

Hazmat Chemistry Study Guide

— Second Edition —



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Firebelle Productions**

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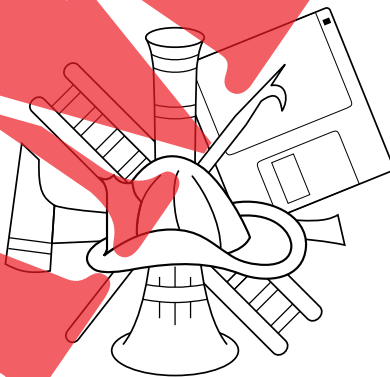
Hazmat Chemistry Study Guide

— Second Edition —

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How Much Chemistry Do You Need to Know?

A lot of students who go through hazardous materials technician training are not fond of chemistry. They view the chemistry class as a necessary (or perhaps unnecessary) evil. They question why they must work so hard to learn information with a half-life of forty hours—information that remains tangible to them (assuming it ever became tangible to begin with) just long enough to pass the final exam on Friday. They argue that chemistry training shouldn't be necessary when responders are repeatedly told to use at least three reference sources at a hazmat incident. So let's look first at why chemistry is important to the hazmat responder, then answer the question of what you need to know to pass the final exam.

What Do You Need to Know at an Incident?

Having a basic knowledge of chemistry helps you understand how chemicals behave and what they are likely to do. This understanding is important for several reasons:

- It gives you something to fall back on when your reference sources aren't immediately available. As a firefighter, I naturally think about the firefighter working an overtime shift on an engine company instead of his or her normal assignment on the hazmat unit. He or she can begin predicting hazards and making appropriate decisions about personal protection without having to wait for reference books to arrive. However, regardless of what agency you work for, you might also be caught in a position where you're without your normal reference sources. You could even find yourself first on scene of a transportation accident while driving around town off duty.
- It helps you understand and interpret the information you find when looking through your reference sources. Clearly, this is important anytime you're trying to assess the hazards and determine a plan of action. However, there will be times when the information you find in reference sources either is misleading or fails to provide the big picture. For example, anhydrous ammonia is placarded as a nonflammable gas, but if you know it has a flammable range of 16% to 25%, you'll realize that it can indeed ignite under the right conditions. The nerve agent sarin is described as being "volatile" and, in fact, is the most volatile of the nerve agents. But with a vapor pressure of only 2.1 mmHg at 68°F (20°C), the liquid is relatively slow to vaporize. (Water, with its vapor pressure of 17.5 mmHg, will evaporate eight times faster.)
- It helps you recognize errors. Yes, the reference books and material safety data sheets we depend on for our safety do sometimes contain errors. Having an understanding of chemistry helps you recognize when something doesn't look right.
- It helps you make judgment calls when reference sources disagree. Different reference sources sometimes have conflicting information. Usually the differences are minor and can be attributed to variations in testing procedures. For example, when different sources list different flash points, it may be because one used data from open-cup testing whereas the other used data from closed-cup testing. However, when the differences are more significant, you're in a better position to interpret the information if you have some background in chemistry.
- It will help you identify what you're dealing with when faced with an unknown hazardous material. Later in your training, you will learn how to do atmospheric monitoring and field identification testing either to identify an unknown chemical or to confirm that a chemical is indeed what a label, placard, MSDS, shipping document, or reporting party indicates it is. Understanding chemistry will enable you interpret test results with more confidence.

What Do You Need to Know to Pass Your Final Exam?

So how much chemistry do you really need to know to pass the final exam? Fortunately, no one expects you to become a chemistry major after only forty hours of training, but you do need to have a good grasp on the basic concepts presented in class. This study guide was written to help you accomplish that. As a result, it focuses on concepts more so than chemicals. The reference to actual hazardous materials is limited to that which is necessary to understand the concepts. So as you go through this study guide (and even as you go through your class), concentrate on recognizing names and formulas and the types of hazardous materials they are associated with. Concentrate on the common characteristics and hazards associated with the different types of materials. When you're able to process information this way, it's much more manageable than trying to memorize the myriad of individual chemicals you'll hear about in your training.

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How Much Chemistry Do You Need to Know? (continued)

Review questions are provided throughout the book to help you test your understanding. The majority are multiple choice, similar to what you can expect to find on the final exam. Some are true/false or short fill-in. The questions provided mid-chapter are mostly recall or recognition questions like the example below. Some questions may require you to look at a periodic table. Others you should be able to answer from memory. The list of potential answers may include things you have not yet encountered, but will always include something familiar. For instance, the question below might be presented in a chapter where you've been introduced to methane (CH_4) but not yet to the other formulas.

Example 1: The formula for methane is:

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

Some of the questions at the end of each chapter may be more complex, requiring you to apply two or more concepts to come up with the right answer. The example below requires you to know how many carbon atoms each compound contains, which you can identify by looking at the prefixes (*but-*, *meth-*, *oct-*, and *pent-*). It also requires you to know that larger molecules have higher flash points. If you know both those things, you can correctly choose octane (c) as your answer.

Example 2: Which of the following has the highest flash point?

- a. Butane
- b. Methane
- c. Octane
- d. Propane

If you can correctly answer all of the questions in this study guide, you will do well on the final exam at the end of your class.

This study guide was developed to loosely parallel the hazmat chemistry curriculum developed by the California Specialized Training Institute (CSTI). (Some of the information in this handout was reprinted with permission from the California Specialized Training Institute.) However, the information applies to training responders receive nationwide.

Important Limitations to This Study Guide

Both this study guide and the hazmat chemistry class you're taking greatly simplify the very complex topic of chemistry. The good news is that you'll have a foundation to better understand hazardous materials. The bad news is that when chemistry is simplified this much, it's easy to forget that these are generalizations only and that there can be important exceptions to the information presented here.

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.

Disclaimer

The basics presented in this book are guidelines only. They are designed to help you manage the initial response phase of a hazmat incident. They are not a substitute for developing preplans for your community or for checking reference sources at an incident. Remember that there are exceptions to every rule, that various factors may change the risks, and that if more than one product is involved, it may be difficult to accurately predict the hazards.

Acknowledgments

I owe a special thanks to the following individuals for their thoughtful review of the first and/or second edition of this *Hazmat Chemistry Study Guide*. Their insight and comments helped make the book something I hope will be a tremendous resource to anyone going through hazmat technician training.

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Former Captain
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Dale Foster
Former Assistant Chief
San Jose (CA) Fire Department

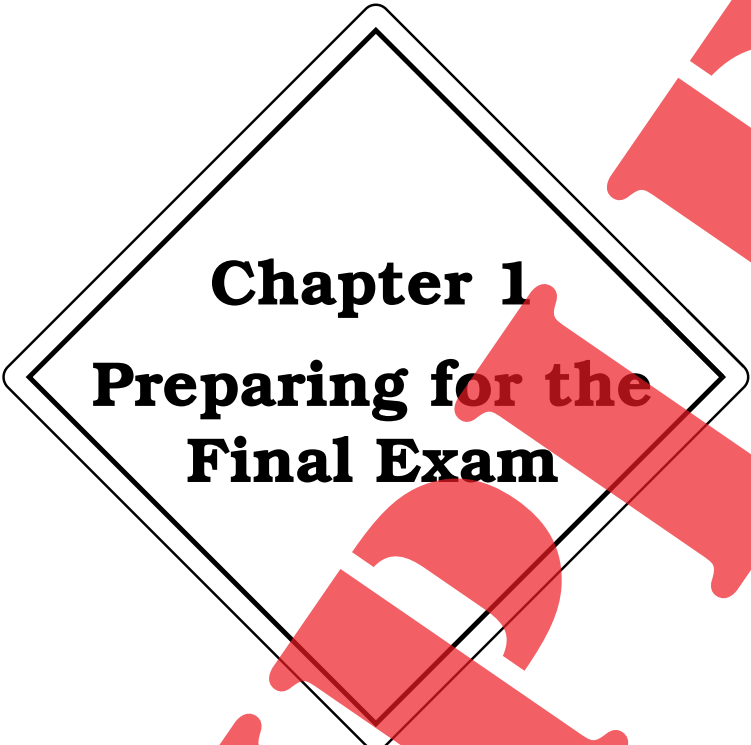
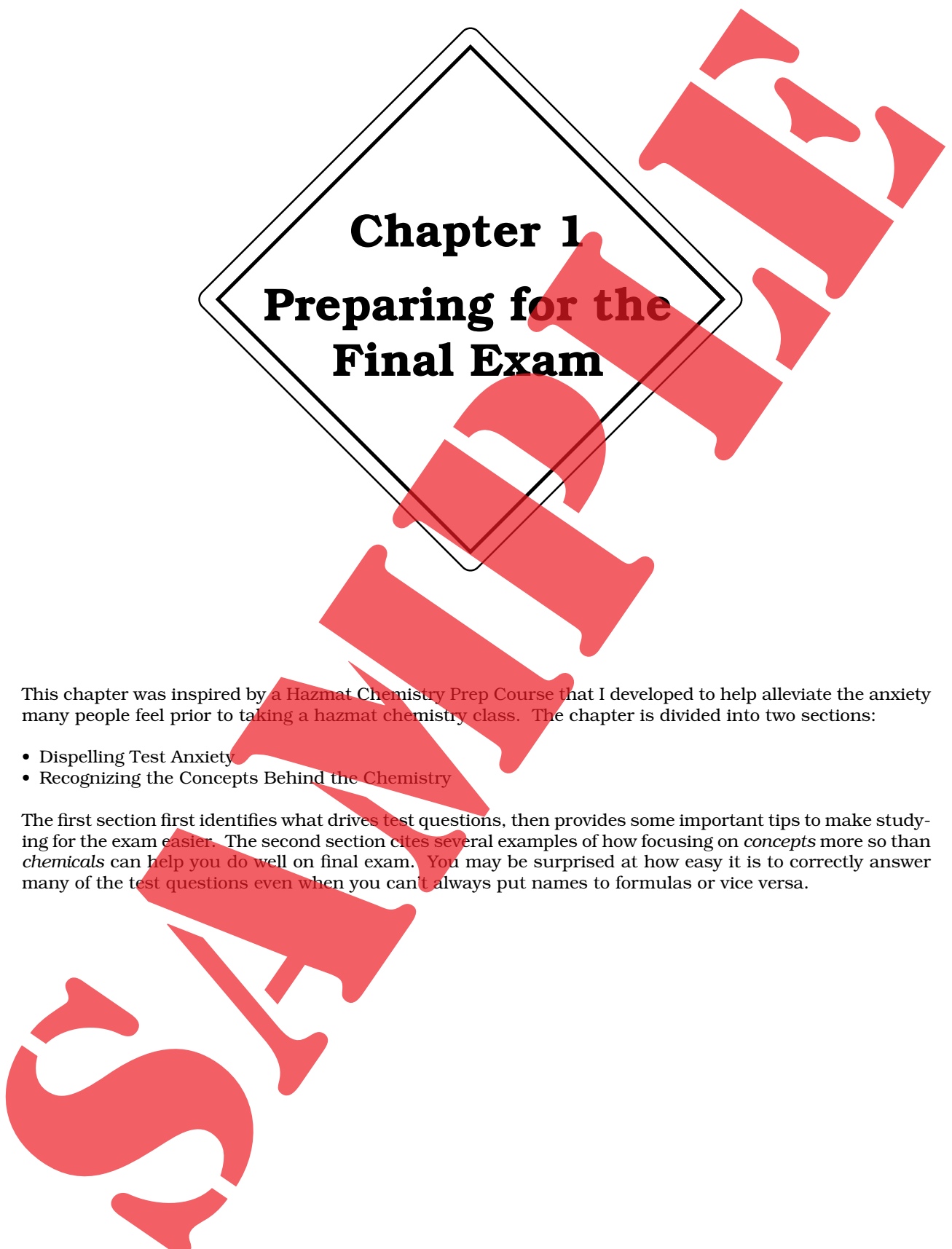
Doug Hansen
Hazardous Materials Specialist
Santa Clara (CA) Fire Department

Finally, I give thanks to the California Specialized Training Institute (CSTI) for giving me the opportunity to help edit and format the 1994 and 1995 revisions of its Hazmat Technician/Specialist curriculum, which ultimately set me on the course of finding clearer ways to communicate this information to emergency responders.

Dedication

To emergency responders everywhere
whose lives may depend on a knowledge of chemistry.

To Robert Charles Innis,
who sparked my imagination in junior high school
and inspired in me a passion for writing.



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.

Hazmat Chemistry Study Guide

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. Three very valuable documents are NFPA 471, 472, and 473. Even better is the NFPA *Hazardous Materials Response Handbook*, which contains the entire texts of 471, 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.

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.

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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?

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Dispelling Test Anxiety (continued)

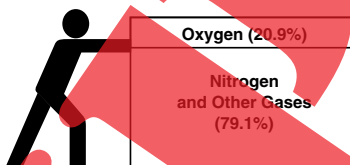
Your meter displays a reading of 19.9% oxygen (a 1% drop from normal). How much of a displacing gas (contaminant) is likely to be present?

- 1%
- 3%
- 5%
- 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?

- The acetone concentration may be below the LEL
- The acetone concentration may be within the flammable range
- The acetone concentration may be above the UEL
- 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

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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?

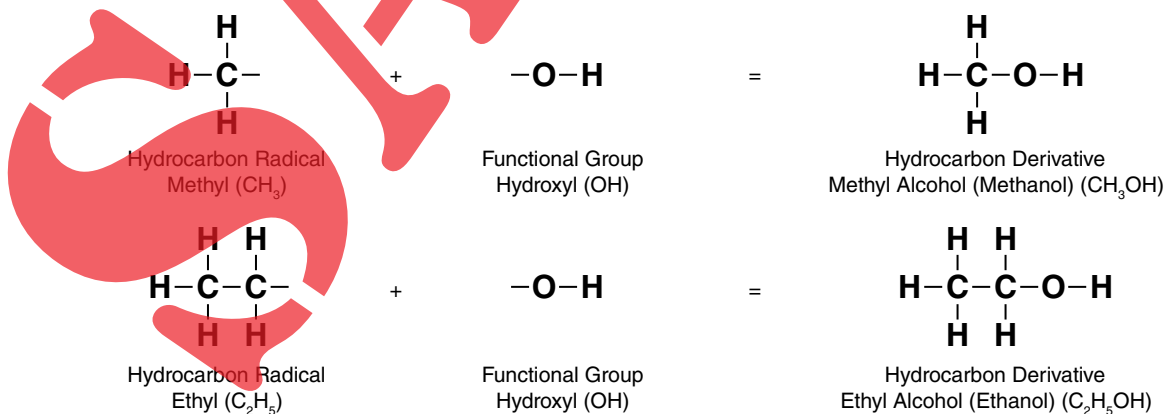
- CaC_2
- KCN
- $\text{C}_2\text{H}_5\text{OH}$
- NaClO

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.

Hazmat Chemistry Study Guide

SAMPLE

Chapter 2

Terms and Definitions

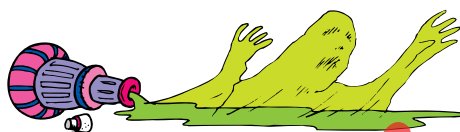
This chapter provides terms and definitions you should be familiar with before proceeding to the other chapters. Other terms will be introduced in subsequent chapters as appropriate. This chapter covers the following:

- Acute Exposure
- 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
- Pyrophoric
- Short-Term Exposure Limit (STEL)
- Sinkers
- 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)

Hazmat Chemistry Study Guide

Vapor Pressure and Vapor Density

Approximately 90% of hazmat injuries are due to inhalation. Obviously, this signals a need to protect against exposure to gases. However, responders must also be concerned about the vapors produced by liquids (and, to some extent, the vapors produced by solids). To determine whether vapors can “get to us,” we need to look at vapor pressure.



Vapor pressure is a significant factor in determining whether vapors can “get to us.”

Vapor pressure is the force exerted by the vapors of a product against the atmosphere or the sides of a closed container at the level of the vapor space above the liquid.

The chart below shows the vapor pressures of a few substances for comparison. (Source: NIOSH Pocket Guide to Chemical Hazards) Note that water has a vapor pressure of 17.5 mmHg at 68°F (20°C). When you're dealing with an unknown substance, you may be able to compare its evaporation rate to that of water to get a relative sense of its vapor pressure.

The Vapor Pressures of A Few Substances

Material	Vapor Pressure
Sulfuric Acid	0.001 mmHg
Turpentine	4 mmHg
Water	17.5 mmHg
Isopropyl Alcohol	33 mmHg
Acetone	180 mmHg
Hydrogen Cyanide	630 mmHg
Chlorine Gas	6.8 atm (roughly 5168 mmHg)

Vapor pressure is normally measured in millimeters of mercury (mmHg) at 68°F (20°C) at sea level. If the vapor pressure of a substance equals or exceeds 760 mmHg at sea level, the product is a gas in its normal state. When it comes to liquids, the closer the vapor pressure is to 760 mmHg, the more vapors the liquid produces and the more you need to protect yourself against the hazards associated with those vapors.

Conversely, the lower the vapor pressure, the lower the risk. Take the example of sulfuric acid in the table above. It's one of the strongest acids known, and its vapors are strong irritants. However, its vapor pressure is so low that the vapors won't travel far.

While there is no official dividing line between a “safe” vapor pressure and an “unsafe” vapor pressure, common sense tells us that a product whose vapor pressure is less than that of water probably isn't going to “reach out and touch someone” who follows the basic principles of “isolate and deny entry.” Obviously, you must look at a product's other properties and incident-specific factors to evaluate overall risk, but if you know the material has a low vapor pressure, it takes the stress level down a notch.

While vapor pressure is normally measured in millimeters of mercury (mmHg), it may be reported in other units of measurement, particularly when the vapor pressure of a substance is very high. The following chart shows equivalent pressures in some of the most common units.

Vapor Pressure Equivalents

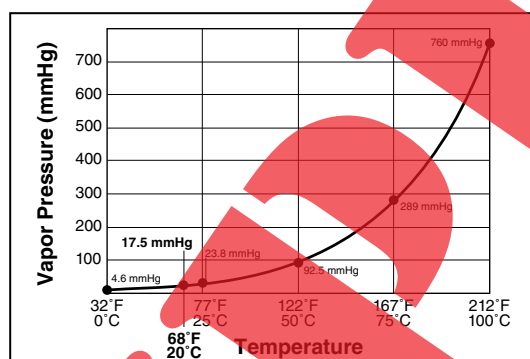
760 millimeters of mercury (mmHg)
29.9 inches of mercury
14.7 pounds per square inch (psi)
1 atmosphere (atm)
760 torr
1.01 bars
101.325 kilopascals (kPa)

Vapor Pressure and Vapor Density (continued)

Vapor pressure is directly related to **volatility**. The higher the vapor pressure, the **more volatile** a material is and the more readily it will evaporate. A material is considered volatile if it evaporates quickly. **Caution:** The nerve agent sarin is often described as being “volatile” because it has the highest vapor pressure of the nerve agents. However, with a vapor pressure of only 2.1 mmHg, it is far less “volatile” than water. It’s a good reminder of why it’s important to look beyond the sometimes misleading English descriptions to determine the actual chemical and physical properties of a substance.

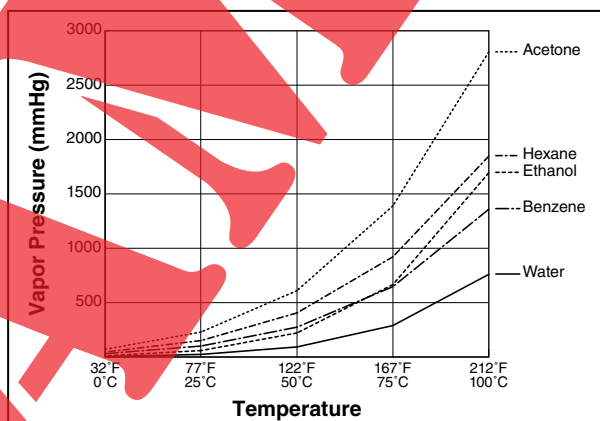
Vapor pressure is temperature-dependent. The greater the temperature, the higher the vapor pressure. The chart below shows the vapor pressure of water at various temperatures.

The Vapor Pressure of Water at Various Temperatures



The chart below compares water with four other substances. Notice that while they’re all fairly close at 32°F (0°C), their vapor pressures vary widely as the temperature increases. The higher the vapor pressure at any given temperature, the greater the potential risks.

Comparison of Vapor Pressure of Five Substances at Various Temperatures



Hazmat Chemistry Study Guide

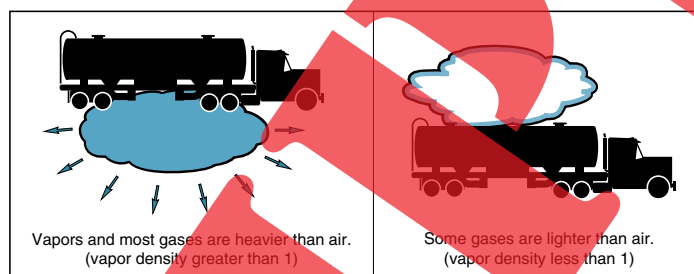
Vapor Pressure and Vapor Density (continued)

Vapor density is the relative weight of a vapor or gas compared with a like volume of air. Air has a molecular weight of 29, but since it is the standard against which all other vapors and gases are measured, it is said to have a vapor density of 1. Vapors or gases with vapor densities greater than 1 (>1) are heavier than air and will settle in low-lying areas. Gases with vapor densities less than 1 (<1) are lighter than air. They will rise and dissipate more readily than those that are heavier than air.

If you don't know something's vapor density but know its molecular weight (or can calculate molecular weight based on chemical composition), you can divide the molecular weight by 29 to determine its vapor density. For example, propane has a molecular weight of 44 and a vapor density of roughly 1.5 ($44 \div 29 = 1.517$). (Molecular weight is the combined weight of all atoms in a compound. See page 62 for more information.)

All vapors are heavier than air. (A vapor is a dispersion of molecules in air from a material that is normally a solid or a liquid.) Gasoline vapors, for example, are almost four times heavier than air. In a gasoline spill, most of the vapors will be close to the ground and will likely accumulate in low-lying areas. Most gases are also heavier than air, with the exception of some very small compounds.

The Location of Gases and Vapors



The chart below shows the vapor densities of the few gases that are lighter than air, many of which are very close to the weight of air.

Gases That Are Lighter Than Air

Gas	Vapor Density
Hydrogen	0.07
Helium	0.138
Natural Gas *	0.550
Methane	0.553
Ammonia	0.589
Hydrogen Fluoride	0.690
Neon	0.696
Acetylene	0.898
Hydrogen Cyanide	0.932
Diborane	0.954
Nitrogen	0.966
Ethylene	0.967
Carbon Monoxide	0.967

* Natural gas consists mostly of methane, with varying amounts of other gases and odorizers.

Although vapor density is independent of other factors, external conditions can have an effect on where a vapor or gas is found. Wind and air currents affect how well gases and vapors mix with the atmosphere and how easily they disperse. Moisture in the atmosphere can be absorbed by gases and vapors, causing them to be less buoyant. Temperature, as already identified, affects vapor pressure, which will cause gases and vapors to disperse at different rates. Likewise, atmospheric pressure at different elevations will either hold gases and vapors down or allow them to disperse more readily. Even concentration plays a part; lower concentrations of heavy gases and vapors won't hug the ground as much as higher concentrations do.

Vapor Pressure and Vapor Density (continued)

Review Questions (answers on page 194)

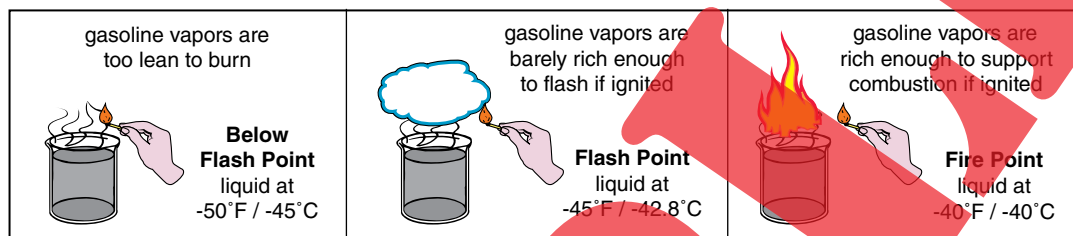
- The majority of hazmat injuries are due to:
 - Absorption
 - Inhalation
 - Ingestion
 - Injection
- Unless otherwise specified, vapor pressure is normally measured in millimeters of mercury (mmHg) at ____ at sea level.
 - 0°F (-18°C)
 - 32°F (0°C)
 - 68°F (20°C)
 - 77°F (25°C)
- Atmospheric pressure is 14.7 psi at sea level. What is the equivalent in millimeters of mercury?
 - 670 mmHg
 - 680 mmHg
 - 760 mmHg
 - 860 mmHg
- Which of the following is the most volatile?
 - Sulfuric acid (vapor pressure 0.001 mmHg)
 - Sarin (vapor pressure 2.9 mmHg)
 - Turpentine (vapor pressure 4 mmHg)
 - Isopropyl alcohol (vapor pressure 33 mmHg)
- Which of the following statements is true?
 - Most gases are lighter than air.
 - All vapors are lighter than air.
 - Most gases are heavier than air.
 - All gases and vapors are heavier than air.
- The lower the vapor pressure, the more volatile a material is.
 - True
 - False
- The higher the temperature of a material, the higher the vapor pressure.
 - True
 - False
- The greater the vapor density, the more readily a vapor will dissipate.
 - True
 - False

Hazmat Chemistry Study Guide

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.

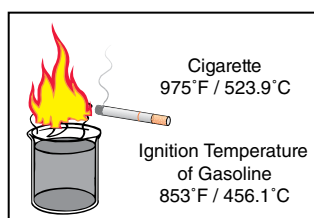
Flash point and fire point refer to the temperature of the liquids rather than to the vapors they produce. The flash point of mixtures, such as kerosene and diesel fuel, may be listed as a range of temperatures instead of a single temperature because the flash point can vary depending on composition. 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 U.S. Department of Transportation defines a combustible liquid as one that has a flash point greater than 141°F/60.6°C.) 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.

The **ignition (autoignition) temperature** of a substance is the minimum temperature required to cause self-sustained combustion of that substance, independent of an ignition source. Put more simply, it's the minimum temperature to which a material must be raised before it will ignite. (It is also the temperature the ignition source must be.) The lower the ignition temperature, the greater the risk of ignition. Ignition temperature is sometimes difficult to measure and should be considered an approximation.

The following illustration shows gasoline vapors (ignition temperature 853°F/456.1°C) being ignited by a lit cigarette at roughly 975°F/523.9°C. This is an example of *pilot ignition*; it is caused by an external ignition source. However, ignition temperature is independent of an ignition source. A good example of *autoignition* is in a fire situation where convection carries hot air and gases to other parts of a building. When the atmosphere becomes hot enough to the point where these gases reach their ignition temperatures, they will ignite automatically without the introduction of any other ignition source. This is called *flashover*.

Ignition Temperature

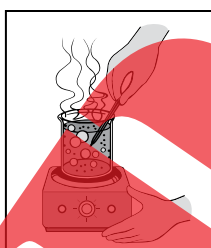


Flammability Factors (continued)

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.

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.

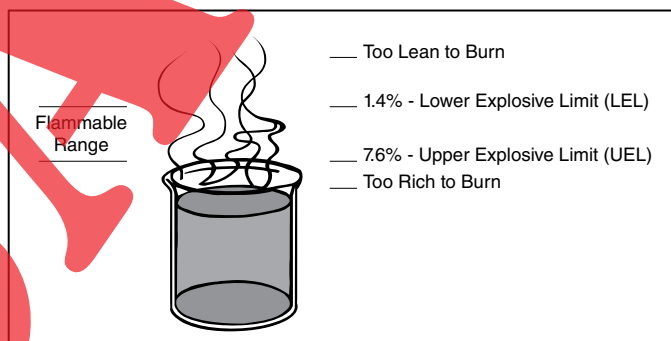
Boiling Point



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



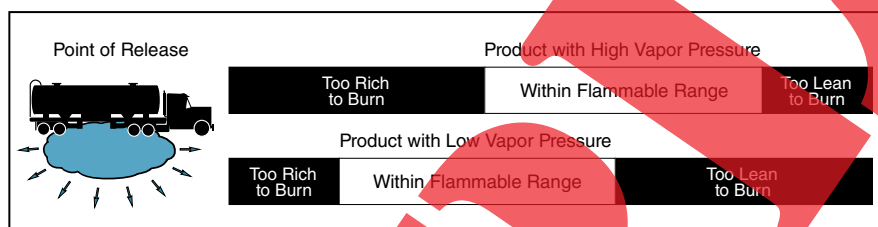
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Flammability Factors (continued)

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



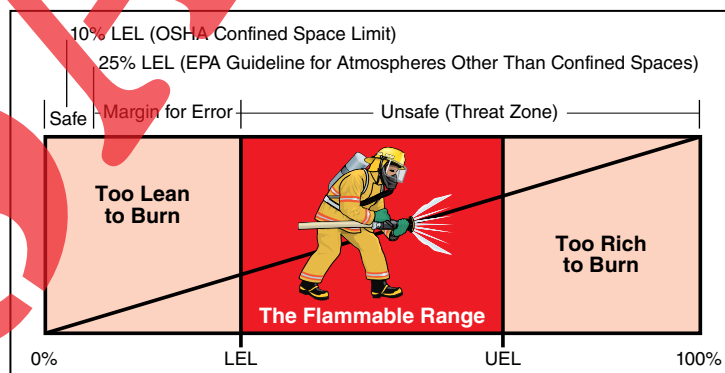
A flammable liquid with a low vapor pressure, on the other hand, will give off less vapor, so the vapors will enter the flammable range closer to the surface of the liquid and become too lean to burn much closer as well. Therefore, flammable liquids with low vapor pressures present a greater risk close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

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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 ignition temperature, the greater the risk of ignition.
 - a. True
 - b. False
11. The higher the ambient temperature, the more easily a flammable or combustible liquid will vaporize.
 - a. True
 - b. False
12. The wider the flammable range, the greater the risk of ignition.
 - a. True
 - b. False
13. Atmospheres above the upper explosive limit are safe to enter because the vapors are too rich to burn.
 - a. True
 - b. False
14. OSHA confined space regulations identify ____ of the LEL as the cutoff prohibiting work in flammable atmospheres.
 - a. 10%
 - b. 15%
 - c. 20%
 - d. 25%

Water Behavior

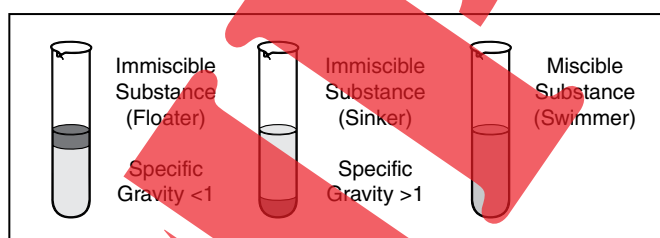
Specific gravity is the weight of a liquid as compared to an equal volume of water. Water weighs 8.33 pounds per gallon. However, since it is the standard against which all other liquids are measured, it is said to have a specific gravity of 1.

Generally speaking, a liquid that has a specific gravity greater than 1 (>1) will sink in water, whereas one with a specific gravity less than 1 (<1) will float on water. These liquids may be referred to as **sinkers** and **floaters**, respectively. If you don't know the specific gravity of a liquid, but do know how much it weighs, you can divide its weight (in pounds per gallon) by 8.33 to determine its specific gravity.

Specific gravity, however, is not the sole factor in determining how a substance behaves with water. For example, ethyl alcohol (drinking alcohol) has a specific gravity of 0.79, but it doesn't float on water; it mixes with it. That's because of its chemical makeup. Ethyl alcohol is what's known as a **polar substance**. But before we jump into an explanation of polarity, let's review some terms you should already be familiar with.

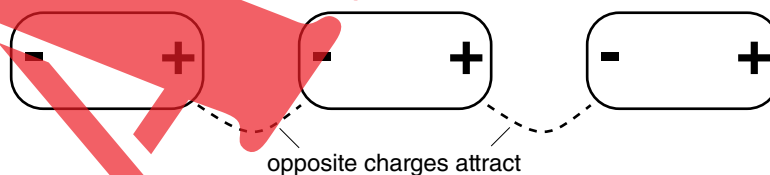
The terms *miscibility* and *solubility* are often used interchangeably. **Miscibility** refers to the ability of products to mix, or form a uniform blend. **Solubility** refers to the ability of a product to dissolve. We usually refer to products mixing with or dissolving in water, but many chemicals can be dissolved in other solvents. Chemicals that mix in water (e.g., ethyl alcohol) are called **miscible** or **soluble** (water-soluble), while those that don't are called **immiscible** or **insoluble**. Chemicals that mix with water may also be called **swimmers**.

Specific Gravity and Miscibility



Solubility is determined by **polarity**, which is a reflection of how strongly one atom attracts the electrons of another atom in a compound. Magnets make a good analogy to help us understand polarity. With their positive and negative poles, magnets are strongly attracted to each other. **Polar** substances also have positive and negative poles, if you will, but in the form of atoms that differ in their electronegativity; the electrons between them are drawn more strongly to one element in the compound than to the others. Such is not the case in **nonpolar** substances.

The Similarity Between Polarity and Magnetic Attraction



Understanding polarity, even to the extent explained here, is beyond what you need to know. What is important, however, is to understand the relation between polarity and miscibility. Water (H_2O or HOH) is a polar substance. Other common polar compounds include those with a double bond between carbon and oxygen ($\text{C}=\text{O}$) and those with a single bond between oxygen and hydrogen ($\text{O}-\text{H}$). (Chemical formulas and chemical bonding will be explained in the following chapter.) Since "like dissolves like," water will dissolve other polar substances (like most alcohols), but not nonpolar substances (like hydrocarbons). When you hear someone refer to polar substances, recognize that these are water-soluble materials. Nonpolar substances are *not* water-soluble, but they may be soluble in other nonpolar substances. For example, wax will dissolve in gasoline. (We'll touch on polarity again briefly in the section on chemical bonding.)

Water Behavior (continued)

Understanding the distinction between specific gravity and miscibility/solubility should help you see the importance of looking at both properties when checking reference sources to determine whether a material floats, sinks, or swims. You can usually find specific gravity reported as a number relative to the weight of water (e.g., benzene is 0.88). Miscibility may be indicated with relative descriptions (e.g., “slightly soluble”) or by percentages. For example, the *NIOSH Pocket Guide to Chemical Hazards* lists benzene as being 0.07% soluble. Its miscibility is measurable but negligible from the first responder’s standpoint.

Temperature affects solubility. In general, the warmer the **solvent** (the substance used to dissolve something else into solution), the greater its capacity to dissolve the **solute** (the substance added to a solvent). Consider, for instance, how much easier it is to dissolve sugar into hot tea than into iced tea. Thus a hazardous material may be more soluble on a hot day than it is on a cold one. (Gases behave differently; the warmer the solution, the less soluble gases become. Carbonated beverages, for example, go flat—lose carbon dioxide—more quickly when warm than when cold.)

Understanding specific gravity and miscibility (solubility) is important in terms of fire control. With flammable liquids that float on water, such as gasoline, it will be necessary to use foam (e.g., AFFF or ATC) to smother a fire and retard vapor production. With liquids that sink in water, such as some solvents, vapor production can be suppressed using light applications of water. Water-soluble (miscible) liquids, such as alcohol, 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.

These factors also influence how to contain spills that have entered waterways. If a spilled material is water-soluble, it will probably be necessary to build a simple dam—one that contains both the product and the water it contaminates. Water can’t be allowed to flow either over or under the dam because everything is contaminated.

If the product is not water-soluble and is heavier than water (specific gravity greater than 1), it may be appropriate to build an *overflow dam* that contains the product while allowing uncontaminated water to flow over the top.

If the product is not water-soluble and is lighter than water (specific gravity less than 1), it may be appropriate to build an *underflow dam* that contains the material floating on the water while allowing uncontaminated water to flow under the dam. The water is channeled through PVC piping or hard suction fire hose buried through the dam.

Understanding water behavior can sometimes help you assess the dangers even when dealing with an unknown substance. Products that are lighter than water (specific gravity less than 1) are usually flammable or combustible hydrocarbons. Those that are heavier than water (specific gravity greater than 1) are usually toxic. Of course, these are generalizations, not hard-and-fast rules you should stake your life on. But when no other details are yet available and you need some direction from which to develop an initial action plan, these little tidbits of information provide a fairly reliable starting point.

Water Behavior (continued)

Review Questions (answers on page 194)

1. A liquid that floats on water has a specific gravity:
 - a. Greater than 1 (>1)
 - b. Less than 1 (<1)
 - c. Equal to 1 ($=1$)
2. Which of the following substances will float on water?

a. Acetic acid	(miscible, specific gravity 1.05)
b. Acetone	(miscible, specific gravity 0.79)
c. Carbon tetrachloride	(miscibility 0.05%, specific gravity 1.59)
d. Pentane	(miscibility 0.04%, specific gravity 0.63)
3. Which of the following substances will sink in water?

a. Methyl alcohol	(miscible, specific gravity 0.79)
b. Methyl acetate	(miscibility 6%, specific gravity 0.96)
c. Trichloroethylene	(miscibility 0.0001% at 77°F, specific gravity 1.46)
d. Benzene	(miscibility 0.07%, specific gravity 0.88)
4. Polar substances are:
 - a. Miscible
 - b. Immiscible
5. In general, the warmer a solvent, the greater its capacity to dissolve a solute:
 - a. True
 - b. False
6. Which of the following would require the use of foam to smother a fire and retard vapor production? (Which, if burning, would generally be the most difficult to extinguish with water alone?)
 - a. Miscible (soluble) substances with a specific gravity equal to 1 ($=1$).
 - b. Miscible (soluble) substances with a specific gravity greater than 1 (>1).
 - c. Immiscible (insoluble) substances with a specific gravity less than 1 (<1).
 - d. Immiscible (insoluble) substances with a specific gravity greater than 1 (>1).
7. Which of the following is most likely a nonpolar substance?
 - a. C_2H_5OH
 - b. $C_2H_4(OH)_2$
 - c. $CH_3COC_2H_5$
 - d. C_6H_{12}

Hazmat Chemistry Study Guide

Physical and Chemical Change

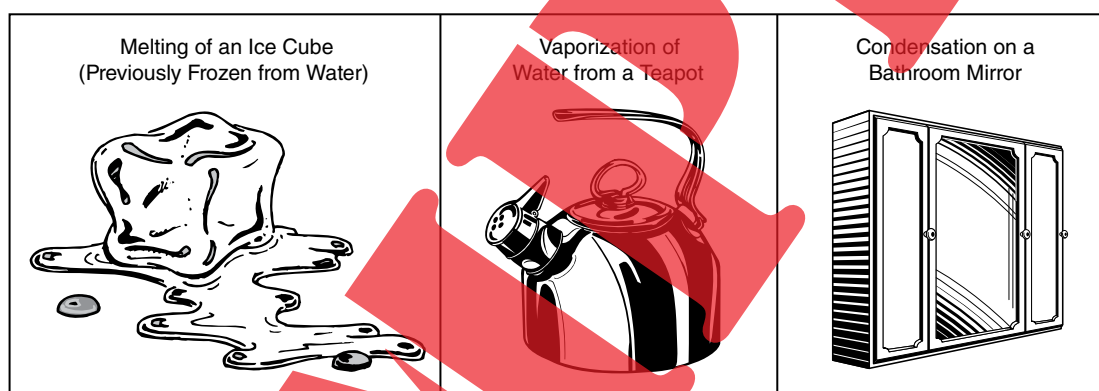
Physical Change

When a substance changes in form (solid, liquid, or gas), but not in chemical composition (the elements that comprise it), it undergoes a **physical change** (or physical reaction). A perfect example is the way water, a liquid in its natural state, becomes a solid (ice) below 32°F (0°C) or a gas (steam) above 212°F (100°C). Water is still H₂O in all three states, even though it has changed form and appearance.

The causative factor in physical change is usually temperature. However, pressure is sometimes used to induce a change in state, as is the case with liquefied compressed gases. Both temperature and pressure are used to transform gases into cryogenic liquids (liquids colder than -130°F/-90°C). (See page 146 for more information.)

Melting is a change from solid to liquid, such as when ice melts to water. The temperature at which this happens is called the **melting point**. The opposite reaction, **freezing**, is a change from liquid to solid, such as when water becomes ice. The temperature at which this happens is called the **freezing point**.

Examples of Physical Change



The change from liquid to gas, such as when water is boiled to create steam, is called **vaporization**. The point of maximum vaporization (or vapor production) is called the **boiling point**. (Boiling point was explained on page 25.)

The change from gas to liquid is called **condensation**. Steam from a hot shower condensing to leave moisture on a bathroom mirror is a good example of this.

Sublimation involves a change from the solid state to a vapor state without the material ever passing through the liquid state. As the temperature increases, so does the rate of sublimation. Sublimation is less common than the four reactions described above. However, examples of materials that sublime are dry ice (carbon dioxide) and naphthalene (used in mothballs).

Deposition, a change from gas to solid, is extremely rare and lasts only for a very brief time. It can occur as a result of a nuclear blast.

Temperature can change the thickness of a liquid—its **viscosity**—without changing its physical state. Viscous liquids (those with high viscosity) are thicker liquids, like heavy oils. Thinner liquids, like water, are less viscous. Viscosity affects risk and product containment options because less viscous liquids flow more easily than viscous ones, expanding the endangered area. However, viscous liquids will flow more easily when heated.

Physical and Chemical Change (continued)

Matter can exist in multiple states at the same incident, such as when a liquefied gas vaporizes as it escapes a breached container. It exists as a liquid inside the container and as a gas outside. Even *within* a container, there is often a liquid space at the bottom and a vapor space at the top—a distinction that impacts the incident. For example, fire impinging on the vapor space stresses a container far more so than fire impinging on the liquid space because the liquid helps absorb the heat, whereas vapors do not.

(The words *gas* and *vapor* were used interchangeably in the previous paragraphs, as they frequently are in the real world. For practical purposes, they mean the same thing. Technically, however, a gas is a material that exists as a gas in its normal state, whereas a vapor is something found as a liquid or solid at normal temperature and pressure.)

The fourth state of matter, **plasma**, starts out as a gas. However, the gas is modified at the atomic level by the application of energy, often in the form of electricity. (Atomic structure is explained in the next chapter.) Extra energy applied to the gas causes some of the electrons to break away from the atoms, leaving an atmosphere of free electrons and positively charged particles (ions). The result is a glowing gaseous mass called plasma.

It takes a special environment to sustain plasma. Plasma exists in nature in stars—big balls of gases whose extremely high temperatures charge the atoms that comprise the gas. However, plasma is also found in fluorescent lights and neon lights. Both contain tubes filled with gases that become plasma when the electricity is turned on.

Supercritical fluids are beyond the scope of this book, but we'll at least define them. A supercritical fluid can be either a gas or a liquid in its natural state. However, by heating that gas above its critical temperature or compressing that liquid above its critical pressure, the material is transformed into something that possesses both gas- and liquid-like properties. (Critical temperature and critical pressure are defined on page 146 as part of the discussion on gases and their behavior.) Density, viscosity, and diffusivity can all be changed by adjusting the temperature and pressure.

Supercritical fluids are able to penetrate other materials much the way gases do, yet their solubility is very much like that of liquids, enabling them to dissolve other substances. The combination of penetration power and solvent capabilities makes supercritical fluids very useful for both cleaning and extraction operations. Supercritical carbon dioxide (scCO_2) and supercritical water (scH_2O), in particular, have been used in the food processing industry since the 1980s in place of more hazardous chemicals.

Chemical Change

Chemical reactivity describes a material's propensity to release energy or undergo change either on its own or in contact with other materials. What distinguishes chemical reactions from physical reactions is that with chemical reactions, the material undergoes a change in composition; a new substance is formed, one that has its own chemical and physical properties and hazards. We'll look at four types of chemical reactivity: air reactivity, water reactivity, polymerization, and chemical incompatibility.

Materials that are **air-reactive** will ignite, decompose, or release energy when exposed to air. Some of these reactions can be quite violent. Air-reactive materials may also be referred to as **pyrophoric**. Technically, pyrophoric materials are those that react in dry air versus moist air. However, one should never assume that the word pyrophoric on a warning label, on a material safety data sheet (MSDS), or in a hazardous materials reference source is meant to exclude reactivity to moist air. Not everyone writing these documents will check the precise definition of a word before using it. Assume that pyrophoric materials will also react with moisture until you've determined otherwise by checking at least three reference sources.

Materials that are air-reactive but not water-reactive (white and yellow phosphorus, for example) may be stored under water to prevent contact with air. But when materials are also so water-reactive that they will react with moisture in the air (for instance, sodium and potassium), they must be stored under some other substance, such as an inert gas, mineral oil, or kerosene.

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Physical and Chemical Change (continued)

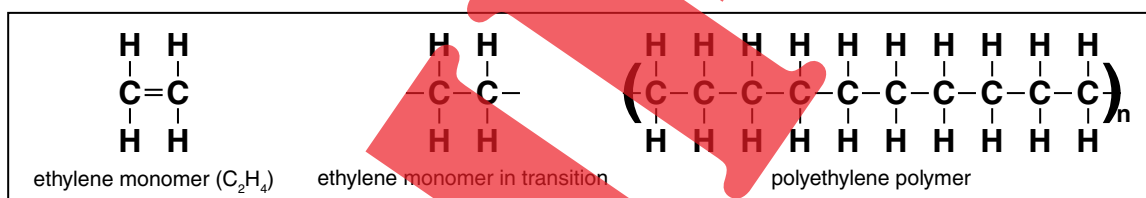
Water reactivity is the tendency of a material to react, or chemically change, upon contact with water. Reactions can range from mild to severe. The more reactive chemicals can release flammable gases, toxic gases, and/or corrosive solutions, generating a lot of heat in the process. (A reaction that generates heat is called **exothermic**.) Some materials can react explosively when exposed to water, ripping the water molecules apart to liberate oxygen. Examples of water-reactive substances include sulfuric acid, sodium, and aluminum chloride.

Water-reactivity has a big impact on how a spilled material will behave on rainy or humid days. Even on a dry day, water-reactive materials present a significant health risk when in contact with the moisture on your skin, in your eyes, or in your respiratory system.

Water reactivity also impacts how you handle a fire emergency. For example, Class D extinguishers can be used on a small fire involving combustible metals. A large fire may require using a defensive attack and protecting exposures instead or withdrawing to a safe distance while the incident runs its course. Using water on the burning material itself can be disastrous.

Polymerization is a chemical reaction in which small compounds called **monomers** react with themselves to form larger molecules called **polymers**. These polymers are "repeating units" that resemble the original molecule. The illustration below shows how ethylene (C_2H_4), the most common monomer, is transformed into polyethylene, a chain of C_2H_4 repeating units. Polyethylene is a very common manmade plastic.

The Making of a Polymer



Ethylene has a double bond between two carbon atoms. (Bonding is covered in the next chapter.) Double bonds between carbon atoms are not as stable as single bonds, so ethylene is prone to polymerization on its own. Human intervention is not necessarily required. However, to create polyethylene, manufacturers initiate a chemical reaction through the careful application of heat, pressure, and a catalyst. The reaction breaks one of the bonds between the carbon atoms, leaving an open bonding site on each. Open bonding sites (unpaired electrons) create a very unstable situation that nature doesn't allow to exist for very long, so these incomplete molecules combine to create more stable compounds (polymers). Different polymers can be created by varying the monomer used and the rate of the reaction.

Polymerization is not dangerous if done in a controlled manner. However, because polymers are not as dense as monomers, they take up more space. The reaction also generates heat. Heat and overpressurization can cause catastrophic container failure in uncontrolled or runaway polymerization.

Catalysts and inhibitors are substances added to other products to control their chemical reactions. **Catalysts** are usually added to speed up the chemical reactions, for instance, to coax individual monomers to hook up and become long-chain polymers. The catalysts themselves are not used up in the reaction; they can be recovered and reused. In the plastics industry, for example, organic peroxides are used to initiate the polymerization process. If catalysts are used improperly, they can increase the speed of a reaction beyond the point where the container can withstand the buildup of pressure and heat.

Inhibitors, sometimes referred to as *stabilizers* or *negative catalysts*, are added to stop or slow a reaction, such as to prevent uncontrolled polymerization. Styrene, for example, can polymerize if mixed with an organic peroxide or if exposed to radiated heat or visible light. The right concentration of the inhibitor *t*-butylcatechol (TCB) will prevent an accident. Inhibitors have a limited shelf life, meaning that they won't stop or slow a reaction indefinitely. If an inhibitor is allowed to degrade, escape, or drop below the necessary concentration, the resulting polymerization can cause the container to rupture violently. Likewise, if an inhibitor is not added where needed, it can spell disaster.

Physical and Chemical Change (continued)

Incompatible chemicals are those that react with each other in ways that generally produce negative consequences. The reactions can range from relatively mild to catastrophic, depending on the type and quantity of chemicals involved. Acids and bases, for example, are incompatible with each other. If the two mix, they can generate a tremendous amount of heat. However, under controlled conditions, weak corrosives can be added to neutralize a spill of the opposite pH (i.e., a weak acid added to a base or a weak base added to an acid). Doing so still involves mixing incompatible chemicals, but the reaction is less violent than one that would result from mixing strong corrosives. (Corrosives are discussed in more detail starting on page 170.)

You must also consider incompatibilities with anything *brought to the scene* to manage the incident, including protective clothing, monitoring equipment, overpack containers, and other tools.

Some compatibility problems aren't apparent right away. Rather, they show up at the next incident. For example, structural firefighting clothing contaminated with an oxidizer at one incident may burn furiously at a subsequent fire. Clothing or other equipment that can't be adequately decontaminated must be disposed of and replaced.

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Physical and Chemical Change (continued)

Review Questions (answers on page 194)

- Physical change involves:
 - Change in form/state (solid, liquid, gas)
 - Change in chemical composition
 - Change in both form and chemical composition
- The factor that most often causes a physical change is:
 - Pressure
 - Temperature
 - Exposure to air or water
 - Exposure to a catalyst
- A material that sublimates is one that:
 - Changes from a liquid to a gas
 - Changes from a gas to a liquid
 - Changes directly from a gas to a solid
 - Changes directly from a solid to a gas
- The change from liquid to gas is called:
 - Condensation
 - Melting
 - Sublimation
 - Vaporization
- _____ are sometimes added to other substances to slow down or stop a reaction.
 - Catalysts
 - Inhibitors
 - Monomers
 - Polymers
- Air-reactive chemicals will ignite or release energy when exposed to air.
 - True
 - False
- Water-reactive chemicals may produce flammable gases, toxic gases, corrosive solutions, and/or heat on contact with water.
 - True
 - False
- Uncontrolled or runaway polymerization can cause catastrophic container failure.
 - True
 - False
- What part of a container will be stressed the most by flame impingement?
 - Liquid space
 - Vapor space

Toxicity and Risk

Hazardous materials can invade the body through several **routes of entry/exposure**:



- **Inhalation** is the most hazardous route of entry because the lungs are so vulnerable to damage and because chemicals that enter the body through the lungs can be rapidly absorbed into the bloodstream and transferred to other organs or body systems. Increasing the exposure potential is the greater surface area (approximately 900 square feet for the average person as compared to an average of 20 square feet surface area for the skin).
- **Absorption** can occur through direct contact between a hazardous material (solid, liquid, or gas) and the skin or eyes. The eyes are particularly susceptible to absorption. So are parts of the body rich in hair follicles (e.g., scalp, underarm, and genital areas). Some hazardous materials are strictly a contact hazard, causing harm at the injury site only. Others can penetrate intact skin and be absorbed directly into the bloodstream. If skin is moist (as from sweating), it increases the risk of absorption.
- **Ingestion** at a hazmat incident occurs most often due to poor hygiene—eating, drinking, or smoking before thoroughly washing one's hands.
- **Injection** can occur through a cut, scratch, or puncture wound from a contaminated object.

Exposures can be either **acute** (one-time or short-term) or **chronic** (repeated or long-term). Hazmat emergencies generally result in acute exposures. Acute exposures can result in effects such as difficulty breathing, dizziness, nausea and vomiting, burns, damage to specific target organs or body systems, or death. The effects may manifest themselves immediately or may not show up until hours or days later. Effects of chronic exposures are often not detectable for years and may include such things as respiratory disease, damage to specific target organs or body systems, cancer, birth defects in unborn children, or ultimately death.

Carcinogens, mutagens, and teratogens are particularly insidious in the damage they cause:

- **Carcinogens** are substances that cause cancer. Many substances are known or suspected carcinogens. Realize that it may take only one very small exposure to get cancer, yet the effects of exposure may not appear for years. Examples of known or suspected carcinogens include asbestos, vinyl chloride, benzene, some pesticides, and many of the materials used to manufacture plastics.
- **Mutagens** are toxins that cause changes to the genetic material of cells (DNA and RNA) that can be inherited by offspring. These genetic changes can have numerous effects, including the failure of important biochemical processes. In some cases they can cause cancer. Examples of known mutagens include ethylene oxide, ethylene dibromide, and benzene.
- **Teratogens** are agents known to cause malformations in an unborn child. Exposure to teratogens during the embryonic stage (the first 8 weeks after implantation) can result in deformed or absent limbs. Exposure during the fetal stage (after the 8th week) can result in physiological and behavioral effects. Examples of teratogens include ionizing radiation, lead compounds, ethyl alcohol, methyl mercury, thalidomide, and dioxins.

Effects of exposure can be local and/or systemic. **Local effects** are those that occur directly to the area exposed. A chemical burn to the skin due to contact with a corrosive material is an example of a local effect. **Systemic effects** are those that impact the entire body. Carbon monoxide poisoning is an example of a systemic effect. Carbon monoxide combines with the hemoglobin in the red blood cells and deprives the body of oxygen. Some of the target organs or body systems that are particularly sensitive to damage from chemicals include the lungs, eyes, skin, liver, kidneys, the central nervous system, and the reproductive system. However, chemicals can affect any part of the body.

The health effects of most chemicals are fairly predictable. However, when two or more chemicals are involved, the **synergistic effect** can produce dramatically different signs and symptoms. Synergism is also a concern when patients have other injuries besides chemical exposure. The combination can be far more serious than either condition alone.

Toxicity and Risk (continued)

Generally, the more toxic a substance is, the more dangerous it is to response personnel. However, other **toxicological risk factors** must be considered for an accurate hazard assessment:

- *Form of the material.* Gases and vapors are the most hazardous due to their mobility and the inhalation hazard. Solids are generally the least dangerous. However, solids in a finely divided state (e.g., dusts and powders) can also be an inhalation hazard.
- *Dose (or concentration) to which a person is exposed.* All chemicals are toxic to some degree, even if toxicity is not the primary hazard. Dose makes the poison. A large exposure to a material with low toxicity can be just as harmful as a small exposure to a highly toxic material.
- *Duration and frequency of exposure.*
- *Sex.* Females are more susceptible to teratogenic and mutagenic substances if pregnant (e.g., lead, formaldehyde, PCBs, and benzene). Males are more susceptible to toxins that target rapidly growing sperm cells (e.g., lead, ethylene dibromide, and hexane).
- *Age.* In general, young children and the elderly are more susceptible to harm from chemical exposures. However, there are times when older persons have an advantage due to their slower metabolism.
- *Individual susceptibilities* (e.g., allergies or pregnancy).
- *State of health.* Illness or poor health can make a person more susceptible to chemical exposures and can mask symptoms of exposure.

Once an exposure does occur, another factor that affects the degree of risk is whether the victim receives prompt, thorough, and appropriate decon and follow-up medical care.

The terms **exposure** and **contamination** are often used interchangeably, in part because a person can be both exposed and contaminated. However, the words mean different things. A *contaminated* person is one who has the hazardous material on his or her body, posing a risk of secondary contamination to others. Someone who is contaminated would also be considered *exposed*. (Obviously, proper personal protective equipment can prevent exposure even when an individual's outer garment is contaminated.)

On the other hand, a person can be *exposed* without being contaminated. For example, a person who inhales a gas or vapor is seldom contaminated unless the concentration of gas or vapor is so heavy that it has condensed onto the person's skin, hair, or clothing. Similarly, a person can be exposed to radiation without being contaminated. A strong dose of gamma or x-ray radiation can cause tissue damage, but it doesn't make an exposed person radioactive. He or she would pose a threat to others only if a radioactive substance (e.g., powder, liquid, or gel) has contaminated his or her body.

The bottom line is that injury can result from either exposure or contamination. However, only contamination poses the risk of continued exposure (continued injury) to patients and secondary contamination to others who come in contact with these patients.

Toxicity and Risk (continued)

Review Questions (answers page 194)

1. Which is generally considered the most dangerous route of entry?
 - a. Inhalation
 - b. Absorption
 - c. Ingestion
 - d. Injection
2. Hazmat emergencies generally result in:
 - a. Chronic health effects
 - b. Acute health effects
3. Which form of material is generally the most hazardous?
 - a. Solids
 - b. Liquids
 - c. Gases and vapors
4. Which of the following are toxins that cause changes to the genetic material of cells (DNA and RNA) that can be inherited by offspring?
 - a. Carcinogens
 - b. Mutagens
 - c. Teratogens
5. _____ poses the risk of continued injury to patients as well as injury to those who care for them.
 - a. Contamination
 - b. Exposure

Hazmat Chemistry Study Guide

Toxicological Values and Exposure Limits

Units of Measure

When evaluating toxicity, it's necessary to use units of measure much smaller than percent by volume in air. The most common is **parts per million (ppm)** or **parts per billion (ppb)**. These are straightforward representations of how much contaminant exists per million or billion units of the atmosphere. A concentration of 1% by volume in air is equal to 10,000 parts per million.

The table below shows the relation between contaminant concentration and oxygen concentration. As indicated on page 14, oxygen represents roughly one fifth of the normal atmosphere, so a 1% drop in oxygen is really a 5% displacement of the overall atmosphere. At the point where OSHA defines the atmosphere as being oxygen-deficient (19.5% oxygen), requiring the use of self-contained breathing apparatus, there can be as much as 70,000 ppm of a contaminant gas.

Relation Between Contaminant Concentration and Oxygen Concentration

Contaminant Concentration		Oxygen Concentration
Parts per Million	Percent in Air	Percent in Air
10,000	1.0	20.7
20,000	2.0	20.5
30,000	3.0	20.3
40,000	4.0	20.1
50,000	5.0	19.9
60,000	6.0	19.7
70,000	7.0	19.5

Toxicity is sometimes measured in **milligrams per cubic meter (mg/m³)**. (One cubic meter is 1.3 cubic yards.) There is no easy correlation between this and either percent by volume or parts per million because milligrams per cubic meter is based on the molecular weight of the material, which is different for every substance. However, it is possible to convert from one to the other with the equations below.

Converting Between Parts per Million and Milligrams per Cubic Meter



$$\text{ppm} = [(\text{mg/m}^3) / (\text{mw})] (24.44)$$

$$\text{mg/m}^3 = [(\text{mw})(\text{ppm})] / (24.44)$$

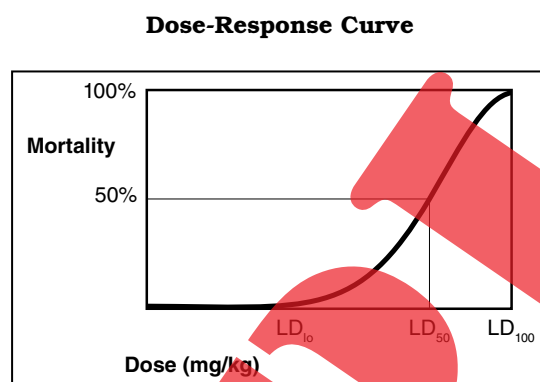
Milligrams per kilogram (mg/kg) measures dose in relation to a person's body weight rather than measuring the atmospheric concentration. One kilogram equals 2.2 pounds.

Two other less common units of measure bear mentioning, even though their use is beyond the scope of this book. *Fibers per cubic meter (fibers/cm³)* is used to measure fibers (e.g., asbestos fibers). *Millions of particles per cubic foot (mppcf)* of air may be used to measure particles and dust (e.g., silica and talc).

In all cases, the smaller the number, the more hazardous the material. It may seem unnecessary to emphasize this point, but it's easy to become confused because of the inverse relation between the dangers reflected in toxicity values versus atmospheric concentration or dose absorbed/ingested. Obviously, the more of a substance one is exposed to, the more harm it can cause. However, it's the substances that are deadly at lower concentrations that present the greatest risk.

Toxicological Values and Exposure Limits (continued)

This relation between exposure and harm can be illustrated by the **Dose-Response Relationship** or the **Dose-Response Curve**. It's that old familiar saying: *The dose makes the poison*. Below a certain threshold, a substance won't cause detrimental effects in the test population being observed. However, as the dose increases, so do the health effects. The illustration below is a generic one. The dose-response curve will look different for each substance. A highly toxic substance will have a very steep curve that climbs quickly, whereas one with low toxicity will have a very shallow curve.



Workplace Environmental Exposure Limits (WEEL)

Workplace environmental exposure limits (WEEL) are established for workers without any special protective equipment. The first three below represent the maximum concentration to which an average person in average health may be exposed repeatedly on a day-to-day basis (40 hours per week, 8 to 10 hours per day) with no adverse health effects. Each is established by a different agency. Often the limits established by each agency are the same, but that's not always the case. Some of these published limits will have a "[skin]" notation, meaning that there's a potential for dermal absorption and that workers should protect against skin exposure.

- **Permissible Exposure Limits (PEL)** are established by the Occupational Safety and Health Administration (OSHA). These are time-weighted average (TWA) concentrations that, unless otherwise noted, must not be exceeded during any 8-hour shift of a 40-hour workweek. (Time-weighted average means that one can exceed the identified concentration, within limits, as long as the average exposure over an 8-hour shift does not exceed the PEL.) Because PELs are OSHA limits, compliance with PELs is mandated by law.
- **Recommended Exposure Limits (REL)** are similar to PELs in that they are also time-weighted averages for a 40-hour workweek. However, RELs differ from PELs in that they allow for a 10-hour shift versus an 8-hour shift and RELs are recommended limits established by the National Institute for Occupational Safety and Health (NIOSH), not regulatory limits from OSHA.
- **Threshold Limit Value—Time-Weighted Average (TLV-TWA)** is also a recommended limit, one from the American Conference of Governmental Industrial Hygienists (ACGIH). It's based on an 8-hour shift and 40-hour workweek.

Workers can exceed the permitted or recommended exposure limits if they stay within the short-term and ceiling exposure limits explained below. Short-term and ceiling exposure limits may be either regulatory limits or recommended limits, depending on whether they're established by OSHA or another agency. (If reference books don't cite the source, err on the side of safety and assume it's a regulatory limit.)

- A **Short-Term Exposure Limit (STEL)** is the maximum concentration to which a worker may be exposed for short durations (15 minutes, unless otherwise noted). Exposures above the STEL should be at least 60 minutes apart and not repeated more than 4 times per day. (Often this is written as TLV-STEL.)
- A **Ceiling Exposure Limit** is the concentration that may not be exceeded at any time. (Often this is written as TLV-C.)

Toxicological Values and Exposure Limits (continued)

Deadly or Dangerous Levels

Let's now look at the other end of the spectrum—levels that can be deadly or dangerous to unprotected persons. Once you're familiar with the two extremes, it's easier to understand the emergency planning levels in the section that follows.

- **Lethal Dose (LD)** and **Lethal Concentration (LC)** reflect the exposure required to kill a given percentage of a test population. The term *lethal dose* is used for solids and liquids and is expressed in milligrams per kilogram (mg/kg) of body weight. *Lethal concentration* is used when describing gases and vapors and is usually expressed in parts per million (ppm) or milligrams per cubic meter (mg/m³). Lethal concentration is independent of body weight.

The subscript notation refers to the percentage of test population affected. LD₅₀ or LC₅₀ is the number most often cited in reference sources. It means that 50% of the test population died from exposure to the specified dose or concentration. LD₁₀₀ or LC₁₀₀ means that 100% died. LD₁₀ or LC₁₀ is the exposure that kills the first individual in a test study.

These numbers are derived from laboratory studies on animals, so they're only an approximation of how humans may be affected. And the information is very limited. If the number cited in reference sources is the LD₅₀ or LC₅₀, there's no way to tell what exposure levels killed the first 49% of the test population. It's the first fatality (the LD₁₀ or LC₁₀) that matters most to emergency responders. Additionally, the data shows only fatalities, with no regard for debilitating health effects suffered by the survivors. It also shows only those fatalities that occurred within the test period (typically 14 days). So if test subjects die a month later as a direct result of the exposure, they're not factored into the statistic.

- An **Immediately Dangerous to Life and Health (IDLH)** atmosphere is one that poses an immediate threat to life, would cause irreversible adverse health effects, or would impair an individual's ability to escape from a dangerous atmosphere.

IDLH values were initially developed as part of a joint project by NIOSH and OSHA as a tool for selecting respirators in the workplace. As a safety margin, IDLH values were based on effects that might occur from a 30-minute exposure, but it was not meant to imply that personnel should stay in the environment without proper protective equipment any longer than necessary. Instead, every effort should be made to exit immediately. IDLH should be thought of like an SCBA low-air alarm. It's a window for escape, not a window for squeezing in additional mitigation measures in the time remaining.

IDLH is often used to distinguish between a rescue and a body recovery operation. If a victim has been exposed to the product at or above an IDLH concentration for more than 30 minutes, the chances of survival drop significantly. However, IDLH is only part of the "risk versus gain" analysis. It is generally not possible to make a positive determination of death from a distance.

IDLH is generally based on toxicological data, but where flammability is a significantly greater risk than toxicity, IDLH may be set at 10% of the lower explosive limit (LEL).

Emergency Planning Levels

The values described next fall between the workplace environmental exposure levels and IDLH atmospheres. These are the ones responders use most often for protecting emergency workers in the cold zone and citizens in the surrounding area.

- **Level of Concern (LOC)** is generally defined as 10% of the IDLH. Unlike the other limits, LOC has no associated description of health effects that might be expected. It is simply a safety margin of 10%—just like 10% of a lower explosive limit (LEL) provides a safety margin to keep from entering the flammable range.

Toxicological Values and Exposure Limits (continued)

- The American Industrial Hygiene Association (AIHA) has recommended **Emergency Response Planning Guideline (ERPG)** levels for about 100 substances. ERPGs provide an estimate of concentrations where one might reasonably anticipate adverse effects for exposures that exceed an hour in duration. ERPGs reflect only acute health effects, not long-term complications. Most of the data is based on animal testing, except where documented human exposures could be factored into the estimates.

Emergency Response Planning Guideline (ERPG) Levels

ERPG Level	Represents the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to one hour ...
1	without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.
2	without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
3	without experiencing or developing life-threatening health effects.

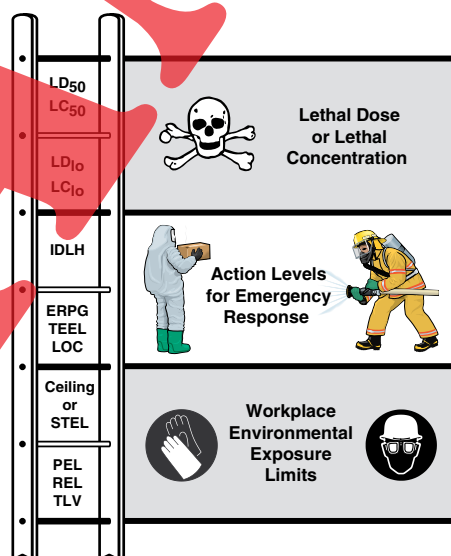
- Temporary Emergency Exposure Limits (TEEL)** are developed by the Subcommittee on Consequence Assessment and Protective Actions (SCAPA) under the U.S. Department of Energy (DOE). TEELs have the same definitions as ERPGs except that TEELs do not specify a one-hour time frame because of the way DOE adjusts for the differences between exposures that are concentration-dependent versus dose-dependent.

As of December 2002, there were more than 2200 substances on the SCAPA list of TEELs, making it a far more extensive list than the AIHA list of ERPGs. However, TEELs are temporary limits, designed to provide guidance until the AIHA publishes ERPGs for the same substances.

Exposure Values Compared

Because the exposure values covered here can be confusing, it often helps to see them on a "hazard ladder" that shows an approximate relation between them. This is obviously not to scale, but it does provide a quick visual representation of how these values stack up against one another.

Simple Hazard Ladder Showing Approximate Relation Between Exposure Values (not to scale)



Toxicological Values and Exposure Limits (continued)

Unfortunately, there may be times when you can't find all of these different values in your reference books, particularly books geared toward workplace exposures. For those occasions, you can estimate IDLH or LOC if you know the TLV-TWA. Remember, however, that these are approximations only.

- LOC is generally defined as 10% of the IDLH or 3 times the TLV-TWA.
- Thus, IDLH is 10 times the LOC or 30 times the TLV-TWA.

One more value, odor threshold, can sometimes be plotted on a hazard ladder. **Odor threshold** is the lowest concentration of a substance in air that can be smelled. If a substance has an odor threshold, it's helpful to know where it stacks up against the toxicity values. Does the substance have adequate warning properties, alerting persons to danger before they can be harmed? Or is it dangerous at concentrations well below the odor threshold?

Of course, some substances have no odor. Others, like chlorine, produce olfactory fatigue. When responders stop smelling chlorine, it's not necessarily because the chlorine has dissipated. It may be because olfactory fatigue has obstructed their ability to detect chlorine by smell alone. Additionally, people vary in their ability to detect odors. For example, at least 25% of the population is genetically unable to smell the bitter almond odor of hydrogen cyanide. So odor threshold is nice to know, but it's far from reliable in judging one's potential exposure.

Toxicological Values and Exposure Limits (continued)

Review Questions (answers on page 194)

1. A contaminant concentration of 1% by volume in air is equal to:
 - a. 1 ppm
 - b. 10 ppm
 - c. 100 ppm
 - d. 1000 ppm
 - e. 10,000 ppm
2. A 1% displacement of oxygen (from a normal concentration of 20.9% to 19.9%) means there may be as much as a ____ concentration of a contaminant gas or vapor.
 - a. 1%
 - b. 3%
 - c. 5%
 - d. 7%
3. What is the legal limit established by OSHA for maximum permitted exposure for an 8-hour time-weighted average?
 - a. TLV-TWA
 - b. PEL
 - c. STEL
 - d. TLV-C
4. LOC is generally described as:
 - a. 10% of the IDLH
 - b. 30% of the LC_{50}
 - c. 10 times the TLV-TWA
 - d. 50% of the IDLH
5. If you're unable to find a material's IDLH in reference sources, you can estimate it as:
 - a. 10% of the LD_{50}/LC_{50}
 - b. 3 times the TLV-TWA
 - c. 10 times the TLV-TWA
 - d. 30 times the TLV-TWA
6. Where flammability is a significantly greater risk than toxicity, IDLH may be set at 10% of the LEL.
 - a. True
 - b. False
7. Lethal dose and lethal concentration values represent death rates only and do not reflect any long-term health effects.
 - a. True
 - b. False
8. When evaluating toxicological values and occupational exposure limits, the _____ the number, the more hazardous the material.
 - a. Higher
 - b. Lower

Hazmat Chemistry Study Guide

Chapter 2 Review

Review Questions (answers on page 194)

- Water has a vapor pressure of ____ at 68°F (20°C) at sea level.
 - 14.7 mmHg
 - 17.5 mmHg
 - 21.1 mmHg
 - 23.8 mmHg
- Which of the following is likely to dissipate fastest (assuming all other conditions are equal)?
 - Methane (vapor density 0.553)
 - Chlorine (vapor density 2.47)
 - Phosgene (vapor density 3.48)
 - Carbon monoxide (vapor density 0.97)
- Which of the following would be considered the most flammable (assuming all are within their flammable ranges)?
 - Octane (flash point 56°F/13.3°C)
 - Isopropyl alcohol (flash point 53°F/11.7°C)
 - Acetone (flash point 0°F/17.8°C)
 - Isopropyl ether (flash point -12°F/-24.4°C)
- Which of the following is likely to present a greater potential for ignition?
 - Ammonia (LEL 16%, UEL 25%)
 - Ethylene oxide (LEL 3%, UEL 100%)
 - Methyl alcohol (LEL 6%, UEL 36%)
 - Pentane (LEL 1.5%, UEL 7.8%)
- If the vapor pressure of methyl alcohol is 96 mmHg at 68°F (20°C), it will be _____ at 90°F (32.2°C).
 - Higher
 - Lower
 - The same
- Which of the following will have vapors likely to travel the furthest from the spill site?
 - Hexane (vapor pressure 124 mmHg)
 - Benzene (vapor pressure 75 mmHg)
 - Toluene (vapor pressure 21 mmHg)
 - Octane (vapor pressure 10 mmHg)
- Which of the following materials sublimates?
 - Mercury
 - Naphthalene
 - Sodium
 - Barium

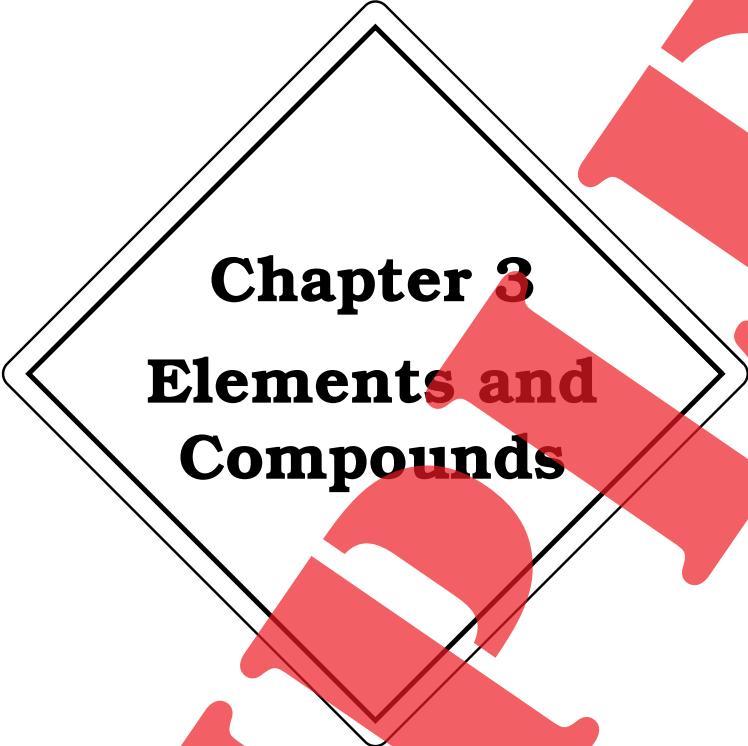
Chapter 2 Review (continued)

8. When at atmosphere containing flammable gases or vapors does *not* meet the definition of a confined space, EPA guidelines suggest hazardous materials technicians can work up to _____ of the LEL if they're cautious and use continuous monitoring.
- 10%
 - 25%
 - 40%
 - 50%
9. Volatility is most accurately described as a measure of:
- Flammability
 - Chemical reactivity
 - Water reactivity
 - Vapor pressure
10. Pure substances that float on water are usually:
- Hydrocarbons
 - Aldehydes
 - Alkyl halides
 - Organic peroxides
11. A person can be exposed to a hazardous material without actually being contaminated.
- True
 - False
12. Which of the following are agents known to cause malformations in an unborn child?
- Carcinogens
 - Mutagens
 - Teratogens
13. Ethylene (ethene) and similar polymers are prone to polymerization due to:
- A double bond between carbon atoms
 - A tendency to be air- or water-reactive
 - Their limited shelf lives
 - Their incompatibility with many other chemicals
14. Emergency response planning guidelines (ERPGs) are based on anticipated health effects for _____ exposures.
- 30-minute
 - 1-hour
 - 2-hour
 - 4-hour
15. Short-term exposure limits (STEL) are based on _____ durations unless otherwise noted.
- 5-minute
 - 15-minute
 - 30-minute
 - 60-minute

Hazmat Chemistry Study Guide

Chapter 2 Review (continued)

16. Which of the following units of measure is based on the molecular weight of the material?
- Parts per million (ppm)
 - Fibers per cubic meter (fibers/cm³)
 - Milligrams per kilogram (mg/kg)
 - Milligrams per cubic meter (mg/m³)
17. Technically, pyrophoric materials are those that:
- React in dry air
 - React in moist air
 - Are spontaneously combustible
 - Have very low ignition temperatures
18. A polar substance is one that is:
- Soluble in water
 - Soluble in hydrocarbons
 - Soluble in only substances made of the same elements
 - Insoluble in anything
19. The vapor density of a vapor or gas can be calculated by dividing the material's molecular weight by:
- 8.33
 - 14.7
 - 17.5
 - 29.0
20. Which of the following is most likely to be used to distinguish between a rescue and a body recovery operation?
- LD or LC
 - TLV-TWA
 - LOC
 - IDLH



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:

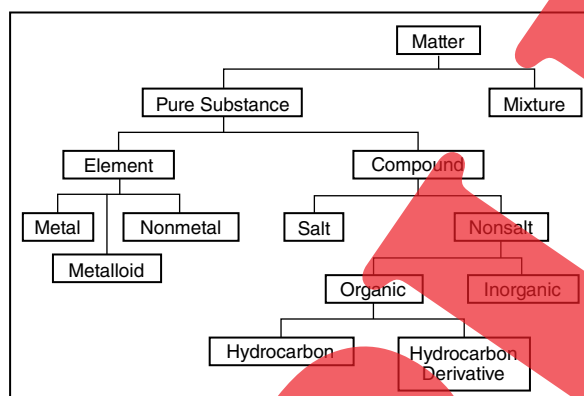
- Matter
- The Periodic Table
- Atomic Structure
- Chemical Bonding
- Isomers

Hazmat Chemistry Study Guide

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).

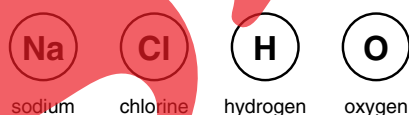
A **mixture** consists of two or more elements or compounds that are physically mixed, but not chemically bonded. For example, sodium chloride (NaCl) and water (H₂O) mix to form salt water, but neither compound is chemically altered during the mixing process. Gasoline, kerosene, and fuel oil are common 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.

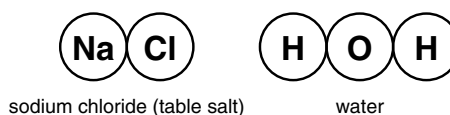
A pure substance may be either a single **element** (such as sodium, chlorine, hydrogen, or oxygen) or a **compound** (such as sodium chloride or water) comprised of two or more elements chemically bonded to form a **molecule**. In other words, compounds can be broken down to release simpler substances (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.

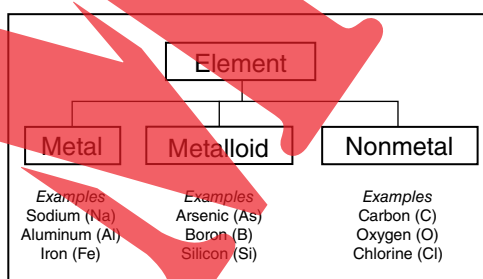
Metals, in general, have a characteristic lustrous (shiny) appearance and are good conductors of heat and electricity. They are malleable (can be hammered into thin sheets) and ductile (can be drawn into wires). Most metals are solids in their natural states. The exceptions are mercury (Hg), cesium (Cs),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

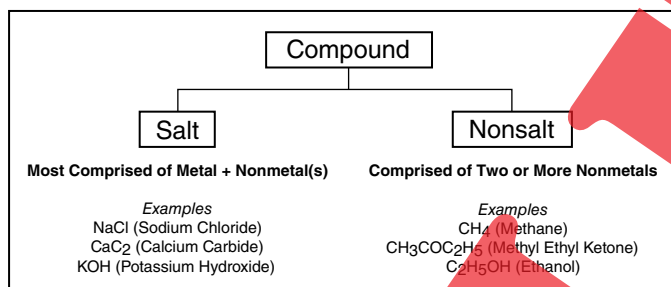


Alloys (or *metal alloys*) are generally described as a mixture of two or more metals, the purpose of which is to create a material that is somehow stronger or better for a particular application than any one metal would be alone. For example, brass is comprised of approximately 70% copper (Cu) and 30% 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.

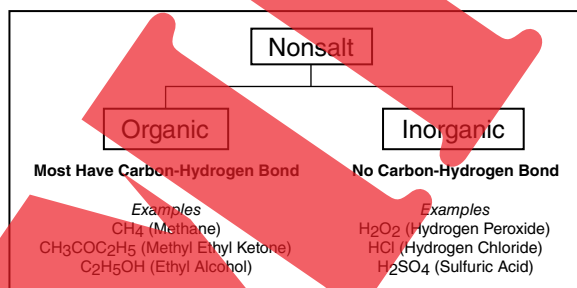
Alloys sometimes contain a small percentage of nonmetal elements. Steel, for example, is comprised primarily of iron (Fe), but contains 0.1% to 1.5% carbon (C). Stainless steel is roughly 80% iron (Fe), 15% chromium (Cr), 4% nickel (Ni), and 0.5% to 1% carbon (C).

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

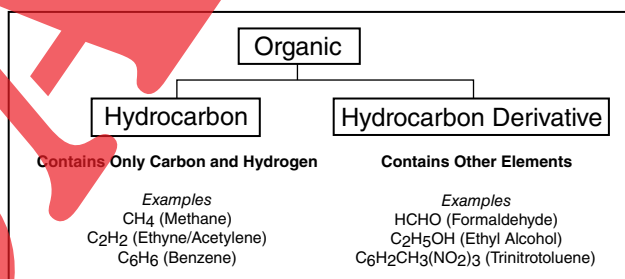
Hazmat Chemistry Study Guide

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 (CO_2), sodium cyanide (NaCN), calcium carbonate (CaCO_3), and carbon tetrachloride (CCl_4). 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

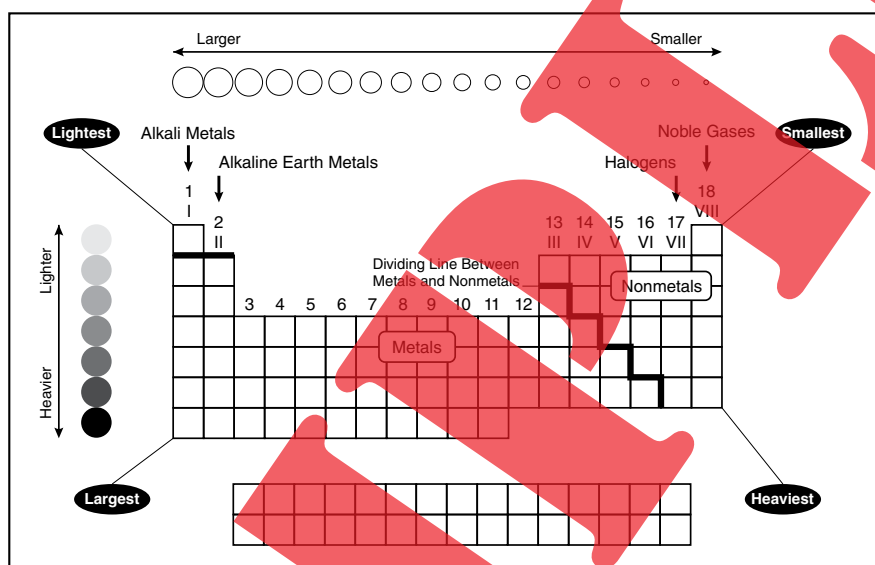
Hazmat Chemistry Study Guide

The Periodic Table

Elements on the periodic table are arranged according to atomic structure. The illustration below is that of a blank periodic table designed to show how an element's position on the periodic table provides some basic information about its characteristics. (A complete periodic table is shown on the following page.)

Metals are located on the left side of the periodic table; nonmetals, on the right. (Notice the dividing line between metals and nonmetals.) Hydrogen, which is located in the upper left-hand corner above the thick dividing line, is also a nonmetal.

Trends on the Periodic Table



The elements become heavier and larger as you look lower on the table, which is significant with respect to vapor density, specific gravity, and other related properties. Elements toward the left side of the periodic table are larger, whereas those toward the right side are smaller and more compact.

The periodic table on the following page shows each element by name, symbol, atomic number, and atomic weight. (The atomic weight was rounded to three decimal points where the number was less than 100. Atomic weights over 100 were rounded to two decimal points.) The symbols consist of either a single capital letter (for example, H for hydrogen) or a capital letter followed by a lowercase letter (for example, He for helium).

Key to Information on the Periodic Table

Atomic Number	1	1.008	Atomic Weight
	H		Symbol
Name	Hydrogen		

Noble Gases																	
VIII																	
18																	
Halogens																	
VII																	
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Hazmat Chemistry Study Guide

The Periodic Table (continued)

The periodic table continues to evolve as new elements are created and named. The one on the previous page is based on a November 2004 periodic table from the International Union of Pure and Applied Chemists (IUPAC). (IUPAC was formed in 1919 by chemists from industry and academia who recognized the need for international standardization in chemistry. More information about this organization and its activities can be found at <http://www.iupac.org>.) Five additional elements (112, 113, 114, 115, and 116) have been reported, but have not been fully authenticated, so they are not included on this periodic table.

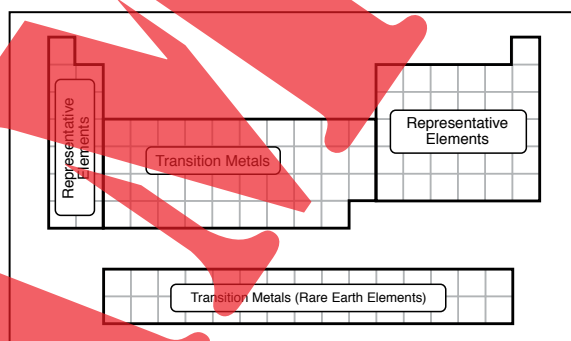
Several elements have two names or spellings, which sometimes accounts for symbols that don't seem to match the element name. Those elements are shown below.

Elements with Alternate Names or Spellings

Symbol	Element Name	Alternate Name	Symbol	Element Name	Alternate Name
Ag	Silver	Argentum	K	Potassium	Kalium
Al	Aluminum	Aluminium	Na	Sodium	Natrium
Au	Gold	Aurum	Pb	Lead	Plumbum
Cs	Cesium	Caesium	Sb	Antimony	Stibium
Cu	Copper	Cuprum	Sn	Tin	Stannum
Fe	Iron	Ferrum	W	Tungsten	Wolfram
Hg	Mercury	Hydrargyrum			

There are three major regions or areas on the periodic table. The **representative elements** on either side of the table are the most important to the study of hazardous materials because, as a category, they're more chemically active than the **transition metals** in the middle of the table and the **rare earth elements** below.

Representative Elements and Transition Metals



Most elements exist as **solids** in their natural physical states. The elements that exist as **gases** are hydrogen, nitrogen, oxygen, chlorine, fluorine, and the noble gases (helium, neon, argon, krypton, xenon, and radon). Periodic tables generally identify bromine, cesium, francium, and mercury as **liquids**. However, some elements are borderline and may exist in different forms, depending on ambient temperature.

If a periodic table is printed in color, solid elements are generally printed in black, gaseous elements in red, and liquid elements in blue. (Some printers may use other color schemes.)

The Periodic Table (continued)

Elements are grouped vertically in **families** based on their chemical behaviors. All members of the same family have similar chemical characteristics, though each will also have its own unique properties. The four families identified below are significant because they are the most predictable; the similarities between each member of the family are greater than they are within other families.

Four Significant Chemical Families

Alkali Metals		Alkaline Earth Metals		Metals										Non Metals		Halogens		Noble Gases	
I	II															VII	VIII		
Li	Be															F	He		
Na	Mg															Cl	Ne		
K	Ca															Br	Ar		
Rb	Sr															I	Kr		
Cs	Ba															At	Xe		
Fr	Ra																Rn		

Group I - The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. These elements are flammable and highly reactive. When in contact with water, they produce flammable hydrogen gas, a strong caustic runoff, and excessive heat. These elements are quite soft compared to metal goods we're used to seeing. They can be cut with a knife much as one would cut through a block of clay.

Sodium and potassium, the most common of the alkali metals, will ignite spontaneously if exposed to moist air. Sodium will even ignite on contact with dry air. Contact between these metals and water rips apart the water molecules, allowing other compounds to be formed from the individual elements. Sodium and potassium combine with free oxygen and hydrogen atoms to form the highly corrosive sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions, respectively. Free hydrogen atoms combine to form the highly flammable hydrogen (H₂) gas. The heat generated from this violent reaction with water is enough to melt the metal and ignite both the hydrogen gas and nearby combustibles.

Group II - The alkaline earths, also metals, are beryllium, magnesium, calcium, strontium, barium, and radium. They are flammable and often water-reactive, though less so than the alkali metals (Group I). The alkaline earth metals are harder than the alkali metals, but still soft compared to many other metals.

A common example from this group is magnesium, which burns with an intense white flame. With an ignition temperature of 1202°F (650°C), magnesium is relatively difficult to ignite in block form. However, the risk of ignition increases in proportion with the amount of surface area exposed to air, so powder, dust, chips, and shavings present a significant fire hazard. Magnesium is very water-reactive when burning. Water intensifies the fire as the water molecule is broken down to form oxygen (O₂) and hydrogen (H₂). Even water molecules not ripped apart can be instantly converted to steam by the heat of the fire, causing a steam explosion.

Group VII - The halogens are fluorine, chlorine, bromine, iodine, and astatine. These elements are highly reactive and toxic. They are nonflammable, but they are powerful oxidizers that support combustion.

Chlorine, with its characteristic suffocating odor, is the most common halogen. Chlorine gas reacts with moisture in the lungs or on the skin to form corrosive hydrochloric acid (HCl). Even more destructive to human tissue is hydrofluoric acid (HF) formed when fluorine reacts with water. Again, these gases don't burn. However, chlorine and fluorine in particular are such powerful oxidizers—more powerful than oxygen itself—that fires can burn intensely in their presence even when no oxygen is present.

Group VIII - The noble gases are helium, neon, argon, krypton, xenon, and radon. These gases are inert, nonreactive simple asphyxiants that are often stored and transported as cryogenic liquids (colder than -130°F/-90°C). The primary risks associated with these gases in an uncontrolled release are frostbite and asphyxiation from oxygen displacement. The high expansion ratios associated with cryogenic liquids greatly increases the risk of catastrophic container failure in the event of a fire or other scenario where the product temperature is elevated beyond the capacity of pressure-relief devices.

Hazmat Chemistry Study Guide

The Periodic Table (continued)

The periodic table can be overwhelming, but let's look at it from a different perspective. Shown below are the thirty most common elements found in hazardous chemicals as originally identified by Ron Edwards, Ph.D. These are the ones you are most likely to encounter, either as individual elements or as part of other compounds.

The 30 Most Common Elements Found in Hazardous Chemicals

Metals

Li - Lithium	Mn - Manganese
Na - Sodium	Fe - Iron
K - Potassium	Co - Cobalt
Be - Beryllium	Cu - Copper
Mg - Magnesium	Hg - Mercury
Ca - Calcium	Al - Aluminum
Ba - Barium	Sn - Tin
Cr - Chromium	

Nonmetals

H - Hydrogen	F - Fluorine
B - Boron	Cl - Chlorine
C - Carbon	Br - Bromine
Si - Silicon	I - Iodine
N - Nitrogen	He - Helium
P - Phosphorus	Ne - Neon
O - Oxygen	Ar - Argon
S - Sulfur	

In his hazmat chemistry classes, respected instructor Dieter Heinz uses "Dieter's Top 13" to help focus attention on substances most commonly encountered and/or of greatest significance to hazmat technicians. These top thirteen metals and nonmetals are similar to those identified by Ron Edwards, but the list has been updated to reflect Dieter's slightly different emphasis. Your community may see more of some elements than others, depending on the industries present. However, narrowing the focus to the elements most abundant in or significant to your community makes the periodic table much less intimidating.

Dieter Heinz's Top 13 Nonmetals

Fuels & Chemicals

C - Carbon
H - Hydrogen

Oxidizers

O - Oxygen
F - Fluorine
Cl - Chlorine
Br - Bromine
I - Iodine

Agricultural & WMD Chemicals

P - Phosphorus
N - Nitrogen
S - Sulfur

Hi-Tech Chemicals

B - Boron
Si - Silicon
As - Arsenic

Dieter Heinz groups the nonmetals based on their most common usage:

- Carbon and hydrogen are found in many chemicals, particularly fuels.
- The halogens are most often found in oxidizers.
- Agricultural chemicals and those used in weapons of mass destruction most often contain phosphorus, nitrogen, and/or sulfur.
- The elements most often encountered in the hi-tech industry are boron, silicon, and arsenic.

Carbon and hydrogen deserve special mention. As emphasized earlier, almost all of the compounds classified as organic are those containing carbon-hydrogen bonds. It's estimated that about 90% of all known compounds are organic and more than 95% of all known compounds contain carbon. It's not because carbon is the most abundant element. Rather, it's a very versatile element, as you'll see in the section on chemical bonding. It can bond with up to four other atoms, including other carbon atoms. It can form double and triple bonds. It can bond in long chains or ring structures. So it's no coincidence that this study guide and your hazmat chemistry class will put such a heavy emphasis on hydrocarbons and hydrocarbon derivatives.

A stylized periodic table is shown, with a red hand pointing to the element Gallium (Ga). The table is a grid where each cell represents an element. The elements shown are: Li, Be, Na, Cr, Cu, Ag, Au, Hg, Ba, Zr, Th, and Ga. The hand is a simple red silhouette with its index finger pointing directly at the cell containing 'Ga'. The background is white, and the grid lines are thin and grey.

- Metals used to conduct electricity (AC or DC) include aluminum, copper, gallium, lithium, silver, and sodium.
- Metals commonly used in nuclear energy applications (for example, to transfer heat out of nuclear reactors) include sodium, thorium, and zirconium.
- Metals and their alloys commonly used in the construction of buildings, vehicles, and aircraft (for strength, heat resistance, and/or reflection of infrared radiation) include aluminum, beryllium, gold, lithium, and zirconium.
- Metals and their alloys commonly used in tools and utensils include aluminum, beryllium, chromium, copper, and silver.
- Metals used in the medical and dental industries for diagnostic or treatment purposes include barium, lithium, mercury, silver, and sodium.
- Metals commonly used in jewelry include gold and silver.

Hazmat Chemistry Study Guide

The Periodic Table (continued)

Review Questions (answers on pages 194 and 195)

- Group I on the periodic table represents the:
 - Transition metals
 - Alkali metals
 - Alkaline earth metals
 - Halogens
- Group II on the periodic table represents the:
 - Transition metals
 - Alkali metals
 - Alkaline earth metals
 - Halogens
- Group VII on the periodic table represents the:
 - Noble gases
 - Alkali metals
 - Alkaline earth metals
 - Halogens
- Group VIII on the periodic table represents the:
 - Noble gases
 - Alkali metals
 - Alkaline earth metals
 - Halogens
- Which of the following lists contains only alkali metals?
 - Sodium, potassium, lithium
 - Calcium, magnesium, barium
 - Potassium, sodium, magnesium
 - Aluminum, magnesium, sodium
- Which of the following will not burn but is an oxidizer that will support combustion?
 - Carbon
 - Chlorine
 - Nitrogen
 - Hydrogen
- Which of the following lists contains only alkaline earth metals?
 - Aluminum, iron, mercury
 - Potassium, sodium, magnesium
 - Beryllium, calcium, magnesium
 - Sodium, potassium, lithium
- Most elements exist as _____ in their natural states.
 - Gases
 - Liquids
 - Solids

The Periodic Table (continued)

9. Elements become heavier as you look lower on the periodic table.

- True
- False

10. Name the following elements.

- | | | | |
|-------|-------|-------|-------|
| a. Na | _____ | f. F | _____ |
| b. C | _____ | g. K | _____ |
| c. Mg | _____ | h. He | _____ |
| d. P | _____ | i. H | _____ |
| e. Cl | _____ | j. O | _____ |

11. Identify the symbol for each of the following elements.

- | | | | |
|-------------|-------|--------------|-------|
| a. Nitrogen | _____ | f. Lithium | _____ |
| b. Calcium | _____ | g. Bromine | _____ |
| c. Sulfur | _____ | h. Potassium | _____ |
| d. Iodine | _____ | i. Aluminum | _____ |
| e. Sodium | _____ | j. Lead | _____ |

12. Identify each of the following elements as being either metal (M) or nonmetal (NM).

- | | | | |
|---------------|-------|--------------|-------|
| a. Lithium | _____ | g. Carbon | _____ |
| b. Chlorine | _____ | h. Hydrogen | _____ |
| c. Nitrogen | _____ | i. Magnesium | _____ |
| d. Sodium | _____ | j. Fluorine | _____ |
| e. Phosphorus | _____ | k. Calcium | _____ |
| f. Potassium | _____ | l. Neon | _____ |

13. Identify which family (Group I, II, VII, or VIII) each of the following elements belongs in.

- | | | | |
|--------------|-------|-------------|-------|
| a. Fluorine | _____ | g. Helium | _____ |
| b. Potassium | _____ | h. Chlorine | _____ |
| c. Argon | _____ | i. Calcium | _____ |
| d. Iodine | _____ | j. Lithium | _____ |
| e. Magnesium | _____ | k. Bromine | _____ |
| f. Sodium | _____ | l. Neon | _____ |

14. Match each of the following families with the description that best fits them.

- Group I - Alkali Metals
- Group II - Alkaline Earth Metals
- Group VII - Halogens
- Group VIII - Noble Gases

- _____ Highly reactive. Toxic. Nonflammable. Powerful oxidizers that will support combustion.
- _____ Flammable. Highly reactive. When in contact with water, produce flammable hydrogen gas, a strong caustic runoff, and excessive heat.
- _____ Inert. Nonreactive. Simple asphyxiants. Often stored and transported as cryogenics.
- _____ Flammable. Often water-reactive.

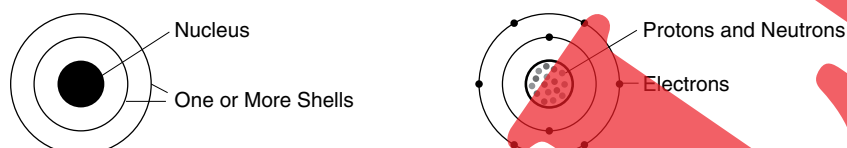
Hazmat Chemistry Study Guide

Atomic Structure

The basic building block of any substance is the **atom**. Every element and compound is made up of one or more atoms. Understanding the structure and behavior of atoms can be very helpful in predicting hazards at an incident and, therefore, in planning a safe, effective response.

As we discuss the makeup of an atom, we'll refer to the **nucleus** (the center of the atom) and **shells**. An atom has only one nucleus but can have several shells.

The Structure of an Atom



Within the nucleus are **protons** and **neutrons**. Every element has a specific number of protons. For example, carbon will always have six protons and oxygen will always have eight protons. The number of protons corresponds to the **atomic number** of the element. Therefore, the atomic number of carbon is 6, while the atomic number of oxygen is 8.

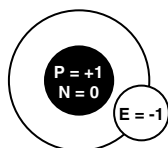
Some elements have an equal number of protons and neutrons, but it's not unusual for elements to have more neutrons than protons. For example, sodium (atomic number 11) has eleven protons and twelve neutrons. (Hydrogen, the smallest of all elements, is an oddity; its dominant form has one proton but no neutrons.)

Electrons orbit the nucleus much the way planets orbit the sun. These electrons are said to reside in shells, sometimes called *orbits* or *rings*. How elements interact with one another is primarily a function of their electrons. Electrons and shells will be discussed in more detail shortly.

An atom's **atomic weight** comes from its protons and neutrons. Electrons are so light that they are considered essentially weightless. Protons and neutrons, on the other hand, each weigh what is referred to as one (1) *atomic mass unit*, or simply "1." For example, oxygen (illustrated above) has eight protons and eight neutrons. Its atomic weight is just shy of 16 (15.999). Molecular weight is the combined weight of all elements in a compound or molecule.

Protons and electrons are electrically charged, protons positively (+1) and electrons negatively (-1). Neutrons have no electrical charge; they are **neutral** and thus have very little bearing on an atom's electrical activity. (Because like charges repel each other, some buffer is needed to keep protons from repelling each other to the point of destroying the nucleus. That's what neutrons are for. Scientists sometimes refer to them as *nuclear glue*.) Atoms must have an equal number of protons and electrons to ensure a balance between positive and negative charges—to ensure the atom is electrically neutral. But when some atoms react (bond) with other atoms, they either gain or lose electrons, becoming "charged" in the process. These charged atoms are called **ions**. (Chemical bonding is covered in the next section.)

Electrical Charges Associated with Parts of the Atom



Summary of Atomic Structure

<u>Part of the Atom</u>	<u>Location</u>	<u>Charge</u>	<u>Weight</u>
Protons	Nucleus	+1	1
Neutrons	Nucleus	0	1
Electrons	Shells/Orbits	-1	0

Atomic Structure (continued)

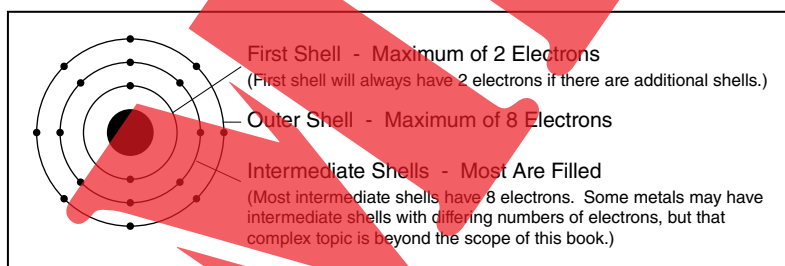
Periodic tables show the predominant, or most stable, form of each element. However, many elements have two or more isotopes. **Isotopes** are merely variations of the same element, the only difference being the number of neutrons in the nucleus. For example, the predominant form of carbon has six protons and six neutrons in the nucleus. Carbon-14 (^{14}C), on the other hand, has six protons and eight neutrons in the nucleus. Thus an atom's identity may also be determined by the number of neutrons in the nucleus.

Isotopes of the same element have the same chemical properties. However, their atomic weights will differ because the number of neutrons is different. Consequently, the physical properties of isotopes may vary slightly. Carbon-14, for example, is radioactive, whereas carbon in its predominant form is not. (Note: The atomic weight indicated on a periodic table is really a weighted average of all naturally occurring isotopes. So for example, if one took every atom of carbon, regardless of isotope, and weighed the entire collection, the average weight of each atom would be 12.011 atomic mass units.)

Again, an atom can have several shells surrounding the nucleus. The number of electrons in the outermost shell is the characteristic that most influences chemical bonding (chemical reactivity). These outer shell electrons are also known as *valance electrons*, though the term *outer shell electrons* will be used throughout this book for clarity. (Some people prefer the term *outermost shell electrons* instead.)

There is a maximum number of electrons that can fit on any one shell. The shell closest to the nucleus can hold no more than two electrons, regardless of how big the atom is. The outer (or outermost) shell can have up to eight electrons. Most intermediate shells have eight electrons. (Some metals play by slightly different rules and can have differing numbers of electrons on their intermediate shells, but that complex topic is beyond the scope of this book.) Hydrogen and helium are so small that they each have only one shell. Hydrogen has one electron on that shell, while helium has two. All other elements have two or more shells.

The Maximum Number of Electrons a Shell Can Hold



By looking at a periodic table, you can easily determine the number of outer shell electrons in the representative elements. It is indicated by the Roman numeral group numbers (I through VIII) at the top of the table. For example, elements in Group I will have one outer shell electron, elements in Group II will have two, and so forth.

Group Number Indicates Number of Outer Shell Electrons

Sodium

Elements in Group I Have One Outer Shell Electron

Oxygen

Elements in Group VI Have Six Outer Shell Electrons

Atomic Structure (continued)

It's this characteristic of having the same number of outer shell electrons that makes the four families introduced earlier (alkali metals, alkaline earth metals, halogens, and noble gases) behave so similarly. Again, it's the number of outer shell electrons that most influences chemical bonding. So because each of the alkali metals, for example, has one electron on its outer shell, they'll all behave similarly in their efforts to bond with another element that can use that one electron. This will be explained in more detail in the next section, but now you can begin to see why we can make generalizations about elements within the same group or family.

Note: Most chemistry classes present atomic structure in far more detail that includes, among other things, a different image of an atom called the *quantum mechanical model*. If you were to look at a regular chemistry text, you would see that many illustrations differ from what is taught in hazmat chemistry classes. Most of what you'll learn in hazmat chemistry has been simplified greatly because the goal is to help emergency responders understand how chemistry relates to the behavior of hazardous materials, not to make chemists out of anyone.

Atomic Structure (continued)

Review Questions (answers on page 195)

1. An element's atomic number is based on the number of:
 - a. Electrons
 - b. Neutrons
 - c. Protons
 - d. Shells
2. An element's atomic weight is based on:
 - a. The weight of its protons
 - b. The weight of its neutrons
 - c. The combined weight of its protons and neutrons
 - d. The combined weight of its protons and electrons
3. The part of an atom that is essentially weightless and has a negative charge is an:
 - a. Electron
 - b. Neutron
 - c. Proton
4. Isotopes are variations of the same element with a different number of:
 - a. Electrons
 - b. Neutrons
 - c. Protons
5. Which of the following has five electrons on its outer shell?
 - a. Sulfur
 - b. Boron
 - c. Phosphorus
 - d. Iodine
6. Which of the following has nine protons in its nucleus?
 - a. Fluorine
 - b. Chlorine
 - c. Magnesium
 - d. Sodium
7. The atomic weight of oxygen in its normal state is closest to:
 - a. 6
 - b. 8
 - c. 12
 - d. 16
8. Which characteristic most influences chemical bonding:
 - a. The number of electrons in the outer shell
 - b. The total number of electrons in all shells
 - c. The number of protons in the nucleus
 - d. The number of neutrons in the nucleus

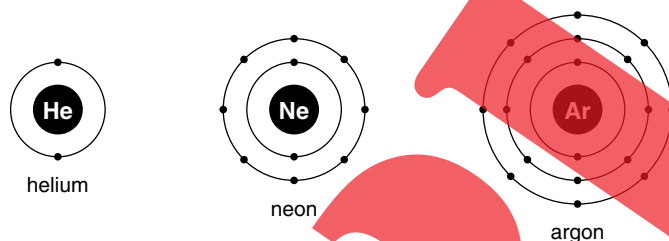
Hazmat Chemistry Study Guide

Chemical Bonding

Once again, all atoms must have an equal number of protons and electrons to be *electrically neutral*. However, to be *stable*, an atom must have a completely filled outer shell (two electrons on hydrogen and helium, eight on all others). Herein lies a conflict and thus the basis for chemical reactivity.

Elements in Group VIII, the noble gases, are the exception to the chemical bonding process described over the next few pages. They already have filled outer shells; thus they have no reason to react with other elements. They are inert. (Inert doesn't mean harmless. Remember, these gases are simple asphyxiants often stored or transported as cryogenic liquids, making them also a thermal hazard with high expansion ratios.)

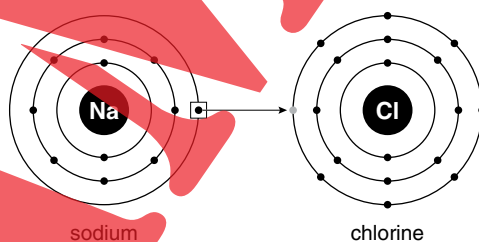
Noble (Inert) Gases with Filled Outer Shells



All the other elements have outer shells that aren't filled to the maximum, so they must bond (combine) with others to create a filled outer shell. Hydrogen, with only one shell, needs one more electron to obtain a total of two. This is called the **duet rule**. The rest will attempt to achieve eight electrons on their outermost shells to fulfill what is called the **octet rule**. (The duet and octet rules are sometimes collectively referred to as the **octet/duet rule**.)

Ionic bonds are formed by the transfer of electrons from a metal element to a nonmetal element. (Here's where it becomes important to know how to distinguish between metals and nonmetals on a periodic table.) In the example below, sodium "donates" the one electron on its outer shell, essentially shedding the outer shell and exposing a filled shell beneath it. Chlorine, with seven electrons on its outer shell, "accepts" the donated electron from the sodium atom, also ending up with a filled outer shell.

Ionic Bond Between Sodium and Chlorine to Form Sodium Chloride



While the two elements are now stable, they're no longer electrically balanced. When the metal element donates electrons to the nonmetal element, it leaves the metal element with a net positive charge (protons outnumber electrons). Conversely, when the nonmetal element accepts electrons from the metal element, it ends up with a net negative charge (electrons outnumber protons). A charged atom is called an **ion**. Positively charged ions (metals) are **cations**, while negatively charged ions (nonmetals) are **anions**.

Summary of Electron Transfer in Ionic Bonds

Type Element	Electron Transfer	Ion Formed	Charge
Metal	Donates	Cation	Positive
Nonmetal	Accepts	Anion	Negative

Chemical Bonding (continued)

Oppositely charged ions attract each other, forming a strong bond that holds them together. In essence, although there has been a transfer of electrons, the atoms involved cannot stray far apart because ions (charged atoms) cannot exist by themselves. The union of a metal element and one or more nonmetal elements creates a **salt compound**. The table below provides some examples.

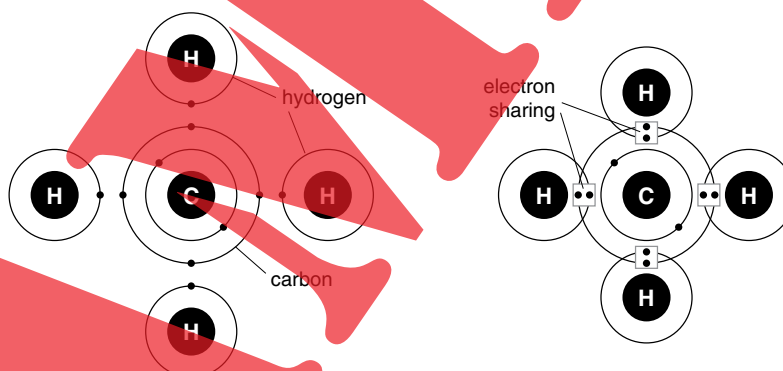
Examples of Salt Compounds Created Through Ionic Bonds

<u>Metal</u>	+	<u>Nonmetal(s)</u>	=	<u>Salt Compound</u>
Calcium (Ca)		Carbon (C)		Calcium Carbide (CaC_2)
Magnesium (Mg)		Oxygen (O)		Magnesium Oxide (MgO)
Sodium (Na)		Oxygen (O)		Sodium Oxide (Na_2O)
Potassium (K)		Carbon and Nitrogen (CN)		Potassium Cyanide (KCN)
Sodium (Na)		Oxygen and Hydrogen (OH)		Sodium Hydroxide (NaOH)
Sodium (Na)		Chlorine and Oxygen (ClO)		Sodium Hypochlorite (NaClO)

Salts are covered in the next chapter. For now, it's sufficient to recognize that most salts are compounds comprised of a metal element bonded to one or more nonmetal elements. There are just a handful of exceptions that don't contain metal, but don't worry about those now.

Covalent bonds are formed between two or more nonmetal elements. These elements share electrons rather than transfer electrons. Their outer shells overlap to the point that electrons seem to belong to each atom at the same time. The union results in a **nonsalt compound** with relatively weak bonds compared to salt compounds. Methane, for example, is formed by the union of one carbon atom and four hydrogen atoms, as shown below.

Covalent Bond Between Carbon and Hydrogen to Form Methane



Covalent compounds are comprised of nonmetal elements only. Most of the ones hazmat technicians encounter consist solely of carbon, hydrogen, and oxygen in various combinations. The bulk of the covalent compounds that contain other elements are limited to nitrogen, phosphorus, sulfur, and the halogens (chlorine, fluorine, bromine, and iodine). The chart below provides a few examples. Many more will be covered in a later chapter.

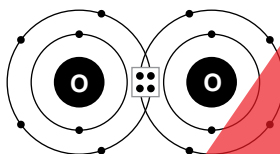
Examples of Nonsalt Compounds Created Through Covalent Bonds

<u>Carbon, Hydrogen, and Oxygen Only</u>	<u>Additional Elements</u>
Propane - C_3H_8	Trinitrotoluene (TNT) - $\text{C}_6\text{H}_2\text{CH}_3(\text{NO}_2)_3$
Acetylene - C_2H_2	Trichloromethane (Chloroform) - CHCl_3
Ethyl Alcohol (Ethanol) - $\text{C}_2\text{H}_5\text{OH}$	Trifluorobromomethane (Halon 1301) - CF_3Br
Dimethyl Ketone (Acetone) - CH_3COCH_3	Parathion - $\text{C}_{10}\text{H}_{14}\text{NO}_5\text{PS}$

Hazmat Chemistry Study Guide

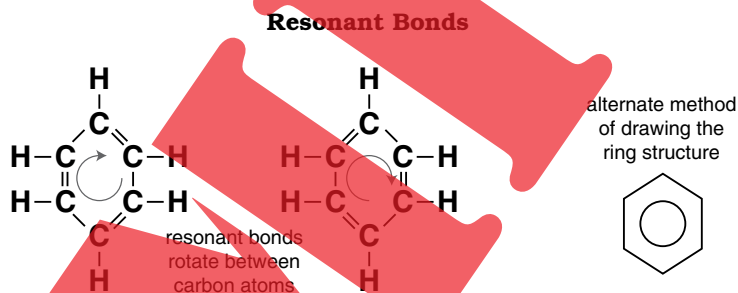
Chemical Bonding (continued)

A covalent compound existing as a molecule of two identical atoms is called a **diatomic molecule** (or, in the cases of gases, a **diatomic gas**). The oxygen we breathe (O_2) is a familiar example. A single atom of oxygen has six electrons in its outer shell; it needs two more to be stable. Yet when two atoms of oxygen bond (share electrons), each essentially winds up with eight electrons in its outer shell. The result is a stable compound.

A Diatomic Molecule of Oxygen (O_2)

The other diatomic gases are hydrogen (H_2), nitrogen (N_2), fluorine (F_2), and chlorine (Cl_2). Diatomic molecules aren't limited to gases. Bromine (Br_2), for example, is a liquid. Iodine (I_2) is a solid.

When compounds contain **resonant bonds**, as do aromatic hydrocarbons (benzene, toluene, xylene, styrene, and cumene), the electrons rotate or alternate very rapidly between the carbon atoms as illustrated with the compound benzene (C_6H_6) below. Benzene's ring structure can be represented either by elements connected with dashes or by a ring within a hexagon.



The table below summarizes the differences between the three types of bonds.

Summary of Ionic, Covalent, and Resonant Bonds

<u>Bond</u>	<u>Composition</u>	<u>Electron Action</u>	<u>Result</u>
Ionic	Metal + Nonmetal	Transfer	Salt Molecule
Covalent	Nonmetal + Nonmetal	Share	Nonsalt Molecule
Resonant	Nonmetal + Nonmetal	Share	Nonsalt Molecule

Every bond stores some amount of energy (bond energy) that is released when the bond is broken. The amount of energy released will depend on the amount and type of elements that comprise the bond and on what causes the bond to be broken. Some compounds can release a tremendous amount of energy (in the form of light and heat) when their bonds are broken.

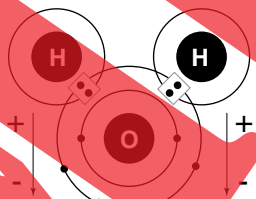
Chemical Bonding (continued)

Now that you've seen the relation between outer shell electrons and chemical bonding, let's go back to the periodic table and the four families of elements considered so important to your understanding of hazardous materials.

- Group I - The alkali metals were described as *highly reactive*. Any element with just one electron on its outer shell is so close to the ideal (stable) condition of having a filled outer shell that it reacts vigorously to donate that one outer shell electron to any element that needs it.
- Group II - The alkaline earth metals are also fairly reactive, but not to the same degree as alkali metals. It takes more effort to shed two outer shell electrons than it does to shed one, so these elements aren't quite as "motivated."
- Group VII - The halogens are also one electron away from having a filled outer shell, so they're highly reactive too. However, they're quite different from the alkali metals. They have seven electrons on their outer shells, so they'll readily grab one more from any metal element with one or more to donate in an ionic bond. But they'll also share electrons with nonmetal elements to form covalent bonds.
- Group VIII - The noble gases have filled outer shells already. They have no reason to react with other elements. They are inert.

Let's also tie in one other concept presented earlier—*polarity*. The simple illustrations used in this study guide don't reflect the fact that electrons are sometimes drawn more strongly to one element than another within a compound. For example, in a water molecule (H_2O), the electrons are more strongly drawn to oxygen than to hydrogen, giving water positive and negative "poles," similar to a magnet. Because opposite charges attract, the negatively charged oxygen atom in one water molecule will attract a positively charged hydrogen atom in another water molecule. Consequently, water molecules are strongly attracted to one another.

Electrons Drawn More Strongly to One Element Than Another



Other polar substances are water-soluble because their electrons are also drawn more strongly to one element than to another. For example, electrons are more strongly drawn to chloride ions (Cl^-) than to sodium ions (Na^+) in sodium chloride (NaCl). However, the attraction between the sodium and chloride ions is not as strong as the attractive forces that want to pair hydrogen (H^+) with the chloride ions (Cl^-) and oxygen (O^-) with the sodium ions (Na^+). So water dissolves the salt (causes it to mix with the water without changing the chemical composition). Some substances are more soluble than others. A substance considered only slightly soluble would be one with weak attractive forces between water and the elements in the other compound.

Nonpolar substances don't have these positive and negative "poles" because the electrons aren't pulled more strongly in one direction than another. So putting them in water won't cause them to mix. The nonpolar substances will either float or sink, depending on specific gravity.

Dash Style Illustrations to Represent Chemical Bonding

Most of the illustrations shown thus far have been useful for picturing the structure of atoms, but they would be too cumbersome for showing complex chemical compounds. So from now on, we'll use a different type of illustration (known as dash style) that shows only the number of available bonding sites on the outer shell of each atom. For example, carbon has four available bonding sites, while hydrogen has only one.

Individual Elements and Their Available Bonding Sites



Carbon



Hydrogen

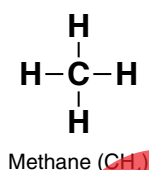
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Chemical Bonding (continued)

As indicated on page 63, the group number identifies the number of electrons on the outer shell. If you subtract that number from 8 (the maximum number of electrons an outer shell can hold), you can determine the number of available bonding sites. For example, phosphorus is in Group V. It has three available bonding sites ($8 - 5 = 3$). (Again, hydrogen is an exception because it can hold only two electrons on its one shell.)

Once elements are bonded in a compound, these dashes show the bond between atoms. In the illustration below, all available bonding sites are taken as one carbon atom is bonded to four hydrogen atoms to form methane (CH_4).

A Compound Made of Five Individual Atoms



Just as atoms need to be balanced (electrically neutral), so do compounds. In other words, all available bonding sites must be filled. The illustration on the left below represents the compound methane (CH_4). It is balanced because all available bonding sites on the five atoms are filled. The illustration on the right represents something discussed later—a hydrocarbon radical. The original methane molecule has lost one hydrogen atom, but that hydrogen atom can be replaced by something else to form a new compound—a hydrocarbon derivative (also discussed later). In that way, the structure will be balanced again.

Balanced (Electrically Neutral) Versus Not Balanced



Note: Chemistry textbooks often contain illustration styles that look considerably different than these. However, the dash style above is the simplest for presenting the concepts most important to the study of hazardous materials, so it's what you're likely to see in your hazmat chemistry class and what will be used throughout this study guide. These illustrations are also referred to as **structural formulas**.

Condensed structural formulas are often used to represent chemical compounds. They differ from **molecular formulas** in that they identify how atoms are arranged. For example, ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$ or $\text{CH}_3\text{CH}_2\text{OH}$) and dimethyl ether (CH_3OCH_3) each have the *molecular formula* $\text{C}_2\text{H}_6\text{O}$. However, without seeing the *condensed structural formulas* ($\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3), you wouldn't know which of the two compounds is represented. The molecular formula identifies the kinds of atoms and the number of each, but it provides no information on how they're arranged. This will become clearer as you see more examples throughout the book.

Chemical Bonding (continued)

Review Questions (answers on page 195)

- Most ionic bonds are those between:
 - Two or more metals
 - Two or more nonmetals
 - Metals and nonmetals
- Covalent bonds are those between:
 - Two or more metals
 - Two or more nonmetals
 - Metals and nonmetals
- In forming ionic bonds, metals _____ electrons.
 - Donate
 - Accept
 - Share
- In forming ionic bonds, nonmetals _____ electrons.
 - Donate
 - Accept
 - Share
- Which of the following is inert?
 - Chlorine
 - Hydrogen
 - Neon
 - Carbon
- Which of the following has a filled outer shell?
 - Carbon
 - Cesium
 - Oxygen
 - Krypton
- Which of the following contains an ionic bond?
 - SiH_4
 - CaC_2
 - C_6H_6
 - CH_4
- Which of the following contains only covalent bonds?
 - NaCN
 - CaO_2
 - KOH
 - C_4H_{10}

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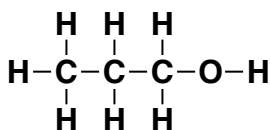
Chemical Bonding (continued)

9. Which of the following will form a cation in the bonding process?
- Mg
 - P
 - He
 - I
10. Which of the following will form an anion in the bonding process?
- Potassium
 - Cesium
 - Fluorine
 - Beryllium
11. Which of the following contain resonant bonds?
- Salt molecules
 - Aromatic hydrocarbons
 - Metal elements
 - Noble gases
12. How many bonding sites are available on the element nitrogen?
- 2
 - 3
 - 4
 - 5
13. Which of the following needs two electrons to create a filled outer shell?
- Calcium
 - Potassium
 - Sulfur
 - Boron
14. Which of the following will form a diatomic molecule?
- Helium
 - Sulfur
 - Magnesium
 - Chlorine
15. Which of the following is inclined to be highly reactive?
- Fluorine
 - Carbon
 - Oxygen
 - Calcium
16. Which of the following represents a condensed structural formula?
- $\text{C}_2\text{H}_5\text{NH}_2$
 - C_4H_{10}
 - $\text{CH}_3\text{COCH}_2\text{CH}_3$
 - $\text{C}_2\text{H}_4(\text{OH})_2$

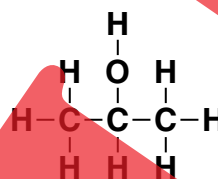
Isomers

Some products can have the same molecular *formula* but different molecular *structures*. These products are known as **isomers** of each other. The structure on the left below represents propyl alcohol, or propanol, (which can be represented by C_3H_7OH or C_3H_8O). The one on the right is isopropyl alcohol (or isopropanol), (also C_3H_7OH or C_3H_8O). The difference is in the way the molecular structure is organized.

Two Isomers of Propyl Alcohol



Propyl Alcohol (Propanol)
 C_3H_7OH

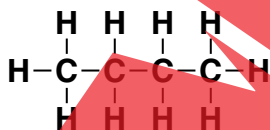


Isopropyl Alcohol (Isopropanol)
 C_3H_7OH

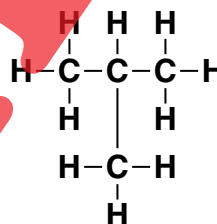
Notice that the formula above (C_3H_7OH) is a variation of the true molecular formula (C_3H_8O). It helps identify both compounds as alcohols, but it isn't as specific as a condensed structural formula. Propyl alcohol's condensed structural formula is $CH_3CH_2CH_2OH$. Isopropyl alcohol's is $CH_3CHOHCH_3$.

Show below are two more examples. The normal configuration of butane (C_4H_{10}) is a straight-chain compound (left), sometimes called *normal butane* or *n-butane*. The branched structure (right) is *isobutane* (also C_4H_{10}).

Two Isomers of Butane



Butane (n-Butane)
 C_4H_{10}



Isobutane
 C_4H_{10}

Despite having the same formulas, isomers can have measurably different characteristics and hazards. Therefore, when researching the hazards of a material, it is vital to identify the name correctly. Notice below some of the differences between propyl alcohol and isopropyl alcohol.

A Sample of How Molecular Structure Affects Other Properties

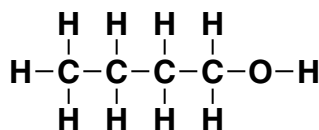
	Propyl Alcohol	Isopropyl Alcohol
Flash Point	77°F (25°C)	53°F (11.7°C)
Ignition Temperature	700°F (371°C)	750°F (399°C)
Boiling Point	207°F (97.2°C)	180.1°F (82.3°C)
Flammable Range	2.1% – 13.5%	2.3% – 12.7%

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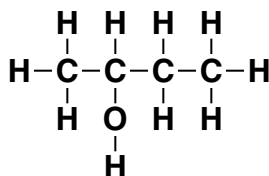
Isomers (continued)

The following are four isomers of butyl alcohol. Again, all have the same molecular formula but different molecular structures.

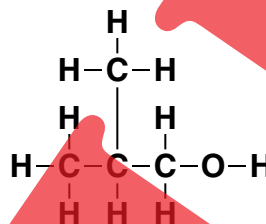
Four Isomers of Butyl Alcohol



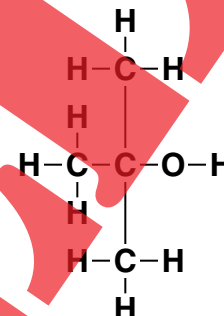
Butyl Alcohol
 $\text{C}_4\text{H}_9\text{OH}$



Secondary
Butyl Alcohol
 $\text{C}_4\text{H}_9\text{OH}$



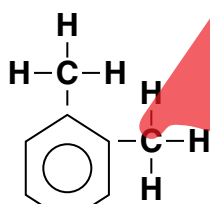
Isobutyl Alcohol
 $\text{C}_4\text{H}_9\text{OH}$



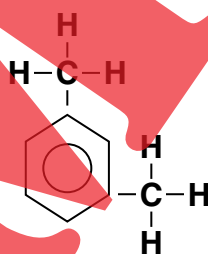
Tertiary
Butyl Alcohol
 $\text{C}_4\text{H}_9\text{OH}$

Prefixes (e.g., *n*-, *i*-, and *iso*-) and numbers are generally used to identify isomers. When numbers are used, they are often an indication as to where the bonds are located. In each of the examples below, there's a bond at the top position (1). The second bond, however, moves clockwise from one position to the next (2, 3, and 4) to create slightly different products. It's not important for you to understand these distinctions, but it is imperative you recognize that prefixes and numbers signify different isomers with characteristics and hazards that can be significantly different.

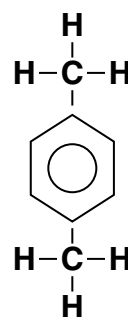
Three Isomers of Xylene



1,2-dimethylbenzene
(ortho-xylene or o-xylene)
 $\text{C}_6\text{H}_4(\text{CH}_3)_2$



1,3-dimethylbenzene
(meta-xylene or m-xylene)
 $\text{C}_6\text{H}_4(\text{CH}_3)_2$



1,4-dimethylbenzene
(para-xylene or p-xylene)
 $\text{C}_6\text{H}_4(\text{CH}_3)_2$

Note: Most chemicals have several names associated with them. It is beyond the scope of this book to cover the different naming systems and synonyms you might encounter. Instead, these pages are designed to reinforce how important it is not to take these name variations for granted. It's too easy for someone who isn't familiar with these distinctions to focus on the root name, ignoring prefixes or numbers for lack of understanding.

Chapter 3 Review

Review Questions (answers on page 195)

- Which of the following is an element?
 - NaF
 - HCN
 - KI
 - Hg
- Which of the following is a compound?
 - As
 - Si
 - CaO
 - Ne
- Alkali metals are Group ____ on the periodic table.
 - I
 - II
 - VII
 - VIII
- Alkali earth metals are Group ____ on the periodic table.
 - I
 - II
 - VII
 - VIII
- Which of the following is a metal?
 - Chlorine
 - Magnesium
 - Silicon
 - Iodine
- Which of the following is a nonmetal?
 - Phosphorus
 - Sodium
 - Potassium
 - Magnesium
- Which of the following is an alkali metal?
 - Calcium
 - Magnesium
 - Aluminum
 - Potassium
- Which of the following is an alkaline earth?
 - Beryllium
 - Lithium
 - Cesium
 - Titanium

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Chapter 3 Review (continued)

9. Which of the following is a highly reactive, toxic, nonflammable oxidizer?
- Chlorine
 - Helium
 - Hydrogen
 - Boron
10. Which of the following is an inert, simple asphyxiant that may be stored as a cryogenic liquid?
- Nitrogen
 - Chlorine
 - Neon
 - Sulfur
11. Which of the following is flammable and highly reactive (even in dry air) and when in contact with water, produces flammable hydrogen gas, a strong caustic runoff, and excessive heat?
- Magnesium
 - Phosphorus
 - Manganese
 - Sodium
12. Nitrogen has ____ electrons in its outer shell.
- 5
 - 6
 - 7
 - 8
13. Carbon has ____ protons in its nucleus.
- 2
 - 4
 - 6
 - 8
14. Which of the following contains an ionic bond?
- MgO
 - Cl₂
 - CO₂
 - CCl₄
15. Which of the following contains only covalent bonds?
- KNO₃
 - CaCO₃
 - CaO₂
 - CH₃Cl
16. Which of the following is balanced (has all available bonding sites filled)?
- C₂H₅
 - C₂H₃
 - C₃H₇
 - C₃H₈

Chapter 3 Review (continued)

17. If the molecular formula for octane is C_8H_{18} , the molecular formula for iso-octane is:
- C_8H_{18}
 - C_8H_{10}
 - C_8H_8
 - $C_{10}H_{18}$
18. If the condensed structural formula for methyl ethyl peroxide is $CH_3O_2CH_2CH_3$, what is the molecular formula?
- $CH_2(CH_3)_2O_2$
 - $C_3H_8O_2$
 - $CH_3O_2C_2H_5$
 - $CH_3OOCH_2CH_3$

Hazmat Chemistry Study Guide

SAMPLE



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.

Hazmat Chemistry Study Guide

Introduction to Salts

Salt compounds are generally formed through an ionic bond between a metal element and one or more nonmetal elements. Only a few exceptions don't contain metal, for example, ammonium chloride (NH_4Cl) and ammonium nitrate (NH_4NO_3). This is because the ammonium ion (NH_4) behaves like a metal element in the way it forms an ionic bond with other nonmetals. But for the most part, when we refer to salts, we are referring to a compound comprised of a metal element bonded to one or more nonmetal elements.

We'll examine six types of salts in this chapter. However, it helps to first be familiar with characteristics that are common to most salts. Some are relatively harmless but, of course, our focus will be on those that are hazardous. Salts are solid. They are nonflammable. Most are water-soluble. Many are also water-reactive and will produce a flammable gas, a toxic gas, a caustic solution, and/or heat when in contact with water. (Reactions that generate heat are called *exothermic*.) Salts are *electrolytes*, meaning they conduct electricity when in a molten state or when dissolved in water. They range from being mildly toxic to very toxic. Some will cause severe environmental damage. Remember, though, that there are exceptions to these generalizations. Sodium chloride (NaCl) is a common example of a binary salt. However, if you failed to recognize that it is ordinary table salt, you might wrongly assume that it, like other binary salts, was very dangerous.

Based on the common hazards listed above, it's safe to assume that you should avoid contact with and inhalation of salts and that you should keep them dry if possible. Some may require greater precautions; others, less. However, you can't go wrong if you apply these guidelines.

General Precautions Required with Salts



The chart below provides an overview of the salts we'll cover in this study guide. Most of what you need to know about salts is summarized in this chart.

An Overview of Salts

Salt	Composition	Naming	Example	Common Hazards of Some of the Worst Salts in Each Category *
Binary Salt	metal + nonmetal (not otherwise listed below)	metal + nonmetal root (ends in "ide")	CaC_2 calcium carbide	Toxic. May be water-reactive. Produce a flammable and/or toxic gas when mixed with water (e.g., calcium carbide produces flammable acetylene gas, aluminum chloride produces nonflammable toxic hydrogen chloride gas). Metal sulfides (metal + sulfur) react with acids to produce toxic hydrogen sulfide gas.
Metal Oxide (Binary Oxide)	metal + oxygen	metal + "oxide"	Na_2O sodium oxide	Water-reactive. Produce heat and a caustic solution when mixed with water. Metal oxides containing alkali metals (Group I) are extremely destructive to skin and metal. (Despite the name, most metal oxides are not oxidizers and do not offgas when exposed to water.)
Metal Cyanide	metal + cyanide	metal + "cyanide"	KCN potassium cyanide	Toxic. React with acids to produce toxic hydrogen cyanide gas.
Metal Hydroxide	metal + hydroxide	metal + "hydroxide" (or alkali, caustic, or base)	NaOH sodium hydroxide	Very caustic and destructive. Water-reactive. Will react with moisture on the skin. Extremely destructive to human skin and other body tissues.
Metal Peroxide	metal (Group I or II) + peroxide	metal + "peroxide"	Na_2O_2 sodium peroxide	Very strong oxidizers; react with reducing agents (fuel). Water-reactive; can react violently. Produce a caustic solution, heat, and oxygen gas when mixed with water.
Metal Oxy salt	metal + element + oxygen	metal + oxyradical (ends in "ate" or "ite") (may include prefix "per" or "hypo")	NaNO_3 sodium nitrate	Very strong oxidizers; react with reducing agents (fuel). The ending "ate," particularly when preceded by the prefix "per" (for example, perchlorate), signifies a high oxygen content. Oxy salts formed with halogens (e.g., chlorates or bromates) or nitrogen (nitrates) are the most hazardous.

* These generalizations apply primarily to salts containing alkali metals (Group I) and alkaline earth metals (Group II). In general, when salts contain transition metals, toxicity and environmental damage are common concerns; reactivity is usually less of a problem.

Introduction to Salts (continued)

Like many other hazardous materials, salts can have multiple names. Your training will focus on the IUPAC (International Union of Pure and Applied Chemists) naming system because the names are designed to reflect a salt's chemical composition. Trivial (slang) names don't do that. What is *lye*, for example? Would you recognize it as potassium hydroxide? In addition, the IUPAC names are universally accepted in chemical references, formal chemistry courses, and scientific and forensic laboratories. It's helpful if you know the trivial (slang) names because you will encounter them in the real world. However, we'll concentrate on the IUPAC names. The chart below is an abbreviated version of the one on the previous page. You may wish to refer to it as you read the information that follows.

Overview of the IUPAC Salts Naming Scheme

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_2O 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_2O_2 sodium peroxide
Metal Oxysalt	metal + element + oxygen	metal + oxyradical (ends in "ate" or "ite") (may include prefix "per" or "hypo")	NaNO_3 sodium nitrate

Again, salts are named according to the elements that comprise them, starting with the metal element and ending with the nonmetal element(s). The binary salt calcium carbide (CaC_2), for example, is comprised of calcium and carbon. The metal oxide salt sodium oxide (Na_2O) contains sodium and oxygen.

Some salts contain two nonmetal elements in addition to the metal one. For instance, in potassium cyanide (KCN), the cyanide portion is comprised of carbon and nitrogen. The hydroxide component of sodium hydroxide (NaOH) is made of hydrogen and oxygen.

The first five salts shown above all contain names ending in *-ide*. Four are even more specific: *cyanide*, *oxide*, *hydroxide*, and *peroxide*. If you see an *-ide* ending, think "salt." Later you'll learn about some nonsalt compounds whose names end in *-ide*, for example, methyl chloride (CH_3Cl). However, these nonsalt compounds won't have metal elements in their structures or their names.

Naming the metal oxysalts is a little more complex. Nonetheless, the name still identifies the elements involved. Sodium nitrate (NaNO_3), for instance, contains sodium, nitrogen, and oxygen. Sodium hypochlorite (NaClO) contains sodium, chlorine, and oxygen.

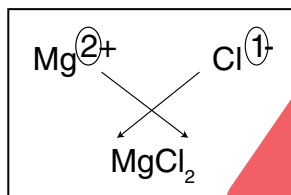
The metal oxysalts have names that end in *-ate* or *-ite* and may include the prefixes *per-* or *hypo-*. These names will be explained later in the chapter when we cover the oxysalts in more detail.

The ratio between metal and nonmetal elements is based on the rules of chemical bonding covered in the last chapter. That chapter provided the example of sodium chloride (NaCl) where sodium (Na) and chlorine (Cl) bonded in a one-to-one ratio because they had one and seven electrons, respectively, on their outer shells. However, with magnesium chloride (MgCl_2), magnesium (Mg) has two electrons on its outer shell, requiring bonds with two atoms of chlorine (Cl) to create a balanced compound.

Introduction to Salts (continued)

The easiest way to determine the formula of a salt compound is to apply something called the **crisscross rule**. Draw a simple diagram like the one below, identifying the electrical charges associated with each ion. Then cross the numbers as shown. The electrical charge of one ion becomes the subscript number for the opposite ion. (Where the number is 1, no subscript is needed.)

The Crisscross Rule



Always reduce the subscripts to the lowest possible numbers without changing the ratio in which the elements are present. For example, calcium (Ca^{2+}) and oxygen (O^{2-}) form calcium oxide (CaO , not Ca_2O_2).

Later in the chapter, you'll learn about *polyatomic ions*, where two or more atoms bonded together act as a single ion. For example, in sodium hydroxide (NaOH), the hydroxide ion (OH) has a charge of 1-. The crisscross rule is applied the same way, with the polyatomic ion treated like one unit.

The elements that comprise salts typically do so only in specific ratios. For example, aluminum chloride (AlCl_3) consists of aluminum and chlorine only in a 1 to 3 ratio. So it is unnecessary to use prefixes such as *mono-*, *di-*, or *tri-* (e.g., aluminum trichloride) to indicate how many atoms are present. The oxysalts are an exception, but the prefixes and endings associated with them are unique. That information will be presented shortly.

Introduction to Salts (continued)

Review Questions (answers on page 195)

- Salt molecules are generally comprised of:
 - Two or more metals elements
 - Two or more nonmetals elements
 - A metal element with one or more nonmetal elements
 - A nonmetal element with one or more metal elements
- Salts are generally flammable.
 - True
 - False
- Many salts are water-reactive.
 - True
 - False
- Salts are generally toxic.
 - True
 - False
- Most of the salts (other than the oxysalts) have names with an ____ ending.
 - ane
 - ate
 - ide
 - ite
- The name for KOH is:
 - Potassium oxide
 - Potassium hydroxide
 - Potassium hydrogen oxide
 - Potassium peroxide
- The name for CaCl_2 is:
 - Calcium chloride
 - Calcium dichloride
 - Calcium dichlorine
 - Dicalcium chloride
- Which of the following is a salt?
 - CO
 - CaO
 - CH_3OH
 - CH_3Cl
- Which of the following is a nonsalt?
 - CaC_2
 - $\text{Ca}(\text{OH})_2$
 - $\text{C}_2\text{H}_5\text{OH}$
 - NaClO

Hazmat Chemistry Study Guide

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

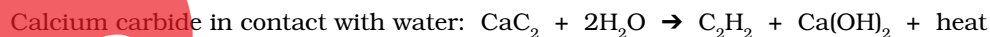
Binary salts consist of only two elements, one metal and one nonmetal (other than oxygen), although there may be more than one atom of either or both elements. The name begins with the metal element, followed by the nonmetal element, modified to provide the *-ide* ending.

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.

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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

<u>Names</u>	<u>Formulas</u>
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

<u>Names</u>	<u>Formulas</u>
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

<u>Oxygen Content</u>	<u>Naming</u>	<u>Oxyradical</u>	<u>Example</u>	<u>Formula</u>
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

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Types of Salts (continued)

Review Questions (answers on page 195)

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

Polyatomic Ions and Multiple Oxidation States

Salts have been presented very simply so far, but the topic is truly not that simple. (Few aspects of chemistry are quite as simple as they are presented in either this study guide or the hazmat chemistry classes taught to emergency responders.) So we're going to dig a bit deeper to better understand a few important concepts.

First, a Review of Binary Salts

The simplest of all salts are those created with only two elements. Let's go back to using sodium chloride as an example. When sodium donates its one outer shell electron, it ends up with a net positive charge of 1 (protons outnumber electrons by one). This is written as 1+ or Na⁺. When chlorine accepts that electron, it ends up with a net negative charge of 1 (electrons outnumber protons by one). This is written as 1- or Cl⁻. Remember, once this electron transfer takes place, sodium and chlorine are no longer called atoms. They are called *ions* (sodium cation and chloride anion, specifically). If this were represented by an equation, it would be written as Na⁺ + Cl⁻ → NaCl. The compound sodium chloride (NaCl) is electrically neutral.

Introduction to Polyatomic (Complex) Ions

The salt examples provided in previous pages included several others made with sodium, so let's stick with sodium as the metal element to introduce the next concept.

Throughout most of this study guide, chemical bonding will focus on the number of outer shell electrons. Sodium chloride (NaCl) was formed because the transfer of one electron from sodium to chlorine resulted in each having a filled outer shell. It satisfied the octet rule of bonding.

Two atoms of sodium (each with a charge of 1+) bond with one atom of oxygen (with its charge of 2-) in a similar fashion: 2Na⁺ + O²⁻ → Na₂O (sodium oxide). So far, so good. However, when we get to sodium peroxide (Na₂O₂), the formula doesn't seem to make sense. "Peroxide" signals two atoms of oxygen. So if a single ion of oxygen has a charge of 2- and the sodium ion has a net charge of 1+, shouldn't the formula for sodium peroxide be Na₄O₂?

Here's where we get into the concept of **polyatomic ions**, sometimes referred to as **complex ions**. These are ions in which two or more atoms bonded together act as a single ion. The electrical charge applies to the unit as a whole, regardless of the charges associated with each individual ion. We'll start by looking at the polyatomic ions in peroxide, cyanide, and hydroxide salts.

Polyatomic (Complex) Ions in Peroxide, Cyanide, and Hydroxide Salts

<u>Ion Name</u>	<u>Ion Symbol</u>	<u>Charge</u>	<u>Salt Example</u>
Peroxide	O ₂ ²⁻	2-	Na ₂ O ₂
Cyanide	CN ⁻	1-	NaCN
Hydroxide	OH ⁻	1-	NaOH

Once you know the electrical charges of these polyatomic ions, you should be able to figure out the correct formulas for other peroxide, cyanide, and hydroxide salts.

Polyatomic (Complex) Ions in Oxysalts

Shown below is part of the table presented in the section on oxysalts. The first column lists the polyatomic ion (sometimes referred to as an *oxyradical*). Each one has a charge of 1-, so regardless of oxygen content, the final salt compound always has just one sodium ion.

Oxysalts Comprised of Sodium, Chlorine, and Oxygen

<u>Polyatomic Ion</u>	<u>Example</u>	<u>Formula</u>
Perchlorate	Sodium Perchlorate	NaClO ₄
Chlorate	Sodium Chlorate	NaClO ₃
Chlorite	Sodium Chlorite	NaClO ₂
Hypochlorite	Sodium Hypochlorite	NaClO

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Polyatomic Ions and Multiple Oxidation States (continued)

Almost all of the polyatomic atoms have negative charges and thus comprise the **nonmetal** portion of a salt compound. However, the ammonium ion (NH_4^+) is one that has a positive charge, so it behaves like a metal element in the ionic bonding process. That's why there's a handful of salts, for example, ammonium chloride (NH_4Cl) and ammonium nitrate (NH_4NO_3), that don't contain a metal element.

There is no easy way to know the electrical charges associated with polyatomic ions. It requires either memorization or a handy reference book. The table below provides some examples. (Note: Oxysalts containing polyatomic ions with a 1- charge are usually the stronger oxidizers.)

Electrical Charges of Some Polyatomic Ions

1+ Charge	1- Charge	2- Charge	3- Charge
Ammonium NH_4^+	Hypochlorite ClO^-	Carbonate CO_3^{2-}	Phosphate PO_4^{3-}
	Chlorite ClO_2^-	Sulfite SO_3^{2-}	Arsenate AsO_4^{3-}
	Chlorate ClO_3^-	Sulfate SO_4^{2-}	Borate BO_3^{3-}
	Perchlorate ClO_4^-	Persulfate $\text{S}_2\text{O}_8^{2-}$	
	Nitrite NO_2^-	Chromate CrO_4^{2-}	
	Nitrate NO_3^-	Dichromate $\text{Cr}_2\text{O}_7^{2-}$	
	Permanganate MnO_4^-	Oxylate $\text{C}_2\text{O}_4^{2-}$	
	Bicarbonate HCO_3^-		
	Acetate CH_3COO^-		
	Bisulfate HSO_4^-		
	Bromate BrO_3^-		

Metal Elements with Multiple Oxidation States

All the metal elements discussed so far have only one charge associated with their ions. However, many of the transition metals have more than one **oxidation state**, meaning that they can donate different numbers of electrons. Let's take iron (Fe) as an example. Iron can donate either two or three electrons. When iron (Fe) combines with chlorine (Cl), it creates some form of iron chloride, either FeCl_2 or FeCl_3 . The first is more correctly called either iron (II) chloride or *ferrous* chloride; the second, either iron (III) chloride or *ferric* chloride. The table below shows some common transition metals with more than one oxidation state. (Note: In each pair, the one with the lower oxidation state has an -ous ending, while the one with the higher oxidation state has an -ic ending.)

Some Common Transition Metals with Multiple Oxidation States

Element	Ion Name	Ion Symbol
Chromium	Chromium (II) or chromous	Cr^{2+}
	Chromium (III) or chromic	Cr^{3+}
Manganese	Manganese (II) or manganous	Mn^{2+}
	Manganese (III) or manganic	Mn^{3+}
Iron	Iron (II) or ferrous	Fe^{2+}
	Iron (III) or ferric	Fe^{3+}
Copper	Copper (I) or cuprous	Cu^+
	Copper (II) or cupric	Cu^{2+}
Mercury	Mercury (I) or mercurous	Hg_2^+
	Mercury (II) or mercuric	Hg^{2+}
Tin	Tin (II) or stannous	Sn^{2+}
	Tin (IV) or stannic	Sn^{4+}
Lead	Lead (II) or plumbous	Pb^{2+}
	Lead (IV) or plumbic	Pb^{4+}

Polyatomic Ions and Multiple Oxidation States (continued)

Review Questions (answers on page 195)

1. Which of the following ions has a positive charge?
 - a. OH
 - b. ClO_3
 - c. NO_3
 - d. NH_4
2. NaClO_3 is the formula for:
 - a. Sodium hypochlorite
 - b. Sodium chlorite
 - c. Sodium chlorate
 - d. Sodium perchlorate
3. What is the correct formula for sodium bicarbonate?
 - a. NaHCO_3
 - b. Na_2HCO_3
 - c. Na_3HCO_3
 - d. $\text{Na}(\text{HCO}_3)_2$
4. Many of the _____ have more than one oxidation state, meaning they can donate different numbers of electrons.
 - a. Alkali metals
 - b. Alkaline earth metals
 - c. Transition metals
 - d. Halogens
5. Which of the following has a higher oxidation state?
 - a. Ferric chloride
 - b. Ferrous chloride
6. Which of the following is a salt?
 - a. CH_3NH_2
 - b. NH_4NO_3
 - c. NH_2COOH
 - d. $\text{C}_6\text{H}_5\text{CH}_3(\text{NO}_2)_3$

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Chapter 4 Review

Review Questions (answers on page 195)

- Which of the following will react with acids to form toxic hydrogen cyanide gas?
 - KOH
 - KClO_4
 - KCN
 - CaC_2
- Which of the following will react with water to form acetylene gas?
 - CaC_2
 - CaO
 - CaCO_3
 - Ca(OH)_2
- Which of the following has the highest oxygen content?
 - Sodium hypochlorite
 - Potassium permanganate
 - Potassium nitrate
 - Sodium peroxide
- Which of the following is a salt?
 - H_2O_2
 - $\text{CH}_3\text{OC}_2\text{H}_5$
 - CH_3CN
 - CaSO_4
- Which of the following is a nonsalt?
 - CaCO_3
 - CH_3Cl
 - CaCl_2
 - MgCl_2
- Which of the following is a salt?
 - Methyl chloride
 - Methyl cyanide
 - Sodium cyanide
 - Hydrogen peroxide
- Which of the following is a nonsalt?
 - Vinyl acetate
 - Sodium nitrate
 - Lithium bromate
 - Ammonium chloride
- Sodium chlorate is a/an:
 - Organic peroxide
 - Metal peroxide
 - Binary salt
 - Metal oxysalt

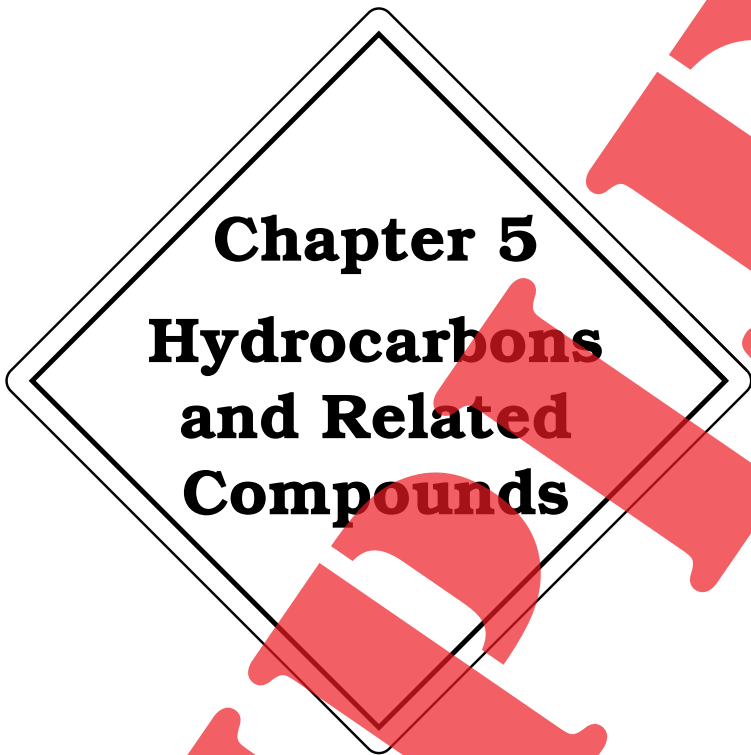
Chapter 4 Review (continued)

9. KNO_3 is:
- Potassium permanganate
 - Potassium nitrate
 - Potassium nitrite
 - Potassium oxide
10. Which of the following produces a caustic solution, heat, and oxygen gas when mixed with water?
- Binary salts
 - Metal peroxides
 - Metal oxysalts
 - Metal hydroxides
11. Which of the following are very strong oxidizers?
- Metal oxysalts
 - Metal oxides
 - Metal hydroxides
 - Metal cyanides
12. Metal sulfides react with _____ to form hydrogen sulfide gas?
- Water
 - Acids
 - Bases
 - Metal
13. Which of the following is *not* an oxidizer and will not offgas when exposed to water?
- Sodium oxide
 - Sodium peroxide
 - Sodium chlorite
 - Sodium perchlorate
14. Which of the following is a very destructive corrosive, particularly to skin and other body tissues?
- KCN
 - AlCl_3
 - NaOH
 - MgO
15. Which of the following is likely to react with water to produce a caustic solution, heat, and oxygen gas?
- NaO
 - Na_2O_2
 - NaClO_3
 - NaCl
16. What is the formula for sodium perchlorate?
- NaClO
 - NaClO_2
 - NaClO_3
 - NaClO_4

Hazmat Chemistry Study Guide

Chapter 4 Review (continued)

17. Salts formed with halogens and having names ending in *-ate* or *-ite* are most likely to be:
- Strong oxidizers
 - Strong caustics
 - Highly flammable
 - Highly water-reactive
18. The reaction between salts and water are often:
- Explosive
 - Exothermic
 - Endothermic
 - Pyrophoric
19. Which of the following is most likely to be a caustic?
- CH_3CHO
 - $\text{C}_2\text{H}_5\text{OH}$
 - NaOH
 - H_2SO_4
20. Acids react with cyanide salts to form:
- Hydrogen cyanide
 - Vinyl cyanide
 - Cyanogen chloride
 - A nitrile hydrocarbon derivative compound
21. Which of the following polyatomic ions has a electrical charge of 1-?
- Carbonate
 - Sulfate
 - Phosphate
 - Perchlorate
22. A compound whose formula begins with _____ is most likely a salt even though it contains no metal.
- NH
 - NH_2
 - NH_3
 - NH_4



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:

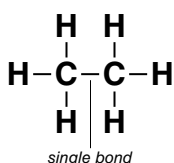
- The Four Types of Hydrocarbons
- Hydrocarbon Names and Formulas
- The Effect of Molecular Size
- Hydrocarbon Radicals
- Overview of Hydrocarbon Derivatives
- Part 1 Hydrocarbon Derivatives - Carbonyls
- Other Part 1 Hydrocarbon Derivatives
- Part 2 Hydrocarbon Derivatives - Nitrogen Based
- Other Part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

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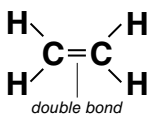
The Four Types of Hydrocarbons

Hydrocarbons, as the name implies, are compounds that consist of hydrogen and carbon. There are four types of hydrocarbons: alkanes, alkenes, alkynes, and aromatics. What distinguishes the four types is the bonds between carbon atoms. **Alkanes** have a single bond between carbon atoms. **Alkenes** have a double bond between carbon atoms. **Alkynes** have a triple bond between carbon atoms. **Aromatics** have a ring (cyclic) structure with resonant bonds. (Resonant bonds were explained in more detail on page 68.) Let's look first at the structures so you'll have a mental picture of hydrocarbons. Then we'll discuss their properties.

Four Types of Hydrocarbons



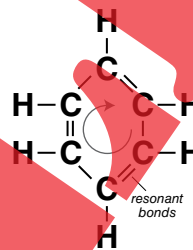
An Alkane
(Ethane • C_2H_6)



An Alkene
(Ethene • C_2H_4)



An Alkyne
(Ethyne • C_2H_2)



An Aromatic
(Benzene • C_6H_6)

All hydrocarbons have common characteristics, making it possible to predict their behavior and hazards even before checking reference sources. All hydrocarbons burn, though some are flammable and others are combustible, depending on flash point. All have some degree of toxicity. All are insoluble in water and will float on the surface.

Common Characteristics of All Hydrocarbons

All are flammable or combustible.
All have some degree of toxicity.
All are insoluble in water and will float on the surface.

Differences in behavior between the types of hydrocarbons are based primarily on the bonds between carbon atoms. Most alkanes (single bonds) are relatively stable. However, double and triple bonds are very reactive, triple bonds more so than double bonds. Therefore, alkenes (double bonds) are less stable than alkanes and are prone to polymerization, particularly the smaller compounds. Alkynes (triple bonds) are highly unstable. They have explosive potential. Most aromatics are very stable, even though they appear to have three double bonds, because the electrons rotate between elements (resonant bonds). As a group, aromatics are fairly toxic. They burn with sooty smoke that often has a spider web appearance. Some are carcinogenic.

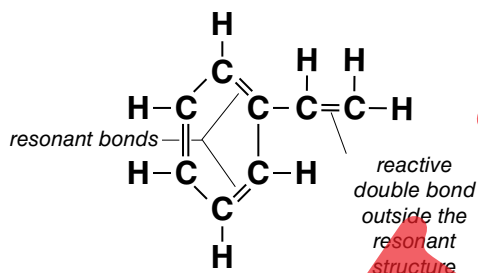
Common Characteristics Based on Type of Hydrocarbon

Type	Bond	Common Characteristics
Alkane	Single	Stable.
Alkene	Double	Less stable. Could polymerize.
Alkyne	Triple	Highly unstable. Could explode.
Aromatic	Resonant	Generally stable. Toxic. Burn with sooty smoke. Some carcinogenic.

Remember that these are generalizations only and that the information does not necessarily apply to all chemicals in a given category. For example, most aromatic hydrocarbons are stable. The aromatic hydrocarbon styrene (C_8H_8), however, contains a double bond between carbon atoms outside the resonant structure. (See next page.) Styrene is less stable than other aromatic hydrocarbons because of this double bond.

The Four Types of Hydrocarbons (continued)

Aromatic Styrene (C_8H_8) with a Double Bond Outside the Resonant Structure

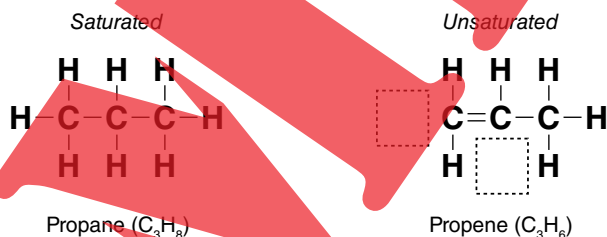


Use the generalizations on the previous page for a quick assessment, but check at least three reference sources to size up the hazards and determine your plan of action.

The alkanes, alkenes, and alkynes pictured so far are all called *straight-chain hydrocarbons* because the carbon atoms are arranged in a straight chain. You'll see variations (*branched hydrocarbons*) shortly.

Two other terms you may hear associated with these hydrocarbons are *saturated* and *unsaturated*. **Saturated** hydrocarbons are those containing only single bonds between the carbon atoms (alkanes). Another way to think of it is that the alkanes are *saturated* with as many hydrogen atoms as they can possibly hold because every available bonding site is filled with hydrogen. The other hydrocarbons are considered **unsaturated** because the multiple bonds between carbon atoms means there is less room for hydrogen in the compound. The term **polyunsaturated**, as in *polyunsaturated fats* and oils, means there is more than one carbon-carbon double bond.

Saturated Versus Unsaturated



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The Four Types of Hydrocarbons (continued)

Review Questions (answers on page 195)

- Which one of the following hydrocarbon groups is least stable?
 - Alkanes
 - Alkenes
 - Alkynes
 - Aromatics
- Which one of the following hydrocarbon groups is prone to polymerization?
 - Alkanes
 - Alkenes
 - Alkynes
 - Aromatics
- Which one of the following hydrocarbon groups burns with sooty smoke?
 - Alkanes
 - Alkenes
 - Alkynes
 - Aromatics
- Which one of the following hydrocarbon groups is saturated?
 - Alkanes
 - Alkenes
 - Alkynes
 - Aromatics
- What distinguishes one hydrocarbon type from another?
 - The number of carbon atoms
 - The number of hydrogen atoms
 - The bonds between carbon atoms
 - The bonds between carbon and hydrogen atoms
- Which of the following aromatic hydrocarbons is less stable than the others?
 - Benzene
 - Toluene
 - Xylene
 - Styrene
- Straight-chain hydrocarbons are:
 - Floaters
 - Sinkers
 - Swimmers

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.

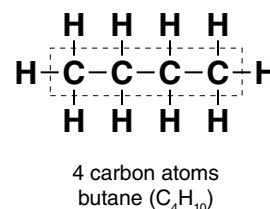
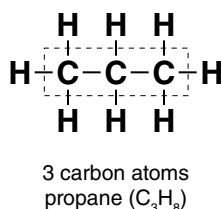
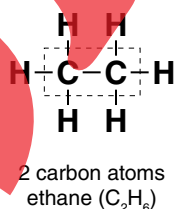
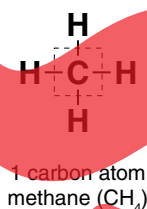
Alkanes, alkenes, and alkynes use common prefixes based on the number of carbon atoms in the formula. Those prefixes are identified below.

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



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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_nH_{2n+2}	C_2H_6 (Ethane), C_3H_8 (Propane)
Alkene	C_nH_{2n}	C_2H_4 (Ethene), C_3H_6 (Propene)
Alkyne	C_nH_{2n-2}	C_2H_2 (Ethyne), C_3H_4 (Propyne)
Aromatic	C_nH_{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.

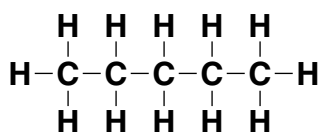
Compound	Generic Formula	Type	Name
C_8H_{18}	$C_8H_{2(8) \text{ +/- } \quad}$	_____	_____
C_5H_{10}	$C_5H_{2(5) \text{ +/- } \quad}$	_____	_____
C_9H_{12}	$C_9H_{2(9) \text{ +/- } \quad}$	_____	_____

Hydrocarbon Names and Formulas (continued)

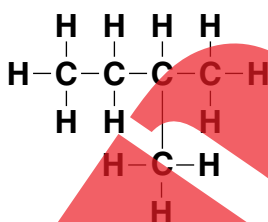
Most of what you need to know about the different types of hydrocarbons is summed up in the preceding pages. However, we'll look briefly at some important variations.

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.

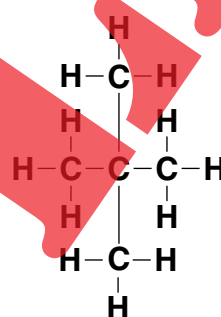
Isomers of Pentane (C_5H_{12})



Pentane (C_5H_{12})



Isopentane (C_5H_{12})

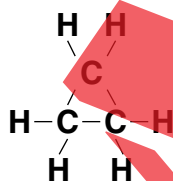


Neopentane (C_5H_{12})

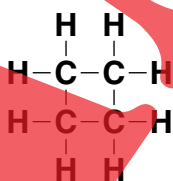
As indicated earlier, the different structure of isomers tends to result in slightly different properties. The difference may not be dramatic, but even a 20°F (6.67°C) difference in flash point, for example, can be significant depending on ambient temperature and the presence of other ignition sources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

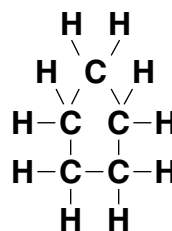
Cyclo Compounds



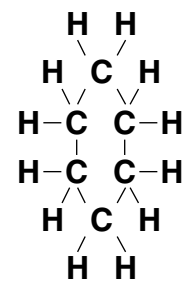
Cyclopropane (C_3H_6)



Cyclobutane (C_4H_8)



Cyclopentane (C_5H_{10})

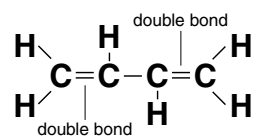


Cyclohexane (C_6H_{12})

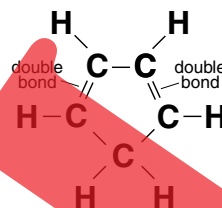
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Hydrocarbon Names and Formulas (continued)

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 double bonds between two 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. $\text{C}_n\text{H}_{2n-6}$

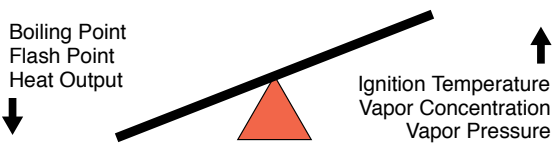
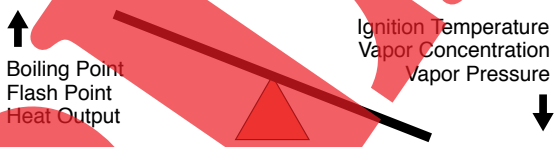
Hydrocarbon Names and Formulas (continued)

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

The Effect of Molecular Size

The more carbon and hydrogen in the compound, the larger the molecule. Molecular size has a direct effect on physical and chemical properties, including those related to flammability. Many of these properties are directly or indirectly proportional to one another. The illustration below shows a few examples. Of course, this is assuming one is comparing similar compounds, such as straight-chain hydrocarbons. When comparing different types of materials (such as a hydrocarbon versus a hydrocarbon derivative), chemical composition has a greater bearing on physical and chemical properties than does molecular size.

The Effect of Molecular Size

Smaller Molecules		Larger Molecules	
			
Significant Characteristics More Active. Contain Less Fuel (Hydrogen).		Significant Characteristics Less Active. Contain More Fuel (Hydrogen).	
Boiling Point Is Lower because it takes less heat to inspire these more active molecules to vaporize.	Ignition Temperature Is Higher because it takes more heat energy to ignite molecules with less hydrogen (fuel).	Boiling Point Is Higher because it takes more heat to inspire these less active molecules to vaporize.	Ignition Temperature Is Lower because it takes less heat energy to ignite molecules with more hydrogen (fuel).
Flash Point Is Lower because it takes less heat to produce enough vapors to form an ignitable mixture.	Vapor Concentration Is Higher because more vapor is being produced by these more active molecules.	Flash Point Is Higher because it takes more heat to produce enough vapors to form an ignitable mixture.	Vapor Concentration Is Lower because less vapor is being produced by these less active molecules.
Heat Output Is Lower because these molecules contain fewer hydrogen atoms (fuel).	Vapor Pressure Is Higher because these more active molecules are more eager to vaporize.	Heat Output Is Higher because these molecules contain more hydrogen atoms (fuel).	Vapor Pressure Is Lower because these less active molecules are less eager to vaporize.

As you can see from the summary above, molecular size determines how active a compound is, which in turn affects the other properties. Small molecules produce *more* vapor (have a higher vapor content) and have a higher vapor pressure because they are *more* active than are larger molecules. Larger molecules, by comparison, produce *less* vapor (have a lower vapor content) and have a lower vapor pressure because they are *less* active than are smaller molecules.

What's often confusing is that flash point and ignition temperature are inversely proportional. The flash point is *lower* in smaller molecules because it takes *less* heat to raise the temperature of the liquid to the point where it produces sufficient vapors to form an ignitable mixture in air. However, it takes *more* heat energy (ignition temperature) to ignite those vapors because they contain less hydrogen (fuel) than do the vapors produced by a larger molecule. Thus the flash point and ignition temperature are further apart in relation to each other.

The opposite is true with larger molecules. The flash point is *higher* because it takes *more* heat to raise the temperature of the liquid to the point where it produces sufficient vapor to form an ignitable mixture in air. However, when the ignitable mixture is produced, the vapors are closer to their ignition temperature; thus it takes *less* heat energy to cause ignition. The flash point and ignition temperature are closer together in relation to each other. Because these larger molecules contain more hydrogen (fuel), they will also output more heat than do smaller molecules.

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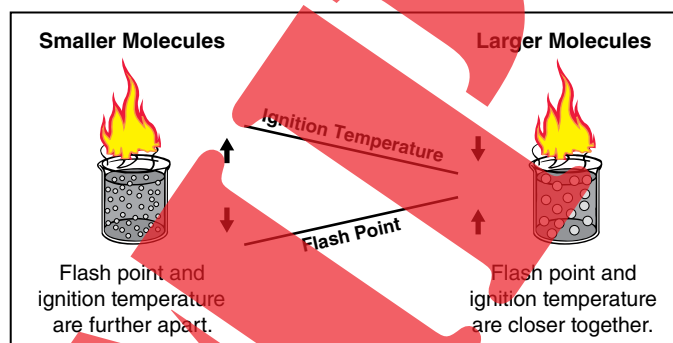
The Effect of Molecular Size (continued)

The chart below gives a more concrete illustration of this concept. Be aware, however, that there can be minor exceptions to the generalizations made above. If you look at the ignition temperatures of the five alkanes listed below, you can see that they drop for the first three, then go up slightly.

The Effect of Molecular Size on Five Alkanes

<u>Alkane</u>	<u>Flash Point</u>	<u>Boiling Point</u>	<u>Ignition Temperature</u>	<u>Vapor Pressure</u>
Pentane	-57°F / (-49.4°C)	97°F / (36.1°C)	500°F / (260°C)	420 mmHg
Hexane	-7°F / (-21.7°C)	156°F / (68.9°C)	437°F / (225°C)	124 mmHg
Heptane	25°F / (3.9°C)	209°F / (98.3°C)	399°F / (203.9°C)	40 mmHg
Octane	56°F / (13.3°C)	258°F / (125.6°C)	403°F / (206.1°C)	10 mmHg
Nonane	88°F / (31.1°C)	303°F / (150.6°C)	401°F / (205°C)	3 mmHg

The illustration below emphasizes that while flash point and ignition temperature are inversely proportional, they will never cross. In other words, the ignition temperature of a product will always be higher than the flash point.

The Relation Between Size, Flash Point, and Ignition Temperature

The Effect of Molecular Size (continued)

Review Questions (answers on page 196)

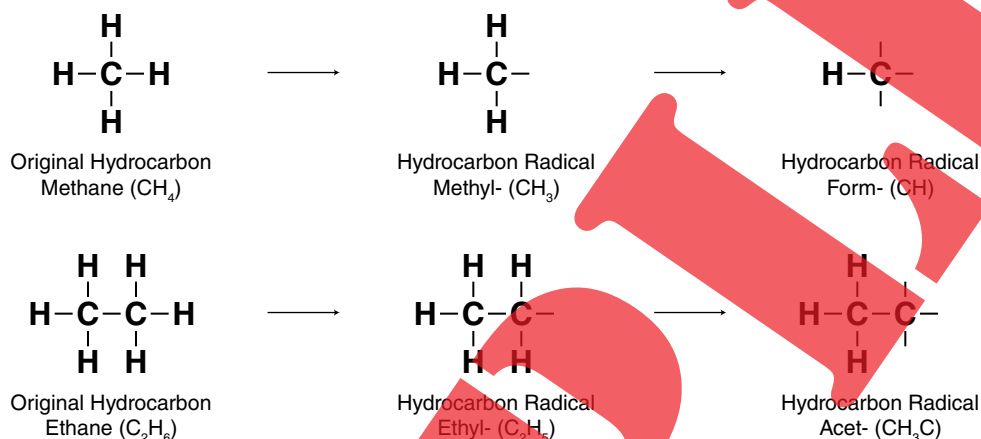
1. Smaller molecules have:
 - a. Lower flash points
 - b. Higher boiling points
 - c. Lower ignition temperatures
 - d. Lower vapor pressures
2. Larger molecules have:
 - a. Lower flash points
 - b. Lower boiling points
 - c. Lower ignition temperatures
 - d. Higher vapor pressures
3. Which of the following has the lowest flash point?
 - a. Hexane
 - b. Heptane
 - c. Octane
 - d. Pentane
4. Which of the following has the highest ignition temperature?
 - a. Butane
 - b. Ethane
 - c. Methane
 - d. Propane
5. Which of the following has the lowest boiling point?
 - a. Decane
 - b. Hexane
 - c. Octane
 - d. Pentane
6. 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}

Hazmat Chemistry Study Guide

Hydrocarbon Radicals

A **hydrocarbon radical** is a hydrocarbon molecule in which one or more hydrogen atoms have been removed. The first example below shows two different hydrocarbon radicals that can be made from methane; the second, from ethane.

The Making of a Hydrocarbon Radical



Hydrocarbon radicals cannot exist by themselves because they are not electrically balanced. The missing hydrogen atoms must be replaced by something else. That something else (called a *functional group*) bonded to a hydrocarbon radical forms a hydrocarbon derivative (which is the next topic covered). The chart below shows the various hydrocarbon radicals and the hydrocarbon compounds from which they come.

Hydrocarbon Radicals

Original Hydrocarbon		Hydrocarbon Radical	
Methane	CH_4	Methyl	$\text{CH}_3\cdot$
Methane	CH_4	Form-	$\text{H}(\text{C})\equiv$
Ethane	C_2H_6	Ethyl	$\text{C}_2\text{H}_5\cdot$
Ethane	C_2H_6	Acet-	$\text{CH}_3(\text{C})\equiv$
Ethene	C_2H_4	Vinyl	$\text{C}_2\text{H}_3\cdot$
Propane	C_3H_8	Propyl	$\text{C}_3\text{H}_7\cdot$
Propene	C_3H_6	Allyl, Acryl	$\text{C}_2\text{H}_3(\text{C})\equiv$
Butane	C_4H_{10}	Butyl	$\text{C}_4\text{H}_9\cdot$
Benzene	C_6H_6	Phenyl, Benzyl	$\text{C}_6\text{H}_5\cdot$

Hydrocarbon Radicals (continued)

Review Questions (answers on page 196)

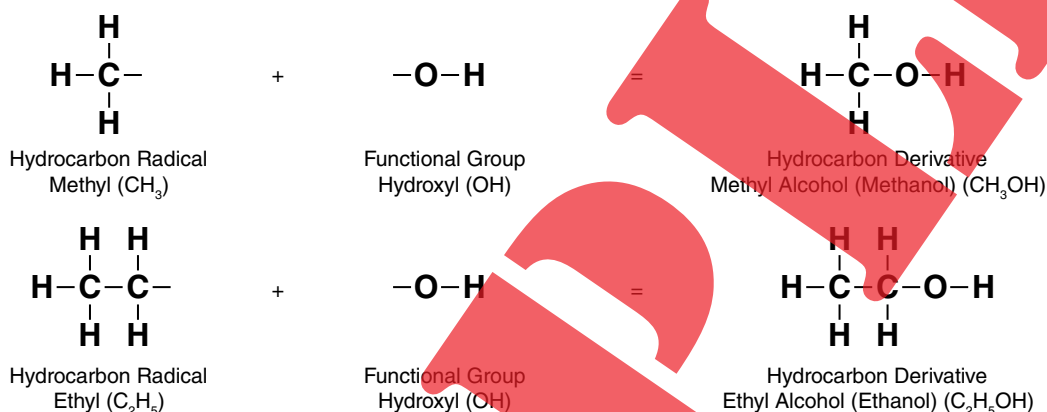
1. The *acet* hydrocarbon radical comes from the _____ molecule.
 - a. Methane
 - b. Ethane
 - c. Ethene
 - d. Propane
2. The *vinyl* hydrocarbon radical comes from the _____ molecule.
 - a. Ethane
 - b. Ethene
 - c. Propene
 - d. Butane
3. The *allyl* hydrocarbon radical comes from the _____ molecule.
 - a. Ethene
 - b. Propane
 - c. Propene
 - d. Butane
4. The *phenyl* hydrocarbon radical comes from the _____ molecule.
 - a. Benzene
 - b. Butane
 - c. Pentane
 - d. Propene
5. Which of the following is a radical of the hydrocarbon methane?
 - a. Acet
 - b. Vinyl
 - c. Form
 - d. Acryl
6. Which of the following is a radical of the hydrocarbon propene?
 - a. Phenyl
 - b. Vinyl
 - c. Acet
 - d. Acryl
7. CH_3 represents:
 - a. The compound methane
 - b. The methyl radical
 - c. The ethyl radical
 - d. The compound ethane
8. C_2H_5 represents:
 - a. The compound ethane
 - b. The compound ethene
 - c. The ethyl radical
 - d. The vinyl radical

Hazmat Chemistry Study Guide

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.

Overview of Hydrocarbon Derivatives (continued)

The chart below shows 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 on the following pages.

Hydrocarbon Derivatives

Part 1 Hydrocarbon Derivatives				Part 2 Hydrocarbon Derivatives			
Type	Structure	Key to Formula	Common Hazards	Type	Structure	Key to Formula	Common Hazards
Ketones	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}$	CO	Toxic. Flammable. Narcotic.	Nitros	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{N}}}-\text{O}$	NO ₂	Highly flammable. Explosive. Toxic.
Aldehydes	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$	CHO	Toxic. Flammable. Wide flammable range. Over time, may form explosive peroxides.	Amines	$\text{R}-\overset{\text{H(R)}}{\underset{\text{H(R)}}{\text{N}}}$	NH ₂	Toxic. Flammable. Corrosive.
Organic Acids	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{H}$	COOH	Toxic. Corrosive. Combustible.	Nitriles (Cyanides)	$\text{R}-\text{C}\equiv\text{N}$	CN	Toxic. Flammable. Some polymerizable.
Esters	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{R}$	COO or CO ₂	Toxic. Flammable. May form polymers (if unsaturated).	Carbamates	$\text{(R)H}-\overset{\text{O}}{\underset{\parallel}{\text{N}}}-\text{C}-\text{O}-\text{R}$	NH ₂ COO	Toxic. Combustible.
Alcohols	$\text{R}-\text{O}-\text{H}$	OH	Toxic. Flammable. Wide flammable range. Undergo slow oxidation.	Amides	$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\overset{\text{H(R)}}{\underset{\text{H(R)}}{\text{N}}}$	CONH ₂	Low to moderate toxicity. Flammable. Some polymerizable.
Glycols	$\text{R}-(\text{O}-\text{H})_2$	(OH) ₂	Toxic. Combustible.	Thiols	$\text{R}-\text{S}-\text{H}$	SH	Flammable. Toxic.
Glycerols	$\text{R}-(\text{O}-\text{H})_3$	(OH) ₃	Toxic. Combustible.	Alkyl Halides	$\text{R}-\text{X}$	F, Cl, Br, or I	Toxic.
Ethers	$\text{R}-\text{O}-\text{R}$	O	Very volatile. Flammable. Wide flammable range. Over time, form explosive peroxide crystals.	Organo-phosphates	$\text{R}-\text{P}$	P	Toxic. May be mixed in flammable liquid.
Organic Peroxides	$\text{R}-\text{O}-\text{O}-\text{R}$	OO or O ₂	Explosive. Extremely unstable. Oxidizer. Temperature-sensitive.	Hi-Tech Compounds	May vary greatly	B, Si, As, Be, Sn, or Ti	May be reactive, pyrophoric, toxic.

Key to Chemical Symbols Above

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

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

Hazmat Chemistry Study Guide

Part 1 Hydrocarbon Derivatives - Carbonyls

Ketones, aldehydes, organic acids, and esters fall into the group known as **carbonyls**. What they have in common is a double bond between carbon and oxygen (C=O). This carbon-oxygen double bond is a very stable one, unlike a double bond between two carbon atoms.

(Technically, the *carbamates* and *amides* [page 127] are also carbonyls, containing a double bond between carbon and oxygen. They are presented separately, however, because the hydrocarbon derivatives in this study guide have been organized to help students grasp them in tangible groupings. The four carbonyls below contain only carbon, oxygen, and hydrogen. The carbamates and amides introduce nitrogen.)

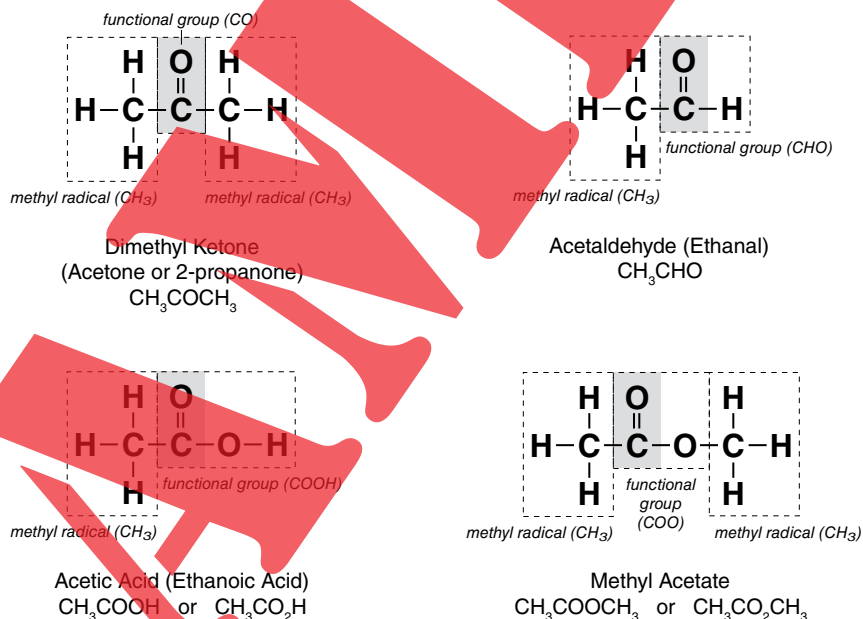
While all four carbonyls have a double bond between carbon and oxygen, each has a slightly different functional group. This is illustrated in a couple ways below. Immediately below is a table in which the functional group is spelled out for each type of derivative, then underlined in a common example.

Four Carbonyl Examples

Derivative Type	Functional Group	Example	Name
Ketone	CO	CH_3COCH_3	Dimethyl Ketone
Aldehyde	CHO	CH_3CHO	Acetaldehyde
Organic Acid	COOH (or CO_2H)	CH_3COOH	Acetic Acid
Ester	COO (or CO_2)	$\text{CH}_3\text{COOCH}_3$	Methyl Acetate

These same four carbonyls are shown below in graphic form. The functional groups and hydrocarbon radicals are outlined in separate boxes. The carbon-oxygen double bond is highlight in gray.

Four Carbonyl Examples Illustrated



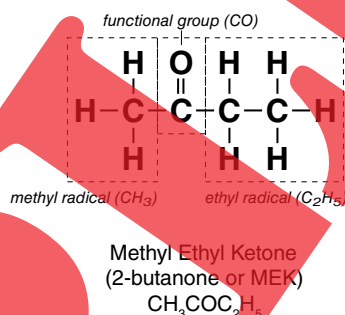
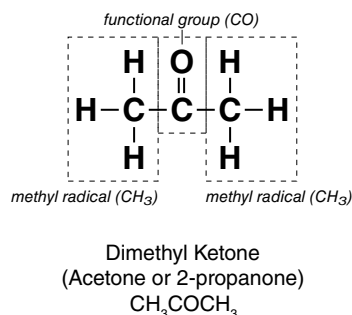
These four carbonyls were chosen because of their graphic similarity. Notice that each has a methyl radical (CH₃) on the left. The ketone (dimethyl ketone) and the ester (methyl acetate) both also have methyl radicals on the right. However, the aldehyde (acetaldehyde) and the organic acid (acetic acid) have nothing on the right because their particular functional groups leave no open bonding sites.

Part 1 Hydrocarbon Derivatives - Carbonyls (continued)

Ketones

Dimethyl ketone (CH_3COCH_3) was pictured on the previous page. If the second methyl radical is replaced by an ethyl radical, it creates methyl ethyl ketone ($\text{CH}_3\text{COC}_2\text{H}_5$), often called MEK. There are other ketones, but two examples are sufficient to illustrate the structure of these compounds. These two are the most important in the ketone family.

Ketone Examples



Ketones can have multiple names. The easiest to recognize are those ending in *ketone* because the name clearly identifies the type of derivative and the hydrocarbon radicals. *Dimethyl ketone* denotes two methyl radicals (CH_3). *Methyl ethyl ketone* clearly indicates CH_3 and C_2H_5 , respectively.

The other names are based on more complex naming conventions. The examples above contain two names beginning with a number (2-propanone and 2-butanone). The number 2 signifies that oxygen connects to the second carbon atom in the chain. The prefixes *prop-* and *but-* identify the total number of carbon atoms (3 and 4, respectively). The *-one* ending signifies a ketone, which says the functional group is simply CO, so the bond between oxygen and the second carbon atom must be a double bond.

Even the name *acetone* is not so mysterious. *Acet-* normally signifies the hydrocarbon radical $\text{CH}_3\text{C}\equiv$. Comparing that to the first illustration above, we see a methyl radical (CH_3) attached to a carbon atom with three available bonding sites. Two are filled with a double bond to oxygen. (Again, our clue is the *-one* ending.) The only thing not so obvious to the chemistry novice is what fills the last bond. However, the simplest ketone has another methyl radical (CH_3) on that side. There is no ketone with only a hydrogen atom in that position. (A hydrogen atom in that position would make the compound an aldehyde— CH_3CHO .)

Ketones are water-soluble solvents that are toxic and flammable, exhibiting a yellow flame with a blue base when burning. They can have a narcotic effect on the central nervous system.

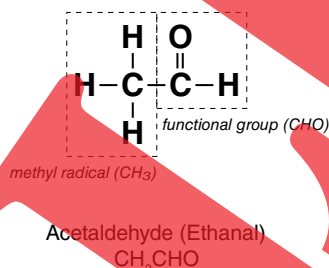
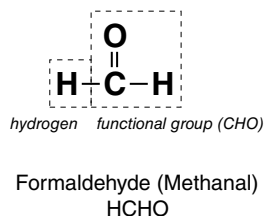
Hazmat Chemistry Study Guide

Part 1 Hydrocarbon Derivatives - Carbonyls (continued)

Aldehydes

Acetaldehyde (CH_3CHO) was pictured earlier, but the simplest of all aldehydes has a single hydrogen atom (H) bonded to the functional group (CHO). All the others have hydrocarbon radicals.

Aldehyde Examples

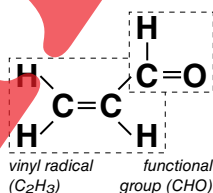


Aldehydes also have multiple names. Those with the *-al* endings use the more familiar prefixes, so let's start there. The *-al* ending signifies an aldehyde. (Don't confuse this with the *-ol* ending in alcohols. *Ethanol* is not *ethanol*.) The prefixes correspond to the number of carbon atoms. *Meth-* means one, *eth-* means two, etc. So methanal is built on a single carbon atom. That leaves no option but to have a lone hydrogen atom on the one bonding site not reserved for the functional group. Ethanal is built on a backbone of two carbon atoms, one of which is not dedicated to the functional group and thus can be filled with three hydrogen atoms.

You may be more familiar with the names formaldehyde and acetaldehyde. Page 108 showed the *form-* and *acet-* radicals with three open bonding sites, rather than the one open bonding site on *methyl-* and *ethyl-*. That allows two for the carbon-oxygen double bond and one for the hydrogen atom. In essence, the carbon atom belonging to the functional group is treated like part of the hydrocarbon radical for naming purposes.

Very seldom will this book focus on exceptions to the rules, but one aldehyde deserves special mention. *Propenal* ($\text{CH}_2\text{:CHCHO}$ or $\text{C}_3\text{H}_4\text{O}$) is more commonly called *acrolein*. Firefighters may recognize it as the major irritant in smoke given off by burning wood, wood products, and other Class A combustibles. (The formula for acrolein is typically depicted with either a colon [:] or an equal [=] sign to signify a double bond between the carbon atoms. Every chemistry book differs in how extensively it uses colons or equal signs to signify double carbon bonds in other compounds. This book leans towards the simpler formulas to keep readers focused on the more relevant topic of hazardous materials.)

Another Aldehyde Example



Aldehydes are water-soluble compounds frequently used as preservatives. Most are liquids. The exception is formaldehyde, which is a gas in its natural state, but which is usually transported dissolved in water. It's commonly called formalin in solution.

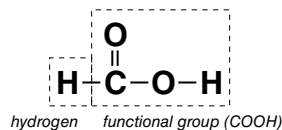
Like ketones, aldehydes are toxic and flammable, exhibiting a yellow flame with a blue base when burning. Aldehydes are sometimes described as having wide flammable ranges, the most dramatic examples being formaldehyde (7% to 73%) and acetaldehyde (4% to 60%). Some aldehydes can form unstable, explosive organic peroxides over time, particularly when exposed to air. While many of the carbonyls are irritants, the aldehydes are particularly noted for choking, suffocating odors.

Part 1 Hydrocarbon Derivatives - Carbonyls (continued)

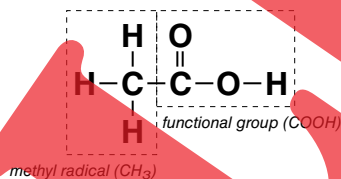
Organic (Carboxylic) Acids

Organic (carboxylic) acids are similar to aldehydes in that the simplest one has a lone hydrogen atom attached to the functional group (COOH). Others have a hydrocarbon radical instead. These compounds have names ending in *-ic acid* or *-oic acid*. The prefixes are determined just as they are for the aldehydes.

Organic (Carboxylic) Acid Examples



Formic Acid (Methanoic Acid)
HCOOH



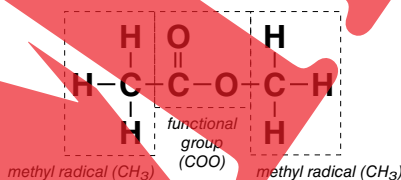
Acetic Acid (Ethanoic Acid)
CH₃COOH or CH₃CO₂H

Organic acids are toxic and corrosive. They are combustible, burning with a blue and yellow flame and clean smoke. They are water-soluble.

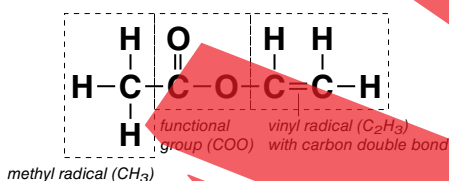
Esters

Esters have the functional group COO (or CO₂). Notice that vinyl acetate and methyl acrylate (bottom) have the same chemical composition, but the radicals are bonded to opposite sides of the functional group.

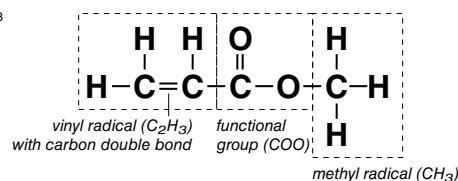
Ester Examples



Methyl Acetate
CH₃COOCH₃ or CH₃CO₂CH₃



Vinyl Acetate
CH₃COOC₂H₃ or CH₃CO₂C₂H₃



Methyl Acrylate
C₂H₃COOCH₃ or C₂H₃CO₂CH₃

Esters have names that end in *-ate*. Often they end in *acetate* or *acrylate*. The overall naming scheme for esters is more complex than the naming schemes covered so far and beyond the scope of this study guide. It's more important to be able to distinguish esters from other compounds. They and a handful of the organic peroxides are the only hydrocarbon derivatives with an *-ate* ending. Metal oxysalts also have names that end in *-ate*, for example, sodium nitrate or calcium hypochlorate. But the metal element identifies them as salts rather than hydrocarbon derivatives.

Esters are flammable, exhibiting a yellow flame with a blue base when burning. Some are toxic. Esters are commonly used in industry to synthesize resins and plastics. Those with a double bond between carbon atoms are particularly valuable in the plastics industry because of their tendency to polymerize. It's this same property that make them so dangerous. Esters are also commonly used in the perfume industry because many of them have pleasant fruity or floral odors. Esters are described as only "slightly soluble."

Hazmat Chemistry Study Guide

Part 1 Hydrocarbon Derivatives - Carbonyls (continued)

Review Questions (answers on page 196)

- CH_3COCH_3 is a/an:
 - Ketone
 - Aldehyde
 - Ester
 - Organic acid
- $\text{CH}_3\text{COOCH}_3$ is a/an:
 - Ketone
 - Aldehyde
 - Ester
 - Organic acid
- CH_3COOH is a/an:
 - Ketone
 - Aldehyde
 - Ester
 - Organic acid
- CH_3CHO is a/an:
 - Ketone
 - Aldehyde
 - Ester
 - Organic acid
- Which of the following hydrocarbon derivatives tend to be toxic and flammable and can have a narcotic effect on the central nervous system?
 - Ketones
 - Aldehydes
 - Esters
 - Organic acids
- Which of the following hydrocarbon derivatives tend to have wide flammable ranges and may, over time, form unstable and explosive organic peroxides?
 - Ketones
 - Aldehydes
 - Esters
 - Organic acids
- Which of the following hydrocarbon derivatives are toxic, corrosive, and combustible?
 - Ketones
 - Aldehydes
 - Esters
 - Organic acids

Part 1 Hydrocarbon Derivatives - Carbonyls (continued)

8. Which of the following hydrocarbon derivatives are often used in the plastics industry due to their tendency to polymerize?
- Ketones
 - Aldehydes
 - Esters
 - Organic acids
9. Chemical names that end in *-ate* (commonly *acetate* or *acrylate*) are often associated with:
- Ketones
 - Aldehydes
 - Esters
 - Organic acids
10. Chemical names that end in *-al* (e.g., *ethanal*) are often associated with:
- Ketones
 - Aldehydes
 - Esters
 - Organic acids
11. The name for 2-butanone is represented by the formula:
- $\text{CH}_3\text{COC}_2\text{H}_5$
 - $\text{C}_2\text{H}_5\text{COCH}_3$
 - CH_3COCH_3
 - $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
12. Acrolein is a/an
- Ketone
 - Aldehyde
 - Ester
 - Organic acid

Hazmat Chemistry Study Guide

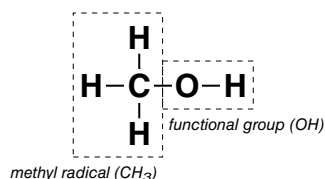
Other Part 1 Hydrocarbon Derivatives

The next five hydrocarbon derivatives also contain carbon, hydrogen, and oxygen, but what sets them apart from the carbonyls is that they do not have a double bond between carbon and oxygen.

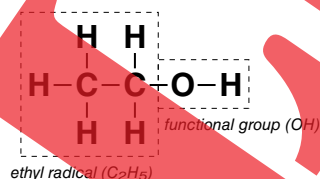
Alcohols

The two most common alcohols (methyl alcohol and ethyl alcohol) were introduced on page 110 to illustrate the making of a hydrocarbon derivative. The functional group (OH) is called a *hydroxyl group*.

Alcohol Examples



Methyl Alcohol (Methanol)
 CH_3OH



Ethyl Alcohol (Ethanol)
 $\text{C}_2\text{H}_5\text{OH}$

Note: Metal hydroxide salts also contain OH in the formula. In that marriage, however, the OH portion is considered a negatively charged hydroxide ion (OH^-). Hydroxyl groups, on the other hand, have no electrical charge. Further details are beyond the scope of this study guide. What is important is to recognize the difference between alcohols (with carbon-based hydrocarbon radicals) and hydroxide salts (containing a metal element instead).

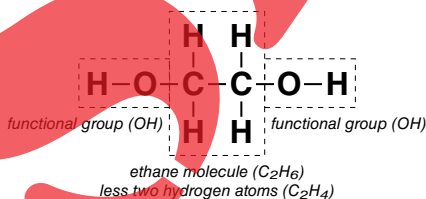
The proper names for these hydrocarbon derivatives end in *-ol*. (Don't confuse this with the *-al* ending associated with aldehydes. *Ethanol* is not *ethanal*.) The prefixes correspond to the number of carbon atoms, just as you've seen with other hydrocarbon derivatives. It's also common to see these compounds referred to as *alcohols*: methyl alcohol, ethyl alcohol, propyl alcohol, and so forth. However, you may also encounter the names wood alcohol (methanol), grain alcohol (ethanol), and rubbing alcohol (isopropyl alcohol). (Remember, isopropyl alcohol is an isomer of propyl alcohol—same molecular formula, different molecular structure.)

Alcohols are either flammable or combustible, burning with a clean blue flame. The smallest alcohols, methyl and ethyl, have relatively wide flammable ranges (6% to 36% and 3.3% to 19%, respectively). These water-soluble compounds are generally toxic, although toxicity varies from one to another. For example, ethanol in alcoholic beverages can be tolerated in significant quantities, even though it still has a toxic effect on the body. Yet, methanol is very toxic. One of the worst consequences of methanol poisoning is blindness resulting from the way the liver metabolizes methanol to release formic acid and formaldehyde into the body.

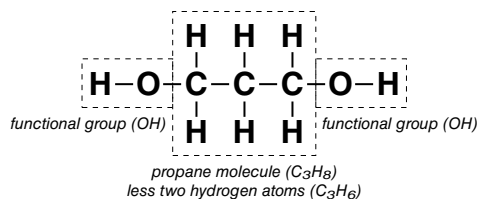
Glycols

Glycols are part of the larger alcohol family, but have two hydroxyl (OH) groups instead of one. The most common is ethylene glycol, commonly used as antifreeze. The only other common one is propylene glycol. Each has the word *glycol* in the name. The prefixes *eth-* and *prop-* signify the number of carbon atoms. Glycols are toxic and combustible. Most are highly soluble in water and are relatively nonvolatile.

Glycol Examples



Ethylene Glycol
 $\text{C}_2\text{H}_4(\text{OH})_2$ or $\text{HO}(\text{CH}_2)_2\text{OH}$



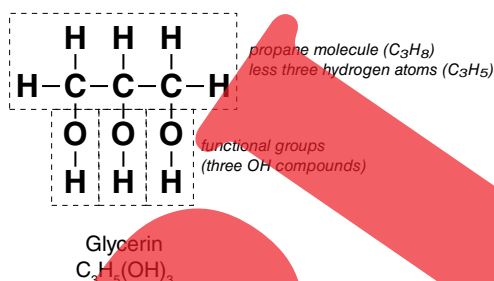
Propylene Glycol
 $\text{C}_3\text{H}_6(\text{OH})_2$ or $\text{HO}(\text{CH}_2)_3\text{OH}$

Other Part 1 Hydrocarbon Derivatives (continued)

Glycerols

Glycerols are also part of the larger alcohol family, but they have three hydroxyl (OH) groups to set them apart. Glycerols, in general, should be considered toxic and combustible. However, the most common one, glycerin, is relatively harmless in low concentrations. Glycerin is used to make a wide variety of products, from dynamite to candy and pharmaceuticals.

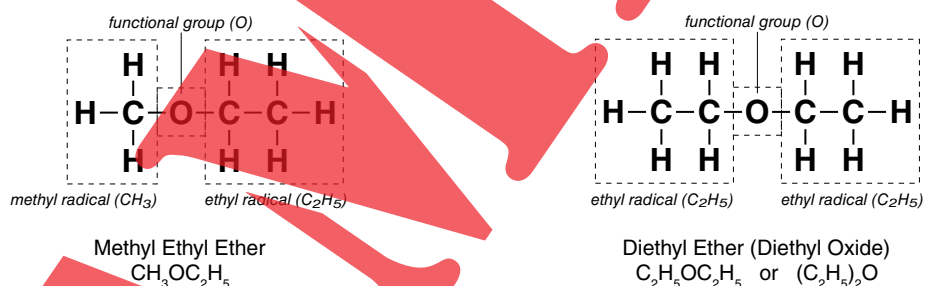
Glycerol Example



Ethers

The functional group in ethers is a single oxygen atom. The name identifies the hydrocarbon radicals followed by the word *ether*. While it's far less common, you may see the word *oxide* instead, as in diethyl oxide illustrated below. It's important to recognize this as an ether, not an oxide salt (which would have a metal element in the name and formula). The simplest ether, not pictured below, has methyl radicals on each side. It is called dimethyl ether (CH_3OCH_3)—*di* meaning *two*.

Ether Examples



Ethers are very volatile. They are flammable. Many have flash points below 0°F (17.8°C), and some have relatively wide flammable ranges, including diethyl ether (1.9% to 36%) and divinyl ether (1.7% to 27%). When ethers burn, they do so with invisible flames.

Ethers have limited shelf lives; they form explosive organic peroxides over time, particularly when exposed to air. For example, methyl ethyl ether ($CH_3OC_2H_5$) bonds with oxygen from the atmosphere to become methyl ethyl peroxide ($CH_3OOC_2H_5$). Crystals developing on the container indicate extreme danger.

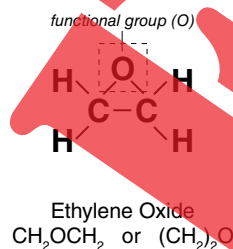
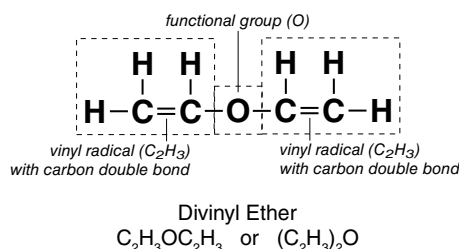
Ethers are insoluble in water; they are floaters. Most have anesthetic properties, which is one reason diethyl ether (commonly referred to simply as "ether") was once widely used as a general anesthetic in hospitals before being replaced by safer products.

Two other ethers are shown on the next page. Divinyl ether ($C_2H_3OC_2H_3$) behaves like most other ethers, but has the added danger of polymerization due to two double carbon bonds. Ethylene oxide (CH_2OCH_2) is unique in name and appearance, but its structure (an oxygen atom between two carbon atoms) qualifies it as an ether. Ethylene oxide is an extremely hazardous gas with a flammable range of 3% to 100%. That plus its composition (a fuel component and an oxidizer component in the same compound), makes it possible for ethylene oxide to burn inside its own container with no air present. It's also subject to polymerization.

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Other Part 1 Hydrocarbon Derivatives (continued)

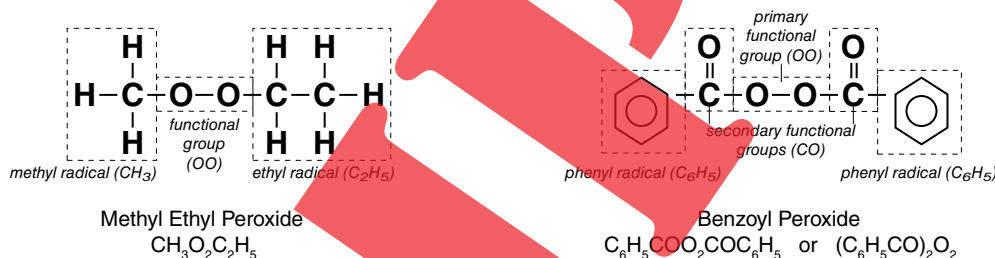
More Ether Examples



Organic Peroxides

Organic peroxides are extremely unstable. Although they are not explosive, *per se*—they are placarded as organic peroxides (DOT Class 5.2)—they are similar to explosives in that they contain both a fuel component and an oxidizer component in the same formula. That oxidizer component is the functional group OO or O_2 . Each oxygen atom is also bonded to a hydrocarbon radical (fuel).

Organic Peroxide Examples



Organic peroxides normally have *peroxide* or *peroxy* in the name. The ones pictured above have relatively simple names that clearly identify the hydrocarbon radicals. However, many of these manmade compounds have names that are complex and difficult to pronounce. They're beyond the scope of this study guide. What's most important is that you can distinguish these compounds from the salts. Remember, peroxide salts (e.g., sodium peroxide) also have *peroxide* in the name and O_2 in the formula. However, it's that metal element that marks them as salts. Some of the organic peroxides have names with a *per-* prefix and *-ate* ending, similar to the oxysalts. Isopropyl percarbonate is one example. But there's no metal element in the name, so it's clearly not a salt.

A few organic peroxides have names that are misleading, for example, peracetic acid (CH_3COOOH). It's a poignant reminder of how important it is to check reference sources at a hazmat incident rather than rely solely on name recognition and a limited knowledge of chemistry. One other common material bears mentioning. Hydrogen peroxide (H_2O_2) is an *inorganic* peroxide, not an organic one, because it doesn't contain carbon.

Organic peroxides have a multitude of hazards, the most significant of which is their unstable nature. They are very sensitive to heat and friction. Many are also very sensitive to contamination. Their chemical composition makes them both flammable and oxidizing. They're highly reactive with other chemicals. Many are toxic. Some are corrosive. All in all, they're quite a challenge. These materials are insoluble in water; they are floaters.

Organic peroxides are often used as catalysts in the plastics industry to initiate the polymerization process. They are prone to runaway polymerization if exposed to elevated temperatures. Consequently, many reference sources will identify *self-accelerating decomposition temperatures* (SADT) for these compounds. The SADT is the temperature at which an organic peroxide begins to decompose. (As a rule of thumb, increasing the temperature by a mere 10 degrees will cause the reaction rate to double.) Once the reaction begins, it cannot be stopped. Organic peroxides should be kept below the *maximum safe storage temperature* (MSST)—a temperature far enough below the SADT to provide a margin of safety.

Other Part 1 Hydrocarbon Derivatives (continued)

Review Questions (answers on page 196)

1. $\text{CH}_3\text{O}_2\text{C}_2\text{H}_5$ is a/an:
 - a. Alcohol
 - b. Ether
 - c. Organic peroxide
 - d. Glycol
2. $\text{CH}_3\text{OC}_2\text{H}_5$ is a/an:
 - a. Alcohol
 - b. Ether
 - c. Organic peroxide
 - d. Glycol
3. $\text{C}_2\text{H}_4(\text{OH})_2$ is a/an:
 - a. Alcohol
 - b. Glycerol
 - c. Organic peroxide
 - d. Glycol
4. CH_3OH is a/an:
 - a. Alcohol
 - b. Glycol
 - c. Glycerol
 - d. Ether
5. $\text{C}_3\text{H}_5(\text{OH})_3$ is a/an:
 - a. Alcohol
 - b. Glycerol
 - c. Glycol
 - d. Ether
6. Which of the following hydrocarbon derivatives are toxic and flammable with wide flammable ranges?
 - a. Alcohols
 - b. Glycols
 - c. Glycerols
 - d. Organic peroxides
7. Which of the following hydrocarbon derivatives have limited shelf lives and tend to form explosive peroxides over time, particularly when exposed to air?
 - a. Ethers
 - b. Glycols
 - c. Glycerols
 - d. Organic peroxides

Hazmat Chemistry Study Guide

Other Part 1 Hydrocarbon Derivatives (continued)

8. Which of the following hydrocarbon derivatives are extremely unstable and, like explosives, contain both a fuel component and an oxidizer in the same formula?
- a. Alcohols
 - b. Glycols
 - c. Glycerols
 - d. Organic peroxides
9. Ethylene oxide is a/an:
- a. Organic peroxide
 - b. Ether
 - c. Aldehyde
 - d. Glycerol

Part 2 Hydrocarbon Derivatives - Nitrogen Based

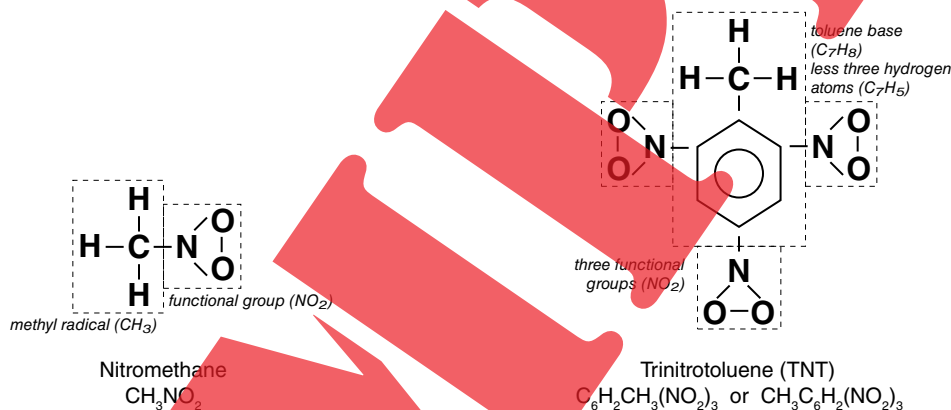
This next group of hydrocarbon derivatives introduces one new element—nitrogen.

Nitros

Nitros are comprised of one or more nitro (NO_2) groups bonded to a hydrocarbon radical. The bonded pair of oxygen atoms makes the nitro group a strong oxidizer. The hydrocarbon radical provides the fuel component. With both an oxidizer and a fuel component in the same structure, two sides of the fire triangle are already complete. Consequently, these compounds are explosive and highly flammable. Many are sensitive to shock and/or heat. They're also toxic by inhalation, ingestion, and skin absorption. Many nitros are vasodilators, exposure to which can cause a sudden drop in blood pressure. They vary in solubility.

Most nitro compounds contain *nitro* in the name. The first example below is a very simple compound in which the name nitromethane clearly indicates a methyl radical attached to the functional group. The second example is a derivative of toluene (C_7H_8). However, three of the original hydrogen atoms have been replaced by nitro compounds (NO_2), hence the name trinitrotoluene, whose formula may be written as $\text{C}_6\text{H}_2\text{CH}_3(\text{NO}_2)_3$ or $\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_3$.

Nitro Examples



Amines

The simplest amines are those containing the functional group NH_2 bonded to a single hydrocarbon radical, as with methyl amine (CH_3NH_2) and ethyl amine ($\text{C}_2\text{H}_5\text{NH}_2$) below. However, secondary and tertiary amines can be created by substituting additional hydrocarbon radicals for hydrogen atoms, as in dimethyl amine ($[(\text{CH}_3)_2\text{NH}]$) and trimethyl amine ($[(\text{CH}_3)_3\text{N}]$). (See next page.) The names follow the common pattern of first identifying the radical, followed by the word *amine*.

Amine Examples

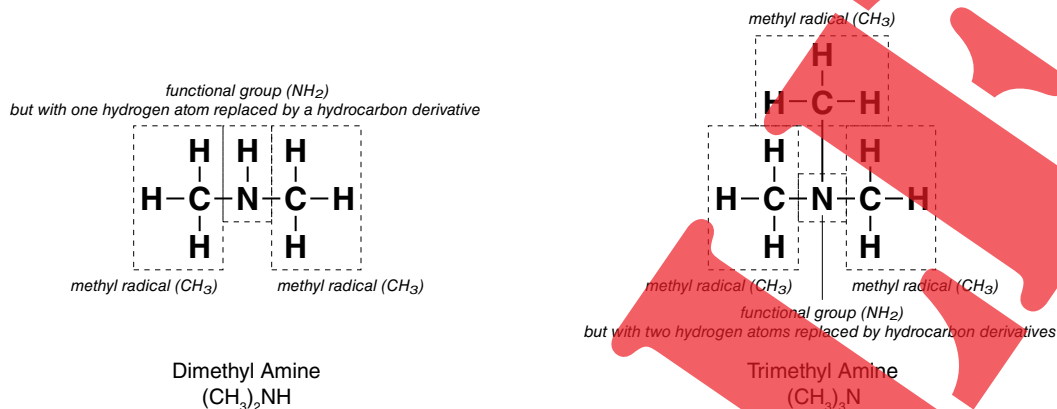


Amines are often called ammonia derivatives since the functional group begins as ammonia (NH_3) before the hydrogen atoms are removed. The ammonia base and hydrocarbon radicals both contribute to the toxicity and flammability of amines. Some amines are also corrosive. Acute exposure could cause a caustic burn, while chronic exposure may cause kidney or liver damage. Amines exhibit a yellow flame when burning. They are water-soluble and have characteristically foul odors.

Hazmat Chemistry Study Guide

Part 2 Hydrocarbon Derivatives - Nitrogen Based (continued)

More Amine Examples



Nitriles (Cyanides)

The nitriles, also called cyanides, contain the functional group CN , with a triple bond between the carbon atom and the nitrogen atom. The easiest names are the ones with the word *cyanide* because we're more familiar with names in which the hydrocarbon radical and functional group are identified separately. The examples below are methyl cyanide (CH_3CN) and vinyl cyanide ($\text{CH}_2\text{:CHCN}$).

The names ending in *nitrile* work differently, where the carbon atom from the functional group is treated like part of the hydrocarbon radical. For example, acetonitrile combines the *acet-* radical ($\text{CH}_3\text{[C}\equiv\text{]}$) with the nitrogen atom (N) to complete the formula CH_3CN . Nitrogen is added to the *acryl-* radical ($\text{C}_2\text{H}_3\text{[C}\equiv\text{]}$) to create acrylonitrile ($\text{CH}_2\text{:CHCN}$).

Nitrile (Cyanide) Examples



Nitriles are toxic due to the cyanide compounds in their structures. They are flammable, exhibiting a yellow flame with a blue base when burning. Some nitriles (e.g., acrylonitrile) are subject to polymerization due to a double bond between carbon atoms. Nitriles are water-soluble solvents.

Note: If cyanide (CN) is bonded to a metal element rather than to a hydrocarbon radical, it forms a highly toxic metal cyanide salt (e.g., sodium cyanide or potassium cyanide).

Part 2 Hydrocarbon Derivatives - Nitrogen Based (continued)

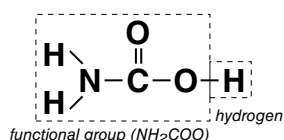
Carbamates

The functional group for carbamates is generally recognized as NH_2COO —essentially a combination of the functional groups seen with amines (NH_2) and esters (COO). Carbamic acid (NH_2COOH) is the simplest example, with a hydrogen atom filling the one open bonding site. Carbaryl ($\text{C}_{12}\text{H}_{11}\text{NO}_2$), below right, is a more complex example, where one of the hydrogen atoms normally attached to nitrogen has been replaced by another hydrocarbon radical. On the other side of the functional group are two benzene rings.

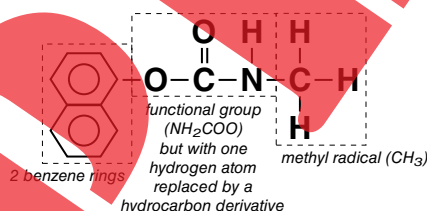
There's no simple naming scheme associated with these compounds, but a *carba-* prefix in a name that doesn't point towards other hydrocarbon derivatives should get you thinking about carbamates.

Carbamates are used as pesticides, often in place of the more toxic organophosphates. Nonetheless, they are still toxic and combustible.

Carbamate Examples



Carbamic Acid
 NH_2COOH

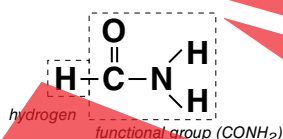


Carbaryl
 $\text{C}_{12}\text{H}_{11}\text{NO}_2$

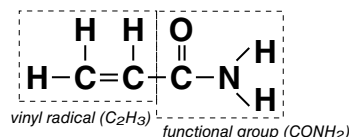
Amides

Amides have a functional group of CONH_2 —essentially a combination of the functional groups seen with ketones (CO) and amines (NH_2). Here again, though not pictured below, more of the hydrogen atoms attached to nitrogen can be replaced by hydrocarbon radicals.

Amide Examples



Formamide
 HCONH_2



Acrylamide
 $\text{C}_2\text{H}_3\text{CONH}_2$

These compounds often contain *amide* in the name. This is another hydrocarbon derivative where the carbon atom from the functional group is treated like part of the hydrocarbon radical for naming purposes. For example, formamide is based on the *form-* radical ($\text{H}[\text{C}]\equiv$). The illustration of acrylamide above depicts the vinyl radical, but the name is based on the *acryl-* radical ($\text{C}_2\text{H}_3[\text{C}]\equiv$).

Amides have low to moderate toxicity. They are flammable. Those with a double bond between carbon atoms (e.g., acrylamide) are subject to polymerization.

Hazmat Chemistry Study Guide

Part 2 Hydrocarbon Derivatives - Nitrogen Based (continued)

Review Questions (answers on page 196)

- $\text{C}_2\text{H}_5\text{NH}_2$ is a/an:
 - Amide
 - Amine
 - Carbamate
 - Nitrile
- $\text{C}_6\text{H}_2\text{CH}_3(\text{NO}_2)_3$ is a/an:
 - Nitro
 - Nitrile
 - Amine
 - Carbamate
- $\text{C}_2\text{H}_5\text{CONH}_2$ is a/an:
 - Nitro
 - Amine
 - Amide
 - Carbamate
- $\text{CH}_2\text{:CHCN}$ is a/an:
 - Amine
 - Carbamate
 - Nitro
 - Nitrile
- Which of the following hydrocarbon derivatives have characteristically foul odors?
 - Amines
 - Amides
 - Carbamates
 - Nitriles
- Which of the following hydrocarbon derivatives are typically used as pesticides?
 - Nitros
 - Amines
 - Nitriles
 - Carbamates
- Many _____ are sensitive to shock and heat.
 - Nitros
 - Nitriles
 - Amines
 - Amides
- Which of the following hydrocarbon derivatives have cyanide compounds in their structures?
 - Amides
 - Amines
 - Carbamates
 - Nitriles

Part 2 Hydrocarbon Derivatives - Nitrogen Based (continued)

9. Which of the following is a nitrile?
- a. KCN
 - b. CH_3NH_2
 - c. $\text{CH}_2\text{:CHCN}$
 - d. $\text{CH}_3\text{COOC}_2\text{H}_5$
10. Which of the following is most likely to polymerize?
- a. CH_3CN
 - b. $\text{CH}_2\text{:CHCN}$
 - c. $(\text{CH}_3)_3\text{N}$
 - d. $\text{C}_6\text{H}_5\text{CH}_2(\text{NO}_2)_3$

Other Part 2 Hydrocarbon Derivatives

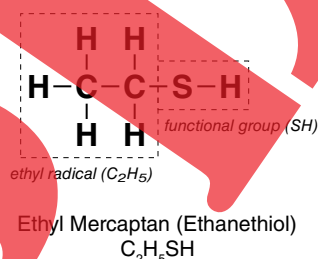
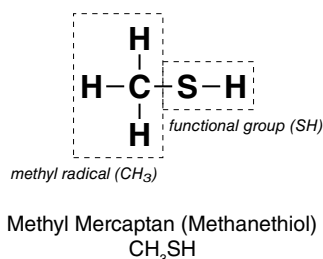
This final section introduces a variety of elements beyond just oxygen and nitrogen seen previously.

Thiols (Mercaptans)

Thiols (or mercaptans) contain the functional group SH (sulfur and hydrogen) bonded to a single hydrocarbon radical. They commonly have either *thiol* or *mercaptan* in the name and, as the examples below show, clearly identify the hydrocarbon radical using familiar prefixes.

These compounds are flammable and toxic. They are also strong irritants. Many have skunk-like odors and are used as odorizers for hydrocarbon fuels, for instance, as a warning agent for natural gas.

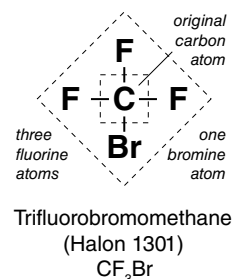
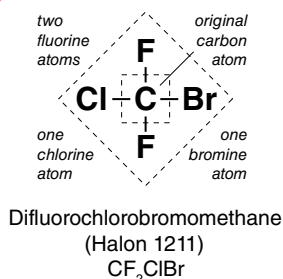
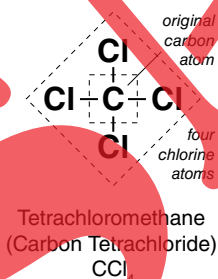
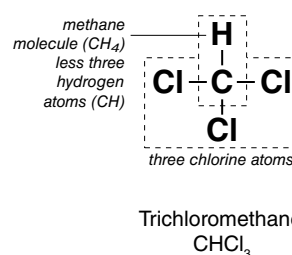
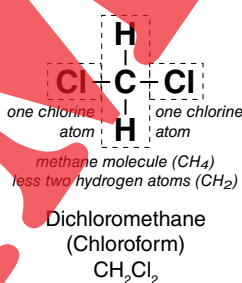
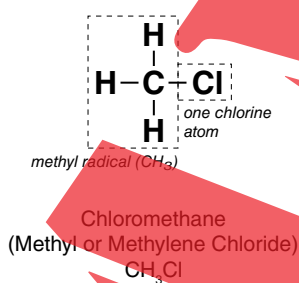
Thiol (Mercaptan) Examples



Alkyl Halides (Halogenated Hydrocarbons)

There is no specific functional group for alkyl halides (also called halogenated hydrocarbons). Rather, what they have in common is that one or more hydrogen atoms in the original hydrocarbon is replaced by a halogen (fluorine, chlorine, bromine, or iodine). The most common are the chlorinated hydrocarbons. The six illustrations below are based on methane, the simplest hydrocarbon. The next page shows examples of alkyl halides produced from ethane and ethene.

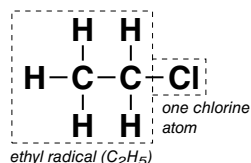
Alkyl Halide (Halogenated Hydrocarbon) Examples



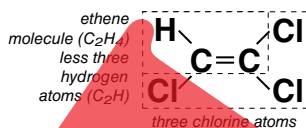
Other Part 2 Hydrocarbon Derivatives (continued)

The proper names of these compounds very clearly identify the original molecule (methane, ethane, ethene, etc.) and the halogens used. The common or alternate names, such as methylene chloride, chloroform, and Halon, are the ones that don't necessarily give a clear indication as to chemical composition. (Note: Some of these names have *-ide* endings, similar to most of the salts. However, the presence of halogens instead of metal elements clearly distinguishes these as alkyl halides.)

More Alkyl Halide (Halogenated Hydrocarbon) Examples



Chloroethane
(Ethyl Chloride)
 C_2H_5Cl



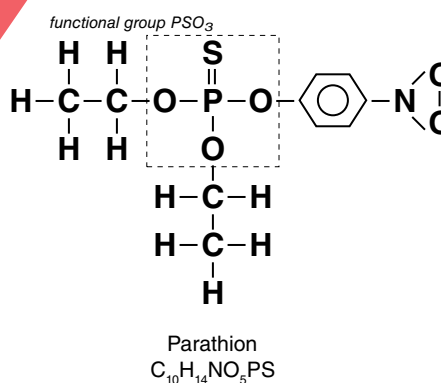
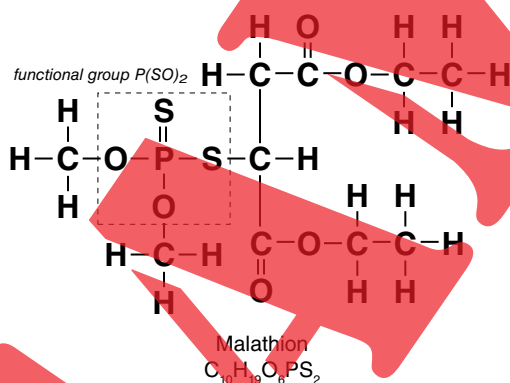
Trichloroethylene
 $ClCH:CCl_2$

Alkyl halides are considered toxic as a group, some more so than others. Some are flammable, although most do not burn. In fact, some are used as extinguishing agents. Most will break down at relatively low temperatures (as low as $325^\circ F / 162.8^\circ C$), giving off toxic decomposition products. For example, carbon tetrachloride, once used as an extinguishing agent, decomposes to toxic phosgene gas when heated. Alkyl halides are insoluble in water; they are sinkers.

Organophosphates

Organophosphates are very large compounds containing phosphorus double-bonded to either sulfur or oxygen. Malathion and parathion, shown below, are two common examples. The first has a functional group of $P(SO)_2$; the second, PSO_3 . These toxic compounds are used as insecticides. They are often mixed with flammable liquids for dissemination.

Organophosphate Examples



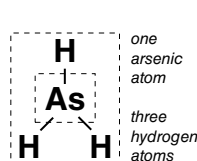
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Other Part 2 Hydrocarbon Derivatives (continued)

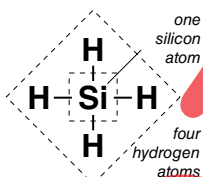
Hi-Tech Compounds

The final category of hydrocarbon derivatives contains what are generally referred to as hi-tech compounds. These are a variety of products that don't fit into any of the other categories. Because these compounds vary so much in composition, there is no pattern in the names, formulas, or structures that would immediately identify the hi-tech compounds. However, these compounds may contain arsenic (As), beryllium (Be), boron (B), silicon (Si), tin (Sn), or titanium (Ti).

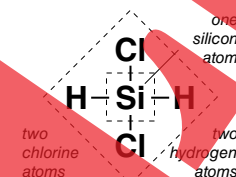
Hi-Tech Compound Examples



Arsine
 AsH_3



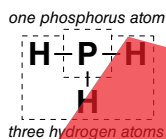
Silane
 SiH_4



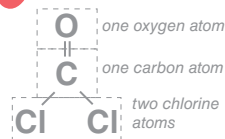
Dichlorosilane
 H_2SiCl_2

Below are two chemicals whose names are very similar. Phosphine (PH_3), left, is a hi-tech compound. Phosgene (COCl_2), right, is not; it's a chlorinated hydrocarbon. However, it's worthwhile showing the two side-by-side as an example of how important it is to make sure you have the correct spelling on a chemical name so that you don't mistake the hazards associated with it. (Some of the synonyms for phosgene suggest it is a chlorinated hydrocarbon. Examples include carbonic dichloride, carbon oxychloride, and carbonyl dichloride. However, phosgene is the name emergency responders are most likely to encounter.)

An Example of Dissimilar Compounds with Similar Names



Phosphine (a hi-tech compound)
 PH_3



Phosgene (a chlorinated hydrocarbon)
 COCl_2

The diversity of the hi-tech compounds makes it difficult to make generalizations about the hazards. However, many are reactive, pyrophoric, and/or toxic. Some are flammable. Until proven otherwise, they should all be treated as very dangerous.

Other Part 2 Hydrocarbon Derivatives (continued)

Review Questions (answers on page 196)

- $C_{10}H_{19}O_6PS_2$ is a/an:
 - Alkyl halide
 - Hi-tech compound
 - Organophosphate
 - Thiol
- SiH_4 is a/an:
 - Alkyl halide
 - Hi-tech compound
 - Organophosphate
 - Thiol
- $CHCl_3$ is a/an:
 - Alkyl halide
 - Hi-tech compound
 - Organophosphate
 - Thiol
- CF_3Br is a/an:
 - Alkyl halide
 - Hi-tech compound
 - Organophosphate
 - Thiol
- CH_3SH is a/an:
 - Alkyl halide
 - Hi-tech compound
 - Organophosphate
 - Thiol
- Which of the following hydrocarbon derivatives have names that sometimes end in *-ide*?
 - Alkyl halides
 - Hi-tech compounds
 - Organophosphates
 - Thiols
- Which of the following hydrocarbon derivatives are toxic compounds used as insecticides?
 - Alkyl halides
 - Hi-tech compounds
 - Organophosphates
 - Thiols
- Which of the following groups contains a number of extinguishing agents?
 - Alkyl halides
 - Hi-tech compounds
 - Organophosphates
 - Thiols

Hazmat Chemistry Study Guide

Other Part 2 Hydrocarbon Derivatives (continued)

9. Which of the following hydrocarbon derivatives have skunk-like odors and are used as warning agents for other chemicals, such as natural gas?
- Alkyl halides
 - Hi-tech compounds
 - Organophosphates
 - Thiols
10. Which of these hydrocarbon derivatives are often mixed with flammable liquids for dissemination?
- Alkyl halides
 - Hi-tech compounds
 - Organophosphates
 - Thiols
11. The most common alkyl halides (halogenated hydrocarbons) are those containing:
- Chlorine
 - Fluorine
 - Bromine
 - Iodine

Chapter 5 Review

Review Questions (answers on page 196)

- Which of the following is a highly unstable alkyne with a triple bond between carbon atoms?
 - Acetylene
 - Ethene
 - Styrene
 - Propene
- C_2H_2 is an:
 - Alkane
 - Alkene
 - Alkyne
 - Aromatic
- C_7H_8 is an:
 - Alkane
 - Alkene
 - Alkyne
 - Aromatic
- C_6H_{14} is an:
 - Alkane
 - Alkene
 - Alkyne
 - Aromatic
- C_2H_4 is an:
 - Alkane
 - Alkene
 - Alkyne
 - Aromatic
- C_3H_6 is:
 - Propane
 - Propene
 - Propyne
 - Propanone
- C_8H_{10} is:
 - Octane
 - Hexane
 - Styrene
 - Xylene
- C_5H_{12} is:
 - Butene
 - Pentane
 - Phenol
 - Benzene

Hazmat Chemistry Study Guide

Chapter 5 Review (continued)

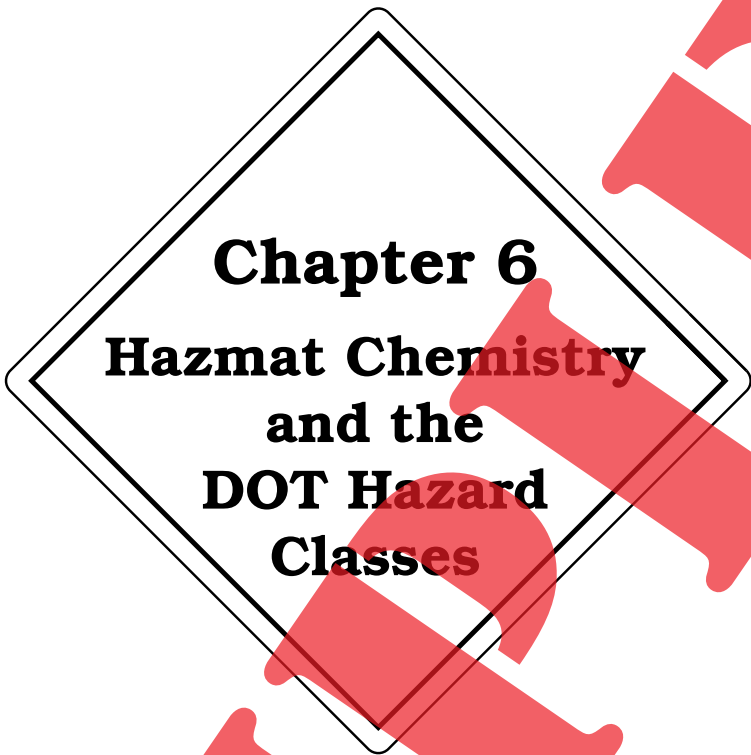
9. The formula for methane is:
- CH_3
 - CH_4
 - C_2H_2
 - C_2H_4
10. Which of the following is an alkyl halide?
- Sodium chloride
 - Potassium chloride
 - Methyl chloride
 - Lithium chloride
11. $\text{CH}_3\text{COC}_2\text{H}_5$ is a/an:
- Ester
 - Ketone
 - Ether
 - Glycol
12. $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ is a/an:
- Ketone
 - Organic acid
 - Ether
 - Ester
13. Which of the following hydrocarbon derivatives tend to have wide flammable ranges and may, over time, form unstable and explosive organic peroxides?
- Ethers
 - Nitros
 - Ketones
 - Glycols
14. Which of the following compounds is most likely to be very reactive and unstable due to its bonding structure?
- Pentane
 - Isopentane
 - Cyclopentane
 - Cyclopentadiene
15. Which of the following contains an unstable double bond?
- C_2H_6
 - C_2H_4
 - C_2H_2
 - C_6H_6
16. Which of the following is an aromatic hydrocarbon?
- Propane
 - Methyl amine
 - Toluene
 - Trinitrotoluene

Chapter 5 Review (continued)

17. Which of the following hydrocarbons is saturated?
- Ethyne
 - Benzene
 - Pentane
 - Propene
18. Which of the following is most likely to polymerize?
- C_3H_8
 - C_3H_6
 - C_8H_{10}
 - CH_4
19. Which of the following has the highest flash point?
- Methyl alcohol
 - Ethyl alcohol
 - Propyl alcohol
 - Butyl alcohol
20. Which of the following is likely to have the highest ignition temperature?
- CH_3NH_2
 - $C_2H_5NH_2$
 - $C_3H_7NH_2$
 - $C_4H_9NH_2$
21. Which of the following has the lowest vapor pressure?
- Methane
 - Propane
 - Pentane
 - Octane
22. Flammable liquids with high vapor pressures have:
- High boiling points
 - Low flash points
 - Low ignition temperatures
 - Low vapor content
23. Flammable liquids with high flash points have:
- Low ignition temperatures
 - High vapor content
 - Low boiling points
 - High ignition temperatures

Hazmat Chemistry Study Guide

SAMPLE



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.

Hazmat Chemistry Study Guide

Class 1 - Explosives

An **explosive** is any substance or article that is designed to function by explosion. Explosives include those compounds that, by chemical reaction within themselves, are able to function in a similar manner, even if not designed to do so. It's important to realize, however, that many materials not classed as explosives will indeed explode under the right conditions. Examples include natural gas, organic peroxides, and grain dusts. Therefore, while the chemistry differs, the precautions that apply to explosives also apply to materials capable of producing similar reactions.



Divisions of This Hazard Class

Explosives are divided into six divisions based on degree of hazard.

Division	Degree of Hazard	Examples
1.1	Mass explosion hazard	Black powder, dynamite, TNT
1.2	Projection hazard	Detonating cord, aerial flares
1.3	Fire hazard with minor blast or projection hazard	Propellant explosives
1.4	Minor explosion hazard	Practice ammo, most fireworks
1.5	Very insensitive explosive	Blasting agents, ANFO
1.6	Extremely insensitive articles	Articles not otherwise specified

The explosives hazard class includes blasting agents (Division 1.5). A **blasting agent** is a chemical mixture that consists largely of ammonium nitrate and that will detonate when initiated by a high-explosive primer or booster. Blasting agents are relatively insensitive to shock, friction, and impact, but are very dangerous when exposed to fire. The two most common ones are ammonium nitrate and water gels (or blasting slurries). If the name ammonium nitrate doesn't set off any alarm bells for you, think about the 1995 bombing of the Alfred P. Murrah federal building in Oklahoma City. That was done with a mixture of ammonium nitrate and fuel oil, otherwise known as ANFO.

It's important to recognize that the divisions above were established based on how the explosives are expected to behave under normal conditions of transport. They do not reflect how these materials will behave when exposed to fire. Many emergency responders have been killed because they underestimated the hazard potential of relatively insensitive explosives. There is little difference between the six divisions from a first responder's perspective. While the degree of risk varies, all Class 1 materials can be just as deadly if they explode. The National Fire Protection Association (NFPA) recommends that firefighters should not attempt to fight a fire involving explosives. Rather, the area should be evacuated to a distance of at least 2000 feet.

Nor do these classifications reflect dangers that other factors can introduce. For example, older explosives are often more unstable than those recently manufactured. Explosives already stressed by heat, shock, or friction, such as those that survived flame impingement or a transportation accident, can detonate hours later, with little to no provocation.

The military uses its own marking system, with explosives divided into four categories based on the relative detonation and fire hazards. Military shipments are sometimes transported in unmarked vehicles for security, and military drivers may be under orders not to identify their cargoes. However, if a military driver rapidly abandons a damaged or burning vehicle, it's a good clue that you should withdraw immediately.

Military Division	Hazard	UN/DOT Equivalent
1	Mass detonation	Class 1.1
2	Explosion with fragments	Class 2.2
3	Mass fire hazard	Class 1.3
4	Moderate fire hazard	Class 1.4

Military Markings

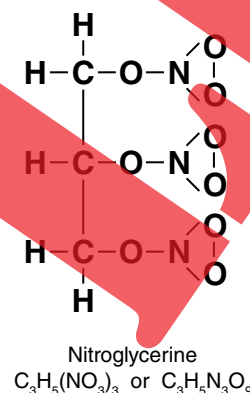
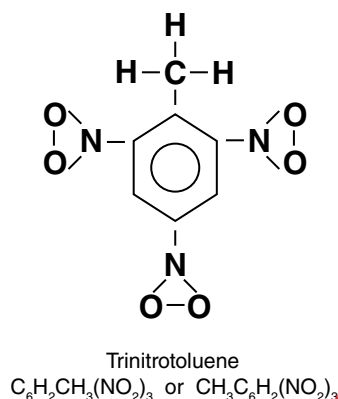


Class 1 - Explosives (continued)

Relation to What You Already Learned About Hazmat Chemistry

One reason explosives are so dangerous is that they contain both an oxidizer and a fuel component in their structures. Two sides of the fire triangle are already complete. Let's look at a couple of examples to see how they relate to the chemistry we've already learned.

Examples of Explosives



Both of the examples above are hydrocarbon derivatives, specifically nitros. In the case of trinitrotoluene (TNT), three nitro (NO_2) groups were added. In the case of nitroglycerin, it was three nitrate (NO_3) groups. The functional groups common to explosives are called **explosophores**; they are strong, highly reactive oxidizers. Other examples of explosophores include chlorite (ClO_2), chlorate (ClO_3), perchlorate (ClO_4), and peroxide (O_2). Notice how each of these are rich in oxygen. (These should look familiar to you too. The first three are the same groups that when added to metal elements create the powerful oxidizers known as oxysalts. And a peroxide group added to a metal element creates metal peroxide salts, also powerful oxidizers.)

Not all explosives depend on oxygen-rich explosophores, however. Heavy metal azides, which are derivatives of hydrazoic acid (N_3H), are extremely explosive. Lead azide ($\text{Pb}[\text{N}_3]_2$) is an example. Fulminates of heavy metals, based on the **CNO functional group**, are also powerful explosives. Mercury fulminate ($\text{Hg}[\text{CNO}]_2$) is an example. Acetylides, such as cuprous acetylide (Cu_2C_2), are metal derivatives of acetylene (C_2H_2), which contains the highly reactive carbon triple bond.

With two sides of the fire triangle already complete, all it takes is the introduction of energy in the form of heat, shock, or friction to cause a reaction. Some explosives are highly sensitive and require very little energy to initiate a reaction, while others are relatively insensitive, requiring an initiating device to function. Explosives are sometimes made "hotter" or more powerful by adding finely powdered metals, such as aluminum, to the mixture.

Other Important Concepts

An **explosion** is broadly defined as the sudden and rapid escape of gases from a confined space, accompanied by high temperatures, violent shock, and loud noise. There are three types:

- A **chemical explosion** is caused by an almost instantaneous conversion of a solid or liquid explosive compound into gases that have a much greater volume than the original substances. With the exception of nuclear explosives, all manufactured explosives are chemical explosives. Most explosions emergency personnel respond to are due to chemical explosives. (This section deals only with chemical explosives.)
- A **mechanical explosion** (or pressure relief explosion) involves a buildup of pressure inside a container, often due to overheating. If the container is not equipped with a safety valve, the internal pressure will eventually exceed the structural capacity of the container, resulting in container failure.
- A **nuclear explosion** may be induced by either fission (the splitting of the nuclei of atoms) or fusion (the joining of the nuclei of atoms under great force).

Class 1 - Explosives (continued)

Explosives are classified as either low explosives or high explosives based on their rate of reaction.

- **Low explosives** are those that **deflagrate**; the reaction is defined as very rapid combustion from the surface inward at a reaction rate slower than the speed of sound. Low explosives have more a “pushing” effect rather than the “shattering” effect associated with high explosives, so they’re used primarily for propulsion. Low explosives can be initiated by a simple flame or acid/ flame reaction. They can also be initiated by shock or friction, but do not require the shock of a blasting cap. Examples of low explosives include black powder, smokeless powder, and solid rocket fuel.
- **High explosives** are those that **detonate**; the reaction is defined as instantaneous combustion, with speeds ranging from 3300 to 29,900 feet per second (faster than the speed of sound—1142 feet per second). High explosives have more of a “shattering” effect rather than the “pushing” effect associated with low explosives. In general, high explosives must be initiated by the shock of a blasting cap.

High explosives are also categorized based on their sensitivity to shock, friction, flame, heat, or any combination of these factors.

- **Primary explosives** are extremely sensitive, which makes them very hazardous to handle. Examples include blasting caps, safety fuses filled with black powder, mercury fulminate, lead styphnate, and lead azide. Primary explosives may be referred to as *detonators or initiation devices* because they are often used to initiate secondary explosives.
- **Secondary explosives**, sometimes referred to as *main charge explosives*, are much less sensitive, making them less hazardous to handle and use. Because of their relative insensitivity, they must be initiated by a strong explosive wave, such as from a primary explosive. Examples of secondary explosives include dynamite, nitroglycerin, TNT, cyclonite (RDX), and pentaerythritol tetranitrate (PETN).

An **explosive train** is a series of two or more explosions arranged to produce the most effective result. Explosive trains are classified based on the final material (low explosive or high explosive) in the chain.

- A pipe bomb filled with smokeless or black powder (a low explosive) is an example of a two-step **low-explosive train**. The first “step” in the train is a safety fuse. When the exposed end of the fuse is ignited, it carries the flame to the powder (the second “step”) inside the pipe, causing it to explode. The majority of low explosives require only a simple two-step train.
- An electric blasting cap connected to a stick of dynamite is an example of a two-step **high-explosive train**. The explosive inside the blasting cap is initiated by heat from an electric current, resulting in a shock wave that causes the dynamite (a high explosive) to detonate. (A three-step explosive train could be set up using a safety fuse to detonate a nonelectric blasting cap, which would in turn detonate the dynamite.)

Boosters are sometimes used to amplify the shock wave from a primary explosive, particularly when the final material in the train is really insensitive. For example, ANFO is insensitive enough that the shock from a blasting cap alone should not cause it to detonate, but it can be detonated by the shock from exploding a smaller amount of another secondary explosive.

Improvised explosive devices (IEDs) are particularly dangerous because they can be concealed in almost anything (backpacks, briefcases, etc.) and can be triggered by innocent actions like opening a door, flipping a light switch, or simply disturbing the innocuous package. Emergency responders don’t have the benefit of standard recognition clues, such as placards, labels, container profiles, and industry preplans. Many of the components required to make improvised explosive devices are so commonplace that anyone can purchase them at a hardware store or supermarket without arousing suspicion.

Class 1 - Explosives (continued)

Review Questions (answers on page 196)

1. All chemical explosives contain:
 - a. A double bond between carbon atoms
 - b. Oxygen-rich explosophores
 - c. Nitro compounds
 - d. An oxidizer and a fuel component
2. Deflagration is defined as:
 - a. Spontaneous combustion
 - b. Very rapid combustion from the surface inward at rates slower than the speed of sound
 - c. Instantaneous combustion at rates faster than the speed of sound
 - d. A pressure relief explosion characterized by overheating and container failure
3. Which of the following must be initiated by the shock of a blasting cap?
 - a. Low explosives
 - b. High explosives
4. What is an explosophore?
 - a. An encapsulated explosive
 - b. An explosive that contains finely powdered metals in the mixture
 - c. A highly reactive oxidizer forming the functional group that makes some hydrocarbon derivatives explosive
 - d. The fuel component of any explosive material
5. Explosives are sometimes made "hotter" or more powerful by:
 - a. Adding an explosophore to the mixture
 - b. Adding finely powdered metals, such as aluminum, to the mixture
 - c. Preheating them
 - d. Using a booster to amplify the shock waves from a secondary explosive
6. What chemical compound is typically the major component of blasting agents?
 - a. Dynamite
 - b. Nitroglycerin
 - c. Ammonium nitrate
 - d. Mercury fulminate
7. Most explosions public safety personnel respond to are:
 - a. Chemical explosions
 - b. Mechanical explosions
 - c. Nuclear explosions
8. Explosives already stressed by heat, shock, or friction can detonate hours later, with little to no provocation.
 - a. True
 - b. False

Hazmat Chemistry Study Guide

Class 2 - Gases

Unlike the other hazard classes, Class 2 is defined by the physical state of its members, not by their primary hazards. So while all Class 2 materials exist as gases in their natural states, their hazards can vary greatly.

Divisions of This Hazard Class

Gases are put into one of three divisions based on their primary hazards.

Division	Description
2.1	Flammable gas (e.g., propane, acetylene)
2.2	Nonflammable, nonpoisonous compressed gas (e.g., anhydrous ammonia, carbon dioxide, nitrogen) (including compressed gas, liquefied gas, pressurized cryogenic gas, and compressed gas in solution)
2.3	Poisonous gas (e.g., arsine, chlorine, methyl bromide)

Division 2.3 (poisonous gases) may be further identified by poison inhalation zone (PIH), sometimes referred to as toxic inhalation zone (TIH). Hazard Zone A is the worst.

Hazard Zone	LC ₅₀ greater than	LC ₅₀ less than or equal to
A	—	200 ppm
B	200 ppm	1000 ppm
C	1000 ppm	3000 ppm
D	3000 ppm	5000 ppm

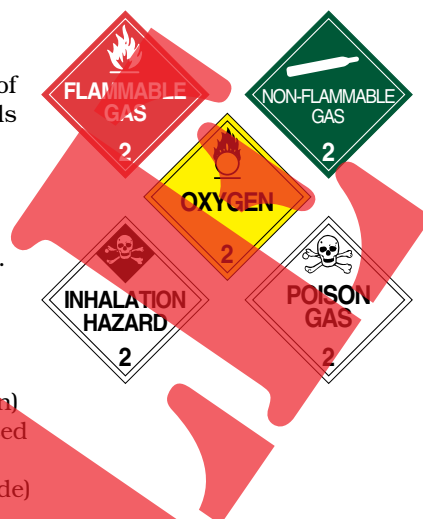
Warning: As emphasized at the beginning of this chapter, materials are put into classes based on their primary hazards, often with little regard to significant secondary hazards. One example above, chlorine, is classed as a poisonous gas. But it's also a very strong oxidizer. However, one can't wholly trust the divisions in this class. In 1984 in Shreveport, Louisiana, one firefighter was killed and another was badly injured when "nonflammable" anhydrous ammonia ignited in an enclosed room. The DOT definition of a flammable gas is one that has a lower explosive limit of not higher than 13.0% (ammonia's is 16%) or has a flammable range of at least 12% regardless of the lower explosive limit. Ammonia, with a lower explosive limit of 16% and an upper explosive limit of 25%, has a flammable range of 9%. It misses the DOT definition on both counts. This is another poignant reminder of how important it is for hazmat technicians to look closely at actual chemical and physical properties and not just at the quick-and-dirty labels sometimes used to describe hazardous materials.

Relation to What You Already Learned About Hazmat Chemistry

Going back to what we learned earlier about basic chemistry, there are a handful of elements that exist as gases. They are hydrogen (H₂), oxygen (O₂), chlorine (Cl₂), fluorine (F₂), helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). The first four exist as diatomic gases (see page 68) because of the need to have a filled outer shell. The last six, the noble gases, already have filled outer shells. They fulfill the octet rule in their natural states and thus have no reason to react with other elements. They are inert.

Other gases can be formed from a combination of solid and gaseous elements. Examples include carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), propane (C₃H₈), acetylene (C₂H₂), and ammonia (NH₃). All of these are nonsalt compounds; they are comprised of covalently bonded nonmetal elements.

Your knowledge of chemistry should also tell you which of the two gases mentioned above are highly reactive oxidizers because of their outer shell electrons. You should be able to predict which ones are likely to be flammable or combustible. You should also be able to identify the one that's highly unstable because of a triple carbon bond.



Class 2 - Gases (continued)

Other Important Concepts

Three variables (temperature, pressure, and volume) dictate how gases behave. Three behavior patterns (called gas laws) are of particular importance to us in assessing risk at incidents involving gases:

- Boyle's Law** For a given quantity of gas at a constant temperature, the volume of the gas is inversely proportional to the pressure. In other words, as the pressure increases, the volume of the gas decreases.
- Charles' Law** For a given quantity of gas at a constant pressure, the volume of the gas is proportional to the temperature. In other words, as the temperature increases, so does the volume.
- Ideal Gas Law** For a given temperature and volume (container size), the pressure of a gas is proportional to the quantity (molecules) of the gas. In other words, as the quantity of gas increases within the container, so does the pressure.

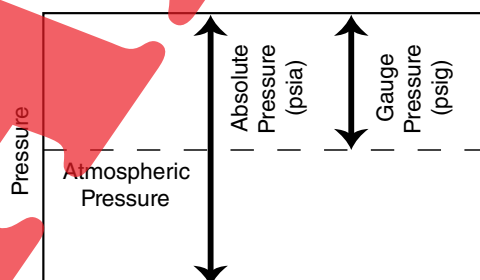
By understanding the relation between temperature, pressure, and volume, you can better assess the risks at incidents involving gases. For example, if a gas cylinder is heated, you can predict that the volume of that gas will increase (Charles' Law), as will the pressure within the cylinder. Direct flame impingement can cause pressure vessels (gas cylinders) to fail catastrophically within as little as ten to twenty minutes. With gases stored in liquid form, there is the added danger of a **BLEVE** (boiling liquid expanding vapor explosion)—catastrophic failure on much bigger scale.

Most compressed gas cylinders are equipped with a pressure relief device to prevent rupture when exposed to fire. Relief devices are prohibited, however, on cylinders containing highly toxic materials. A rising sound from a venting relief device and discoloration of the cylinder or tank due to fire are indications of impending container failure.

Gas properties listed in reference sources are usually based on **standard temperature and pressure (STP)**, conditions that provide a consistent baseline we can relate to. Standard temperature is defined as 0°C (32°F). (Meteorologists and oceanographers may use a standard temperature of 25°C [77°F], but chemists use 0°C.) Standard pressure is considered 1 atm (atmosphere) or 14.7 psia (pounds per square inch absolute).

What is pounds per square inch absolute (psia) and how does it differ from plain old pounds per square inch (psi)? Almost all pressure gauges read zero when open to the atmosphere, regardless of whether one is at sea level (atmospheric pressure 14.7 psi), a mile above sea level (atmospheric pressure 12.2 psi), or anywhere else. What we see on a pressure gauge, therefore, is most accurately recorded as *psig* (gauge pressure). Absolute pressure (psia) represents the sum of gauge pressure and atmospheric pressure. It's a reflection of pressure measured above a perfect vacuum.

Comparison Between psi, psia, and psig



Gases are typically stored in one of three ways: as compressed gases, as liquefied compressed gases, or as cryogenic liquids. **Compressed gases** are those that have been pressurized sufficiently to permit putting a larger volume of gas into a fixed container. Two good examples are oxygen used for medical purposes and compressed air used in self-contained breathing apparatus.

Class 2 - Gases (continued)

Liquefied compressed gases have been compressed even further (through cooling, pressurization, or both) to increase the storage capacity. Compressing the gases this much reduces the distance between gas molecules to the point where the gas behaves like a liquid. Liquid propane (LPG) and liquefied natural gas (LNG) are common examples.

Cryogenic liquids are gases that have been compressed so much through cooling and pressurization that they exist not as gases but as very cold liquids (colder than $-130^{\circ}\text{F}/-90^{\circ}\text{C}$). (Note: Some sources define cryogenic liquids as being below $-150^{\circ}\text{F}/-101.1^{\circ}\text{C}$.) Examples include liquid oxygen, liquid nitrogen, and liquid hydrogen. Cryogenic liquids don't have specific labels or placards; they generally have the same labels or placards as are used for gases. However, many of the containers used for bulk transportation of cryogenic liquids are not placarded, but are instead stenciled with the words "Refrigerated Liquid" and the name of the product.

Contact with cryogenic liquids can immediately freeze human tissue. Even their vapors can cause severe tissue damage. Other materials, such as steel, rubber, and plastic, can become very brittle in contact with cryogens, increasing the risk of container failure and related problems. Some gases in the cryogenic state can be so reactive that they form extremely shock-sensitive mixtures when in contact with combustible materials (e.g., liquid oxygen on asphalt).

Liquefying a gas can be done by cooling it to a temperature below its boiling point and/or by pressurizing it sufficiently. However, the ability to liquefy a gas is dependent on critical temperature and pressure. **Critical temperature** is the temperature above which it is impossible to liquefy a gas, regardless of how much pressure is applied. In other words, all the pressure in the world won't force the gas into a liquid state once it reaches its critical temperature. Or from an emergency response perspective, once a liquefied gas exceeds its critical temperature, the liquid converts instantaneously to gas, potentially causing container failure. **Critical pressure** is the pressure that must be applied to liquefy a gas at its critical temperature.

Propane, for example, has a boiling point of -44°F (-42.2°C). If propane is cooled below -44°F (-42.2°C), it will undergo a change from its natural gaseous state to a liquid state. Cooling a gas that much can be expensive, however. So propane is normally liquefied through a combined effort of cooling and pressurization. Propane's critical temperature is 206°F (96.7°C). Once it exceeds this temperature, it cannot remain in a liquid state no matter how much pressure is applied. Propane's critical pressure is 617 psi. That's how much pressure is required to liquefy propane at 206°F (96.7°C). The lower the temperature, the less pressure is required. Some gases have extremely low critical temperatures. For example, the critical temperature of nitrogen is -231°F (-141.6°). So it can't be liquefied by pressure alone. It must be cooled significantly.

Because gases are compressed, responders need to be concerned about how much space those gases will take up if released from their containers. **Expansion ratio** is the comparison between the volume of a product in a gaseous state versus the volume of that same product in a compressed or liquefied (cryogenic) state. For example, liquefied propane (LPG) has an expansion ratio of 270 to 1, and liquefied natural gas (LNG) has an expansion ratio of 635 to 1. The higher the expansion ratio, the more volume a gas will occupy once released from its container, which can greatly increase the scope of the incident. When the product expands, it can also displace oxygen in the atmosphere, immediately creating an asphyxiation hazard, particularly in an enclosed space.

Another consequence of gases being released from a cylinder (compressed or cryogenic) is that the cylinder cools. An example of this cooling effect can easily be seen when discharging a carbon dioxide fire extinguisher. Cooling due to release of gases is called **adiabatic decompression**. Conversely, a cylinder heats up when gases are compressed into it. Filling a cylinder too quickly can cause the cylinder to fail from overheating. This is why, for example, firefighters must be careful when refilling self-contained breathing apparatus (SCBA) bottles. Heating caused by compressing gases into a cylinder is called **adiabatic compression**.

Class 2 - Gases (continued)

Review Questions (answers on page 197)

- Critical temperature is the temperature:
 - Required to liquefy a gas
 - Above which it's impossible to liquefy a gas, regardless of how much pressure is applied
 - At which a gas begins to decompose in a reaction that cannot be stopped once it begins
 - At which the vapor expansion ratio is at its greatest
- As the temperature of a gas increases, the pressure within a closed cylinder:
 - Increases
 - Decreases
 - Stays the same
- Cryogenic liquids are generally described as being at temperatures:
 - At or below freezing (-32°F/0°C)
 - At or below 0°F (17.8°C)
 - At or below -50°F (-45°C)
 - At or below -130°F (-90°C)
- Critical pressure is the pressure:
 - That will cause a gas cylinder to fail
 - Required to liquefy a gas
 - That must be applied to liquefy a gas at its critical temperature
 - That corresponds to atmospheric pressure (760 mmHg or 14.7 psi or 1 atmosphere)
- Which of the following is placarded as a nonflammable gas even though it will burn when present within its flammable range?
 - Propane
 - Acetylene
 - Methyl bromide
 - Anhydrous ammonia
- Gas properties are usually based on conditions of standard temperature and pressure (STP), meaning:
 - Room temperature at 1 atm
 - 0°C (32°F) at 14.7 psia
 - 20°C (68°F) at 1 atm
 - 25°C (77°F) at 14.7 psia
- Adiabatic compression is:
 - The process used to compress a gas
 - The process used to liquefy a gas
 - Heating caused by compressing gases into a cylinder
 - Overpressurization from compressing more gas into a cylinder than it can safely hold
- A Division 2.3 label or placard on a gas cylinder or tank indicates the primary hazard associated with the gas is:
 - Flammability
 - Toxicity
 - Corrosivity
 - Oxidation

Hazmat Chemistry Study Guide

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 141°F (60.6°C), which comes from the more global 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 less than or equal to 141°F (60.6°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 greater than 141°F (60.6°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.

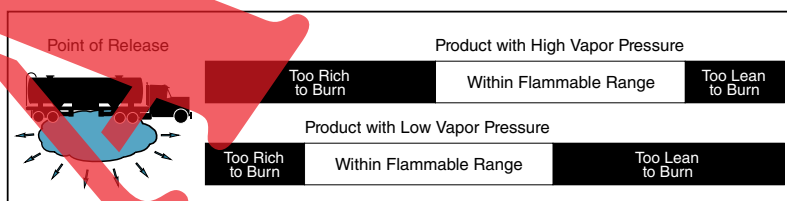
Review of Flammability Factors Presented Earlier

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



Hazmat Chemistry Study Guide

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

Smaller Molecules	Larger Molecules

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 of 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)

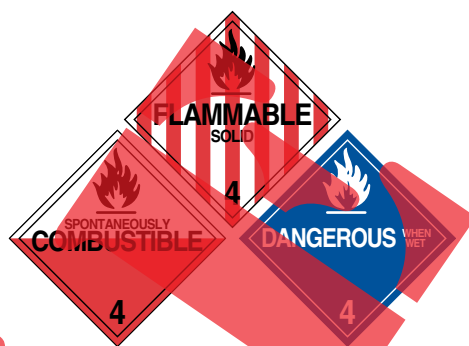
Review Questions (answers on page 197)

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. 141°F (60.6°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. 141°F (60.6°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

Hazmat Chemistry Study Guide

Class 4 - Flammable Solids, Spontaneously Combustible Materials, and Dangerous When Wet Materials

Class 4 includes any solid material, other than an explosive, that is liable to cause fires through friction or through retained heat from manufacturing or processing. It also includes solids and liquids that can be ignited readily on exposure to water or air or that are highly reactive to water or air.



Divisions of This Hazard Class

Class 4 consists of three divisions:

Division	Description
4.1	Flammable solids (e.g., magnesium [pellets, turnings, or ribbons], nitrocellulose)
4.2	Spontaneously combustible materials (e.g., aluminum alkyls, charcoal briquettes, phosphorus)
4.3	Dangerous when wet materials (e.g., magnesium powder, calcium carbide, sodium)

Relation to What You Already Learned About Chemistry

The materials in Class 4 also have diverse backgrounds. Examples include:

- Group 1 (alkali) metals (e.g., lithium, sodium, potassium)
- Group II (alkaline earth) metals (e.g., magnesium, calcium, barium)
- Other finely divided metals (e.g., aluminum and titanium in powder form)
- Binary salts (e.g., calcium carbide, sodium phosphide, lithium hydride)
- The nonmetal elements carbon and phosphorus (red and white/yellow)
- Naphthalene (a hydrocarbon)
- Some hydrocarbon derivatives (e.g., nitrocellulose, picric acid, phosphorous pentasulfide, trichlorosilane, dinitrophenol, wet trinitrotoluene)

As you may recall, the alkali metals are highly reactive due to a single electron on their outermost shells. While they bond with many elements, it's their affinity for the oxygen in water that puts them in Class 4. They're so starved for oxygen that they'll rip apart water molecules to get it. Alkaline earth metals, with two electrons on their outermost shells, won't react as violently, but are still sufficiently water-reactive to be a threat. Also emphasized in earlier chapters is the way these flammable metals and the binary salts will release flammable and/or toxic gases, corrosive solutions, and often a lot of heat when in contact with water.

Chapter 2 identified that materials which ignite spontaneously in contact with air are called **pyrophoric**. Those materials that react in clean, dry air (e.g., white and yellow phosphorus) can be stored under water to prevent hazardous reactions. Those that react in moist air (e.g., sodium and potassium) must be stored under some other substance, such as an inert gas, mineral oil, or kerosene.

Other Important Concepts

A common consideration in this hazard class is **surface-area-to-mass ratio**. Some materials that are not considered hazardous in large pieces can be very dangerous as finely divided powders (e.g., aluminum and titanium). Likewise, carbon in the form of diamonds is very safe; carbon in the form of wood charcoal, which has a high surface-area-to-mass ratio because it's so porous, is regulated as a spontaneously combustible material.

Class 4 - Flammable Solids, Spontaneously Combustible Materials, and Dangerous When Wet Materials (continued)

The combustion process that takes place when metals or other solids burn is different than when liquids burn. Liquids themselves don't burn; rather, what burn are the vapors those liquids produce. However, solids don't vaporize the way liquids do. When solid organic compounds (hydrocarbons and hydrocarbon derivatives) are heated, the molecules that comprise them begin to vibrate rapidly. The more heat that's applied, the faster the molecules move, causing many of the carbon-carbon and carbon-hydrogen bonds to break. This breakdown by heat is called **pyrolysis**. The compounds are broken into more simple fuels (such as methane, ethane, and propane) and free radicals (such as methyl [CH₃] and hydrogen [H]). It is these simpler fuels and the intermediate products of combustion formed from free radicals that actually burn when mixed in the right concentration with air. This concept—the chemical chain reaction—is explained in more detail starting on page 182.

Wood, coal, and other solid organic fuels will also burn on their surfaces. With **surface burning**, or glowing, the solid char that remains after flammable gases are burned off will continue to produce a glow. Examples of surface burning can be seen when flames in a fireplace die down or when charcoal burns.

Metals burn in much the same way. They don't pyrolyze (break down when heated to produce flammable gases). Rather, combustion takes place as a direct combination of the metal with oxygen at the surface of the metal. Metal fires are particularly difficult to extinguish because burning metals can be so hungry for oxygen that they'll fragment water and carbon dioxide to get it, dramatically intensifying the fire. They will even combine with chlorine, fluorine, and other halogens in Halon to intensify the fire. Fires involving combustible metals are best suffocated with dry sand or Class D extinguishers.

Class 4 - Flammable Solids, Spontaneously Combustible Materials, and Dangerous When Wet Materials (continued)

Review Questions (answers on page 197)

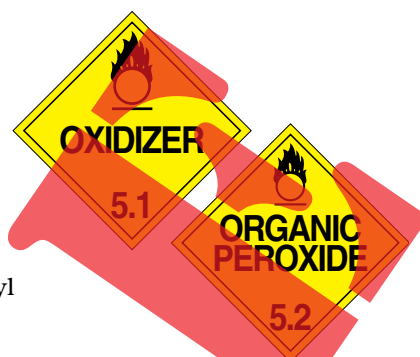
1. Pyrophoric materials are those that:
 - a. Surface burn
 - b. Ignite spontaneously in contact with air
 - c. React with water to form a flammable or toxic gas, a caustic solution, and heat
 - d. Are not considered hazardous in large pieces, but can be very dangerous as finely divided powders
2. Which of the following materials is pyrophoric?
 - a. White or yellow phosphorus
 - b. Calcium carbide
 - c. Magnesium powder, pellets, turnings, or ribbons
 - d. Nitrocellulose
3. Fires involving combustible metals are often best extinguished by:
 - a. Cooling with water
 - b. Smothering with carbon dioxide
 - c. Suffocating with sand or Class D extinguishers
 - d. Using Halon to interrupt the chemical chain reaction
4. Which of the following are most likely to be Class 4 materials?
 - a. Alkali metals
 - b. Alkyl halides
 - c. Metal oxysalts
 - d. Metal peroxides
5. Pyrolysis is:
 - a. The breakdown of organic compounds by heat
 - b. The spontaneous ignition of materials in contact with air
 - c. The decomposition of materials exposed to contaminants
 - d. The decay of radioactive materials to form more stable isotopes

Class 5 - Oxidizers and Organic Peroxides

Divisions of This Hazard Class

Class 5 consists of two divisions:

Division	Description
5.1	Oxidizers (e.g., ammonium nitrate, bromine trifluoride, and calcium hypochlorite)
5.2	Organic peroxides (e.g., dibenzoyl peroxide, methyl ethyl ketone peroxide, and peroxyacetic acid).



NFPA divides oxidizers into four classes, from Class 1, which may increase the burning rate of combustible materials, to Class 4, which can undergo an explosive reaction if exposed to contaminants, heat, shock, or friction.

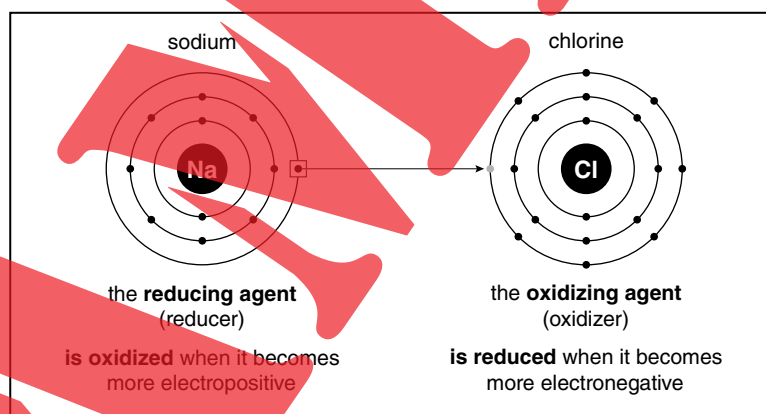
Organic peroxides are further divided into seven types (A through G) in 49 CFR 173.128 based on whether or not they detonate or deflagrate and how they're affected when heated under confinement. Type A is the most hazardous.

Relation to What You Already Learned About Hazmat Chemistry

Oxygen, as you might expect, is a powerful oxidizer. However, so are many other chemicals, including some that don't contain oxygen in their composition. So let's first identify what an oxidizer is.

We introduced the concept of electron transfer in Chapter 3, showing an ionic bond between sodium and chlorine to form sodium chloride. Let's look at this same example again. The illustration below shows one electron being transferred from sodium to chlorine.

Simple Bond Between Sodium and Chlorine Demonstrates an Oxidation-Reduction Reaction



In the example above, sodium is the **reducing agent** (or reducer), sometimes referred to as *fuel*. When it reacts with chlorine (transfers an electron to it), it *reduces* chlorine's electrical charge (makes it more negative). Remember, electrons have a negative charge, so when chlorine acquires another electron, it becomes more electronegative. Chlorine is an **oxidizing agent** (or oxidizer). It *oxidizes* sodium when it accepts the electron, making sodium more electropositive.

Despite the emphasis on electron transfer, oxidation-reduction reactions aren't restricted to ionic compounds. When oxygen (or some other oxidizer) combines with another substance, it oxidizes that substance. It chemically changes the substance, such as when methyl ethyl ether ($\text{CH}_3\text{OC}_2\text{H}_5$) becomes methyl ethyl peroxide ($\text{CH}_3\text{O}_2\text{C}_2\text{H}_5$). We can see the evidence of that oxidation process in the form of crystals on the container. The rusting of iron is another example of an oxidation-reduction reaction. So is fire. The reactants are different, as are the speed of the reactions and the energy produced. But in all cases, oxygen or another oxidizer is chemically combining with other elements or compounds.

Class 5 - Oxidizers and Organic Peroxides (continued)

There are two important points to understand here. One, as emphasized already, materials other than oxygen can fill the role of an oxidizer. So when you think of oxidizers, don't limit your thinking to oxygen. Two, strong oxidizing agents are not always placarded as such. Chlorine, for example, is placarded as a poison gas (Division 2.3) because toxicity is its primary hazard. Fluorine is one of the most powerful oxidizers known. It, too, is placarded as a poison gas, although it requires a subsidiary oxidizer label. For that matter, oxygen is placarded as a nonflammable gas with a subsidiary oxidizer label. So when you think about oxidizers, recognize that Division 5.1 materials are actually a subset of chemicals that can be significant oxidizers.

Division 5.1 materials include many of the salts that have oxygen in their makeup. A common one is ammonium nitrate (NH_4NO_3)—one of the few salts that don't contain metal. Other examples include barium chlorate ($\text{Ba}(\text{ClO}_3)_2$), sodium chlorite (NaClO_2), and sodium peroxide (Na_2O_2). You may recall from the section on salts (page 86) that oxysalts are very strong oxidizers. So when you see a chemical name that starts with a metal element and ends in *-ate* or *-ite*, you should suspect it is an oxidizer. Metal peroxides are also very strong oxidizers. If you see the word *peroxide* in the name (e.g., any of the metal peroxides or hydrogen peroxide, depending on the concentration), suspect it's an oxidizer. Organic peroxides are oxidizers too, but their explosive and unstable nature makes them more dangerous than ordinary oxidizers, so they are distinguished by a different division (5.2).

Many other chemicals are not classed as oxidizers but are powerful oxidizers nonetheless. We already discussed chlorine and fluorine. Other likely suspects include compounds containing a halogen (e.g., chlorine trifluoride and nitrogen trifluoride), nitrogen oxides (e.g., nitrous oxide and nitrogen dioxide), and some oxyacids (e.g., perchloric acid and nitric acid).

Concentration sometimes plays a role in how materials are placarded. Hydrogen peroxide (H_2O_2), for instance, is classed as an oxidizer in concentrations of 8% or more. Perchloric acid is classed as an oxidizer in concentrations of 50% to 72%. Below 50%, it is classed as a corrosive.

Organic peroxides (Division 5.2) are one of the hydrocarbon derivatives covered in Chapter 5. They consist of two oxygen atoms bonded to each other on one side and to hydrocarbon radicals on the other. Examples include methyl ethyl peroxide ($\text{CH}_3\text{O}_2\text{C}_2\text{H}_5$) and dimethyl peroxide ($\text{CH}_3\text{O}_2\text{CH}_3$). Most of the organic peroxides are easy to recognize by name; they either end in *peroxide* or have *peroxy* as part of the name. (Note: Because hydrogen peroxide doesn't contain carbon, it isn't considered an organic peroxide. However, it is a strong oxidizer.)

Organic peroxides are extremely unstable and are very sensitive to heat and friction. They are similar to explosives in that they contain both a fuel component and an oxidizer component in the same formula. Some organic peroxides can form highly unstable crystals on the container when exposed to air. Organic peroxides are often used as catalysts in the plastics industry to initiate the polymerization process. They, more than any other hazard class, are prone to runaway polymerization. (Polymerization was defined on page 34.)

There are no special markings to warn of the polymerization hazard: no separate UN/DOT class, no special placards or labels, no unique containers. So until you find out otherwise, it's a good idea to treat Division 5.2 materials as polymerizable. However, materials from other hazard classes can also polymerize, such as the flammable gases ethylene (ethene), propylene (propene), and butylene (butene). Sometimes the first clue you'll have comes from looking at the *Emergency Response Guidebook* (ERG), which identifies products subject to polymerization with the letter "P" next to the appropriate guide number.

While elevated temperature is the most common cause of uncontrolled polymerization, it can also be triggered by shock, friction, contamination, or the evaporation of an inhibitor over time. The last two, in particular, are not things the hazardous materials technician is likely to know about, unless the container is bulging to a point where it's noticeable.

Overpressurized containers don't always fail when expected to. They can fail much later, when it appears the incident is under control and the danger is past. Such delayed reactions often cause death and injury that could have been prevented had the risks been adequately assessed.

Class 5 - Oxidizers and Organic Peroxides (continued)

Polymerization reactions are exothermic, so responders need to be concerned not only about catastrophic container failure but also about fires from nearby combustibles being ignited. Particularly when organic peroxides are used in the plastics industry, responders need to also be concerned about the toxicity of combustion by-products.

Other Important Concepts

Self-accelerating decomposition temperature (SADT) is the temperature at which an organic peroxide begins to decompose. Once the reaction begins, it cannot be stopped. Unless the quantity of material is small and all exposures can be protected from the ensuing fire, the reaction can be very dangerous. Therefore, it's vital to keep organic peroxides below their SADTs. Better yet, a material should be kept below its **maximum safe storage temperature (MSST)**—a temperature that provides a margin of safety to prevent ever getting to the SADT. Many organic compounds have MSSTs; it's not limited to organic peroxides.

Preventing emergencies with organic peroxides depends on protecting these materials from elevated temperatures, friction, and contamination from contact with other products. However, temperature control is generally the most important safeguard you can employ. As a rule of thumb, increasing the temperature by a mere 10 degrees will cause the chemical reaction rate to double, which shows how vitally important temperature control can be.

Hazmat Chemistry Study Guide

Class 5 - Oxidizers and Organic Peroxides (continued)

Review Questions (answers on page 197)

- Organic peroxides (Division 5.2) are most similar to which other hazard class?
 - Oxidizers
 - Corrosives
 - Explosives
 - Flammable solids
- Which of the following would you expect to be a Class 5.1 oxidizer?
 - Vinyl acetate
 - Sodium chlorite
 - Calcium carbide
 - Potassium chloride
- Which of the following would you expect to be a Class 5.1 oxidizer?
 - NaOH
 - NaCl
 - Na₂O
 - Na₂O₂
- Which of the following is the *most* powerful oxidizer?
 - Oxygen
 - Fluorine
 - Sodium
 - Iodine
- SADT is:
 - The *maximum* safe storage temperature for oxidizers and organic peroxides
 - The *minimum* safe storage temperature for oxidizers and organic peroxides
 - The temperature at which organic peroxides will ignite on contact with air
 - The temperature at which organic peroxides begin to decompose
- When exposed to air, some organic peroxides:
 - Ignite spontaneously
 - Form highly unstable crystals
 - Begin runaway polymerization
 - Oxidize nearby fuels
- The salts most likely to be oxidizers are those with names that end in:
 - ate or -ite
 - Hydroxide
 - ide
 - ine
- Organic peroxides are a class of hydrocarbon derivatives with the functional group:
 - NO₂
 - COOH
 - O₂
 - NH₂COO

Class 6 - Poisonous and Infectious Substances

While all chemicals are toxic to some degree, toxicity is the primary threat with Class 6 materials. As with any hazard class, these materials can have multiple hazards. They may be flammable or combustible. They may be corrosive. They may be oxidizers. Often these secondary hazards are significant, but they take a back seat to toxicity.



Divisions of This Hazard Class

Class 6 has two divisions:

Division	Description
6.1	Poisonous materials (e.g., arsenic compounds, carbon tetrachloride, hydrocyanic acid, tear gas)
6.2	Infectious substances (e.g., anthrax, botulism, rabies, tetanus) (<i>Infectious Substance</i> is used for labels only, not for placards.)

Class 6 materials may be further identified by hazard zone. Hazard Zone A is the worst.

Hazard Zone	LC ₅₀ greater than	LC ₅₀ less than or equal to
A	—	200 ppm
B	200 ppm	1000 ppm

Relation to What You Already Learned About Hazmat Chemistry

Some of the heavy metals (e.g., mercury and lead) are part of Class 6, as are the metal cyanides (e.g., potassium cyanide, sodium cyanide, and calcium cyanide). Several of the hydrocarbon derivatives also contribute heavily to Class 6, including:

- Nitriles, also referred to as cyanides, (e.g., adiponitrile and chloroacetonitrile)
- Amines (e.g., phenylamine)
- Alkyl halides (e.g., chloroform, dichloromethane, and carbon tetrachloride)
- Organophosphates (e.g., malathion and parathion)

The bacteria, viruses, rickettsiae, and toxins that comprise the infectious substance division (6.2) of this hazard class are beyond the scope of this chemistry study guide.

Other Important Concepts

One can break this class into two groups: materials that *happen* to be poisonous and materials that are *designed to kill*. Within the latter group, the two we'll cover briefly are pesticides and chemical warfare agents.

Although **pesticides** are designed to kill specific target organisms (e.g., insects, rodents, or weeds), many can be very toxic to both humans and the environment. Pesticides are sometimes referred to as *crop protection chemicals* because the term doesn't have the same negative connotation as the word *pesticide*. However, changing the name doesn't change the toxicity or other hazards associated with these materials.

Pesticide container labels must include additional **signal words**: *danger* (meaning high toxicity), *warning* (moderate toxicity), or *caution* (relatively low toxicity). The words *extremely flammable* are also displayed on the label if the contents have a flash point below 80°F (26.7°C).

Class 6 - Poisonous and Infectious Substances (continued)

The **active ingredient** in a pesticide is the one that controls or kills the target organism. The **inert ingredients** include the carrier for the active ingredient. Other additives may be used to increase effectiveness by reducing surface tension, increasing uptake by the target organism, or protecting against wash-off. Often it's the presence and concentration of these frequently unlisted inert ingredients and other additives that comprise what manufacturers call their "trade secrets." However, just because they're considered inert or aren't listed on labels and MSDSs doesn't mean they're not hazardous. They can have a variety of hazardous properties.

The Environmental Protection Agency regulates more than 18,000 pesticide products licensed for use in the United States. Unlicensed pesticides, pesticides still under development, and pesticides banned in the United States but used elsewhere drive the total number of these products up even further. The one category we'll emphasize in this section is organophosphates because of their popularity and their similarity to chemical nerve agents.

Organophosphate pesticides account for the majority of insecticide poisonings in the United States. They are often the insecticide of choice in the agricultural world because of their effectiveness and their unstable chemical structure. The word *unstable* as it applies to pesticides means that the products degrade to relatively harmless compounds in just a few days. They don't persist in the environment or the body as other pesticides might. Three organophosphate pesticides whose names should be familiar are parathion, malathion, and diazinon. The chemical structures of these first two hydrocarbon derivatives are illustrated on page 131.

Organophosphates are **acetylcholinesterase inhibitors**. They work by disrupting the nervous system. The nervous system functions by sending electrical impulses from the brain to other parts of the body and back again. Nerve cells don't touch one another; there's a gap (the *synaptic gap*) between the end of one cell and the beginning of the next one. Nerve impulses cross that gap with the aid of a neurotransmitter called *acetylcholine*, which stimulates the receptor site. Another chemical, the enzyme *acetylcholinesterase*, then breaks down the acetylcholine so the nerve cells can relax before the next transmitted signal.

Organophosphate pesticides bind with *acetylcholinesterase* so it can't do its job. Consequently, nerve cells are overstimulated by an excess of *acetylcholine*, causing the seizures commonly seen in poisoned individuals. Ultimately, the nerves become paralyzed and stop functioning. Patients quickly die if they don't receive proper treatment. Even with prompt treatment, effects may linger for days or weeks until the body is able to produce sufficient *acetylcholinesterase* to restore balance.

Organophosphates are toxic by all routes of entry. Onset of signs and symptoms is very rapid for inhalation and eye exposure, whereas it may take several minutes or several hours for signs and symptoms to show up with skin absorption. The effects vary with the route and amount of exposure. A minute exposure may manifest with little more than flu-like symptoms. Signs and symptoms of acute exposure may include headaches, fatigue, dizziness, increased salivation and lacrimation (tearing), miosis (pinpoint pupils), profuse sweating, nausea, vomiting, diarrhea, loss of bowel and bladder control, tightness in the chest, muscle twitching, and bradycardia (slow heartbeat). Severe exposures result in seizures and rapid loss of consciousness.

Chemical **nerve agents** are similar to organophosphate pesticides in their chemical makeup and in the way that they attack the nervous system. However, they are 100 to 500 times more potent. Exposure to even minute quantities can kill very quickly. The signs and symptoms are very much like those of organophosphate poisoning, but usually far more severe.

Nerve agents are considered the most dangerous of the chemical warfare agents. The common ones are tabun (GA), sarin (GB), soman (GD), and V agent (VX). Although people will sometimes use the term *nerve gas*, nerve agents are liquids at ambient temperatures. (The term *nerve gas* is a misnomer.)

G agents are described as volatile and nonpersistent. However, as emphasized earlier, they are less volatile than water, which has a vapor pressure of 17.5 mmHg at 68°F (20°C). These agents are sometimes made more persistent by adding various thickeners. VX, on the other hand, is a persistent, oily liquid that evaporates about at about the same rate as motor oil. The vapors of all four agents are heavier than air.

Class 6 - Poisonous and Infectious Substances (continued)

Blister agents (or **vesicants**) such as mustard, Lewisite, and phosgene oxime are also found in Class 6. Blister agents produce immediate irritation to eyes, skin, and mucous membranes. Mustard is an exception; the pain and irritation can be delayed by as much as 24 hours, even though the damage begins upon contact. (Mustard is the only chemical warfare agent that does not produce symptoms within minutes of exposure.) Blisters are the most distinguishing characteristic of these warfare agents.

Within the **blood agents** is another Class 6 material—hydrogen cyanide. It's a flammable, volatile, colorless liquid under pressure, although at higher temperatures, it's found as a gas. Cyanide prevents oxygen in the bloodstream from entering other cells in the body, causing those cells to suffocate. The primary route of entry is inhalation, but cyanide can also be absorbed through the skin or eyes. Onset of signs and symptoms is very rapid. Low concentrations produce an increase in the rate and depth of respiration, dizziness, nausea, vomiting, and headache. High concentrations initially stimulate the respiratory system, sometimes to the point where patients cannot voluntarily hold their breath. Violent convulsions occur within 30 seconds, followed shortly thereafter by respiratory arrest and cardiac arrest. Death occurs within a few minutes of exposure.

Class 6 also includes tear gas, mace, and adamsite—all **riot control agents**. Riot control agents (also known as *irritants*, *irritating agents*, or *harassing agents*) cause temporary incapacitation by irritating the eyes and respiratory system. The effects seldom persist more than a few minutes once patients are removed to fresh air.

While it's beyond the scope of this book to discuss biological warfare agents and other Division 6.2 materials, it's helpful to understand the major distinctions between chemical and biological warfare agents:

Most chemical warfare agents are characterized by:

- Rapid onset of medical symptoms (usually minutes to hours following exposure).
- Easily observed signatures (e.g., residue, pungent odor, dead insect and animal life, and dead foliage).

Most biological agents are characterized by:

- Delayed onset (usually days to weeks after exposure).
- No characteristic signatures. Biological agents are usually odorless and colorless.
- Widespread reports of illness throughout a greater geographical area.

Hazmat Chemistry Study Guide

Class 6 - Poisonous and Infectious Substances (continued)

Review Questions (answers on page 197)

1. Of the following hydrocarbon derivative groups, which is most likely to have the greatest percentage that fall into Class 6?
 - a. Amides
 - b. Alkyl halides
 - c. Alcohols
 - d. Esters
2. Which of the following salts is most likely to be a Class 6 material?
 - a. KCN
 - b. KOH
 - c. LiH
 - d. NaClO_2
3. The majority of insecticide poisonings in the United States are due to:
 - a. Carbamates
 - b. Organochlorine compounds
 - c. Organophosphates
4. Nerve agent vapors are:
 - a. Heavier than air
 - b. Lighter than air
5. Nerve agents are _____ in their normal states.
 - a. Solids
 - b. Liquids
 - c. Gases
6. The only chemical warfare agent that does not produce symptoms within minutes of exposure is:
 - a. VX
 - b. Lewisite
 - c. Phosgene oxime
 - d. Mustard

Class 7 - Radioactive Materials

Radioactive materials (e.g., cobalt-60 and uranium hexafluoride) are those that contain unstable atoms decaying through nuclear emission.

Divisions of This Hazard Class

The designation of Radioactive I, II, or III is based on the radiation level (dose rate) as measured both at the surface of the package and 1 meter (3 feet) away. (The units of radiation measure below are defined on page 167.)

Maximum Allowable Radiation Level

Label	At Package Surface	At 1 Meter (3 Feet) from Package
I	0.5 mR/hr	none
II	50 mR/hr	1 mR/hr
III	200 mR/hr	10 mR/hr

Labels reflect the maximum potential radiation exposure a person could receive in close proximity to an intact package. Placards are required on transport vehicles only when transporting Radioactive III materials (those that emit the highest level of radiation.)

The Radioactive II and Radioactive III labels contain a **transportation index (TI)**. (The transportation index is also indicated on shipping papers.) This number identifies the maximum radiation level (measured in mR/hr) allowed at 1 meter (3 feet) from an undamaged package.

For example, if the transportation index is 4 (as in the illustration below), the radiation intensity at 1 meter (3 feet) should be no more than 4 mR/hr. If your survey meter is reading something higher, you should suspect that the package has been breached.

Radioactive Transportation Index (TI)



Relation to What You Already Learned About Hazmat Chemistry

Radioactive elements are often easy to identify by name because the name has been modified by a number, for example, carbon-14 (^{14}C) or cobalt-60 (^{60}Co). The number indicates that the element contains more neutrons in the nucleus than normal. The predominant form of carbon, for example, contains six protons and six neutrons in its nucleus. Carbon-14 has six protons and eight neutrons. (These two forms of carbon are isotopes of each other.) However, many elements with atomic numbers 84 (polonium) and above may give off radioactivity in their natural forms, so their names can be written with or without numbers. Examples include uranium and plutonium. In fact, when looking at a periodic table, you should consider any element from polonium on (atomic number 84 and above) potentially radioactive in its natural form.

When atoms give off radioactivity, what they are really doing is throwing off from the nucleus whatever is causing them to be unstable, basically an excess of either protons or neutrons. While it is beyond the scope of this study guide to explain how this complex process works and the variations that exist among the different radioactive elements and compounds, the bottom line is that atoms cast off bits of themselves to achieve a stable balance between protons and neutrons in the nucleus.

Class 7 - Radioactive Materials (continued)

Many radioactive materials have multiple hazards. For example, they may be flammable, toxic, or corrosive in addition to being radioactive.

Other Important Concepts

There are three primary **types of ionizing** (damaging) **radiation**: alpha, beta, and gamma. All radioactive materials give off at least one type of radiation. Many give off two or three.

- **Alpha particles** are relatively large particles that can travel only a few inches in air and are stopped by shielding as light as a thin sheet of paper. They cannot penetrate intact skin. However, they may enter the body through inhalation, ingestion, or contamination of an open wound. Alpha particles are an internal hazard only.
- **Beta particles** are much smaller than alpha particles, but they are far more penetrating. Beta particles can travel several yards in air. They can also penetrate intact skin, damaging the skin and possibly internal organs as well. Beta particles can be inhaled or ingested like alpha particles. It takes heavier shielding, such as a thick piece of metal or an inch of wood, to stop beta radiation.
- **Gamma rays** are electromagnetic waves of high energy and short wavelength. Gamma radiation has strong penetrating power, able to travel considerable distances and through heavy objects. It travels at the speed of light. It, also, can penetrate intact skin, causing skin burns and severe internal damage. Dense shielding, such as lead, is required to stop gamma radiation. In some cases, several inches of lead is required.

Although the chances of encountering x-rays and neutron radiation at a hazmat incident are remote, it pays to know about them.

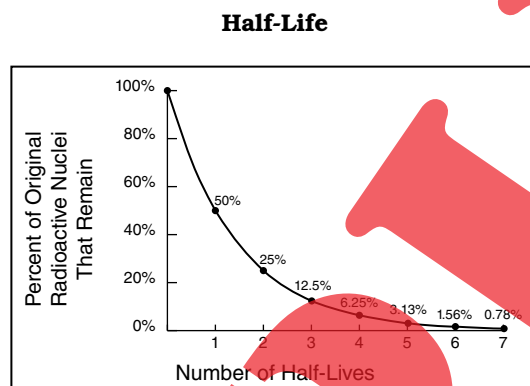
- **X-rays** are similar to gamma rays, although not quite as hazardous. X-rays are of little concern to emergency responders since they are produced primarily by machines; they are rarely a by-product of natural radioactive decay.
- **Neutron particles** are considerably larger than beta particles but smaller than alpha particles. Neutron radiation is normally associated with nuclear power plants, but it is becoming more common in medical treatment. It has very strong penetrating power and presents health hazards similar to that of other forms of radiation.

Other terms identify radioactive materials based on specific uses:

- **Fuel rods**—long tubes filled with ceramic pellets created from uranium, a radioactive element abundant in the earth's crust—are a key component of nuclear power plants. In a process called *fission*, uranium atoms split and release neutrons from the nucleus. The heat produced through this process boils the water circulating around the fuel rods. The water becomes steam, which turns a turbine connected to a generator, creating a magnetic field which then produces electricity.
- The uranium pellets used in nuclear power plants have a limited life span, so the fuel rods must be replaced roughly every 18 months. The **spent fuel**—fuel rods removed from the reactor—is still highly radioactive. Although it eventually loses most of its radioactivity through radioactive decay (approximately 50% in three months, 80% in one year, and 90% in ten years), spent fuel is still very much a concern.
- Three isotopes (uranium-233, uranium-235, and plutonium-239) are referred to as **special nuclear materials**. They're of particular concern because they can be used to create an atomic bomb. It's highly unlikely that emergency responders will encounter these materials because of the tight restrictions governing their production and use. However, if a terrorist were to gain access to any of these materials, it would pose a great threat.
- Nuclear power plants, hospitals, universities, and other industries that use radioactive materials generate contaminated waste. **Low-level waste**, such as lab supplies, discarded protective equipment, cleaning rags, and filters, emit only small amounts of radiation. These items are not a cause for alarm, but they must be handled according to regulations.

Class 7 - Radioactive Materials (continued)

Half-life is the measure of how long it takes for one half of a given amount of radioactive material to decay, or change, to something else. For example, as uranium-238 decays, it changes first to thorium-230, which becomes radium-226, which decays to radon-218, which changes to bismuth-214, which finally becomes the stable element lead. As a rule of thumb, a radioactive isotope decreases to less than 1% of its original value after seven half-lives.



Uranium-238 has a very long half-life of 4.47 billion years. It's not the record holder, but it's certainly among the leaders. Half-lives can vary from only a few seconds to thousands or millions of years. Most are somewhere in between. For example, carbon-14, the material used in carbon dating, has a half-life of 5730 years. Americium-241, used in smoke detectors, has a half-life of 432.2 years. The half-life of iodine-131, used to treat thyroid cancer, is 8.04 days. Sodium-24, another isotope used in medicine, has a half-life of 14.97 hours. These are just a handful of common examples.

Half-life is significant in determining how long an area must be sealed off and whether the incident can be allowed to self-mitigate. If a material's half-life is only a few days, it may be best to simply seal off the site for a couple of weeks until the hazard is no longer present. Conversely, if the half-life is several years, it will probably be necessary to bring in a cleanup company to mitigate the hazard.

There's a difference between **exposure** and **contamination**. A person can be exposed to radiation without being contaminated (e.g., when receiving a medical x-ray). A strong dose of gamma or x-ray radiation can cause tissue damage, but it won't make an exposed person radioactive. That person poses no threat to others. However, a person who has a radioactive substance (e.g., a powder, liquid, or gel) on his or her body is contaminated. He or she acts as a radioactive source and can both expose and contaminate other people.

We all receive a small amount of ionizing radiation (average 360 mrem) every year, roughly 82% from natural sources and 18% from manmade sources. The National Council on Radiation Protection and Measurement estimates the sources of radiation exposure to break down as shown below.

Average Annual Dose of Ionizing Radiation

- 55% Radon (a naturally occurring gas formed from radioactive decay of uranium-238 in rock and soil)
- 11% X-rays and other medical and dental procedures
- 11% Internal (materials such as potassium and carbon in the food we eat and the air we breathe)
- 8% Terrestrial (other naturally occurring radioactive materials in the Earth's crust)
- 8% Cosmic radiation
- 4% Nuclear (emissions from power plants and fallout from past nuclear weapons testing)
- 3% Consumer products (e.g., cigarettes, smoke detectors, color televisions)
- 1% Other

The average annual doses shown above are not a problem. Acute exposures received at a hazmat incident, however, can be.

Class 7 - Radioactive Materials (continued)

Initial signs and symptoms of radiation exposure usually do not appear for 2 to 6 hours, even with high doses. Others may not become apparent for days, weeks, or months. The effects of **radiation sickness** will vary depending on the type of radiation, how much of the body was exposed, the depth of penetration, the dosage received, and whether the exposure is from a single event or multiple events. (Radiation exposures are cumulative.) The following effects apply to **whole-body exposures**:

- Below 100 rems, patients are not likely to have any observable effects. Minor blood changes may result above 50 rems, but they will have little impact on the body. (Rems are defined on the next page.)
- Whole-body exposures above 100 rems may cause nausea and vomiting for 1 to 2 days and a temporary drop in the production of new blood cells.
- As the exposure increases, so do the signs and symptoms of radiation sickness. Initial effects may include nausea, vomiting, diarrhea, dizziness, fatigue, headache, and loss of appetite. Higher doses may also cause fever, sweating, and difficulty breathing.
- Above 350 rems, the initial effects will be followed by a period of apparent wellness. But usually within 2 to 3 weeks, patients will become sick again and experience infection, electrolyte imbalance, diarrhea, bleeding, cardiovascular collapse, and sometimes lapses in consciousness. Medical care is required.
- A whole-body exposure of 450 rems is considered the $LD_{50}/30$ days, meaning that 50% of patients exposed to this level of radiation will die within 30 days if untreated. However, all can survive with proper medical attention.
- Above 1000 rems, the chances of survival drop significantly, even with aggressive treatment.
- Patients exposed to 5000 rems will die within 48 hours. There is no effective treatment for such acute exposures. Treatment is limited to making patients as comfortable as possible.

Radiation often has long-term effects as well, including sterility or other damage to the reproductive system, damage to blood vessels, cancer, and genetic changes.

Partial-body exposure results in radiation burns that develop slowly, although patients may also experience the early nausea and vomiting typical of whole-body exposures.

- Roughly 2 to 3 weeks after partial-body exposures of 300 to 1000 rems, effects may resemble a first-degree sunburn.
- Higher exposures (up to 2500 rems) will produce blisters within 1 to 2 weeks.
- Partial-body exposures exceeding 3000 rems may cause slow-healing ulcers or gangrene.
- Extremely high exposures manifest with tingling, pain, redness, and swelling very soon after exposure.

Radiation exposures should always be kept as low as reasonably achievable. (This is what is known as the *ALARA Principle*.) The U.S. EPA recommends the **radiation exposure limits** below. The first is geared for workers in the nuclear industry. The second two are for personnel performing emergency services; these limits are considered maximum exposures when lower doses are not practicable. (See next page for information on units of radiation measurement.)

U.S. EPA Recommended Radiation Exposure Limits

<u>rem limit</u>	<u>mrem equivalent</u>	<u>exposure/activity</u>
5/year	5,000/year	working in nuclear industry
10/event	10,000/event	mitigating an incident
25/event	25,000/event	saving a life

These limits still leave a considerable margin for error since people are not likely to have any observable effects below 100 rems. However, the limits also take into account that radiation exposures are cumulative. Therefore, the 25-rem limit for saving a life should be considered a once-in-a-lifetime limit. A person who receives this exposure at an incident should not work around radiation again.

Class 7 - Radioactive Materials (continued)

The **English units of radiation measure** are used most often in the United States:

- **Roentgen (R)** is used to measure the amount of radiation produced by gamma and x-rays. Detectors that measure gamma radiation do so in roentgens per hour (R/hr) or milliroentgens per hour (mR/hr). One roentgen equals 1000 milliroentgens.
- **Rad** (radiation absorbed dose) is used to describe radiation energy absorbed by an exposed material or person. It is expressed in rads per hour (rads/hr).
- **Rem** (radiation equivalent man) describes the biological damage done by the absorbed dose of radiation; it reflects both the dose rate and potential harm to the body. It is expressed in rems per hour (rems/hr) or millirems per hour (mrems/hr).
- A **curie (Ci)** is the quantity of radioactive isotope that produces 37 billion disintegrations per second. Curies measure specific activity (or rate of decay) rather than the quantity of radioactive material. For example, the specific activity of radium 226 is 1 Ci/gm. In other words, 1 gram of radium 226 produces 37 billion disintegrations per second. However, the rate of decay would remain the same whether you had 1 gram or 100 grams of radium 226. When comparing radioactive sources, the higher the number (curie), the more hazardous the isotope.
- Many meters that detect alpha and beta particles measure radiation in **counts per minute (cpm)**, which, like the curie, reflects specific activity.

The following are the international (SI) units of measure:

- **Gray (Gy)** measures absorbed dose. It replaces the rad, although 1 gray equals 100 rads.
- **Sievert (Sv)** measures dose equivalent. It replaces the rem, although 1 sievert equals 100 rems.
- **Becquerel (Bq)** measures specific activity (or rate of decay). It replaces the curie, although 1 becquerel equals 1 disintegration per second. Thus 1 curie equals 37 billion becquerels.

The following equation shows the relation between five of the units of measure. It is not precisely accurate, but it is close enough to be used for practical purposes.

$$1 \text{ gray} = 1 \text{ sievert} = 100 \text{ roentgens} = 100 \text{ rads} = 100 \text{ rems}$$

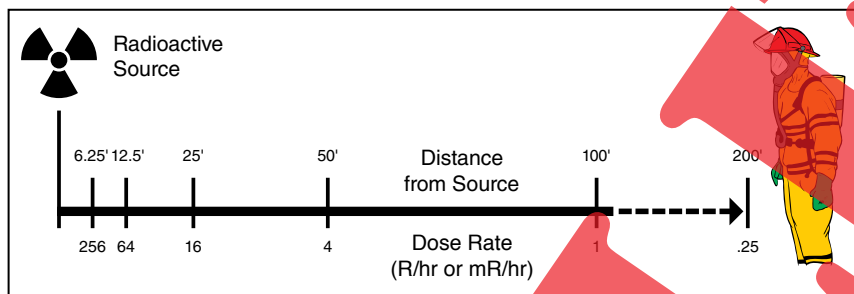
Therefore, if your meter read 100 R/hr, you would be exposed to 100 rems over a 60-minute exposure. Note: Gray and rad both measure the radiation absorbed dose, and sievert and rem both measure the biological damage. However, there is no metric equivalent for roentgens, which measures the amount of radiation produced by gamma rays and x-rays.

Keeping radiation exposures as low as reasonably achievable is done by employing the principle of **time, distance, and shielding**.

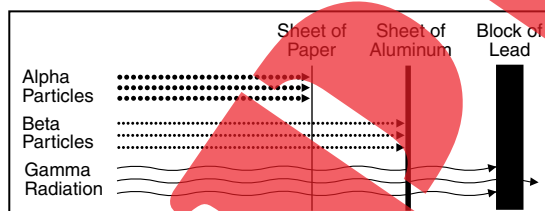
- Radiation doses are directly proportional to length of exposure. Cutting exposure **time** in half cuts the exposure (or dose) in half.
- **Distance** is generally a much more important factor than time is in controlling exposure. Whereas cutting exposure time in half cuts the dose in half, doubling your distance from the radioactive source reduces the exposure by 75%. (See illustration next page.) This is known as the **Inverse Square Law**. Distance is also effective in reducing the type of exposure. Alpha particles travel only a few inches in air. Beta particles travel several meters. Unless you have the contaminant on you or the radioactive material is being spread by wind, rain, or other forces, once you back out of the area, you are no longer at risk from alpha and beta particles; you need worry only about gamma radiation.
- Appropriate **shielding** will help reduce exposure, although shielding is never a substitute for time and distance. The relatively large alpha particles are stopped by shielding as thin as a sheet of paper. It takes heavier shielding, such as a thick piece of metal or an inch of wood, to stop beta radiation. Gamma radiation is so penetrating that far denser shielding, such as several inches of lead, is required.

Class 7 - Radioactive Materials (continued)

Inverse Square Law

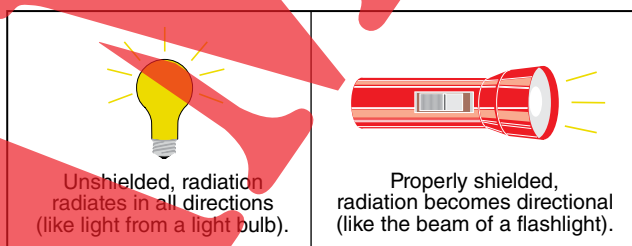


Effect of Shielding on Alpha, Beta, and Gamma Radiation



Properly shielded, radiation is directional, like the beam of a flashlight. If a radioactive package is breached, but the radioactive source is still contained within the package, radiation will be projected in the direction of the breach. Any radiation detected in another direction should be within normal limits of what is permissible from an undamaged package. This obviously requires you to be more diligent in your monitoring efforts. At the same time, it tells you that you may be able to approach the source from another direction and receive no greater exposure than if approaching an intact package.

Effect of Shielding on How Radiation is Projected



Class 7 - Radioactive Materials (continued)

Review Questions (answers on page 197)

1. Radioactive elements are generally those that have _____ in the nucleus than do their stable isotopes.
 - a. More protons
 - b. More neutrons
 - c. Less protons
 - d. Less neutrons
2. Which form of radiation involves relatively large particles that can't penetrate intact skin but can enter the body through inhalation, ingestion, or contamination of an open wound?
 - a. Alpha
 - b. Beta
 - c. Gamma
3. Half-life measures how long it takes for:
 - a. Radioactive materials to decay to something nonhazardous
 - b. One half of a given amount of radioactive material to decay to something else
 - c. Stable atoms to become radioactive once exposed to a source of radiation
 - d. Half an exposed population to exhibit effects of radiation sickness
4. A contaminated person is:
 - a. Anyone who has been exposed to radiation
 - b. Anyone who has suffered tissue damage from a strong dose of radiation
 - c. Anyone who poses a threat of contact with bodily fluids (e.g., from vomiting and diarrhea) following an exposure to radioactive materials
 - d. Anyone who has a radioactive substance on his or her body
5. The average annual dose of ionizing radiation people are exposed to is between:
 - a. 0 and 100 mrem
 - b. 100 and 200 mrem
 - c. 200 and 300 mrem
 - d. 300 and 400 mrem
6. According to the EPA, the maximum radiation exposure one should receive to save a life is:
 - a. 10 rem
 - b. 25 rem
 - c. 50 rem
 - d. 100 rem
7. Which of the following English units of radiation measure describes the biological damage done by the absorbed dose of radiation?
 - a. Roentgen
 - b. Rad
 - c. Rem
 - d. Curie
8. Doubling your distance from a radioactive source cuts your exposure by:
 - a. 25%
 - b. 50%
 - c. 75%
 - d. 100%

Hazmat Chemistry Study Guide

Class 8 - Corrosive Materials

Corrosives (e.g., sulfuric acid, nitric acid, and sodium hydroxide) are materials that degrade metals and cause destruction to living tissue on contact. **Corrosivity** is a measure of a material's ability to corrode—to dissolve or wear away by chemical action.

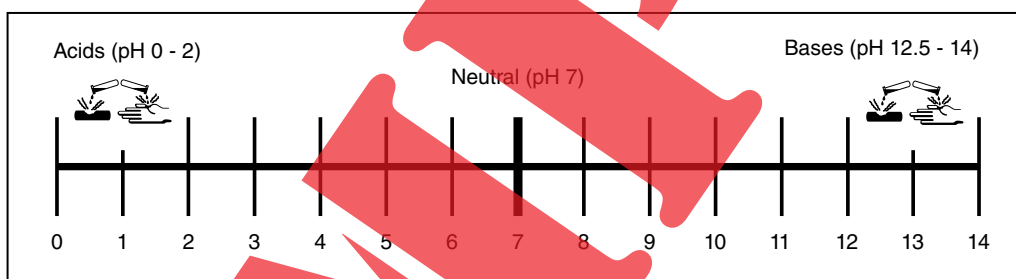
Corrosive materials may be in the form of solids or liquids. (Some gases are also corrosive, but Class 8 doesn't include gases.)

Divisions of This Hazard Class

Corrosives are classified as either acids or bases. **Acids** are those compounds that release hydronium ions (H_3O^{+1}) when dissolved in water. **Bases** (also called **caustics** or **alkalis**) release hydroxide ions (OH^{-1}) when dissolved in water. (The superscript notations $^{+1}$ and $^{-1}$ refer to positive and negative charges, respectively.) We can't see the release of ions, but we can measure them with **pH** (which stands for *power of hydrogen*).

The **pH scale** goes from 0 to 14, with 7 being neutral. Chemicals with a pH of 0 to 6.9 are acidic, while those with a pH of 7.1 to 14 are basic (or caustic or alkaline). However, when it comes to actually classifying corrosives, the Code of Federal Regulations, Title 40, Section 261.22 defines acids as those materials with a pH of 2 or less and bases as those with a pH of 12.5 or more.

The pH Scale



The pH scale is a logarithmic scale, meaning each number reflects a ten-fold difference in corrosivity. For example, a solution with a pH of 1 is ten times more acidic than one with a pH of 2 and a hundred times more acidic than one with a pH of 3. At the opposite end of the scale, a solution with a pH of 13 is ten times more alkaline than one with a pH of 12 and a hundred times more alkaline than one with a pH of 11.

The chart below shows the pH of some common substances. These should be considered approximate values, since it's not unusual to see different values or a range of values, depending on the reference source.

pH of Some Common Substances



Class 8 - Corrosive Materials (continued)

Relation to What You Already Learned About Hazmat Chemistry

Acids fall into two categories: organic and inorganic. **Organic (carboxylic) acids** are hydrocarbon derivatives containing the COOH functional group. Examples include formic acid (HCOOH), acetic acid (CH₃COOH), and acrylic acid (C₂H₃COOH). (Organic acids were addressed on page 117.) In general, organic acids are less corrosive than their inorganic counterparts. Often their other hazardous properties (toxicity, flammability, oxidizing ability, instability, or polymerization potential) are more significant.

The **inorganic acids** can be divided into two groups. The halogen acids—hydrochloric acid (HCl), hydrofluoric acid (HF), hydrobromic acid (HBr), and hydriodic acid (HI)—are very strong acids made when the corresponding acid gas (hydrogen chloride, hydrogen fluoride, hydrogen bromide, and hydrogen iodide) is dissolved in water. (The acid gases have the same formulas [HCl, HF, HBr, and HI] as do the solutions.) The acid gases are extremely soluble in water, so much so that they'll readily dissolve in moisture on a person's body and form the corresponding acid, particularly when present in high concentrations. Halogen acids are noncombustible but will react with metal to release flammable hydrogen gas.

The other inorganic acids consist of hydrogen bonded to a radical containing oxygen. Examples include nitric acid (HNO₃), sulfuric acid (H₂SO₄), and chlorosulfonic acid (ClHO₃S or HSO₃Cl). Inorganic acids (including the halogen acids above) are typically stronger than organic acids. Although they don't burn, some are oxidizers. Most will react with water to produce flammable hydrogen gas. They also tend to be more chemically reactive than organic acids.

The most common **bases** (caustics) are the metal hydroxide salts, including sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide (Ca[OH]₂). Bases also include some of the metal oxides, for instance, sodium oxide (Na₂O) and calcium oxide (CaO), and some of the metal oxysalts, such as sodium hypochlorite (NaClO) and sodium chlorite (NaClO₂). Some of the metal oxysalts, however, form weak caustic solutions that aren't classed as corrosives. Examples include sodium bicarbonate (NaHCO₃) and potassium carbonate (K₂CO₃).

Two examples of nonsalt compounds considered caustics are hydrogen peroxide (H₂O₂) in concentrations of 20% or greater and hydrazine (N₂H₄) at concentrations of 64% or less. Hydrogen peroxide, as identified earlier is also a strong oxidizer, while hydrazine is a powerful reducing agent (fuel).

Other Important Concepts

One of the most significant differences between acids and bases is the way in which they damage human tissue. An acid in contact with the skin will cause the tissue to harden even as it eats away at that tissue, thereby limiting the damage to some degree. A base, on the other hand, will soften and dissolve the tissue, creating far more penetrating and severe injuries. In both cases, however, the damage will continue until the corrosive is thoroughly flushed from the body. And often the extent of the injury is not immediately obvious, something corrosive burns have in common with thermal burns.

Corrosives often produce immediate irritation, but it's not uncommon for pain to be delayed. This is particularly true with corrosives in solid form, which don't really start eating away at the tissue until they react with the moisture on the skin. Such a corrosive on dry skin might not be noticed until a person starts sweating or takes a shower later in the day.

The following table highlights other easily observed differences between acids and bases:

Easily Observed Differences Between Acids and Bases

Observation	Acids	Bases
Taste	Sour taste	Bitter taste
Olfactory response	May burn nose	Usually odorless (except ammonia)
Sensation on skin contact	Painful on skin contact	Slippery sensation
Reactivity	React with some metals to produce H ₂	React with many oils, fats, greases
Reaction with litmus paper	Turn litmus paper red	Turn litmus paper blue

Hazmat Chemistry Study Guide

Class 8 - Corrosive Materials (continued)

Two terms important to the understanding of corrosivity are strength and concentration. **Strength** refers to how thoroughly an acid or base dissociates (dissolves and/or ionizes) in water. Strong acids or bases dissociate more so than weak ones. Strong acids or bases are more corrosive than weak ones. Strength is measured with the pH scale shown earlier.

Concentration is the amount of acid or base in water. Concentration may be expressed in several ways. The most common measurement is percentage (by weight) of an acid or base to water. The higher the percentage, the more concentrated the solution. *Molarity* and *normality*, two other ways of expressing concentration, are beyond the scope of this study guide. However, once again, the higher the number, the more concentrated the solution. For example, a 4M (molar) or 4N (normal) solution is more concentrated than a 3M or 3N solution.

Solutions with more than 35% acid by volume are considered “concentrated,” while those with less than 10% acid by volume are referred to as “dilute.” Other terms used to identify concentrated acids include **anhydrous**, **glacial**, and **fuming**.

There is no easy way to measure concentration in the field. However, it is possible to do a quick estimate by comparing the weight of a solution with an equal amount of water. Corrosives are typically much heavier than water. The more concentrated the solution, the heavier that solution is.

It is important to consider both strength and concentration when looking at corrosives. However, between the two, concentration is more important. A strong acid or base in low concentrations (dilute) may pose little risk. However, weak acids or bases in concentrated solutions can be quite dangerous.

There's a difference between the terms *anhydrous* (mentioned above) and *anhydride*. An **anhydrous** compound is an organic molecule that contains no water. (*Anhydrous* means “without water.”) Ammonia and anhydrous ammonia, for instance, are the same substance, the difference being that “ammonia” most accurately describes a solution of anhydrous ammonia in water.

An **anhydride** is the compound that results when a water molecule is removed from an inorganic or organic corrosive (usually an acid). Instead of taking a substance out of solution, the original compound is altered by the removal of two hydrogen atoms and one oxygen atom. For example, removing a water molecule (H_2O) from sulfuric acid (H_2SO_4) leaves sulfur trioxide (SO_3), a completely different substance. Sulfur trioxide is a very powerful oxidizer that can ignite combustibles on contact.

If extra sulfur trioxide (SO_3) is dissolved into sulfuric acid (H_2SO_4), it forms *fuming* sulfuric acid ($H_2S_2O_7$), also known as *oleum*. Likewise, if nitrogen dioxide (NO_2) is dissolved into nitric acid (HNO_3), it forms *fuming* nitric acid (HN_2O_5). These fuming acids are much more dangerous than the less concentrated forms.

Corrosive spills are generally handled in one of three ways. They can be **absorbed** into an absorbent, assuming it is compatible with the particular corrosive. They may be **diluted** with water. However, this often is not a viable option. It can take a tremendous amount of water to dilute a strong corrosive. And because many acids are water-reactive, adding water can result in a violent reaction. Sometimes the best option is to **neutralize** a corrosive with a *weak* product of the opposite pH. Thus an acid spill would be neutralized with a weak base, such as baking soda or agricultural lime, and a caustic spill would be neutralized with a weak acid, such as citric acid or acetic acid. Using strong acids or bases to neutralize a spill can produce violent reactions with wide pH swings.

Class 8 - Corrosive Materials (continued)

Review Questions (answers on page 197)

- What does pH measure?
 - Strength of a corrosive
 - Concentration of a corrosive
- Which end of the pH scale represents bases (caustics)?
 - pH of 0 to 2
 - pH of 12.5 to 14
- A solution with a pH of 2 is _____ as corrosive as a solution with a pH of 3.
 - Half
 - Twice
 - Ten times
 - A hundred times
- Litmus paper turns _____ in contact with an acid.
 - Blue
 - Black
 - Red
 - Green
- Which type of corrosive generally causes more penetrating and severe injuries?
 - Acids
 - Bases
- _____ tend to feel slippery on skin contact.
 - Acids
 - Bases
- Which of the following is an organic acid?
 - Acetic acid (CH_3COOH)
 - Hydrochloric acid (HCl)
 - Nitric acid (HNO_3)
 - Sulfuric acid (H_2SO_4)
- Which are generally stronger and more reactive?
 - Organic acids
 - Inorganic acids
- Anhydrous*, *glacial*, and *fuming* are terms used to describe:
 - A weak acid
 - A dilute acid
 - A strong acid
 - A concentrated acid

Hazmat Chemistry Study Guide

Class 8 - Corrosive Materials (continued)

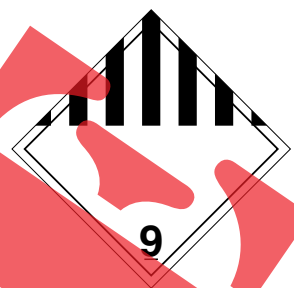
10. Some of the more common bases are those that contain:
- An oxysalt
 - A hydrogen atom bonded to a radical containing oxygen
 - The COOH functional group
 - The hydroxide ion (OH)
11. _____ means “without water.”
- Anhydride
 - Anhydrous
 - Glacial
 - Fuming
12. An acid spill should be neutralized with:
- Water
 - A weak acid
 - A weak base
 - A strong base

Class 9 - Miscellaneous Hazardous Materials

Miscellaneous hazardous materials (also known as *miscellaneous dangerous goods*) are those that present a hazard during transportation but *do not meet the definition of any other hazard class*. This class includes:

- Materials that have an anesthetic, noxious, or other similar property that **could** cause extreme annoyance or discomfort to a flight crew member so as to **prevent** the correct performance of assigned duties.
- Any materials that meet the definition in 49 CFR for an elevated temperature material, a hazardous substance, a hazardous waste, or a marine pollutant.

Examples of Class 9 materials include adipic acid, PCBs, and **molten sulfur**.



Hazmat Chemistry Study Guide

Chapter 6 Review

Review Questions (answers on page 197)

- Which of the following is an explosive?
 - $\text{C}_3\text{H}_5(\text{OH})_3$
 - $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$
 - $\text{C}_2\text{H}_5\text{CONH}_2$
 - $\text{C}_6\text{H}_2\text{CH}_3(\text{NO}_2)_3$
- Detonation is defined as:
 - Spontaneous combustion
 - A pressure relief explosion characterized by overheating and container failure
 - Very rapid combustion from the surface inward at rates slower than the speed of sound
 - Instantaneous combustion at rates faster than the speed of sound
- Which of the following are generally more sensitive to heat, shock, and friction?
 - Primary explosives
 - Secondary explosives
- 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
- Which materials, more than any other hazard class, are prone to runaway polymerization?
 - Gases
 - Explosives
 - Organic peroxides
 - Spontaneously combustible materials
- A Division 2.1 label or placard on a gas cylinder or tank indicates the primary hazard associated with the gas is:
 - Flammability
 - Toxicity
 - Corrosivity
 - Oxidation
- Which of the following gases is the most reactive?
 - Argon
 - Chlorine
 - Helium
 - Neon
- Poisonous gases are further defined by poison inhalation zone (PIH) _____ is the worst.
 - Hazard Zone A
 - Hazard Zone B
 - Hazard Zone C
 - Hazard Zone D

Chapter 6 Review (continued)

9. As the temperature of a gas increases, the pressure within a closed cylinder:
- Increases
 - Decreases
 - Stays the same
10. The higher the expansion ratio, the more volume a gas will occupy once released from its container.
- True
 - False
11. If a compressed gas cylinder is filled too quickly:
- It will result in a BLEVE
 - It can fail due to overheating
 - It can fail due to overpressurization
 - It will become very cold, posing a risk of thermal injury to anyone who touches it
12. Which of the following materials tend to be very sensitive to heat and friction?
- Division 2.3
 - Division 4.1
 - Division 5.2
 - Division 6.1
13. Flammable liquids with low flash points usually have:
- High boiling points
 - Low vapor pressures
 - Low ignition temperatures
 - High ignition temperatures
14. With flammable liquids that _____, it will be necessary to use foam to smother a fire and retard vapor production.
- Sink in water
 - Float on water
 - Are miscible in water
15. Which of the following are most likely to form highly unstable crystals on the container when exposed to air?
- Class 1 materials
 - Division 4.2 materials
 - Division 5.2 materials
 - Class 8 materials
16. Which of the following is likely to be a Division 4.3 (dangerous when wet) material?
- Nitrocellulose
 - White phosphorus
 - Sodium hydroxide
 - Calcium carbide

Hazmat Chemistry Study Guide

Chapter 6 Review (continued)

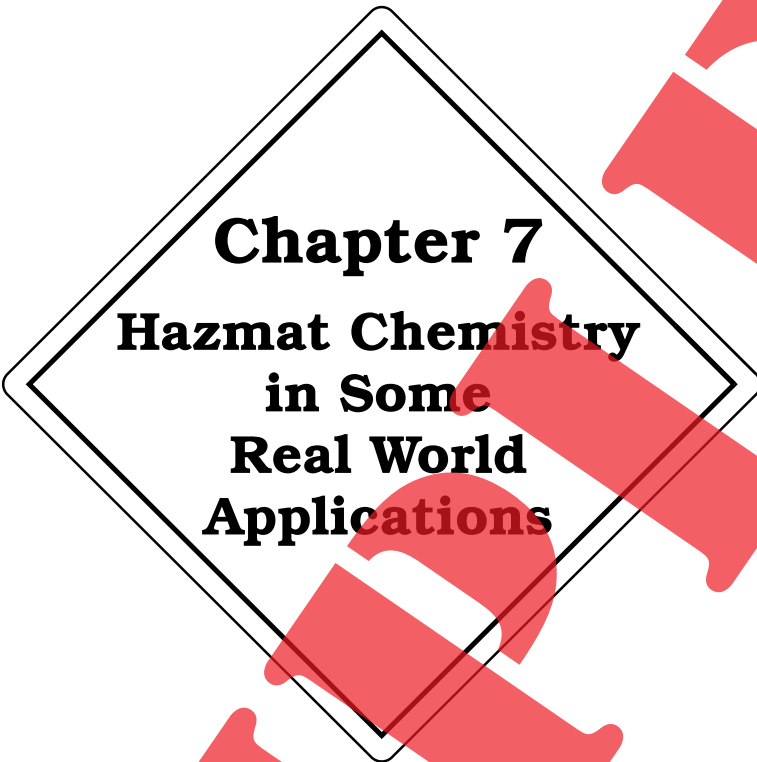
17. What factor makes some otherwise safe products dangerous enough to be designated Class 4 materials?
- Temperature of the product
 - Exposure to water
 - Tendency to surface burn
 - Surface-area-to-mass ratio
18. Which of the following is an organic peroxide?
- NH_4NO_3
 - Na_2O_2
 - $\text{CH}_3\text{CO}_2\text{CH}_3$
 - $\text{CH}_3\text{O}_2\text{C}_2\text{H}_5$
19. Generally the *most* important thing you can do to prevent emergencies with organic peroxides is to protect them from:
- Friction
 - Elevated temperatures
 - Exposure to water
 - Exposure to contaminants
20. The signal word *warning* on a pesticide container label means:
- High toxicity
 - Moderate toxicity
 - Relatively low toxicity
21. The designation of Radioactive I, II, or III) is based on the radiation level as measured both at the surface of an intact package and _____ away.
- 1 foot
 - 3 feet
 - 5 feet
 - 10 feet
22. Which form of radiation has the strongest penetrating power, able to travel considerable distances and through heavy objects?
- Alpha
 - Beta
 - Gamma
23. According to EPA recommendations, the maximum radiation exposure one should receive to mitigate an incident (not involving saving a life) is:
- 10 rems
 - 25 rems
 - 50 rems
 - 100 rems
24. Which of the following measures is the *most* effective for minimizing exposure to radioactive materials?
- Reducing the amount of time in proximity to the materials
 - Maintaining a greater distance from the source
 - Using more shielding

Chapter 6 Review (continued)

25. When looking at a periodic table, you should consider any element from _____ on potentially radioactive in its natural state.
- Lead (atomic number 82)
 - Bismuth (atomic number 83)
 - Polonium (atomic number 84)
 - Uranium (atomic number 92)
26. Which end of the pH scale represents acids?
- pH of 0 to 2
 - pH of 12.5 to 14
27. pH measures the:
- Strength of a corrosive
 - Concentration of a corrosive
28. Which is more important when looking at corrosives? Which represents a greater danger?
- Strength of a corrosive
 - Concentration of a corrosive
29. Using *strong* acids or bases to neutralize a *corrosive spill* of the opposite pH:
- Will neutralize the spill faster and more effectively than will a weak acid or base
 - Will neutralize the spill slower and less effectively than will a weak acid or base
 - Can produce violent reactions with wide pH swings
 - Won't affect the pH of the original spill

Hazmat Chemistry Study Guide

SAMPLE



Chapter 7

Hazmat Chemistry in Some Real World Applications

This chapter covers a couple of other chemistry-related topics with which you should be familiar:

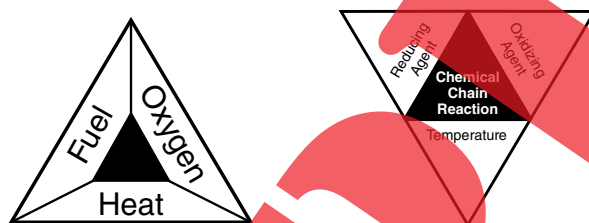
- Fire Chemistry
- Chemical Reactions/Incompatibility

Fire Chemistry

Let's start the discussion of fire chemistry by looking at what we already know about fire. We often refer to the **fire triangle** to describe the components necessary for fire to occur: *fuel*, *heat*, and *oxygen* (or another oxidizer).

However, the fire triangle fails to reflect the way products produced in the combustion process further propagate the fire. To incorporate the fourth component, we use the **fire tetrahedron**. The fire tetrahedron starts with the same elements as does the fire triangle, although it uses different terminology: *reducing agent* (fuel), *oxidizing agent* (either oxygen or another oxidizer), and *temperature* (heat). The fourth element is the *chemical chain reaction*, which will be explained shortly.

The Fire Triangle and the Fire Tetrahedron



There are **four methods of fire extinguishment** based on the fire tetrahedron:

- Reduce the temperature of the fuel
- Remove the reducing agent (remove the fuel)
- Remove the oxidizing agent (smother the fire)
- Interrupt the chemical chain reaction

Reducing fuel temperature is done by applying water.

Removing the fuel can be done in different ways, depending on the circumstances. Closing an emergency shutoff valve is often a safe and easy option. Foam can be used to suppress vapors and provide a barrier between oxygen and the fuel. (Using foam both removes the fuel and smothers the fire.) Allowing the fire to burn itself out—consume all the fuel—is sometimes safer than attempting extinguishment.

Removing the oxidizing agent (smothering the fire), like removing the fuel, can be done by applying a foam barrier. Using dry powder extinguishing agents on combustible metals is another example of excluding oxygen. In some cases, it may be appropriate to smother a fire by introducing inert gases (such as carbon dioxide or nitrogen) into an enclosed space.

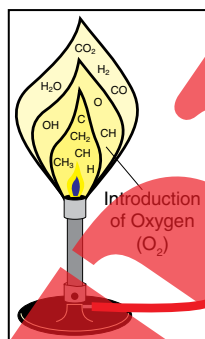
Dry chemical and halon extinguishers can be used to interrupt the chemical chain reaction. They, too, “separate the fuel from the oxygen,” but they do so on a molecular level by breaking down and bonding with free radicals produced during combustion.

The **chemical chain reaction** is a complex process not understood in its entirety. In general, however, it's a process in which compounds (fuels) are broken down by the heat of the fire, and the free radicals formed from their components combine with other free radicals to form new compounds (**products of combustion**). Some of these compounds (the intermediate by-products) break down again, releasing new free radicals to repeat the process until what remains either has been dispersed into the atmosphere (where it is no longer available to the combustion process) or is stable enough that it no longer reacts. We could say that the compounds have been consumed by the fire, but that's somewhat misleading. Matter isn't destroyed when it burns. Rather, it is transformed into another form or state. And when matter burns, it produces heat, flame, smoke, and other fire gases.

Fire Chemistry (continued)

Imagine a simple fuel like methane (CH_4), consisting only of carbon and hydrogen. Once ignited, the methane molecule breaks apart, yielding free radicals, such as methyl (CH_3) and atomic hydrogen (H). As you may recall from earlier chapters, free radicals are not electrically balanced. They must react with something else, for instance, the oxygen in the air, to fill the available bonding sites. Oxygen, also, is broken down in this process, yielding free radicals (O) of its own. Ultimately, all of these free radicals combine to form the more stable compounds diatomic hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and water vapor (H_2O).

Breakdown of a Simple Hydrocarbon (Methane)



Products of combustion are often hazardous in one or more ways. For example, carbon monoxide and hydrogen are both flammable. They will continue to react as part of the chemical chain reaction, propagating the fire even further. Carbon monoxide is also toxic.

Products of combustion vary, depending on the fuel. Methane is a very simple fuel, yielding very common combustion by-products. Other fuels can yield more complex and more dangerous materials. Carbon monoxide (CO) and carbon dioxide (CO_2) are usually produced in large quantities at any fire. Some of the other more common and more toxic fire gases include the following:

- Hydrogen cyanide (HCN) - Produced from the burning of nitrogen-containing materials, such as wool, silk, nylon, and polyurethane
- Nitrogen oxides, particularly nitrogen dioxide (NO_2) and nitric oxide (NO) - Also produced from the burning of nitrogen-containing materials
- Hydrogen chloride (HCl) - Produced from the burning of chlorine-containing materials, such as polyvinyl chloride (PVC)
- Acrolein ($\text{CH}_2=\text{CHCHO}$ or $\text{C}_3\text{H}_4\text{O}$) - Formed from smoldering cellulosic materials

The fire gases produced can vary with oxygen content too. Carbon dioxide (CO_2), for instance, is a product of **complete combustion**, which requires sufficient oxygen to react with the available fuel. When the oxygen content is insufficient to oxidize all of the fuel molecules present, the resulting **incomplete combustion** produces carbon monoxide (CO). Both gases are present at most fires because the fuel doesn't burn evenly throughout. However, the percentages of each will vary with oxygen content.

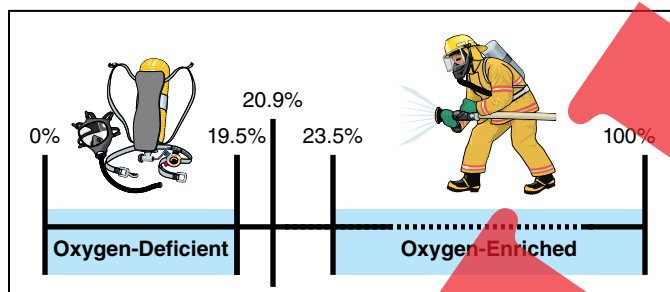
Even products that don't burn can give off **hazardous decomposition products** when they break down at elevated temperatures. For example, carbon tetrachloride (CCl_4), once used as an extinguishing agent before its dangers were known, forms toxic phosgene gas (COCl_2) when broken down by sufficient heat.

Oxygen content affects not just the fire gases produced but also the intensity of the fire and how quickly it spreads. The normal atmosphere is comprised of roughly 78% nitrogen, 20.9% oxygen, and 1.1% argon and other gases. An **oxygen-enriched** atmosphere will cause any flammable or combustible material to ignite more readily and burn more fiercely. If the oxygen level is above 23.5%, the atmosphere is considered to be potentially explosive. Atmospheres with less than 19.5% oxygen are considered **oxygen-deficient**. While fire will continue to burn at this concentration, it won't burn as well. As the concentration drops, so does flame propagation.

Hazmat Chemistry Study Guide

Fire Chemistry (continued)

Oxygen-Deficient and Oxygen-Enriched Atmospheres



Backdraft and flashover are two situations in which fire intensifies very quickly. However, the mechanisms by which each occurs are different. **Backdraft** is related to oxygen content. It occurs when oxygen (air) is suddenly introduced into an area where fire has been smoldering from lack of adequate oxygen. This can happen when someone opens a door or window to the fire room. Fire goes from the smoldering stage to the free-burning stage with explosive force, producing dangerous pressure waves similar to an explosion.

Flashover is the sudden simultaneous ignition of combustibles that have become heated to their ignition (autoignition) temperatures by radiated heat from the fire. Smoke and superheated gases accumulate at ceiling level, but also radiate heat back to other combustibles in the room. In the moments before flashover occurs, one can see heavy smoke developing at upper levels, followed by flame rolling across the ceiling.

Fire (combustion) is actually a form of oxidation. **Oxidation** is defined as the chemical combination of oxygen with any substance. In other words, when oxygen combines chemically with any substance, that substance will have been oxidized.

Fire is rapid oxidation producing heat and light. However, oxidation takes other forms besides fire. The rusting of iron is an oxidation reaction, but it takes place so slowly that no light is produced and the amount of heat produced is almost immeasurable. The formation of organic peroxides over time when ether is exposed to air is also an oxidation reaction. So is the process that takes place when rags soaked with animal or vegetable oils generate heat prior to igniting (spontaneous combustion).

Thus far when we've talked about materials burning, we've talked about the materials themselves. However, as covered in previous chapters, liquids and solids don't actually burn; what burn are the vapors given off by those products either through vaporization (liquids) or pyrolysis (solids).

Fire Chemistry (continued)

Review Questions (answers on page 197)

- Simple hydrocarbons such as methane and propane produce _____ when burning.
 - Carbon dioxide, carbon monoxide, hydrogen, and water vapor
 - Hydrogen, acrolein, and water vapor
 - Carbon monoxide, hydrogen, hydrogen cyanide, and water vapor
 - Carbon dioxide, nitrogen oxides, and hydrogen
- Chlorine-containing materials produce _____ when burning.
 - Acrolein
 - Nitrogen oxides
 - Hydrogen cyanide
 - Hydrogen chloride
- Hydrogen cyanide and nitrogen oxides are common combustion by-products of:
 - Simple hydrocarbons
 - Cellulosic materials
 - Chlorine-containing materials
 - Nitrogen-containing materials
- An oxygen-enriched atmosphere will cause flammable and combustible materials to ignite more readily and burn more fiercely.
 - True
 - False
- Which of the following is most directly related to a sudden increase in oxygen content?
 - Flashover
 - Backdraft
 - Oxidation
 - Pyrolysis
- Heavy smoke developing at upper levels, followed by flame rolling across the ceiling are characteristic of:
 - Flashover
 - Backdraft
 - Oxidation
 - Pyrolysis
- Oxidation is:
 - The process by which compounds give off oxygen
 - Any reaction that causes an oxygen-enriched atmosphere
 - Any reaction that causes an oxygen-deficient atmosphere
 - The chemical combination of oxygen with any substance
- The breakdown of solids under the influence of heat to produce combustible gases is called:
 - Vaporization
 - Evaporation
 - Oxidation
 - Pyrolysis

Chemical Reactions/Incompatibility

We've touched on chemical incompatibility several times throughout this study guide. In Chapter 2, we defined chemical reactivity and gave examples of what it means for chemicals to be air-reactive or water-reactive. We identified that water-reactivity has ramifications beyond the obvious scenarios of simply mixing something with water or allowing it to get wet in the rain. Water-reactive chemicals can also react with moisture on the skin, in the eyes, or in the respiratory tract. In subsequent chapters, we introduced specific types of chemicals that are incompatible with air, water, and sometimes other chemicals as well. Now, however, we'll look specifically at the incompatible reactions between two or more chemicals should they happen to mix.

First, let's identify some potential scenarios so that we don't overlook anything important. The most obvious scenarios are those that trigger an emergency response: the transportation accident, earthquake, or other big shake-up where multiple containers break and two or more chemicals mix; the fire impinging on numerous chemicals at once; the citizen who didn't read labels and foolishly mixed bleach and ammonia (or worse); the worker who filled a tank that hadn't been cleaned and purged of its previous contents; the discovery of a clandestine drug lab where numerous chemicals are stored and used improperly; the terrorist intent on doing harm; and so forth.

Sometimes mixing between incompatible chemicals is not the triggering event but rather a dangerous consequence of the initial release and specific circumstances surrounding that release. For example, a release of liquid oxygen from a cryogenic cargo tank stopped along the highway presents more danger than a similar leak from a tank at a fixed facility designed with some built-in safeguards, the difference being that liquid oxygen in contact with asphalt on the highway forms an extremely shock-sensitive mixture.

Chemical incompatibility is a major consideration in the selection of personal protective equipment at a hazmat incident. Obviously, you don't want to go into the hot zone wearing chemical protective clothing that will disintegrate on contact with the spilled material. Nor do you want to wear chemical protective clothing the hazardous material will permeate in a short amount of time. So you'll want to check **chemical compatibility charts** provided by suit, glove, and boot manufacturers to ensure the equipment provides adequate protection against the specific hazardous material you are dealing with. In the event that the chemical's identity is still unknown, you want to choose chemical protective clothing that was tested to ensure good overall protection against a wide range of common chemicals.

Incompatibility is a concern with monitoring equipment as well. For example, you need intrinsically safe equipment in a potentially flammable atmosphere. Otherwise, your equipment may provide an ignition source. You should monitor an unknown atmosphere for corrosive vapors before exposing sensitive electronic devices to potential damage. Corrosive vapors are likely to lead to false readings and may destroy the sensors altogether.

Chemical incompatibility may affect your mitigation measures and cleanup options. For example, you may be able to neutralize an acid spill with a weak base if you do so carefully. If you use a strong base, however, you'll produce a violent reaction that may injure responders and make the incident much worse. If you try to collect spilled acid in a metal container versus a plastic one, the acid will react with the metal and compound the problem. So, as you can see, chemical incompatibility has significant ramifications at many levels.

Several outcomes are possible when two or more chemicals mix. The resulting product(s):

- May be no more hazardous than the original materials.
- May be less hazardous than the original materials.
- May be more hazardous than the original materials (a situation referred to as the "synergistic effect"). For example, the resulting product may be toxic at lower doses or toxic by different routes of entry (e.g., by inhalation versus ingestion).
- May present entirely different hazards from those of the original materials. For example, if nitric acid and acetic acid (both corrosives) are mixed, the result is a shock-sensitive explosive.

Chemical Reactions/Incompatibility (continued)

The mixing of incompatible chemicals can have several results. The reaction:

- Can be explosive or otherwise violent, such as rapidly overpressurizing a container.
- Can be strongly **exothermic**, releasing sufficient heat to ignite nearby combustibles.*
- Can be strongly **endothermic**, absorbing heat from the air and forming dangerous compounds.*
- Can produce flammable products.
- Can form toxic products.
- Can form corrosive products.

* The majority of chemical reactions are exothermic. Very few are endothermic.

Types of Chemical Reactions

While you don't necessarily need to know the mechanisms behind these incompatible reactions, it's helpful to understand the various types of chemical reactions below. Although these reactions are presented in the context of chemical incompatibility, they're the same types of reactions that take place in beneficial processes too. It's basic chemical bonding, as presented in Chapter 3, except now that you have a better understanding of hazmat chemistry, the concepts aren't so overwhelming.

- **Synthesis reactions** (sometimes called *combination reactions*) are those in which two or more substances combine to form a new one. For instance, when hydrogen (H) and fluorine (F) combine, they create highly toxic hydrogen fluoride (HF) gas, which in solution becomes the very corrosive hydrofluoric acid (also written as HF).



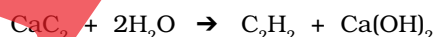
- **Decomposition reactions** are the reverse of synthesis reactions; a single compound is broken down into the elements or molecules that comprise them. When ammonium nitrate (NH_4NO_3) thermally decomposes, the potentially explosive reaction produces nitrous oxide (N_2O) and water (H_2O).



- In **single replacement reactions**, one element or compound breaks away from its original "partner" and joins another. For instance, when sodium (Na) is exposed to water (H_2O), a hydroxyl (OH) group breaks away from the original water molecule and joins the sodium atoms, resulting in flammable hydrogen gas (H_2) and a caustic solution of sodium hydroxide (NaOH).

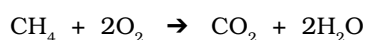


- In **double replacement reactions**, elements or compounds from each substance change "partners," forming two entirely new compounds. In the example below, when calcium carbide (CaC_2) reacts with water (H_2O), both molecules split. Their components change partners to form flammable acetylene gas (C_2H_2) and a caustic solution of calcium hydroxide ($\text{Ca}(\text{OH})_2$).



Although the four reactions identified above cover the basic mechanics, you should also be familiar with the reaction types below.

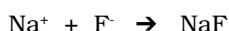
- **Combustion reactions** are what we know as *fire* or *burning*. Organic materials combine with oxygen to produce carbon dioxide (CO_2), water vapor (H_2O), and heat. The following equation represents the combustion of methane (CH_4).



While the equation above is a combustion reaction, mechanically it's also a double replacement reaction. And it's also a redox reaction. (See next page.)

Chemical Reactions/Incompatibility (continued)

- **Redox reactions** (or **reduction-oxidation reactions**) are generally defined as ones in which electrons are exchanged. Shown below is the ionic bond between a positively charged sodium ion (Na^+) and a negatively charged fluorine ion (F^-) to form the electrically neutral sodium fluoride compound (NaF). Notice that this is also a synthesis (combination) reaction.



Every redox reaction involves the simultaneous loss and gain of an equal number of electrons. Neither reaction (reduction or oxidation) can happen without the other.

Despite the focus on electron exchange, redox reactions aren't limited to ionic bonding. Oxidation is the chemical combining of oxygen (or other oxidizers) with another substance. The reaction can be a very slow one (as when oxygen combines with iron to create rust) or a very fast one (as manifested by a fire or explosion). In fact, fire (combustion) is nothing more than a complex redox reaction involving a reducing agent (fuel), an oxidizing agent (usually oxygen), and temperature. So while we stopped looking at electron action once we began looking at covalent compounds in this study guide, covalent compounds can indeed participate in redox reactions.

- **Acid-base reactions** (or **neutralization reactions**) are double replacement reactions between an acid and a base. The reaction below is a very dangerous one involving two strong corrosives. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) are on opposite ends of the pH scale. If mixed, the reaction will generate a tremendous amount of heat. That's why whenever hazmat technicians attempt neutralization of an acid or a base, they must do so with a weak corrosive of the opposite pH.



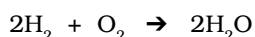
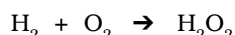
Balancing Chemical Equations

Balancing chemical equations is beyond the scope of what is taught in many hazmat chemistry classes, but we'll touch on it briefly because it demonstrates how elements and compounds must be present in specific ratios to create specific reactions. We can compare this to the concept of complete combustion versus incomplete combustion. The two equations below represent the burning of coal (carbon). If enough oxygen is present to create complete combustion, it produces carbon dioxide (CO_2). But the ratio of carbon to oxygen is doubled because of an oxygen-deficient atmosphere, the result is incomplete combustion, characterized by carbon monoxide (CO).



There's a law in chemistry, the *Law of Conservation of Mass*, that says matter is neither created nor destroyed in chemical reactions. So elements must be present in the same numbers on both sides of the equation. In a simple equation, such as the one above, balancing is easy. But often it becomes necessary to change the proportion of elements or compounds to achieve a balance.

Let's take the simple example of making water (H_2O) from the diatomic gases hydrogen (H_2) and oxygen (O_2). Combining these two diatomic gases in a one-to-one ratio doesn't produce water. It produces hydrogen peroxide (H_2O_2) because there are two atoms of each element. Creating a compound with twice as many hydrogen atoms as oxygen atoms requires starting out with the same ratio, as in the second equation below.



The most important thing to remember in trying to balance equations is not to change any of the formulas on either side of the arrow. Only the coefficients (the numbers in front of elements or compounds) can change. That's why the last equation above has two molecules of diatomic hydrogen (2H_2), not one molecule of H_4 (something that doesn't exist).

Chemical Reactions/Incompatibility (continued)

It's often possible to balance equations simply by creating a table that shows how many atoms of each element exist on both sides of the arrow and adjusting the coefficients until the numbers are the same. Using water (H_2O) as an example, the following table shows first what the numbers would look like if the diatomic gases were used in a one-to-one ratio, then what happens when the coefficients are adjusted to double diatomic hydrogen and the resulting water molecule.

Using a Simple Table to Balance the Equation in Making Water (H_2O)

Element	Before Adjusting Coefficients $\text{H}_2 + \text{O}_2 \neq \text{H}_2\text{O}$		After Adjusting Coefficients $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$	
	Before the Arrow	After the Arrow	Before the Arrow	After the Arrow
H	2	2	4	4
O	2	1	2	2

Quite often, particularly with more complex reactions, balancing equations is more of a trial-and-error process of fiddling with the coefficients until the numbers work. The equation below represents what happens when someone lights a butane (C_4H_{10}) lighter. However, a quick look at the number of atoms of each element on both sides of the arrows shows that the equation isn't balanced.



There's no quick way to identify the right coefficients. It takes trying different numbers until things work. However, one good guideline is to start with the most complicated-looking reactant first, in this case, butane (C_4H_{10}). Try putting a 2 in front of it, then see if adjusting the other numbers makes everything come out even. If not, put a 3 there and repeat the process. Eventually, you'll find the right combination. In this case, it isn't necessary to go beyond two molecules of butane. The equation balances as shown below.



It helps to work one element at a time. In other words, in the example above, once you put a 2 in front of butane, turn your attention to the carbon-containing compound (CO_2) on the other side of the arrow. It's clear we need eight atoms of carbon to match what is on the left side of the equation. There's no carbon anywhere else, so you can now turn your attention to hydrogen. There are twenty atoms of hydrogen before the arrow, so ten molecules of water will give us the same thing after the arrow. The only thing remaining to tinker with is oxygen, and by counting the number of atoms on the right side of the arrow, we know what we need on the left.

Hazmat Chemistry Study Guide

Chemical Reactions/Incompatibility (continued)

Review Questions (answers on page 197)

- The *synergistic effect* describes what happens when two or more chemicals mix and the resulting product:
 - Is less hazardous than the original materials
 - Is equally hazardous as (no more hazardous than) the original materials
 - Is more hazardous than the original materials
 - Presents entirely different hazards than the original materials
- The *best* description of an exothermic reaction is one that is characterized by:
 - The formation of toxic and/or flammable gases
 - The formation of corrosive solutions
 - Catastrophic container failure from overpressurization
 - The generation of heat, sometimes sufficient to ignite nearby combustibles
- The equation $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ is an example of a _____ reaction.
 - Synthesis
 - Decomposition
 - Single Replacement
 - Double Replacement
- Which of the following is an example of synthesis reaction?
 - $\text{NaCN} + \text{HCl} \rightarrow \text{NaCl} + \text{HCN}$
 - $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$
 - $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{HCl} + \text{CH}_3\text{Cl}$
 - $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
- Which of the following is an example of a double replacement reaction?
 - $\text{FeS} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2\text{S}$
 - $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$
 - $\text{NaCl} + \text{O}_3 \rightarrow \text{NaClO} + \text{O}_2$
 - $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$
- Which of the following represents a balanced equation?
 - $\text{H}_2\text{SO}_4 + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{Na}_2\text{SO}_4$
 - $\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{H}_2\text{O} + 2\text{Na}_2\text{SO}_4$
 - $\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$
 - $2\text{H}_2\text{SO}_4 + \text{NaOH} \rightarrow 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$
- Which of the following represents a balanced equation?
 - $2\text{CO} + 3\text{H}_2 \rightarrow 2\text{CH}_3\text{OH}$
 - $\text{H}_2\text{S} + 3\text{O}_2 \rightarrow \text{H}_2\text{O} + 2\text{SO}_2$
 - $4\text{Al} + 2\text{MnO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 2\text{Mn}$
 - $2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
- Which equation accurately depicts how the gases nitrogen and hydrogen combine to form ammonia?
 - $\text{N}_2 + \text{H}_6 \rightarrow 2\text{NH}_3$
 - $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
 - $2\text{N} + 3\text{H}_2 \rightarrow 2\text{NH}_3$
 - $2\text{N} + 2\text{H}_3 \rightarrow 2\text{NH}_3$

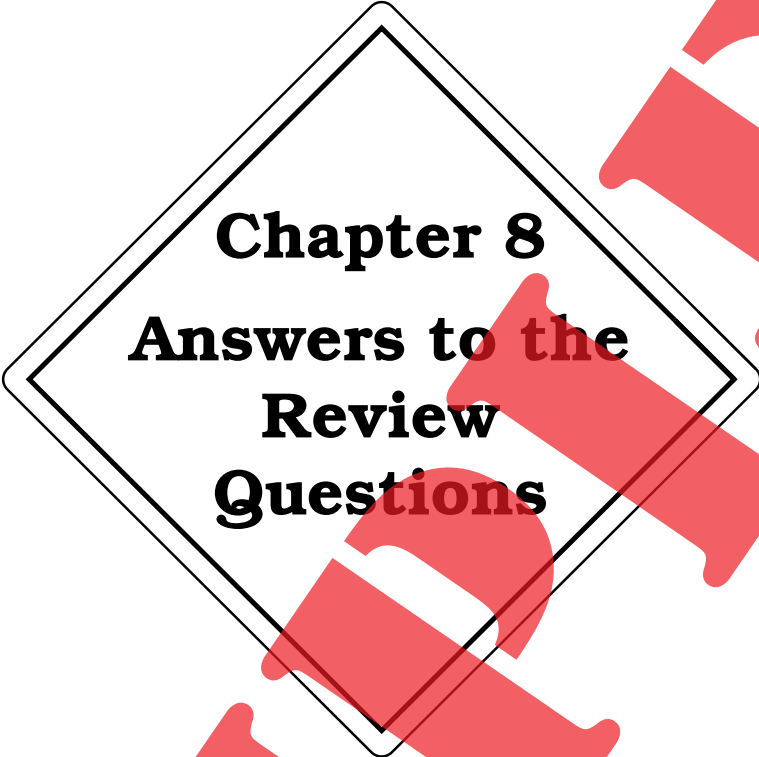
Chapter 7 Review

Review Questions (answers on page 197)

- The sudden simultaneous ignition of combustibles that have become heated to their ignition temperatures by radiated heat from the fire is called:
 - Flashover
 - Backdraft
 - Oxidation
 - Pyrolysis
- Oxygen-deficient atmospheres are defined as having less than ____ oxygen.
 - 20.9%
 - 20.1%
 - 19.5%
 - 18.6%
- Oxygen-enriched atmospheres are defined as having more than ____ oxygen.
 - 21.5%
 - 22.5%
 - 23.5%
 - 24.5%
- When carbon tetrachloride is broken down by heat, it forms:
 - Chlorine
 - Methyl chloride
 - Trichloromethane
 - Phosgene
- Which of the following is an example of decomposition reaction?
 - $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
 - $\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$
 - $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$
 - $\text{CCl}_4 + \text{H}_2\text{O} \rightarrow \text{COCl}_2 + 2\text{HCl}$
- Which of the following is an example of a single replacement reaction?
 - $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - $2\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{HCl}$
 - $2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow 2\text{HCl} + \text{Na}_2\text{SO}_4$
 - $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$
- Which of the following is an example of a chemical reaction producing one or more end products more hazardous than the original chemical(s).
 - $\text{Na} + \text{Cl} \rightarrow \text{NaCl}$
 - $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{Ca(OH)}_2$
 - $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

Hazmat Chemistry Study Guide

SAMPLE



Chapter 8

Answers to the Review Questions

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

Hazmat Chemistry Study Guide

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. b
11. a
12. a
13. b
14. a

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

Hazmat Chemistry Study Guide

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

Hazmat Chemistry Study Guide

SAMPLE



Appendix

Hazmat Chemistry Study Guide

Acronyms and Abbreviations

The following is a list of acronyms and abbreviations used in this *Hazmat Chemistry Study Guide*.

ACGIH	American Conference of Governmental Industrial Hygienists
AFFF	Aqueous Film Forming Foam
AIHA	American Industrial Hygiene Association
ALARA	As Low As Reasonably Achievable
ammo	Ammunition
ANFO	Ammonium Nitrate and Fuel Oil
ATC	Alcohol-Type Concentrate
atm	Atmospheres
BLEVE	Boiling Liquid Expanding Vapor Explosion
Bq	Becquerel
CFR	Code of Federal Regulations
Ci	Curie
cpm	Counts per Minute
DNA	Deoxyribonucleic Acid
DOT	Department of Transportation
EPA	Environmental Protection Agency
ERPG	Emergency Response Planning Guideline
Gy	Gray
Hazmat	Hazardous Materials
IDLH	Immediately Dangerous to Life and Health
IUPAC	International Union of Pure and Applied Chemists
LC	Lethal Concentration
LD	Lethal Dose
LEL	Lower Explosive Limit
LOC	Level of Concern
LOX	Liquid Oxygen
LNG	Liquefied Natural Gas
LPG	Liquid Petroleum Gas
mmHg	Millimeters of Mercury
mg/kg	Milligrams per Kilogram
mg/m ³	Milligrams per Cubic Meter
mR/hr	Millirems per Hour
MSST	Maximum Safe Storage Temperature
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
ORM	Other Regulated Materials
PCB	Polychlorinated Biphenyl
PEL	Permissible Exposure Limit
PIH	Poison Inhalation Zone
PPE	Personal Protective Equipment
ppb	Parts per Billion
ppm	Parts per Million
psi	Pounds per Square Inch
psia	Pounds per Square Inch Absolute
psig	Pounds per Square Inch Gauge
Rad	Radiation Absorbed Dose
Redox	Reduction-Oxidation (Reactions)
REL	Recommended Exposure Limit
Rem	Roentgen Equivalent Man
RNA	Ribonucleic Acid
SADT	Self-Accelerating Decomposition Temperature
SCBA	Self-Contained Breathing Apparatus
SOGs	Standard Operating Guidelines
SOPs	Standard Operating Procedures
STEL	Short-Term Exposure Limit

Acronyms and Abbreviations (continued)

STP	Standard Temperature and Pressure
Sv	Sievert
TEEL	Temporary Emergency Exposure Limit
TI	Transportation Index
TIH	Toxic Inhalation Zone
TLV-C	Threshold Limit Value–Ceiling
TLV-TWA	Threshold Limit Value–Time-Weighted Average
TNT	Trinitrotoluene
UEL	Upper Explosive Limit
WEEL	Workplace Environmental Exposure Limit

Hazmat Chemistry Study Guide

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Hazmat Chemistry Study Guide

About the Author

Jill Meryl Levy owns her own business, "Firebelle Productions." She is an author and publisher, with several full-length books to her credit. She wrote the first edition of *The First Responder's Pocket Guide to Hazardous Materials Emergency Response* in 1996 and a greatly expanded second edition in 2000. That book is now in its third edition, with a new title: *The First Responder's Field Guide to Hazmat & Terrorism Emergency Response*. In 1998, she released *Take Command of Your Writing*, a comprehensive guide to more effective writing geared specifically for emergency services personnel. The *Hazmat Chemistry Study Guide* was first published in 2002 and revised in 2005. Her latest book, *Crimes Against the English Language*, another book on more effective writing, was published in September 2005. Jill also produces brochures, booklets, and newsletters for fire departments and industry.

Jill has worked in the field of safety education since 1981 when she was hired by the City of Santa Clara Fire Department (CA). Later, during her employment at Hewlett-Packard Company in Cupertino (CA), Jill began producing brochures, booklets, and newsletters as a means to communicate safety information to a large employee population. The publications became so popular that she was soon producing brochures and booklets on a corporate-wide basis.

Jill first got involved with hazardous materials while working with the Governor's Office of Emergency Services California Specialized Training Institute (CSTI) on the 1994 and 1995 revisions of its *Hazardous Materials Technician/Specialist* curriculum. In 1995 she became a CSTI-certified hazardous materials specialist and a first responder outreach instructor. Jill has also assisted the California State Fire Marshal's Office with curriculum revision projects.

Jill has been a volunteer firefighter for the Santa Clara County Fire Department (CA) since 1980. In her spare time, Jill helps build homes with Habitat for Humanity.

Products by Firebelle Productions

The First Responder's Field Guide to Hazmat & Terrorism Emergency Response

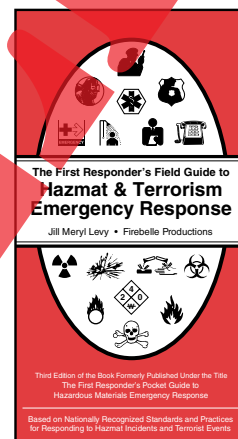
The First Responder's Field Guide to Hazmat & Terrorism Emergency Response puts the contents of a 24-hour Hazardous Materials First Responder course at your fingertips. This field guide is designed to help first responders manage a hazardous materials incident until a trained hazmat team arrives. It also provides good information for individuals at the technician, specialist, and incident commander levels. (This book is the third edition of the book previously titled *The First Responder's Pocket Guide to Hazardous Materials Emergency Response*.)

Contents

- ✓ Quick Reference Guide
- ✓ Recognizing and Responding to a Hazmat Incident
- ✓ Labels, Placards, and Other Marking Systems
- ✓ Container Recognition
- ✓ Assessing the Hazards
- ✓ Medical Management of Hazmat Exposures
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Hazmat Chemistry Study Guide

Products by Firebelle Productions (continued)***Hazmat Chemistry Study Guide (Second Edition)***

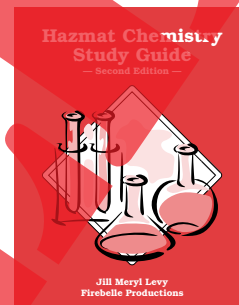
The *Hazmat Chemistry Study Guide (Second Edition)* is a powerful tool to help responders study for the final exam in a basic hazmat chemistry class. It provides a condensed summary of the major concepts taught in most hazmat chemistry classes nationwide and follows each concept with sample test questions similar to what students can expect to see on the final exam.

Contents

- ✓ Preparing for the Final Exam
- ✓ Terms and Definitions
- ✓ Elements and Compounds
- ✓ Salts
- ✓ Hydrocarbons and Related Compounds
- ✓ Hazmat Chemistry According to the DOT Hazard Classes
- ✓ Hazmat Chemistry in Some Real World Applications

Price

A single copy of the *Hazmat Chemistry Study Guide (Second Edition)* is \$29.95 plus \$5 for shipping and handling (plus sales tax in California). Volume discounts are available.

***The Hazmat Chemistry Mini Review***

The *Hazmat Chemistry Mini Review* puts in the palm of your hand the most important information taught in hazmat chemistry classes nationwide. And the small format (6 inches by 4.25 inches) makes for quick reading, without skimping on vital content. This book is a handy companion to the *Hazmat Chemistry Study Guide*. The study guide goes into greater depth and provides hundreds of sample test questions, making it an outstanding resource for anyone going through a hazmat chemistry class. The *Hazmat Chemistry Mini Review*, on the other hand, provides a quick summary of the key concepts that is easy to grasp in a matter of minutes. It's great for that last-minute review before the test at the end of class or for a quick refresher months later, when what you learned in class has become a distant memory.

Contents

- ✓ Terms and Definitions
- ✓ Elements and Compounds
- ✓ Chemical Bonding
- ✓ Salts
- ✓ Hydrocarbons
- ✓ Hydrocarbon Derivatives
- ✓ Fire Chemistry and Chemical Reactions
- ✓ Toxicity and Risk

Price

A single copy of the *The Hazmat Chemistry Mini Review* is \$12.95 plus \$3 for shipping and handling (plus sales tax in California). Volume discounts are available.



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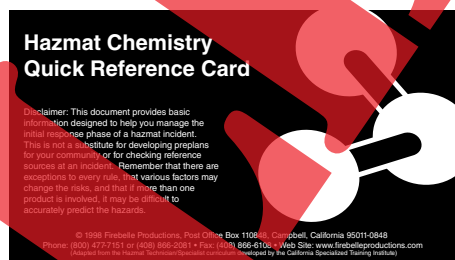
Hazmat Chemistry Quick Reference Card

The *Hazmat Chemistry Quick Reference Card* provides responders with a condensed summary of the chemistry information taught in many hazardous materials technician classes throughout the United States.

Contents

This ten-panel folding card covers several topics:

- ✓ The Classification of Matter
- ✓ Hydrocarbons
- ✓ Hydrocarbon Radicals and Hydrocarbon Derivatives
- ✓ Salts
- ✓ Behavioral Clues
- ✓ The Effect of Molecular Size
- ✓ The Periodic Table of Elements



Price

A single *Hazmat Chemistry Quick Reference Card* is \$3.50 (plus sales tax in California). Volume discounts are available.

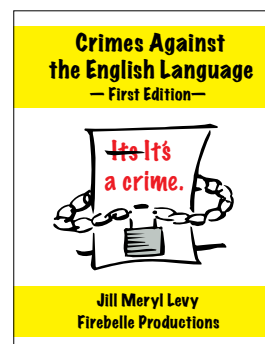
Crimes Against the English Language

Crimes Against the English Language helps readers improve their writing by reviewing common problems in grammar, punctuation, and word choice, cleverly presented as “criminal cases.” Readers will learn common mistakes and how to prevent them, then have the opportunity to test their knowledge with interactive worksheets titled “You Be the Detective.”

Contents

Crimes Against the English Language helps readers recognize and avoid common “violations,” including:

- ✓ Creating comma splices and run-on sentences.
- ✓ Punctuating sentences incorrectly.
- ✓ Misusing abbreviations and acronyms.
- ✓ Using apostrophes incorrectly to form plurals and possessives.
- ✓ Using the wrong words (words correctly spelled but wrong for the context of the sentence).
- ✓ Cluttering documents with redundant, weak, or superfluous words.
- ✓ Omitting important details or words necessary for grammatical or logical completeness.
- ✓ Creating awkward, confusing, or embarrassing sentences with needless shifts, misplaced modifiers, and dangling modifiers.



Price

A single copy of *Crimes Against the English Language* is \$29.95 plus \$5 for shipping and handling (plus sales tax in California). Volume discounts are available.

Products by Firebelle Productions (continued)

Take Command of Your Writing

Take Command of Your Writing is the first comprehensive guide to more effective writing geared specifically for emergency services personnel. This reference book contains 670 pages packed with useful information on grammar, punctuation, spelling, capitalization, abbreviations and acronyms, numbers, word choice, and more. It contains a chapter on writing for special applications, such as letters and memos, reports, and multiple-choice tests. It even contains a chapter on making documents look more professional and user-friendly.

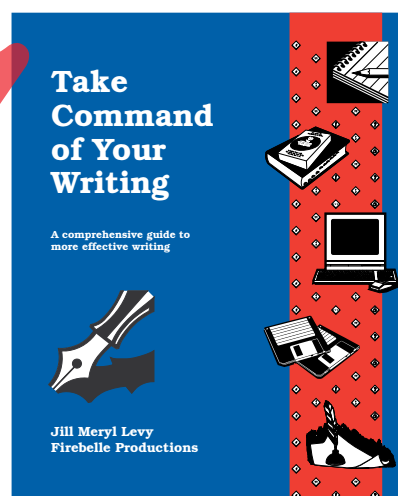
Highlights

- ✓ Each chapter provides a thorough coverage of the rules, answering many questions that other grammar books leave unanswered.
- ✓ The most important rules are highlighted in easy-to-read sidebars for quick reference.
- ✓ Thousands of examples make it easy to understand how to apply the rules.
- ✓ Professionally drawn illustrations provide an attractive, user-friendly format.
- ✓ A thorough index makes information easy to find.

Contents

Take Command of Your Writing contains 17 informative chapters that can help you become a more effective writer.

- ✓ Commas
- ✓ Other Marks of Punctuation
- ✓ Parts of Speech
- ✓ Subject-Verb Agreement
- ✓ More on Verbs
- ✓ Adjectives and Adverbs
- ✓ Pronouns and Antecedents
- ✓ Spelling
- ✓ Compound Words
- ✓ Finding the Right Words
- ✓ Capitalization
- ✓ Abbreviations and Acronyms
- ✓ Numbers
- ✓ More Effective Writing
- ✓ Writing for Special Applications
- ✓ In the Eye of the Beholder
- ✓ Glossary



Price

A single copy of *Take Command of Your Writing* is \$49.95 plus \$5 for shipping and handling (plus sales tax in California). Volume discounts are available.