
propane (C_3H_8)



4 carbon atoms
butane (C_4H_{10})

Hydrocarbon Names and Formulas (continued)

The five substances listed below are aromatic hydrocarbons. Like the alkenes, these have names with *-ene* endings. However, the aromatic hydrocarbons use different prefixes than do the other hydrocarbons. The aromatics you'll most likely learn about in your hazmat training are benzene, toluene, xylene, styrene, and cumene. (If you understand the different bonds, as illustrated on page 96, and the chemical formulas, as explained below, you'll better understand why the aromatics with their *-ene* endings are not the same as the alkenes.)

Five Aromatics

Name	Formula
Benzene	C_6H_6
Toluene	C_7H_8
Xylene	C_8H_{10}
Styrene	C_8H_8
Cumene	C_9H_{12}

Hydrocarbons can also be recognized by formula. First, they contain only carbon and hydrogen, so when you see only those two elements in a formula, you know the compound is a hydrocarbon versus a hydrocarbon derivative or something else. Second, each of the four types of hydrocarbons have formulas that follow a certain pattern. Those patterns are shown below. (Note: "n" represents the number of carbon atoms in the structure.) Styrene (C_8H_8) is the one exception. It doesn't follow the pattern for other aromatics.

Hydrocarbon Formulas

Type	Formula	Examples
Alkane	$C_n H_{2n+2}$	C_2H_6 (Ethane), C_3H_8 (Propane)
Alkene	$C_n H_{2n}$	C_2H_4 (Ethene), C_3H_6 (Propene)
Alkyne	$C_n H_{2n-2}$	C_2H_2 (Ethyne), C_3H_4 (Propyne)
Aromatic	$C_n H_{2n-6}$ (n≥6) (except styrene)	C_6H_6 (Benzene), C_7H_8 (Toluene)

A little practice with these formulas will help you see how they work. In each problem below, the type of hydrocarbon and generic formula are provided. If you recognize the prefix for each compound, you can plug the associated number into the generic formula, do the math, and find the final formula.

Compound	Type	Generic Formula	Final Formula
Hexane	Alkane	$C \quad H_{2(\quad)+2}$	$C \quad H \quad$
Butene	Alkene	$C \quad H_{2(\quad)}$	$C \quad H \quad$
Acetylene *	Alkyne	$C \quad H_{2(\quad)-2}$	$C \quad H \quad$
Xylene	Aromatic	$C \quad H_{2(\quad)-6}$	$C \quad H \quad$

* Remember: Acetylene is an exception to the naming scheme. Its other name is ethyne.

You can also work backwards. In each problem below, the compound's formula is provided along with most of the generic formula. After determining how many hydrogen atoms must be added to or subtracted from the generic formula, you can easily pick the type of hydrocarbon, which should give you the name ending. The prefix is determined by looking at the number of carbon atoms.

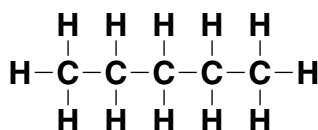
Compound	Generic Formula	Type	Name
C_8H_{18}	$C_8H_{2(8) \text{ +/- } \quad}$	<u> </u>	<u> </u>
C_5H_{10}	$C_5H_{2(5) \text{ +/- } \quad}$	<u> </u>	<u> </u>
C_9H_{12}	$C_9H_{2(9) \text{ +/- } \quad}$	<u> </u>	<u> </u>

Hydrocarbon Names and Formulas (continued)

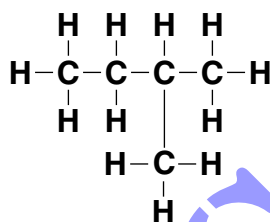
Most of what you need to know about the different types of hydrocarbons is summed up in the preceding pages. However, we'll look briefly at some important variations.

The section on chemical bonding introduced you to the concept of **isomers**—compounds with the same molecular formula, but different molecular structure. Not all hydrocarbons have isomers, but many of them do. The following illustration shows three compounds we didn't look at earlier: *pentane*, *isopentane*, and *neopentane*. The arrangement of carbon atoms—a straight chain for pentane and a branched appearance for its isomers—is what's referred to with the terms **straight-chain hydrocarbon** and **branched hydrocarbon**, respectively.

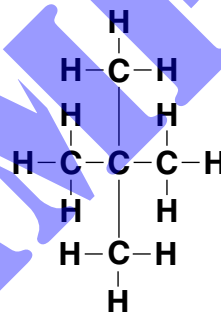
Isomers of Pentane (C_5H_{12})



Pentane (C_5H_{12})



Isopentane (C_5H_{12})

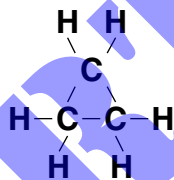


Neopentane (C_5H_{12})

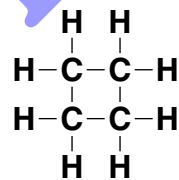
As indicated earlier, the different structure of isomers tends to result in slightly different properties. The difference may not be dramatic, but even a 20°F (6.67°C) difference in flash point, for example, can be significant depending on ambient temperature and the presence of other ignition sources on scene.

Cyclo compounds appear to have a ring structure like the aromatic hydrocarbons, but they have single bonds between carbon atoms, not resonant bonds that set the aromatics apart. As is the case with branched isomers, cyclo compounds can have different properties than their straight-chain cousins. (Note that the cyclo compounds don't follow the formula patterns that their straight-chain cousins do.)

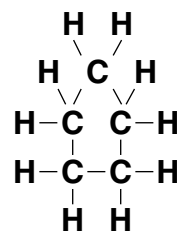
Cyclo Compounds



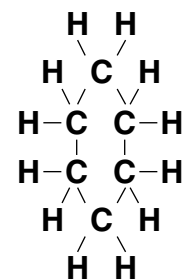
Cyclopropane (C_3H_6)



Cyclobutane (C_4H_8)



Cyclopentane (C_5H_{10})

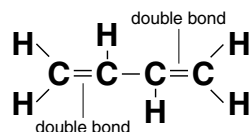


Cyclohexane (C_6H_{12})

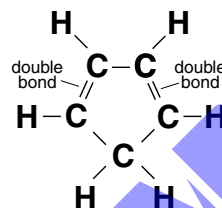
Hydrocarbon Names and Formulas (continued)

If one double bond between carbon atoms is very reactive and unstable, multiple double bonds in the same compound will be much worse. Shown below are butadiene (C_4H_6) and cyclopentadiene (C_5H_6). Butadiene, a flammable and toxic monomer used in the plastics industry, will polymerize so easily that DOT regulations prohibit shipping it without the addition of an inhibitor. (It is usually shipped as a liquefied compressed gas.) Cyclopentadiene is so reactive that it explodes if heated.

Compounds with Multiple Double Bonds



Butadiene (1,3-Butadiene)
(C_4H_6)



Cyclopentadiene (1,3-Cyclopentadiene)
(C_5H_6)

Note that the names butadiene and cyclopentadiene above still give us clues to formula and structure. *But-* and *pent-* indicate four and five carbon atoms, respectively. The *-ene* ending signals an alkene (double bond), with the prefix *cyclo* in cyclopentadiene further indicating a cyclo compound. The secondary prefix *di-* in each name warns of *two* double bonds between carbon atoms versus just one.

Hydrocarbon Names and Formulas (continued)

Review Questions (answers on page 196)

1. List the prefixes used to name alkanes, alkenes, and alkynes based on the number of carbon atoms.

1 carbon atom _____
 2 carbon atoms _____
 3 carbon atoms _____
 4 carbon atoms _____
 5 carbon atoms _____

6 carbon atoms _____
 7 carbon atoms _____
 8 carbon atoms _____
 9 carbon atoms _____
 10 carbon atoms _____

2. The formula for methane is:

- a. CH_3
- b. CH_4
- c. C_2H_2
- d. C_2H_4

3. The formula for ethylene (ethene) is:

- a. C_2H_2
- b. C_2H_4
- c. C_2H_5
- d. C_2H_6

4. The formula for acetylene is:

- a. C_2H_2
- b. C_2H_4
- c. C_2H_6
- d. C_3H_4

5. What is the generic formula for alkanes?

- a. C_nH_{2n}
- b. $\text{C}_n\text{H}_{2n+2}$
- c. $\text{C}_n\text{H}_{2n-2}$
- d. $\text{C}_n\text{H}_{2n-6}$

6. What is the generic formula for alkenes?

- a. C_nH_{2n}
- b. $\text{C}_n\text{H}_{2n+2}$
- c. $\text{C}_n\text{H}_{2n-2}$
- d. $\text{C}_n\text{H}_{2n-6}$

7. What is the generic formula for alkynes?

- a. C_nH_{2n}
- b. $\text{C}_n\text{H}_{2n+2}$
- c. $\text{C}_n\text{H}_{2n-2}$
- d. $\text{C}_n\text{H}_{2n-6}$

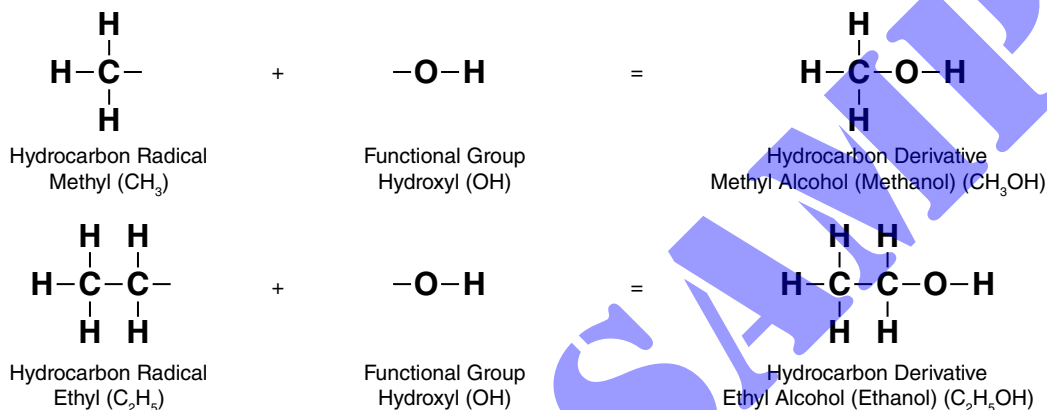
Hydrocarbon Names and Formulas (continued)

8. What is the generic formula for aromatics?
- C_nH_{2n}
 - C_nH_{2n+2}
 - C_nH_{2n-2}
 - C_nH_{2n-6}
9. Which of the following has multiple double carbon bonds?
- Acetylene
 - Butadiene
 - Cyclopentane
 - Styrene
10. Which of the following would you expect to be least stable?
- C_5H_6
 - C_6H_6
 - C_5H_{10}
 - C_5H_{12}
11. Which aromatic hydrocarbon has a formula that does not follow the generic pattern for aromatics?
- Benzene
 - Toluene
 - Xylene
 - Styrene

Overview of Hydrocarbon Derivatives

Hydrocarbon derivatives are comprised of one or more hydrocarbon radicals attached to a **functional group**. (Hydrocarbon radicals were explained on page 108.) A functional group is essentially another compound, although it, too, is electrically unbalanced and must be bonded to something else. The examples below illustrate two different alcohols (methanol and ethanol) created by joining the same functional group (OH) to different hydrocarbon radicals. (These examples were chosen, in part, because so many people are familiar with the “shorthand formula” often associated with ethanol—ETOH—the primary component of any alcoholic beverage.)

The Making of Hydrocarbon Derivatives



The hydrocarbon derivatives can be divided into groups based on the elements that comprise them. Part 1 hydrocarbon derivatives contain only carbon, hydrogen, and oxygen. The group is further divided by general structure. The **carbonyls** all have a double bond between the carbon and oxygen atoms within their structures; the others do not. Part 2 hydrocarbon derivatives may contain carbon, hydrogen, or oxygen, but they also contain other elements.

Hydrocarbon Derivatives by Group

Part 1 Hydrocarbon Derivatives (contain only carbon, hydrogen, and oxygen)		Part 2 Hydrocarbon Derivatives (contain other elements)	
<u>Carbonyls</u> Ketones Aldehydes Organic Acids *	<u>Others</u> Alcohols Glycols Glycerols Ethers Organic Peroxides	<u>Contain Nitrogen</u> Nitros Amines Nitriles ** Carbamates Amides	<u>Contain Other Elements</u> Thiols Alkyl Halides *** Organophosphates Hi-Tech Compounds

* Organic acids may also be referred to as carboxylic acids.

** Nitriles may also be referred to as cyanides.

*** Alkyl halides may also be referred to as halogenated hydrocarbons.

The charts on the following page show the structure of each hydrocarbon derivative, as well as the key to recognizing each in a chemical formula. The hazards listed are common hazards for some of the worst chemicals in each category. Each of these hydrocarbon derivatives are covered in more detail throughout this chapter.

Overview of Hydrocarbon Derivatives (continued)

Hydrocarbon Derivatives Part 1

Type	Structure	Key to Formula	Common Names	Common Hazards and Other Behaviors
Ketones	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}$	CO	ketone or -one	Toxic. Flammable. Burn with yellow flame and blue base. Can have narcotic effect on central nervous system. Water-soluble.
Aldehydes	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$	CHO	aldehyde or -al	Toxic. Flammable. Burn with yellow flame and blue base. May have wide flammable ranges. May eventually form unstable, explosive peroxides if exposed to air. Have choking, suffocating odors. Water-soluble.
Organic Acids	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{H}$	COOH	-ic acid or -oic acid	Toxic. Corrosive. Combustible. Burn with blue and yellow flame and clean smoke. Water-soluble.
Esters	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{R}$	COO or CO ₂	-ate or acetate or acrylate	Flammable. Burn with yellow flame and blue base. May be toxic. May be subject to polymerization. Slightly soluble.
Alcohols	$\text{R}-\text{O}-\text{H}$	OH	alcohol or -ol	Generally toxic. Flammable or combustible. Burn with clean blue flame. May have wide flammable ranges. Water-soluble.
Glycols	$\text{R}-(\text{O}-\text{H})_2$	(OH) ₂	glycol	Toxic. Combustible. Highly soluble. Relatively nonvolatile.
Glycerols	$\text{R}-(\text{O}-\text{H})_3$	(OH) ₃	glycerol or glycerin	(The most common one, glycerin, is relatively harmless. Others should be considered toxic and combustible until proven otherwise.)
Ethers	$\text{R}-\text{O}-\text{R}$	O	ether or oxide	Very volatile. Flammable. Burn with invisible flames. May have flash points below 0°F. May have wide flammable ranges. May be subject to polymerization. Limited shelf lives; form explosive organic peroxides if exposed to air. May have anesthetic properties. Insoluble (floaters).
Organic Peroxides	$\text{R}-\text{O}-\text{O}-\text{R}$	OO or O ₂	peroxide or peroxy-	Explosive. Extremely unstable. Very sensitive to heat and friction (possibly to contamination also). Prone to runaway polymerization if heated. Flammable. Oxidizing. Highly reactive with other chemicals. May be toxic. May be corrosive. Insoluble (floaters).

Hydrocarbon Derivatives Part 2

Type	Structure	Key to Formula	Common Names	Common Hazards and Other Behaviors
Nitros	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{N}}}$	NO ₂	nitro-	Explosive. Highly flammable. May be sensitive to shock or heat. Toxic. May be vasodilators. May or may not be water-soluble.
Amines	$\text{R}-\overset{\text{H(R)}}{\underset{\text{H(R)}}{\text{N}}}$	NH ₂	amine	Toxic. Flammable. Burn with yellow flame. May be corrosive. Water-soluble. Have characteristically foul odors.
Nitriles (Cyanides)	$\text{R}-\text{C}\equiv\text{N}$	CN	nitrile or cyanide	Toxic. Flammable. Burn with yellow flame and blue base. May be subject to polymerization. Water-soluble.
Carbamates	$\text{(R)H}-\overset{\text{O}}{\underset{\parallel}{\text{N}}}-\text{C}-\text{O}-\text{R}$	NH ₂ COO	carba-	Toxic (commonly used in pesticides, often in place of the more toxic organophosphate compounds). Combustible.
Amides	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\overset{\text{H(R)}}{\underset{\text{H(R)}}{\text{N}}}$	CONH ₂	-amide	Low to moderate toxicity. Flammable. May be subject to polymerization.
Thiols (Mercaptans)	$\text{R}-\text{S}-\text{H}$	SH	-thiol or mercaptan	Flammable. Toxic. Strong irritants. Have skunk-like odors.
Alkyl Halides (Halogenated Hydrocarbons)	$\text{R}-\text{X}$	F, Cl, Br, or I (a halogen versus a specific functional group)	-ide or -methane	Generally toxic. May be flammable. (Most do not burn. Some are used as extinguishing agents.) May break down at relatively low temperatures, giving off toxic decomposition products. Insoluble (sinks).
Organo-phosphates	$\text{R}-\text{P}$	P (double bonded to sulfur or oxygen)	varies	Toxic (often used in insecticides). May be mixed with flammable liquids for dissemination.
Hi-Tech Compounds	May vary greatly	B, Si, As, Be, Sn, or Ti	varies	May be reactive, pyrophoric, and/or toxic. May be flammable. Should be treated as very dangerous until proven otherwise.

Key to Chemical Symbols Above

As = Arsenic	Br = Bromine	F = Fluorine	N = Nitrogen	R = Hydrocarbon Radical	Sn = Tin
B = Boron	C = Carbon	H = Hydrogen	O = Oxygen	S = Sulfur	Ti = Titanium
Be = Beryllium	Cl = Chlorine	I = Iodine	P = Phosphorus	Si = Silicon	X = Alkyl Halide

Overview of Hydrocarbon Derivatives (continued)

One additional naming system bears mentioning at this point. The naming system isn't limited to hydrocarbon derivatives, but you'll see it more often over the next few pages. It's one used with *binary covalent compounds*, meaning those containing two nonmetal elements. It uses the prefixes below to indicate the number of each element present.

Common Prefixes for Binary Covalent Compounds

<u>Number of Atoms</u>	<u>Prefix</u>
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

Two familiar examples are carbon monoxide (CO) and carbon dioxide (CO₂). (The prefix *mono-* is rarely needed and is used only with the element oxygen.) Carbon tetrachloride (CCl₄) is another example, addressed later in this chapter.

Even though the naming system is designed for binary compounds, it is also used liberally with hydrocarbon derivatives containing more than two elements. Trichloromethane (CHCl₃), for instance, has three chlorine atoms joined to a hydrocarbon radical that started life as methane (CH₄). Conversely, dimethyl ketone (CH₃COCH₃) has two methyl radicals joined to a ketone (CO) functional group. You'll see illustrations of these compounds shortly.

A few very familiar compounds don't follow this naming system. The hydrocarbons identified earlier have their own system. Other significant examples include ammonia (NH₃) and water (H₂O).

Overview of Hydrocarbon Derivatives (continued)

Review Questions (answers on page 196)

- Hydrocarbon derivatives can be divided into two main groups based on the elements that comprise them. Part 1 hydrocarbon derivatives contain only:
 - Carbon and hydrogen
 - Carbon, hydrogen, and oxygen
 - Carbon, hydrogen, and nitrogen
 - Carbon, hydrogen, oxygen, and nitrogen
- What is it that the carbonyls all have in common?
 - A double bond between carbon atoms
 - A double bond between carbon and oxygen atoms
 - The presence of nitrogen in their structures
 - The OH functional group they contain
- What part of the hydrocarbon derivative formula C_2H_5OH represents the functional group?
 - C_2H_5
 - H_5O
 - H_5OH
 - OH
- What part of the formula CH_3CN represents the hydrocarbon radical?
 - CH_3
 - CN
 - H_3
 - N
- Which of the following statements is most correct regarding the hydrocarbon derivative hazards identified in this chapter?
 - The hazards identified for each type of hydrocarbon derivative apply to every member of the group.
 - The hazards identified for each type of hydrocarbon derivative apply to most members of the group.
 - The hazards identified are common hazards for some of the worst chemicals in each hydrocarbon derivative category.
 - The hazards identified are those that apply to the most commonly manufactured chemicals in each hydrocarbon derivative category.
- Carbon tetrachloride has ____ chlorine atoms.
 - 1
 - 2
 - 3
 - 4

Chapter 6

Hazmat Chemistry and the DOT Hazard Classes

Responders are generally more accustomed to viewing hazardous materials according to their DOT classifications than by any other way. So this chapter looks at each of the DOT hazard classes, providing the following information:

- A brief description of the hazard class.
- The divisions each class consists of.
- A look at the relation between the hazard class and what you've learned so far about hazmat chemistry. This section draws some correlation to what was presented earlier about elements, salts, hydrocarbons, and hydrocarbon derivatives so that you can see how what you learned about chemical composition and behavior relates to hazard classification.
- Other important concepts relative to the hazard class.

Keep in mind that hazardous materials are put into hazard classes based on their primary hazards (or in the case of gases, based on their physical form in their natural state). However, many materials have multiple hazards, and those secondary hazards can often be significant.

Class 3 - Flammable and Combustible Liquids

Divisions in This Hazard Class

Class 3 consists of flammable and combustible liquids. The distinction between the two is in their flash points. The U.S. Department of Transportation uses a cutoff of 140°F (60°C), which comes from the hazardous materials regulations sponsored by the United Nations for international transportation.

- **Flammable liquids** (e.g., gasoline, acetone, and toluene) are generally defined as those with flash points not more than 140°F (60°C).
- **Combustible liquids** (e.g., fuel oil, mineral oil, and peanut oil) are those that do not meet the definition of any other hazard class and have flash points above 140°F (60°C) but below 200°F (93.3°C).

In contrast, the National Fire Protection Association (NFPA) and the Occupational Safety and Health Administration (OSHA) define a flammable liquid as one whose flash point does not exceed 100°F (37.8°C) and a combustible liquid as one whose flash point is 100°F (37.8°C) or higher. The table below provides additional details.

Flammable Versus Combustible Liquids Per NFPA 30 (Not the Same as DOT Definitions)

Class	Flash Point	Boiling Point
1A (Flammable)	< 73°F (22.8°C)	< 100°F (37.8°C)
1B (Flammable)	< 73°F (22.8°C)	≥ 100°F (37.8°C)
1C (Flammable)	≥ 73°F (22.8°C) but < 100°F (37.8°C)	—
II (Combustible)	≥ 100°F (37.8°C) but < 140°F (60°C)	—
IIIA (Combustible)	≥ 140°F (60°C) but < 200°F (93.3°C)	—
IIIB (Combustible)	≥ 200°F (93.3°C)	—

Another way to think of it is that flammable liquids can ignite easily at ambient temperatures, whereas combustible liquids must be heated first. This is not a precise definition, but it's a handy approximation for field use.

Note: You may also encounter the word *inflammable*. It's a very confusing term because the prefix *in-* is often used to mean "not," as in *inorganic* (not organic), *inaccessible* (not accessible), and *incomplete* (not complete). However, *inflammable* means the same thing as *flammable*. It does not mean nonflammable.

Although flammability is the primary hazard associated with these materials, most have multiple hazards (e.g., toxicity, corrosivity, or water-reactivity). Responders must take these other hazards into consideration when assessing the risk and determining a plan of action.

Relation to What You Already Learned About Chemistry

The materials in Class 3 come from many different areas. The following are examples:

- Simple hydrocarbons (e.g., pentane, octane, hexene, isooctene)
- Aromatic hydrocarbons (e.g., benzene, toluene, xylene)
- Ketones (e.g., acetone, methyl ethyl ketone)
- Aldehydes (e.g., acetaldehyde, paraldehyde)
- Esters (e.g., methyl acrylate, vinyl acetate)
- Alcohols (e.g., methyl alcohol, ethyl alcohol, isopropyl alcohol)
- Amines (e.g., butylamine, isopropyl amine)
- Nitriles (e.g., acetonitrile, isobutyl nitrile)
- Ethers (e.g., vinyl ethyl ether, methyl tert-butyl ether)
- Some alkyl halides (e.g., isobutyl chloride, propylene dichloride), although most are nonflammable

Class 3 also contains many mixtures, which we didn't explore in the chemistry section. Common examples include gasoline, kerosene, diesel, and other fuel oils.



Class 3 - Flammable and Combustible Liquids (continued)

You may recall from Chapter 5 that all hydrocarbons are floaters, meaning they are insoluble in water and have a specific gravity of less than 1. Chapter 5 also provided water-solubility information on most of the hydrocarbon derivatives. For example, the ketones, aldehydes, esters, alcohols, amines, and nitriles are generally water-soluble. Solubility is affected somewhat by molecular size, however. So even within these groups, the larger the molecule, the less soluble it is. Ethers are insoluble floaters. Alkyl halides are insoluble sinkers.

Water solubility is important when determining how to fight a fire or control vapor production. With flammable liquids that float on water, it will be necessary to use foam to smother a fire and retard vapor production. With liquids that sink in water, vapor production can be suppressed using light applications of water. Water-soluble (miscible) liquids, can be managed either by diluting the product to reduce vapor production so that vapors are no longer within the flammable range or by smothering the fire with an alcohol-type concentrate (ATC) foam.

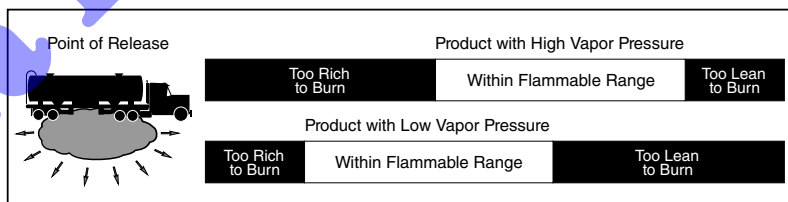
Review of Flammability Factors Presented Earlier

The following is a quick recap of some of the definitions presented in Chapter 2. For more complete information, review pages 24 through 26.

- **Flash point** is the minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air. Flash point is generally considered to be the most important property in assessing the hazards of flammable and combustible liquids.
- **Fire point** is the temperature at which enough vapors are given off to support continuous burning even after the source of ignition has been removed.
- The **ignition (autoignition) temperature** of a substance is the minimum temperature required to cause self-sustained combustion independent of an ignition source.
- **Boiling point** is the temperature at which the vapor pressure at the surface of the liquid is equal to or slightly greater than the atmospheric pressure. It's the point of maximum vapor production.
- **Flammable (explosive) range** is the percentage of vapor in air within which ignition is possible. Below the **lower explosive limit (LEL)**, the vapors are too lean to burn, whereas above the **upper explosive limit (UEL)**, the vapors are too rich to burn.
- **Vapor pressure** is the force exerted by the vapors of a product against the atmosphere or the sides of a container.
- **Vapor content** is a reflection of how much vapor is produced by the product.

Page 26 demonstrated the relation between vapor pressure and flammable range. In general, flammable liquids with low vapor pressures present a greater risk closer to the source, whereas those with higher vapor pressures present a risk of ignition at greater distances.

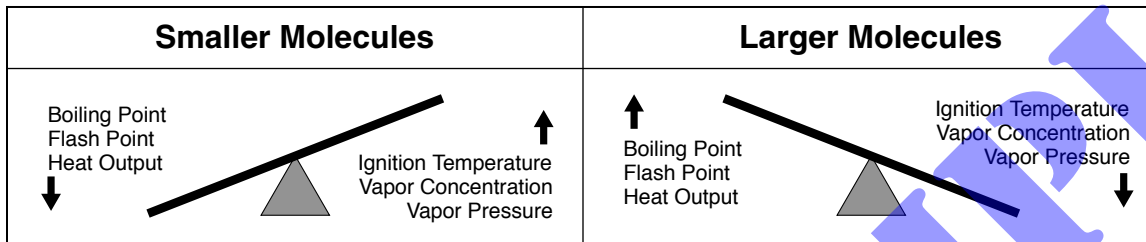
The Effect of Vapor Pressure on the Distance at Which the Flammable Range Is Found



Class 3 - Flammable and Combustible Liquids (continued)

Pages 105 and 106 identified how many chemical and physical properties are directly or indirectly proportional to one another and how these properties are related to molecular size.

Proportional Relation Between Various Properties of Flammable Liquids



Other Important Concepts

Some fuels within this hazard class (such as crude oil) present an added danger of boilover, frothover, or slopover.

- If an open-topped tank of crude oil is burning, there is a danger of a violent **boilover** caused by steam expansion beneath the hot oil. This requires a combination of the right conditions: a fuel with a wide range of boiling points, the roof being off, and water at the bottom of the tank. It generally takes a few hours to develop. However, boilovers are extremely dangerous, and the risk should not be underestimated. There are documented incidents where numerous lives have been lost.
- **Frothover** is similar to boilover in that it also involves steam expansion beneath a hot product, which forces the product out of the tank. However, the product isn't burning. Rather, a product already at elevated temperatures is added to a tank that has residual water in it.
- When a water stream is applied to the hot surface of burning oil, it causes the water to boil, which in turn ejects some the oil. This is called **slopover**. This is relatively mild compared to a boilover, but can be dangerous nonetheless.

Class 3 - Flammable and Combustible Liquids (continued)

Review Questions (answers on page 197)

1. The DOT generally defines flammable liquids as having flash points less than or equal to:
 - a. 100°F (37.8°C)
 - b. 135°F (57.2°C)
 - c. 140°F (60°C)
 - d. 212°F (100°C)
2. NFPA and OSHA put the line of demarcation between flammable and combustible liquids at:
 - a. 100°F (37.8°C)
 - b. 135°F (57.2°C)
 - c. 140°F (60°C)
 - d. 212°F (100°C)
3. Which is generally considered to be the most important property in assessing the hazardous of flammable and combustible liquids?
 - a. Boiling point
 - b. Flash point
 - c. Ignition temperature
 - d. Vapor pressure
4. Of the following groups, which is most likely to contain flammable liquids that float on water?
 - a. Alcohols
 - b. Ketones
 - c. Alkyl halides
 - d. Straight-chain and aromatic hydrocarbons
5. Of the following groups, which is most likely to contain flammable liquids that are miscible in water?
 - a. Ethers
 - b. Alcohols
 - c. Alkyl halides
 - d. Hydrocarbons
6. Boilover involves:
 - a. Steam expansion beneath burning crude oil in an open-topped tank
 - b. Steam expansion beneath a product at elevated temperatures added to a tank that has residual water in it
 - c. Water applied to the hot surface of burning oil, causing the water to boil and ejecting some of the oil
 - d. Catastrophic bubbling over of burning crude oil within an open-topped tank
7. Inflammable means:
 - a. Flammable
 - b. Nonflammable

Chapter 8
Answers to the
Review
Questions

This chapter provides answers to the review questions throughout the book.

Answers to the Review Questions

Vapor Pressure and Vapor Density (page 23)

1. b
2. c
3. c
4. d
5. c
6. b
7. a
8. b

Flammability Factors (pages 27-28)

1. c
2. a
3. d
4. a
5. c
6. b
7. b
8. a
9. b
10. a
11. a
12. b
13. a
14. b

Water Behavior (page 31)

1. b
2. d
3. c
4. a
5. a
6. c
7. d

Physical and Chemical Change (page 36)

1. a
2. b
3. d
4. d
5. b
6. a
7. a
8. a
9. b

Toxicity and Risk (page 39)

1. a
2. b
3. c
4. b
5. a

Toxicological Values and Exposure Limits (page 45)

1. e
2. c
3. b
4. a
5. d
6. a
7. a
8. b

Chapter 2 Review (pages 46-48)

1. b
2. a
3. d
4. b
5. a
6. a
7. b
8. b
9. d
10. a
11. a
12. c
13. a
14. b
15. b
16. d
17. a
18. a
19. d
20. d

Matter (page 53)

1. a
2. c
3. c
4. d
5. b
6. c
7. b
8. c

The Periodic Table (pages 60-61)

1. b
2. c
3. d
4. a
5. a
6. b
7. c
8. c
9. a
10. a. Sodium
b. Carbon
c. Magnesium
d. Phosphorus
e. Chlorine
f. Fluorine
g. Potassium
h. Helium
i. Hydrogen
j. Oxygen
11. a. N
b. Ca
c. S
d. I
e. Na
f. Li
g. Br
h. K
i. Al
j. Pb
12. a. M
b. NM
c. NM
d. M
e. NM
f. M
g. NM
h. NM
i. M
j. NM
k. M
l. NM

Answers to the Review Questions (continued)

The Periodic Table (pages 60-61)

13. a. VII
b. I
c. VIII
d. VII
e. II
f. I
g. VIII
h. VII
i. II
j. I
k. VII
l. VIII
14. c (Group VII)
a (Group I)
d (Group VIII)
b (Group II)

Atomic Structure (page 65)

1. c
2. c
3. a
4. b
5. c
6. a
7. d
8. a

Chemical Bonding (pages 71-72)

1. c
2. b
3. a
4. b
5. c
6. d
7. b
8. d
9. a
10. c
11. b
12. b
13. c
14. d
15. a
16. c

Chapter 3 Review (pages 75-77)

1. d
2. c
3. a
4. b
5. b
6. a
7. d
8. a
9. a
10. c
11. d
12. a
13. c
14. a
15. d
16. d
17. a
18. b

Introduction to Salts (page 83)

1. c
2. b
3. a
4. a
5. c
6. b
7. a
8. b
9. c

Types of Salts (page 88)

1. b
2. a
3. c
4. a
5. d
6. c
7. d
8. b

Polyatomic Ions and Multiple Oxidation States (page 91)

1. d
2. c
3. a
4. c
5. a
6. b

Chapter 4 Review (pages 92-94)

1. c
2. a
3. b
4. d
5. b
6. c
7. a
8. d
9. b
10. b
11. a
12. b
13. a
14. c
15. b
16. d
17. a
18. b
19. c
20. a
21. d
22. d

The Four Types of Hydrocarbons (page 98)

1. c
2. b
3. d
4. a
5. c
6. d
7. a

Answers to the Review Questions (continued)

Hydrocarbon Names and Formulas (pages 103-104)

- | | |
|----------|-----------------|
| 1. Meth- | 1 carbon atom |
| Eth- | 2 carbon atoms |
| Prop- | 3 carbon atoms |
| But- | 4 carbon atoms |
| Pent- | 5 carbon atoms |
| Hex- | 6 carbon atoms |
| Hept- | 7 carbon atoms |
| Oct- | 8 carbon atoms |
| Non- | 9 carbon atoms |
| Dec- | 10 carbon atoms |

2. b
3. b
4. a
5. b
6. a
7. c
8. d
9. b
10. a
11. d

The Effect of Molecular Size (page 107)

1. a
2. c
3. d
4. c
5. d
6. a

Hydrocarbon Radicals (page 109)

1. b
2. b
3. c
4. a
5. c
6. d
7. b
8. c

Overview of Hydrocarbon Derivatives (page 113)

1. b
2. b
3. d
4. a
5. c
6. d

Part 1 Hydrocarbon Derivatives Carbonyls (pages 118-119)

1. a
2. c
3. d
4. b
5. a
6. b
7. d
8. c
9. c
10. b
11. a
12. b

Other Part 1 Hydrocarbon Derivatives (pages 123-124)

1. c
2. b
3. d
4. a
5. b
6. a
7. a
8. d
9. b

Part 2 Hydrocarbon Derivatives—Nitrogen Based (pages 128-129)

1. b
2. a
3. c
4. d
5. a
6. d
7. a
8. d
9. c
10. b

Other Part 2 Hydrocarbon Derivatives (pages 133-134)

1. c
2. b
3. a
4. a
5. d
6. a
7. c
8. a
9. d
10. c
11. a

Chapter 5 Review (pages 135-137)

1. a
2. c
3. d
4. a
5. b
6. b
7. d
8. b
9. b
10. c
11. b
12. d
13. a
14. d
15. b
16. c
17. c
18. b
19. d
20. a
21. d
22. b
23. a

Class 1 - Explosives (page 143)

1. d
2. b
3. b
4. c
5. b
6. c
7. a
8. a

Answers to the Review Questions (continued)

Class 2 - Gases (page 147)

1. b
2. a
3. d
4. c
5. d
6. b
7. c
8. b

Class 3 - Flammable and Combustible Liquids (page 151)

1. c
2. a
3. b
4. d
5. b
6. a
7. a

Class 4 - Flammable Solids, etc. (page 154)

1. b
2. a
3. c
4. a
5. a

Class 5 - Oxidizers and Organic Peroxides (page 158)

1. c
2. b
3. d
4. b
5. d
6. b
7. a
8. c

Class 6 - Poisonous and Infectious Substances (page 162)

1. b
2. a
3. c
4. a
5. b
6. d

Class 7 - Radioactive Materials (Page 169)

1. b
2. a
3. b
4. d
5. d
6. b
7. c
8. c

Class 8 - Corrosive Materials (pages 173-174)

1. a
2. b
3. c
4. c
5. b
6. b
7. a
8. b
9. d
10. d
11. b
12. c

Chapter 6 Review (pages 176-179)

1. d
2. d
3. a
4. a
5. c
6. a
7. b
8. a
9. a
10. a
11. b
12. c
13. d
14. b
15. c
16. d
17. d
18. d
19. b
20. b
21. b
22. c
23. a
24. b

Chapter 6 Review (pages 176-179)

25. c
26. a
27. a
28. b
29. c

Fire Chemistry (page 185)

1. a
2. d
3. d
4. a
5. b
6. a
7. d
8. d

Chemical Reactions/Incompatibility (page 190)

1. c
2. d
3. b
4. b
5. a
6. c
7. d
8. b

Chapter 7 Review (page 191)

1. a
2. c
3. c
4. d
5. a
6. d
7. c

Index

A

Abbreviations 200–201
 About the author 208
 Acetylcholinesterase inhibitors 160
 Acid-base reactions 188
 Acids 170–174
 Organic acids 117
 Acknowledgments 7
 Acronyms 200–201
 Active ingredient in pesticides 160
 Acute exposure guideline levels (AEGL) 43, 44
 Acute exposures 37
 Adiabatic compression 146
 Adiabatic decompression 146
 AEGL 43, 44
 Air-reactive chemicals 33, 152, 186
 ALARA principle 166
 Alcohols 111, 120, 148
 Aldehydes 111, 114, 116, 148
 Alkali metals 57, 69
 Alkaline earths 57, 69
 Alkalis. *See* Bases
 Alkanes 96–98, 99–104
 Alkenes 96–98, 99–104
 Alkyl halides (halogenated hydrocarbons)
 111, 130–131, 148, 159
 Alkynes 96, 99–104
 Alpha particles 164, 167
 Amides 111, 127
 Amines 111, 125–126, 148, 159
 Anhydride 172
 Anions 66
 Answers to review questions 194–197
 Aromatic hydrocarbons 96, 99–104, 148
 Atmospheric displacement 14, 40
 Atomic number 62
 Atomic structure 62–65
 Atomic weight 62

B

Backdraft 184
 Bacteria 159
 Balancing chemical equations 188–189
 Base states of oxyradicals 86–87
 Bases 170–174
 Becquerel (Bq) 167
 Beta particles 164, 167
 Bibliography 202
 Binary oxide salts. *See* Metal oxide salts
 Binary salts 84, 89, 152. *See also* Salts
 Blasting agents 140
 BLEVE 145
 Blister agents 161
 Boiling point 20, 25, 105, 149
 Boilover 150
 Bonding 66–72. *See also* Chemical bonding
 Bonding sites 69–70

Boosters 142
 Boyle's Law 145
 Branched hydrocarbon 97, 101

C

Carbamates 111, 127
 Carbonyls 110, 114–119
 Carcinogens 37
 Catalysts 34, 156
 Cations 66
 Caustics. *See* Bases
 Ceiling exposure limit (TLV-C) 41, 44
 Chapter 1 review 46–48
 Chapter 2 review 75–77
 Chapter 3 review 92–94
 Chapter 4 review 135–137
 Chapter 5 review 176–179
 Chapter 6 review 191
 Characteristics of hydrocarbons 96
 Charles' Law 145
 Chemical and physical change 32–36
 Chemical bonding 66–72
 Bonding sites 69–70
 Covalent bonds 67
 Double (pi) bonds 96, 102
 Hydrocarbons 96
 Ionic bonds 66, 80
 Octet/duet rule 66, 144
 Resonant bonds 68, 96
 Single bonds 96
 Triple bonds 96
 Chemical chain reaction 182
 Chemical compatibility charts 186
 Chemical explosions 141
 Chemical incompatibility 35, 186–190
 Chemical reactions (types of) 187–189
 Chemical reactivity 33
 Chemical structures 69
 Chemical warfare agents 160–161
 Chronic exposures 37
 Combustible liquids 24–28, 148–151
 Combustion 183
 Combustion reactions 187
 Complete combustion 183, 188
 Complex ions 89–91
 Compounds (defined) 50
 Compounds and elements 49–77
 Compressed gases 145–146
 Concepts versus chemicals 12, 15–17
 Condensation 32
 Condensed structural formulas 70
 Confined spaces and LEL 26
 Contamination 38, 165
 Corrosives 170–174
 Concentration 172
 Neutralization of 172, 186
 Strength 172
 Corrosivity 170

Index (continued)

Covalent bonds 67
Critical pressure 146
Critical temperature 146
Cryogenic liquids 57, 146
Curie (Ci) 167
Cyclo compounds 101

D

Dangerous when wet materials 152–154
Decomposition products 183
Decomposition reactions 187
Dedication 8
Deflagration 142
Deposition 32
Detonation 142
Diatomic gases 12, 68, 144
Dispelling test anxiety 10–14
Dose-response curve 41
DOT hazard classes 139–179
 Class 1 - Explosives 140–143
 Class 2 - Gases 144–147
 Class 3 - Flammable and combustible liquids 148–151
 Class 4 - Flammable solids, etc. 152–154
 Class 5 - Oxidizers and organic peroxides 155–158
 Class 6 - Poisonous and infectious substances 159–162
 Class 7 - Radioactive materials 163–169
 Class 8 - Corrosive materials 170–174
 Class 9 - Miscellaneous hazardous materials 175
Double replacement reactions 187
Duet rule 66

E

Effect of molecular size 15, 105–107, 150
Electrical charges of polyatomic ions 90
Electrons 62–63, 66–69
Elements 50, 54, 62
 Dieter's top 13 metals 59
 Dieter's top 13 nonmetals 58
 Most common 58
Elements and compounds 49–77
Emergency response planning guideline (ERPG) 43, 44
Endothermic reactions 187
Energy 33, 68
ERPG 43, 44
Esters 111, 114, 117, 148
Ethers 111, 121, 148
Exothermic reactions 34, 187
Expansion ratio 10, 146
Explosions, types of 141
Explosives 11, 140–143

Explosophores 141
Exposure 38, 165
Exposure limits 40–45
 radiation 166

F

Fire chemistry 182–185
Fire extinguishment 30, 34, 149, 153, 182
Fire point 24, 149
Fire tetrahedron 182
Fire triangle 182
Fissile materials 164
Flammability factors 24–28, 149
 Boiling point 25, 106, 149
 Fire point 24, 149
 Flammable (explosive) range 25, 149
 Flash point 24, 105, 148, 149
 Ignition (autoignition) temperature 24, 105, 149, 184
 Lower explosive limit (LEL) 25, 149
 Spontaneous combustion 24
 Upper explosive limit (UEL) 25, 149
 Vapor pressure 20–21, 25, 26, 105, 149
Flammable (explosive) range 25, 149
Flammable liquids 24–28, 148–151
Flammable solids 152–154
Flashover 184
Flash point 24, 105, 148, 149
Foam 30
Freezing 32
Freezing point 32
Free radicals 182–183
Frothover 150
Fuel rods 164

G

Gamma radiation 164, 167
Gases 32, 56, 144–147
 Adiabatic compression 146
 Adiabatic decompression 146
 Compressed gases 145–146
 Critical pressure 146
 Critical temperature 146
 Cryogenic liquids 57, 146
 Diatomic gases 12, 68, 144
 Expansion ratio 10, 146
 Liquefied compressed gases 146
 Noble gases 57, 66, 69, 144
 Vapor density 22
Gas laws 145
Glycerol 111, 121
Glycols 111, 120
Gray (Gy) 167

Index (continued)

H

Half-life 165
 Halogenated hydrocarbons (alkyl halides) 111, 130–131, 159
 Halogens 57, 69, 130–131
 Hazardous decomposition products 183
 Hazard ladder 44
 Hazard zone 144, 159
 Hi-tech compounds 111, 132
 High explosives 142
 Hydrocarbons and related compounds 95
 Alkanes 96–98, 99–100
 Alkenes 96–98, 99–100
 Alkynes 96–98, 99–100
 Aromatic hydrocarbons 96–98, 99–100, 100, 148
 Branched hydrocarbon 97, 101
 Characteristics of hydrocarbons 96
 Effect of molecular size 15, 105–107, 150
 Functional group (defined) 110
 Hydrocarbon derivatives 16–17, 52, 152, 159
 Alcohols 111, 120, 148
 Aldehydes 111, 114, 116, 148
 Alkyl halides (halogenated hydrocarbons) 111, 130–131, 148, 159
 Amides 111, 127
 Amines 111, 125–126, 148, 159
 Carbamates 111, 127
 Carbonyls 110, 114–119
 Cyanides. *See* Nitriles
 Esters 111, 114, 117, 148
 Ethers 111, 121, 148
 Glycerol 111, 121
 Glycols 111, 120
 Halogenated hydrocarbons (alkyl halides) 111, 130–131, 148, 159
 Hi-tech compounds 111, 132
 Ketones 111, 114, 115, 148
 Mercaptans (thiols) 111, 130
 Nitriles (cyanides) 111, 126, 148, 159
 Nitros 111, 125, 141
 Organic acids 111, 114, 117, 171
 Organic peroxides 111, 122, 184
 Organophosphates 111, 130, 159
 Overview 110–113
 Part 1 - Carbonyls 114–119
 Part 1 - Others 120–124
 Part 2 - Nitrogen Based 125–129
 Part 2 - Others 130–134
 Thiols (mercaptans) 111, 130
 Hydrocarbon radicals 108–109, 110
 Molecular size 15, 105–107, 150
 Naming hydrocarbons 99–104
 Saturated hydrocarbons 97
 Straight-chain hydrocarbon 97, 101
 Unsaturated hydrocarbons 97

Hydrocarbon derivatives. *See* Hydrocarbons and related compounds
 Hydrocarbon formulas 99–104

I

Ideal Gas Law 145
 IDLH 42–44
 Ignition (autoignition) temperature 24, 105, 149, 184
 Immediately dangerous to life and health (IDLH) 42–44
 Incompatibility 35, 186–190
 Incomplete combustion 183, 188
 Inert ingredient 160
 Infectious substances 159
 Inflammable 25, 148
 Inhibitors 34
 Inorganic acids 171
 Inorganic compounds 52
 Inverse Square Law 167–168
 Ionic bonds 66, 80
 Ionizing radiation 164
 Ions 66, 89–91
 Irritants 161
 Isomers 73–74
 Isotopes 63

K

Ketones 111, 114, 115, 148

L

Lethal concentration (LC) 42, 44, 144, 159
 Lethal dose (LD) 42, 44
 Level of concern (LOC) 42–44
 Liquefied compressed gases 146
 Liquids 32, 56
 Local effects of hazmat exposures 37
 Low explosives 142
 Low-level waste 164
 Lower explosive limit (LEL) 25–26, 149

M

Matter 50–53
 Maximum safe storage temperature (MSST) 122, 157
 Mechanical explosions 141
 Melting 32
 Melting point 32
 Mercaptans (thiols) 111, 130
 Metal cyanide salts 85, 159. *See also* Salts
 Metal hydroxide salts 85. *See also* Salts
 Metal oxide salts 85. *See also* Salts
 Metal oxysalts 86–88, 89–91, 171. *See also* Salts
 Metal peroxide salts 86. *See also* Salts
 Metalloids 51

Index (continued)

Metals 51, 54, 66, 141, 159

Alkali metals 57, 69

Alkaline earths 57, 69

Combustible 34, 152–153

in Salts 79–94

Transition metals 56, 90

Milligrams per cubic meter (mg/m³) 40

Milligrams per kilogram (mg/kg) 40

Miscibility 29–30

Mixtures 6, 50, 148

Molecular formulas 70

Molecular size 15, 105–107, 150

Monomers 34

Mutagens 37

N

Nerve agents 160

Neutralization 172, 186

Neutralization reactions 188

Neutron particles 164

Neutrons 62

NFPA 472 10

Nitriles (cyanides) 111, 126, 148, 159

Nitros 111, 125, 141

Noble gases 57, 66, 69, 144

Nonmetals 51, 54, 66, 67

in Salts 79–94

Nonsalts 15–16, 51, 67

Nuclear explosions 141

Nucleus 62

O

Octet/duet rule 66, 144

Octet rule 66

Odor threshold 44

Organic acids 111, 114, 117, 171

Organic compounds 52

Organic peroxides 11, 111, 122, 155–158, 184

Organophosphates 111, 130, 159, 160

Outer (outermost) shell electrons 63–64

Oxidation 184

Oxidation-reduction reaction 155

Oxidation states 90

Oxidizers 57, 86, 155–158, 182

Oxidizing agent 155, 182

Oxygen-deficient atmosphere 183–184

Oxygen displacement 14, 40

Oxygen-enriched atmosphere 183–184

Oxyradicals 86–88

Base states 86–88

Electrical charges 90

Polyatomic ions 89

P

PAC 43

Parts per billion (ppb) 40

Parts per million (ppm) 40

PEL 41, 44

Periodic table 54–61, 63

Families 57, 69

Trends 54

Permissible exposure limits (PEL) 41, 44

Pesticide signal words 159

Pesticides 159–160

Organophosphates 160

pH 170, 172

pH scale 170, 172

Physical and chemical change 32–36

Physical state 56

Plasma 33

Poisonous substances 159–162

Poison inhalation zone (PIH) 144

Polarity 29, 69

Polyatomic ions 89–91

Polymerization 13, 34, 96, 122, 156

Polymers 34

Preparing for a hazmat chemistry exam 9–17

Primary explosives 142

Products of combustion 182–183

Protective action criteria (PAC) 43

Protons 62

psi, psia, and psig 145

Pure substance 50

Pyrolysis 153

Pyrophoric materials 152

R

Rad 167

Radiation exposure

ALARA Principle 166

Average annual dose 165

Exposure limits 166

Inverse Square Law 167

Partial-body exposure 166

Radiation measurement 167

Radiation sickness 166

Time, distance, and shielding 167–168

Whole-body exposures 166

Radiation sickness 166

Radioactive elements 63, 163

Radioactive materials 163–169

Alpha particles 164, 167

Beta particles 164, 167

Contamination 165

Exposure 165

Fuel rods 164

Gamma rays 164, 167

Half-life 165

Inverse Square Law 167

Ionizing radiation 164

Isotopes 63

Low-level waste 164

Neutron particles 164

Special nuclear materials 164

Spent fuel 164

Index (continued)

Time, distance, and shielding 167–168
 Transportation index (TI) 163
 X-rays 164
 Rare earth elements 56
 Recommended exposure limits (REL) 41, 44
 Redox reactions 188
 Reducing agent 155, 182
 REL 41, 44
 Rem 167
 Representative elements 56
 Resonant bonds 68, 96
 Review questions answers 194–197
 Rickettsiae 159
 Riot control agents 161
 Risk factors (toxicological) 38
 Roentgen (R) 167
 Routes of entry / exposure 37

S

Salts 15–16, 51, 67, 79–94, 156, 171
 Binary salts 84, 89, 152
 Composition 84
 General precautions 80
 Introduction 80–83
 Metal cyanide salts 85, 159
 Metal hydroxide salts 85
 Metal oxide salts 85, 171
 Metal oxysalts 81, 86–88, 89–91, 171
 Base states 86–88
 Metal peroxide salts 86
 Naming 81
 Overview chart 80
 Oxyradicals 86–88
 Types 84–88
 Saturated hydrocarbons 97
 Secondary explosives 142
 Self-accelerating decomposition temperature (SADT) 122, 157
 Shells 62–63, 66–69
 Shielding 167–168
 Short-term exposure limit (STEL) 41, 44
 Sievert (Sv) 167
 Single replacement reactions 187
 Slopover 150
 Solids 32, 56
 Solubility 29–30, 149
 Solute 30
 Solvent 30
 Special nuclear materials 164
 Specific gravity 29–30, 54
 Spent fuel 164
 Spontaneous combustion 24, 184
 Spontaneously combustible materials 152–154
 Standard temperature and pressure (STP) 145
 STEL 41, 44
 Straight-chain hydrocarbon 97, 101
 Structural formulas 70
 Sublimation 32

Supercritical fluids 33
 Surface-area-to-mass ratio 152
 Surface burning 153
 Synergistic effect 37
 Synthesis reactions 187
 Systemic effects of hazmat exposures 37

T

Table of contents 3–4
 TEEL 43, 44
 Temperature, effects of 21, 24–25, 32, 56, 145, 157
 Temporary emergency exposure limits (TEEL) 43, 44
 Teratogens 37
 Terms and definitions 19–46
 Test anxiety 10–14
 Thiols (mercaptans) 111, 130
 Threshold Limit Value-Ceiling (TLV-C) 41, 44
 Threshold Limit Value (TLV-TWA) 41–44
 Time, distance, and shielding 167–168
 TLV-C 41, 44
 TLV-TWA 41–44, 44
 Toxic inhalation zone (TIH) 144
 Toxicity and risk 37–39
 Toxicological risk factors 38
 Toxicological values and exposure limits 40–45
 Toxins 159
 Transition metals 56, 90
 Transportation index (TI) 163
 Types of hydrocarbons 96

U

Units of measure 40
 Unsaturated hydrocarbons 97
 Upper explosive limit (UEL) 25, 26, 149

V

Vaporization 32
 Vapor content 105, 149
 Vapor density 22, 54
 Vapor pressure 20–21, 25, 26, 105, 149
 Vesicants 161
 Viruses 159
 Volatility 21

W

Water behavior 29–31
 Water-reactive chemicals 57, 152, 186
 Salts 79–94
 Water reactivity 33
 Workplace environmental exposure limits 41

X

X-rays 164