Module 5:

Practical Chemistry
Module 5: Practical Chemistry

Module Description

This module discusses chemistry and chemical principles in terms of practical applications for fire fighters. The first half of the module focuses on chemical and physical properties; the second half covers chemicals structure hazards, bonding, formulas, and structures.

Prerequisites

- Students should have completed a hazardous materials operations level training program.
- Students should have access to the equipment and materials common to a fire department technician level hazardous materials team.
# Objectives

Upon completion of this module, participants will be able to:

<table>
<thead>
<tr>
<th>Objectives</th>
<th>NFPA Standards</th>
<th>OSHA Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Identify and interpret the types of hazard and response information available from key resources and apply this information for the purpose of hazard analysis.</td>
<td>NFPA 472</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
</tr>
<tr>
<td>• Describe the following terms and explain their significance in the risk assessment process:</td>
<td>NFPA 472,</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
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<tr>
<td>• vapor pressure</td>
<td>4-2.2.1</td>
<td></td>
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<tr>
<td>• vapor density</td>
<td>4-2.2.2</td>
<td></td>
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<tr>
<td>• flash point</td>
<td>4-2.2.3</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
</tr>
<tr>
<td>• acid</td>
<td>4-2.2.4</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
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<tr>
<td>• caustic</td>
<td>4-2.2.5</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
</tr>
<tr>
<td>• air reactivity</td>
<td>4-2.2.6</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
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<td>• Describe the heat transfer processes that occur in a cryogenic liquid spill.</td>
<td>NFPA 472</td>
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<td>• Given the scenario of a domestic gas line break and the readings from a combustible gas indicator, determine the area of evacuation.</td>
<td>4-2.2.2</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
</tr>
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<td>• Identify two methods for determining the pressure in bulk packaging or facility containers.</td>
<td>NFPA 472</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
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<td>• Discuss key classic chemical definitions to better understand the “why’s” of chemical nomenclature and how these chemicals interact with each other and the environment.</td>
<td>4-2.2.3</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
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<td>• Identify additional continuing educational opportunities available to the hazmat technician in the area of chemistry.</td>
<td>NFPA 472</td>
<td>29 CFR 1910.120 (q) (6) (iii) (I)</td>
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<td>4-2.2.4</td>
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Instructor Preparation

Read this entire unit, practice the demonstrations and prepare student stations for hands-on activities. Contact local industrial and/or academic experts to help you conduct the demonstrations and develop relevant hands-on training.

If you intend to do the optional Chemical Structures section beginning on page 5-61, it is preferable to cover that material before the Physical Properties section.

Make sure you are properly staffed to conduct the hands-on exercises. Typically you will need at least one assistant instructor to help you distribute materials and act as a safety officer during hands-on exercises. Capable assistants can divide the class into small groups for selected exercises, minimizing the student-to-instructor ratio, and improving the overall learning experience and class safety.

Research the common hazardous materials in your response area by volume, location, and transportation methods. Obtain MSDSs on those materials and study their physical characteristics. Using hazardous materials that your team is likely to encounter will increase the relevancy of this unit and improve the readiness of your team. Collect adequate technical references (books, MSDSs, databases, specialists, etc.) for the students to refer to in small group activities during the class. Also, collect local case studies that show practical application of the material in this module.

Schedule site visits to industrial locations that manufacture, use, store or transport hazardous materials common in your area. Prepare your students by covering the relevant material in this unit and having them research the hazardous materials prior to visiting the industrial location. Have them predict the types of containers, pressures, states of matter, etc. they expect to see at that location.

Demonstrations and hands-on activities are interwoven with lecture and discussion throughout this unit. The classroom setting should allow for both activities to take place. Typically, putting students at tables with some room to work is sufficient. An alternative arrangement may be to conduct the lecture and discussion activities in a classroom setting and all hands-on activities in an apparatus bay, covered garage, outside, or in an actual chemistry laboratory at a local school.

Explain to students that fundamental concepts of practical chemistry covered in First Responder Operations training will be revisited and expanded in this Technician program. There will be a strong emphasis on hands-on activities, demonstrations, and case studies. Traditional chemistry covering chemical nomenclature, bonding, etc. is included as a supplement at the end of this unit. The “Chemical Structures” portion of this module is optional and reflects a more academic approach to chemistry. You may choose to teach this section if you feel students will benefit from this information, or if they express an interest in these concepts.

Participants should have the opportunity to review this unit before beginning training.
Plan on giving the Prerequisite Quiz at the beginning of this module. If any students fail to answer at least half the questions correctly, they should be directed to read *Training for Hazardous Materials Response: Your Rights and Responsibilities* and Unit 3 of *Hazardous Materials Training for First Responders*. Both programs are available through the IAFF’s Hazardous Materials Department.

**Equipment and Supplies**

**Hazardous Materials Supplies**

- Reference materials (books, computer databases, MSDSs)
- Detection devices
  - CGI/O₂ meter
  - Radiation survey meter w/check source

**Chemicals (hardware store, grocery store)**

- 1 pint of acetone
- 1 jug of Listerine or similar alcohol-based mouthwash
- 1 small container of liquid dishwasher rinse
- 1 small bottle of molasses
- 3-6 additional kinds of commonly found solvents (gasoline, diesel, motor oil, alcohol, cooking oil, etc.)
- 5-10 lbs. of dry ice (look in the yellow pages under ice)
- 1 jug of ammonia cleaning solution (or 1 small box of ammonia inhalant ampules)

**Hardware**

- 65 mm watch glasses (chemical glassware company, approx. $2 ea.) or similar item, 2-3 ea. per group of 2-3 students
- 5 ml disposable pipettes (chemical supply company, approx. $32/box of 500)
  - 1 box of 500 (you’ll supply a dozen or so to each group of 2-3 students)
- pH paper (chemical supply company, approx. $10/box)
  - 1 box per group of 2-3 students (pH range of 0-14) or pH indicator strips
- KI paper strips (oxidizer test strips)
- 1 test tube rack per group of 2-3 students, approx. $12 ea.
- 1 box of test tubes, 13x100mm, borosilicate, approx. $50/box of 250
  - (you’ll supply a dozen or so to each group of 2-3 students)
- 1 metal test tube holder (clamp) per group of 2-3 students, approx $3 ea.
- Small aluminum pans, 2 per group of 2-3 students
- Tongs or forceps for holding matches at least 6” away from your hand
- 1 gallon Rubbermaid™ or Tupperware™ jug, one of the open top ones with a lid that covers the entire opening (like a small open top drum); it should be made of relatively
pliable rubberized plastic. Generally the clear ones are too brittle. These should be available in most supermarkets in the kitchen utensil ‘plastic container’ area.

- 12 candles
- Lighter
- 1 box of wooden matches per group
- 2 wooden clothespins per group (used to hold lit matches in Flash Point exercise)
- 1 small funnel
- Roll of aluminum foil
- 1 permanent marking pen for each group (to write on the side of test tubes)
- Paper towels
- Squirt bottles w/water for cleaning purposes (1 per group)
- Food coloring
- 2-liter pop bottle
- 3 each 5-gallon buckets
- Hose and source of water for outside activities
- Sticks or wooden spoons for stirring contents of 5-gallon buckets
- 1 road flare
- Chemical cold packs and chemical heat packs
- SCBA cylinder

**Safety Items**

- Duct tape
- Fire extinguisher
- Fire fighter gloves
- Approved safety glasses for everyone in the room
- Disposable gloves (check compatibility with the solvents you’ll be using)
- Eyewash station
- Sink for washing hands when exercise is over
- Paper towels, squirt bottles of water and garbage cans for cleanup purposes
- Marked containers to hold used glass test tubes as waste (milk jugs work well)
- Marked containers to hold waste flammable solvents (1 gallon plastic gas can)
- Tabletops with 2 foot long strips of aluminum foil
- Adequate ventilation so fumes don’t build up in the training room
- MSDSs for the hazardous materials you are bringing into the room

**Chemical supply companies**

- Check your local phone book under chemical supplies
- All World Scientific, WA, 800-289-6753
- HazTech Systems, Inc., CA, 800-543-5487
Audiovisual Equipment

- VCR and videos:
  - Team Member: Properties of Hazardous Materials
  - Team Member: Basic Chemistry
- Recommended videos:
  - Chemical Manufacturers Association lending library—(703) 741-5726
    - Flammable Solids
    - Oxidizers
  - Emergency Film Group—(800) 842-0999
    - Introduction to Hazardous Chemicals
    - Hazardous Wastes
      The Emergency Film Group also produces training videotapes on specific chemicals and classes of chemicals.
  - BLEVE (Boiling Liquid Expanding Vapor Explosions) NFPA
    - BLEVE: Response and Prevention (Canadian version)
      Transport Canada Communications Group—(613) 993-0055 or
      Library Research Services Centre—(613) 990-2309
      Note: The videotape discusses units of measure in metric terms. If you obtain this videotape, it may be helpful to convert distances, quantities and other measurements before you discuss the tape with your students.
- Transparencies and overhead transparency projector

References

- Hazmat databases (CAMEO, CCINFO, etc.)
- Maps and diagrams (facility diagrams, preplans, LEPC info, etc.)
- Monitoring equipment (available to your hazmat team)
- Reference manuals (SAX - Dangerous Properties of Industrial Materials; NIOSH Pocket Guide to Chemical Hazards; CHRIS; Railroad Manuals, etc.)
- Technical information centers (CHEMTREC, CANUTEC, SETIQ, local Poison Control Centers)
- Technical information specialists (local industry specialists, chemists, etc.)
- Chemical Manufacturers’ Association (CMA)
  1300 Wilson Blvd.
  Arlington, VA 22209
  800-262-8200
Approximate Length

This module requires approximately three to five days to complete. As a competency-based program, the length of instruction will be determined by:

- The experience and capabilities of the students and instructors
- Whether you choose to conduct the optional “Chemical Structures” section
- The degree of customization that the instructors include in this program with relation to local hazardous materials and industries
- The use of specialists to provide hands-on demonstrations and instruction
- The use of site visits to industries in the team’s response area that manufacture, use, store or transport hazardous materials
Module 5
Prerequisite Quiz

1. Air is assigned a vapor density of:
   A. 0
   B. 1
   C. .7
   D. Air has no vapor density

2. If a material is “water miscible”, it is:
   A. Insoluble in water
   B. Partially soluble in water
   C. Soluble at a one-to-one ratio
   D. Infinitely soluble in water

3. Substances with high vapor pressures are:
   A. More likely to evaporate
   B. Less likely to evaporate
   C. More likely to sink in air
   D. More likely to rise in air

4. The rate of a chemical reaction can usually be increased by:
   A. Increasing temperature and concentration and reducing pressure
   B. Reducing temperature and pressure and increasing concentration
   C. Reducing pressure and increasing temperature and concentration
   D. Increasing temperature, concentration, and pressure

5. Vapors and gases with molecular weights greater than 29 tend to:
   A. Rise in air
   B. Sink in air
   C. Evaporate quickly
   D. Evaporate slowly

6. Although specific gravity has no unit of measure, it does have a value relative to:
   A. The weight of air
   B. The weight of water
   C. The effect of gravity
   D. Parts per million

7. “Ignition temperature” refers to:
   A. The flash point
   B. The upper explosive limit
   C. The flammable range
   D. The temperature at which a material burns without a flame
8. A “pyrophoric” material describes a material that spontaneously ignites in air at or below:
   A. 130°F
   B. 100°F
   C. 85°F
   D. 32°F

9. All gases have vapor pressures higher than:
   A. 0 mm Hg
   B. 120 mm Hg
   C. 540 mm Hg
   D. 760 mm Hg

10. A chemical’s “explosive limit” depends on its:
    A. Ignition temperature
    B. Specific gravity
    C. Reactivity
    D. Concentration
Introduction

Questions

1. Which is more flammable, gasoline or diesel fuel?

2. Which is more flammable, methyl ethyl ketone or toluene?

3. Will ammonia vapors tend to rise or sink in air?

4. Why is propane found as both a gas and liquid in five-gallon propane bottles? What is the typical pressure in those bottles? How does this compare to an industrial sized tank of propane?

5. How can you evaluate whether a material will readily evaporate, posing a potential inhalation or flammable threat?

6. Why doesn’t grease dissolve in water? Why does soap dissolve in water, and dissolve grease?

This module will focus on a practical approach to chemistry often described as “bucket or street chemistry” by fire fighter hazardous material responders. Why do you need to understand chemical principles? Consider the following:

Your department is on-scene at a propane gas leak from a rail car. Will the gas rise or sink? How does that affect your response?

Your department responds to an incident involving a solvent leak at an industrial facility. The MSDS indicates that the vapor pressure is 20 mm Hg and the flash point is 350°F. What does this tell you about the flammability of the product. What type of cleanup methods should be used?

Your department is on-scene at a loading dock where a container of sulfuric acid is leaking. Some of the acid has already entered a storm drain; you are able to contain the rest. Will simply pouring a few gallons of water down the storm drain remove the environmental threat to a nearby stream?
These are examples of how understanding the physical properties of a material can help protect you and other team members, and enable you to take effective action at the scene of a hazardous material incident.

Also, risk assessment is more accurate if you have a background knowledge of chemicals and their properties. If risks are accurately evaluated, then:

- You are able to develop the most appropriate strategies and tactics.
- You can select the equipment and protective clothing that will offer the greatest protection.
- The effects of exposure become clearer if you have a knowledge of chemicals and their properties.

This unit will focus on hazardous materials most commonly encountered in North America, including gasoline, diesel, acetone, natural gas, propane, ammonia, sulfuric acid, hydrochloric acid, nitric acid, caustic soda and 111 trichloroethane. Additional hazardous materials, those common in your response area can be included in accompanying exercises. Practical information covered in this module can also be applied to materials that are less common or unique to your location.

Know what you’re dealing with. It is strongly recommended that fire fighter hazardous materials teams work closely with manufacturers, distributors and users of hazardous materials used in their area. Pre-planning and training with these organizations can help teams determine the type of hazard they may encounter, develop strategies for controlling these hazards, and identify specialists within those organizations who can provide timely, safe and practical information during an actual incident. In addition, chemical specialists are often available from governmental groups including water and wastewater treatment labs and educational institutions. As with fire fighting, there is little substitute for experience when it comes to dealing with chemistry and hazardous materials. Start by learning the basic language of chemistry and developing a contact list of experts, then improve your chemistry skills as you progress.
A section on standard chemical terminology is included to broaden your knowledge base and provide valuable perspective on some of the ‘why’s behind the practical chemistry approach used in this unit. Additional academic chemistry instruction can be obtained through community colleges, universities, textbooks and workbooks, or computer based courses. Technicians are encouraged to broaden their chemistry backgrounds in a manner that best prepares them for the hazards they are likely to encounter and is commensurate with the time and resources they have available to maintain those skills.
**Physical and Chemical Properties**

**Temperature**

**Question**

Does water boil at a lower temperature at 10,000 feet than it does at sea level?

**Definition and Measurement**

**Temperature** is a scale measure of heat energy and is key in determining how materials will react. Temperature can be measured in Centigrade (°C) (also known as Celsius) or Fahrenheit (°F) units. The relationship between the two scales is illustrated below.

To convert between these two temperature scales, the following formulas are used:

- degrees Centigrade = \( \frac{5}{9} \times (\text{degrees Fahrenheit} - 32) \)
- degrees Fahrenheit = \( \frac{9}{5} \times \text{degrees Centigrade} + 32 \)

<table>
<thead>
<tr>
<th>Centigrade</th>
<th>Fahrenheit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Freezes</td>
<td>0°C</td>
</tr>
<tr>
<td>Body Temperature</td>
<td>37°C</td>
</tr>
<tr>
<td>Water Boils</td>
<td>100°C</td>
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</tbody>
</table>

Throughout this material, the Fahrenheit scale and other units of measurement customary in the United States will be used. Responders, however, should also be familiar with other systems, such as the metric system, for measuring temperature as well as pressure and volume.
**Melting Point**

**Melting point** is the temperature at which a solid becomes a liquid. When this happens, the tightly compacted molecules of the substance gain energy. There is movement among the molecules as those with higher energy at the surface break away and enter the liquid state.

**Freezing Point**

The **freezing point** is the temperature at which a liquid becomes a solid. When this happens, the molecules lose energy, for example, as a result of cooling. At some temperature, unique to each substance, the rate of solid particles becoming liquid and the rate of liquid particles becoming solid is the same. That is, the melting point of a solid is the same as the freezing point of its liquid. For example, the melting point of ice is 32°F and the freezing point of water is 32°F.

**Boiling Point**

As the temperature of a liquid increases, the molecules of a liquid gain energy and, as a result, move around more. At the **boiling point** of liquid, the most highly energized molecules rise to the top. Once they reach the surface of the liquid, these molecules enter the surrounding air as vapor. The boiling point of a liquid is affected by atmospheric pressure, that is, the pressure the atmosphere exerts on the liquid. The influence of pressure will be described in greater detail later in this unit, but it is important to know that the standard or normal boiling point of a liquid is its boiling point at one standard atmosphere, which equals 760 mm Hg on a barometer, or 14.7 psi—pounds per square inch. As discussed later, the boiling point of a liquid is related to the liquid’s vapor pressure.

You respond to a liquid chemical spill involving a material with a boiling point of 100°F. The outside temperature is 80°F. Because the chemical is near its boiling point, it will be evaporating very quickly. There will be a higher concentration of vapors in the atmosphere. As a result, you need to be concerned with the vapors as well as the liquid.
States of Matter

At normal room temperature and pressure, all substances exist in one of three physical states: gas, liquid, or solid. Substances can change from one state to another as changes occur in temperature or pressure, or both. A change in a material’s state of matter can affect the degree of hazard posed by the material and consequently, appropriate tactics for controlling the hazard. For example, a toxic substance may be more hazardous in a gaseous state than in a liquid state because it is easier to inhale when it is in the gaseous state.

It is important to keep in mind that a change from solid to liquid or gas is a physical transformation, not a chemical one. Often, temperature is responsible for the change, but an increase or decrease in pressure can also bring about a change in state. The effects of pressure will be discussed later in this unit with regard to compressed gases.

Compressed Gases

- Pressurized (Gaseous state)
- Liquefied (Liquid state)
- "liquefied" cryogenic

Categories of Compressed Gases

Solids

A solid is a substance that retains a definite size and shape under normal conditions. The molecules (individual units of matter) that make up the substance are compacted together in a stationary, regular, and ordered shape. The solid state is usually the most dense of the three states of matter. (Water is one exception, with ice being less dense than water.) Solids become liquid at the melting point of the substance. A few solids can change directly to a gas without going through a liquid state; this process is known as sublimation. Carbon dioxide (dry ice) or moth balls (naphthalene) are examples of solids that sublimate.
**Liquids**

A **liquid** is a substance that flows easily and has a specific volume, but no specific shape. Liquid molecules are not tightly bound together, allowing liquid to flow. The temperature at which a liquid becomes solid is the freezing point. Evaporation is the process of a liquid changing to the gaseous state which occurs at the substance’s boiling point.

**Gases**

A **gas** is a substance that expands to fill any given volume, has no independent shape, and is readily compressed. Gases are the least dense of the three states. A gas begins to condense to form a liquid when it is cooled to its boiling point. Gas molecules move with a great deal of energy, often away from each other. This action is what creates pressure.

**Activity (Optional)**

**Vapor Pressure**

**Questions**

1. A hazardous materials team with a combustible gas meter responds to a 4” rupture in a 30” natural gas pipeline under 750 psi. It will take an hour or two for the pipeline company to remotely valve off the line allowing the remaining pressurized gas to escape. The temperature is 70°F with winds less than 2 mph. The terrain is hilly and lightly populated. What are the immediate hazards? What should they do?

2. A hazardous materials team responds to a five-gallon spill of muriatic acid in an asphalt parking lot. What are the immediate hazards? What can be done to clean up the spilled acid?

3. A hazardous materials team responds to a one pound spill of grungicide. Chemical information on the product is researched in books, in CAMEO and on the
**MSDS. The vapor pressure is 0.003 mmHg. Is this product likely to evaporate? Does this tell you about the toxicity of the material?**

**4. A hazardous materials team responds to a 500 gallon spill of an industrial solvent. Will the vapors tend to sink and move downward toward the school below?**

**Definition and Measurement**

Many liquids pose the greatest hazard to health when they are in a gaseous or vapor state. Flammable materials in a gaseous or vapor state are more hazardous than those in liquid form, because the vapor from a liquid burns and is more readily inhaled.

**Vapor pressure** is a measure of the ability of a material to evaporate, that is, change from a liquid state to a vapor or gaseous state. The pressure exerted by the vapor above a liquid at a certain temperature is called its equilibrium vapor pressure. The higher the vapor pressure of a material, the faster it will evaporate. Comparing the vapor pressures of water and acetone, it is evident that acetone, with a vapor pressure of approximately 180 mm Hg, will evaporate more quickly than water, with a vapor pressure of 25 mm Hg.

In addition to vapor pressure, temperature also influences evaporation. As temperature increases, vapor pressure increases. For example, water evaporates faster at 200°F than at 40°F. Molecules with more energy (heat) are more likely to move from a liquid state to a gaseous state than molecules with less energy.

The effect of temperature is also easily demonstrated by comparing vapor pressures:

- Water at 212°F = VP of 760 mm Hg—water rapidly evaporates at its boiling point
- Water at 122°F = VP of 93 mm Hg
- Water at room temperature = VP of 25 mm Hg

Vapor pressure and boiling point are related. At its boiling point, 212°F (100°C), the vapor pressure of water is equal to atmospheric pressure (760 mm Hg). In fact, boiling
point is defined technically as the temperature at which a liquid’s vapor pressure equals atmospheric pressure.

The units most often used to describe vapor pressure are mm Hg (millimeters of mercury). These units are probably familiar to fire fighters as they are often used to describe barometric or atmospheric pressure as well as blood pressure. Some examples of vapor pressures at room temperature are:

- Acetylene gas: VP of approximately 2500 mm Hg (gas)
- Acetone: VP of approximately 180 mm Hg on a warm day
- Water: VP of approximately 25 mm Hg (evaporates slowly)
- Most solids: VP of near 0 mm Hg (do not evaporate)

Another term often used in conjunction with pressure is atm (atmosphere). One atmosphere is equal to 760 mm Hg, the pressure that the atmosphere exerts at sea level.

Common units for measurement of one atmosphere of pressure are: 1 atm = 760 mmHg = 14.7 psi = 760 torr = 101 kPa.

Materials with vapor pressures greater than atmospheric pressure (760 mm Hg) evaporate immediately and are gases.

Substances that have high vapor pressures at room temperature, such as acetone and gasoline, evaporate readily and are sometimes loosely termed volatile. Substances that have low vapor pressures at room temperature, such as solids, are sometimes loosely called nonvolatile, meaning that they do not evaporate easily.

While off-loading a tank container at a warehouse, workers spill about 100 gallons of toluene diisocyanate (TDI). The vapor pressure of TDI is around .05 mm Hg at 77°F, but much lower under cold conditions. So if the weather is warm, the TDI may evaporate quickly. If not, there may be liquid remaining and your control techniques will be different.
Activities

Vapor Density

Questions

1. Can you list three hazardous materials that tend to be heavier than air?

2. Can you list three hazardous materials that tend to be lighter than air?

3. Why is it important to know whether a hazardous material tends to be heavier or lighter than air?

Definition and Measurement

Some gases and vapors such as carbon dioxide, are heavier than air, causing them to sink. Others, such as helium, are lighter than air and tend to rise. Gases and vapors with vapor densities around 1.0 will be influenced more by wind conditions and temperature than by their vapor densities. **Vapor density** is the measure of this tendency to either sink or rise.

Air has a vapor density of 1.0. Vapors or gases with a vapor density greater than 1.0 tend to sink in air. Propane with a vapor density of 1.5 tends to settle in low-lying areas. Vapors or gases lighter than air, such as methane (with a vapor density of 0.55), tend to rise. Vapor densities are often listed in reference material with the notation ‘Air = 1’ as a reminder.

Another common way to determine the vapor density of a gas or vapor is to research its molecular weight (MW). This property can often be found on the MSDS and is listed in the NIOSH Pocket Guide. Again, there is a simple rule for determining whether a gas or vapor will rise compared to air, based on its molecular weight. Air has a molecular weight of 29. Materials with a molecular weight more than 29 (propane, MW = 44) will tend to sink. Materials with a
molecular weight less than 29 will tend to rise (methane, MW = 16).

Gases/vapors that tend to rise

- hydrogen
- ammonia
- acetylene and carbon monoxide
- propane, carbon dioxide
- gasoline vapors

Gases/vapors that tend to sink

The property of vapor density is particularly important in confined spaces. Gases and vapors that are heavier than air, such as propane and carbon dioxide gas, can accumulate in low areas of confined spaces. This accumulation causes air to be displaced. Entry to such a space without self-contained breathing apparatus will quickly cause unconsciousness and death due to lack of oxygen. This can also occur in terrain where low-lying areas allow the pooling of gases that are heavier than air. Detection equipment must be used to assess the risks involved in entry to such areas and confined spaces. Vapor density becomes less significant as gases and vapors mix with air. Gases and vapors mix more quickly when air is turbulent, for example, when mechanical ventilation is being used.

Your team responds to a leaking gasoline tank truck near a ditch. There is little wind movement. Where do you think the highest concentration of gasoline vapors might be? If you understand vapor density, you know they will tend to collect in the ditch. The most flammable atmospheres will be in this area.

Activities
Flash Point

Question

Of the solvents used in the vapor pressure demonstration, which are the least flammable? Which are the most flammable?

Definition and Measurement

The minimum temperature of a liquid at which a spark or flame can cause an instantaneous flash in the vapor space above the liquid is called flash point. A flammable liquid, by NFPA definition, is a liquid that has a flash point below 100°F (38°C). Liquids that have flash points of 100°F to 200°F are classified as combustible liquids. The United States Department of Transportation defines a flammable liquid as a liquid with a flash point below 140°F (60°C). The lower the flash point, the higher the flammability of the liquid.

Some references describe the flash point of a flammable liquid in terms of “o.c.” or “c.c.” These abbreviations simply refer to the method used to test the flash point. The term o.c. stands for open cup and c.c. for closed cup types of testing chambers. Both tests measure temperature readings using an open flame that is passed over the sample as a source of ignition. A sample is placed into a cup and the temperature is lowered well below the flash point. The flame is turned on and the temperature of the substance is slowly raised. When a “flash” occurs, the liquid has reached its flash point. Open cup tests approximate the conditions found in an open puddle of liquid. Closed cup tests approximate the conditions in closed tanks or vessels.

Again, flash points are expressed in terms of temperature of the liquid being tested. The lower the flash point of a liquid, the higher its flammability.
For example:

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Flash Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>gasoline</td>
<td>-45°F</td>
</tr>
<tr>
<td>acetone</td>
<td>0°F</td>
</tr>
<tr>
<td>kerosene</td>
<td>150 to 185°F</td>
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</tbody>
</table>

Generally, liquids do not burn. Rather, it is the vapors of flammable liquids that burn. Determining how readily a liquid will vaporize is one consideration when confronted with a flammable liquid. Other properties, such as solubility, will also influence the choice of appropriate control techniques.

Remember, liquids that are classified as FLAMMABLE or COMBUSTIBLE LIQUIDS are often very toxic as well.

*Your team responds to a solvent spill with a material that has a flash point of 50°F. The outside temperature is also 50°F. If you understand flash point, you know that while the solvent will not spontaneously ignite, it will produce enough vapors to form an ignitable mixture. You should make sure all possible ignition sources are shut off.*

*Your team responds to a liquid hazardous materials release with a material that has a flash point of 350°F and is described in references as “may burn.” There is also a diesel fuel leak. Which spill poses the greatest flammability hazard? If you understand flash point, you know that diesel fuel (with a flash point of 150°F to 185°F) is the lesser hazard.*

**Activities**
Concentration

Questions

How does the principle of concentration apply to the following?

1. Fire fighting foam, applied at a specified percentage

2. Medications that are delivered are often dissolved in a water based solution at a certain concentration (milligrams/liter)

3. ‘Wetting’ agent added to a tank in a specified concentration

Definition and Measurement

The term concentration refers to how much of one material there is in relation to another. Percent (%), parts per million (ppm), and parts per billion (ppb) units are used for measuring the concentration of gases and vapors in air.

One part per million is equal to 1/1,000,000. For example, one cup of ammonia gas mixed with one million cups of air yields one part per million of ammonia gas. Most people can smell ammonia at around 1 to 5 ppm. The concentration of ammonia at 1 ppm is roughly equivalent to one cup of a gas in a 32 by 33 foot room with an eight foot ceiling.

“Parts per billion” indicates extremely minute concentrations of substances in liquids, solids, or gases. One part per billion equals 1/1,000,000,000 or .001 ppm.

Solids can also be measured in terms of their weight, in grams (g), milligrams (mg = 1/1,000g), or micrograms (µ = 1/1,000,000g).

Concentration is one factor that determines the toxicity of a substance. The following poison lines illustrate the toxicities of hydrogen sulfide, methyl chloride, and gasoline according to concentrations.
**POISON versus FLAMMABLE**

Hydrogen Sulfide (H₂S)
(not to scale)

<table>
<thead>
<tr>
<th>%</th>
<th>LFL</th>
<th>UFL</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.3</td>
<td>45</td>
<td>43,000</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td>450,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1,000,000</td>
</tr>
</tbody>
</table>

**Flammable Range**

- 100 ppm IDLH (one, one ten thousandth %)
- 15 ppm TLV-STEL
- 10 ppm TLV-TWA (one, one hundred thousandth %)

---

**POISON versus FLAMMABILITY**

Methyl Chloride (CH₃Cl)
(not to scale)

<table>
<thead>
<tr>
<th>%</th>
<th>LFL (ppm)</th>
<th>UFL (ppm)</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.1</td>
<td>17.2</td>
<td>81,000</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td>170,200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1,000,000</td>
</tr>
</tbody>
</table>

**Flammable Range**

- 2,000 ppm IDLH (.2 %)
- 100 ppm TLV-STEL (one, one ten thousandth %)
- 50 ppm TLV-TWA (one half, one ten thousandth %)
POISON versus FLAMMABILITY
Gasoline
(not to scale)

0 %
0 ppm

1.4% (LFL)
14,000 ppm

7.4% (UFL)
74,000 ppm

100 %
1,000,000 ppm

300 ppm TLV-TWA (three ten thousandths %)
500 ppm TLV-STEL (five ten thousandths %)
One ppm of a solid in a solid is equal to 1 microgram (1/1,000,000 of a gram) per gram. So, a plot of soil contaminated at a level of 25 micrograms of pesticide per gram of soil is contaminated at the 25 ppm level.

For the concentration of a solid in a liquid, 1 ppb is equal to 1 microgram of substance per liter of liquid. So, a river contaminated at a level of 10 micrograms of pesticide per liter of water is contaminated at the 10 ppb level.

**Activities**

**Flammable Limits**

**Questions**

1. Of propane and butane, which has the greater flammable range?

2. Which is flammable at a lower concentration? Are both gases flammable at room temperature?

**Definition and Measurement**

**Lower Explosive (Flammable) Limit (LEL) and Upper Explosive (Flammable) Limit (UEL)** refer to the concentration of a flammable liquid (in its vapor form) or a flammable gas in air. Below the LEL, the mixture is too lean to ignite. Above the UEL, the mixture is too rich to ignite. Between the LEL and UEL, the mixture is said to be explosive or flammable.

Temperature affects the flammability range of substances. Figure 5.1 illustrates the relationship between increasing temperature and the concentration of a vapor in the air. As the temperature increases, more of the liquid is vaporized and the flash point is reached.

It is important to keep in mind that adding air to the mixture (by ventilating an enclosed space, for example) will bring the concentration back into the flammable (or explosive) range.
Detection devices are used to measure the concentration of vapors or gases in air. The most common instrument used for this purpose is the combustible gas indicator (CGI). The CGI measures the concentration of a gas or vapor in air as it relates to the explosive limit of the gas or vapor being measured. It is important to understand the significance of its readings. For example, if you obtain a CGI reading of 25% LEL near a leaking propane tank, the air contains one fourth of the propane needed to readily ignite. References give the flammable range of propane as 2.1% to 9.5%. The CGI is, therefore, reading that 0.53% of propane exists in the air (that is, 25% of the LEL of 2.1%). Percentages can be converted to parts per million (ppm) with the formula: 1% = 10,000 ppm. So the concentration in the above example is 5,300 ppm. Additionally, the conversion factor or response curve for the type of CGI must be factored in to determine the true concentration.

Another method for calculation of true concentration is to first convert the LEL to parts per million. In the above example, an LEL of 2.1% volume in air can be converted to 21,000 ppm. Next, the 21,000 ppm is multiplied by the CGI reading of 25%, which is 5,250 ppm. An example conversion factor might be 1.5. The 5,250 ppm is multiplied by the conversion factor of 1.5, which provides a true concentration of 7,875 ppm, plus or minus the accuracy of the CGI.

You respond to a rupture in a natural gas pipeline. The temperature is moderate and there is no wind. Would you expect concentrations to be above the UEL, and if so, where? Concentrations in the pipeline would be above the UEL and most likely continue a short distance from the opening. As the gas leaked out it would mix with air and enter the flammable range. Further from the opening, it would dilute further, eventually passing below the LEL concentration.
Flammable Solids

Questions

1. Identify at least one flammable solid.

2. Identify the common flammable solid carried on almost every emergency vehicle.

Definition

As fire fighters know, most liquids and solids can burn if subjected to enough heat. DOT (Department of Transportation) has created a class for substances that either self-ignite, burn spontaneously when mixed with air or water, or burn so vigorously they are difficult to extinguish using normal methods. DOT has created a special class for these substances called flammable solids.

Flammable solids are materials that can ignite through friction, absorption of moisture, or chemical reaction. However, they are not classified as explosives. Flammable solids ignite readily and burn vigorously. Some flammable solids can autoignite, which means they can begin to burn without a flame or other ignition source. Gases or vapors
are consumed in fire as quickly as they are produced, and
the material continues self-sustained combustion. Pyrophoric solids spontaneously ignite in air at or below 130°F.

**Specific Gravity**

**Questions**

1. What are examples of solids and liquids that float?
2. What are examples of solids and liquids that sink?
3. Why is it important to know whether a hazardous material will either float or sink in water?

**Definition and Measurement**

Specific gravity is the weight of a material compared to the weight of a reference substance, usually water, with a specific gravity of 1.0. There are no specific measurement units used for specific gravity. If a liquid or solid weighs more than water, it has a specific gravity greater than 1.0 and will sink in water. Materials with a specific gravity less than 1.0 will float on water. For example, gasoline with a specific gravity of 0.9 floats on water. Mercury, with a specific gravity of 13.5, sinks in water.

Your department responds to a spill of toluene from a rail car. The chemical is flowing into a stream. What actions can you take to help contain the toluene that has already entered the stream?

If you are familiar with the specific gravity of toluene (0.87), you know it will float on water. An underflow dam may help contain some of the spilled toluene. A vacuum truck may be able to pick up some of the toluene from the surface of the containment area.

**Activities**
Water Solubility

Question

Is it possible to dissolve a pound of sugar in a cup of water? Why or why not?

Definition and Measurement

Solubility refers to the degree that one substance will mix completely with another substance. The mixture is called a solution. The substance present in a greater amount is called the solvent. Water can be a solvent, though in common usage the term refers to petroleum-based chemicals. The substance present in lesser amount is called the solute. A solute may be a gas, liquid, or solid.

If a liquid mixes completely in a solvent, it is said to be miscible with that solvent. For example, alcohols such as methyl, ethyl, and propyl alcohol are miscible with water. Water miscible means that the liquid is infinitely soluble in water. Regardless of the amount of methyl alcohol added to water, it will all mix. Most liquids (and all solids) are either very soluble, soluble, sparingly soluble, or insoluble. Any liquid that is soluble but not completely miscible, has a solubility limit. Solubility limits are usually expressed as percentages. For example, toluene is only 0.07% soluble in water.

Gasoline is not water soluble, and is therefore immiscible. If a liquid is not miscible with a solvent, the excess that cannot dissolve will form a separate layer. This layer will float if it is lighter than the solvent, or sink if it is heavier than the solvent.

Solubility is related to the polarity of the solute relative to the polarity of the solvent.
Polarity

Polarity results from an uneven distribution of positive (+) and negative (-) charges within a molecule. Some molecules are highly polar, some nonpolar, and many have both polar and nonpolar parts.

Polar Substances

In polar substances, positive and negative charges are present, similar to a bar magnet. In a water molecule, oxygen has a strong affinity for electrons, as compared to hydrogen. The oxygen atom utilizes the electron that each hydrogen has. This makes one end positive and the other negative. For example, water is a highly polar solvent (see figure below). Other polar materials will dissolve readily in water, making dilution possible.

\[
\begin{array}{c}
\text{O}^{-} \\
\text{H}^{+} & \text{H}^{+}
\end{array}
\]

Water Molecule

Liquids whose molecules are polar, such as water and many alcohols, dissolve when mixed together. The structure of ethyl alcohol in the figure below depicts the polarity of this molecule. Many other solvents other than alcohols are also polar. Tactically, polarity is significant in controlling vapor production. Foam that is U.L. listed for controlling flammable vapors from a polar solvent is necessary. Typically, most foam concentrates that are listed for polar solvent application are applied at a 6% concentration.
Nonpolar Substances

The molecules of nonpolar substances have positive and negative charges evenly distributed within their structures thereby balancing each other out. There are no significant separations between positive (+) and negative (-) charges, giving them an overall neutral charge, like hexane, represented below.

Nonpolar materials, such as most oils, gasoline, and other petroleum based products, will not readily dissolve in water. Adding water to a nonpolar material, such as a gasoline fire, will only spread the nonpolar molecules. Nonpolar and polar molecules (such as oil and water, respectively) don’t readily mix.

Polar/Nonpolar Molecules

Some molecules have both polar and nonpolar sections. Ethyl alcohol, as shown previously, is one example. Soaps are another example. Though soaps dissolve in water (a polar substance), they are also able to remove grease (a nonpolar substance) during washing. This is because soap molecules have small polar ends attached to very large nonpolar sections. The grease particles attract the nonpolar sections of the soap molecules, leaving the polar ends protruding from the grease particles to dissolve in water. In this way, the grease particles are coated with a water soluble layer of soap molecules. When decontaminating clothing and equipment that are contaminated with oily substances, soapy water may be the only decontamination solution needed.
The same principles that apply to the solubility of liquids apply to solids. Solids whose molecules are polar will be soluble in polar solvents. The molecules of table salt are polar (see below), so they will dissolve in water, but not in gasoline.

\[
\text{Salt Molecule} \\
\text{\textcolor{white}{(+)}Na — Cl\textcolor{white}{(-)}}
\]

Unlike polar liquids, however, polar solids are not miscible with water. They have a limited capacity to dissolve in water. For example, table salt is water soluble, but not infinitely. If water and salt are mixed, a certain amount of the salt will dissolve. After enough salt was been added, the water will be “saturated” and unable to dissolve any more salt.

**Activities**

You respond to a liquid spill at a garden center and your chemical protective clothing becomes contaminated with malathion, a pesticide with a solubility of 0.02%. What type of decontamination solution should you use? Is water alone sufficient?

If you understand polarity, you know that a polar/nonpolar solution will be necessary because malathion will not dissolve in water alone (a polar liquid).
Oxidation

Questions

1. Does diesel fuel burn?

2. What happens if diesel fuel is mixed with ammonium nitrate?

3. What common materials do you work with that are packed with oxidizers, and burn very rapidly with lots of energy?

Oxidizers and Peroxides

Oxidizers

Oxidizers can make a fire burn hotter, faster, and may cause explosions. Some oxidizers are unstable or very reactive. Oxygen is an example of a powerful oxidizer, but by itself it is nonflammable. When added to other materials (even nonflammable protective clothing) it dramatically accelerates combustion. Oxidizers often continue to burn even when sources of air are removed from the fire because they provide their own oxidizing capability and usually need no air to burn.

Inorganic Peroxides

Inorganic peroxides act as both oxidizers and corrosives. One common inorganic peroxide is hydrogen peroxide. Medicinal hydrogen peroxide is typically only in a 3% solution mixed with water. Commercial grade hydrogen peroxide can be found from 30% to 70% in strength. A spill of concentrated hydrogen peroxide can spontaneously combust if mixed with organic materials such as wood, leaves, cardboard, or other Class A materials. Peroxides are capable of supporting combustion, perhaps explosive combustion, even in the absence of air.

Organic Peroxides

Organic peroxides typically contain both an oxidizer and a compound that can act as a fuel. The fire tetrahedron
model suggests that for fire to occur, heat, oxygen, fuel, and 
a chemical reaction are necessary. An organic peroxide has 
the fuel and oxygen built into the molecule. Consequently, 
for most of these materials, the application of a small 
amount of heat is all that is necessary for a fire or explosion 
to occur. For this reason, unless research indicates other-
wise, organic peroxides should be treated as Class 1 explo-
sives by emergency responders.

Common uses for organic peroxides include catalysts and 
initiators in polymerization reactions. Organic peroxides 
can be liquids or solids and may be dissolved in a solvent, 
sometimes a flammable one. Often, organic peroxides are 
shipped refrigerated and stored in cold storage cabinets or 
special refrigerators.

The DOT classifies organic peroxides into seven categories: 
Types A, B, C, D, E, F and G. Type A organic peroxides 
are the most unstable and are forbidden in transport. Type 
G are considered relatively stable for organic peroxides. 
Common organic peroxides include: methyl ethyl ketone 
peroxide (MEKP), benzoyl peroxide and ether peroxides.

**Chlorates and Perchlorates**

Chlorates and perchlorates are unstable molecules con-
taining excess oxygen. While they are not flammable, they 
decompose rapidly when subjected to heat, releasing oxy-
gen and supporting the rapid burning of any nearby combus-
tible material. The disastrous explosion at Henderson, 
Nevada in May, 1988 demonstrated the behavior of one of 
these chemicals, ammonium perchlorate. In the plant in 
which the explosion occurred, ammonium perchlorate was 
mixed with combustible materials to produce rocket fuels. 
A fire, accidentally started by a welding torch, spread to 55-gallon plastic drums containing ammonium perchlorate. 
The product exploded as the fire reached them, resulting in 
a series of seven large explosions. The two largest explo-
sions reportedly registered 3.0 and 3.5 on the Richter scale 
at an observatory in California.

**Activities**
Polymerization

Questions

1. What are some examples of polymers in the classroom?

2. What are some examples of materials in a manufacturing environment that may be polymerized?

Definition and Measurement

Polymerization is the process of combining single chemical units—monomers—to form larger chemical units called polymers. A monomer can be thought of as one link in a chain, with all of the links forming a polymer chain. Though many monomers that form polymers are classified only as flammable or combustible liquids or gases, polymerization can be explosive. Table 5.1 on the following page lists some common monomers.

Activity
### Table 5.1 Common Monomers

<table>
<thead>
<tr>
<th>Name</th>
<th>Physical Description</th>
<th>Properties</th>
<th>Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile</td>
<td>Colorless to pale yellow liquid with a pungent odor</td>
<td>Boiling point: 171°F</td>
<td>Polymerization may occur spontaneously in absence of oxygen or with exposure to light or excessive heat or in presence of alkili</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LEL: 3%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>UEL: 17%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor pressure: 83mm</td>
<td></td>
</tr>
<tr>
<td>Butadiene</td>
<td>Colorless gas with a mild aromatic or gasoline-like odor, a liquid below 24°F, shipped as a liquefied compressed gas</td>
<td>Boiling point: 24°F</td>
<td>May contain inhibitors (such as tributylcatechol) to prevent self-polymerization. May form explosive peroxides upon exposure to air. Reactive with phenol, chlorine dioxide, copper, crotonaldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LEL: 2.0%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>UEL: 12.0%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor pressure: 1,824mm</td>
<td></td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>Colorless liquid or gas with an ether-like odor, irritating at high concentrations</td>
<td>Boiling point: 51°F</td>
<td>May polymerize violently if contaminated with alkaline or acidic materials and metal oxides or chlorides</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LEL: 3%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>UEL: 100%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor pressure: 1,095mm</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>Colorless liquid with a sweet, aromatic odor at low concentrations; sharp, penetrating, disagreeable odor at higher concentrations</td>
<td>Boiling point: 293°F</td>
<td>Polymerization may occur if heated above 150°F; metals, salts, peroxides, and strong acids may also cause polymerization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LEL: 1.1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>UEL: 6.1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor pressure: 4.5mm</td>
<td></td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>Colorless gas; liquifies in a freezing mixture</td>
<td>Boiling point: 7°F</td>
<td>Polymerizes in presence of air, sunlight, or heat unless stabilized by inhibitors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LEL: 3.6%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>UEL: 33%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor pressure: 2,580mm</td>
<td></td>
</tr>
</tbody>
</table>

Information summarized from NIOSH Pocket Guide to Chemical Hazards, June 1997, DHHS (NIOSH) Publication No. 97-140
Polymerization reactions are controlled by catalysts and inhibitors. Catalysts are substances that can start the polymerization process or control its speed. Inhibitors are substances added to monomers to prevent them from polymerizing. Some inhibitors are time-dependent and may lose their effectiveness during the course of transportation if unexpected delays are encountered. Other inhibitors may escape by evaporation, particularly if there is a source of heat present, as in a fire. If the inhibitor loses its effectiveness, polymerization begins again. Polymerization reactions in closed containers can result in tremendous, rapid expansion of the material and buildup of heat, causing container failure.

The word “stabilized” means the same as “inhibited” when used in shipping documents. Products likely to polymerize are indicated in the NAERG with a “P” following the guide number; for example, styrene monomer, inhibited—Guide 128P.

**Corrosivity**

**Questions**

1. What are some common acids you work with or use at home?

2. What are some common bases you work with or use at home?

3. What are the hazards of corrosives?

4. Are corrosives solids, liquids, or gases?

**Definition and Measurement**

A corrosive is a material (solid, liquid, or gas) that burns, irritates, or destructively attacks organic tissues, most notably the skin. When taken internally, a corrosive can affect the tissue it contacts, such as the lungs if inhaled, or the stomach if ingested. There are two classes of corrosives: acids and bases. Bases are also known as alkalis or caustics. It is important to remember that both acids and bases can be equally damaging to the body.
The pH scale is used to determine whether a material is an acid or base. The scale ranges from 0 to 14 with 7 as a mid-point. Materials with a pH of 0 to 7 are considered acidic. Materials with a pH of 7 to 14 are considered basic. Materials with a pH of 7, such as water, are considered neutral. The pH scale is a logarithmic scale. That means that since 7 is the center of this logarithmic scale, the difference in acidity from pH 6 to pH 7 is small, while the difference from pH 3 to pH 4 is greater, and the difference in acidity between pH 1 to pH 2 is very great, which is why pH refers to concentration.

It is important to obtain information about the strength and concentration of the acid or base you encounter. For acids or bases to assume their corrosive characteristics, they both must be dissolved into water. By doing so, the water breaks (ionizes) the acid or base molecules into different components, or ions. The amount of ions formed, versus the amount of acid or base molecules available, is known as strength. For example, 100 out of 100 hydrogen chloride molecules will disassociate in water (up to saturation), which creates a strong acid. On the other hand, approximately 1 out of 100 acetic acid molecules disassociate, which creates a weak acid.

**Question**

*Can you measure the pH of gasoline?*

Hydrochloric acid is a strong acid because it is almost completely ionized in water and the concentration of hydronium ions is very high. Acetic acid is a weak acid because only about 0.0001 of the acetic acid is ionized, so the concentration of ions is very low. Sulfuric acid is a stronger acid than acetic acid, and the pH of sulfuric acid is lower (more acidic) than the pH of acetic acid at similar concentrations. Vinegar, which has a concentration of 5% acetic acid in water, has a pH of about 2 to 3, while a concentration of 1% sulfuric acid has a pH of about 1.

Both acids and bases can cause injury. Those with very low or very high pH are the most hazardous. Any highly concentrated acid or base should be carefully assessed before action is taken.
It is important to note the difference between concentration and strength in a corrosive. Acids and bases in water may be labeled according to the concentration of the acid or base in water, such as 40% sulfuric acid or 98% potassium hydroxide. Highly concentrated solutions of any acid or base are likely to be very corrosive. Also, some acids and bases are stronger than others.
Neutralization

Neutralization is considered by emergency responders to be the process where mixtures of acid, base, and water are created in an attempt to reach a neutral pH of 7. In the field it is difficult and time consuming to reach a pH of 7; consequently, a pH of 5 to 9 is considered ‘neutral.’

Fire departments will generally not be required to neutralize large spills of corrosives. This is the responsibility of private industry. Your department may, however, be required to oversee this procedure.

The neutralization of acids can be accomplished by adding a weak base, such as baking soda. It is important to remember that strong acids react with water to produce heat, splattering, and fumes. If an acid is diluted by adding water, the acid cannot absorb the heat of the reaction, and injury can result from spattering corrosive material. Bases should likewise be neutralized by adding a weak acidic solution. Be extremely careful if you choose to neutralize a spill. Neutralization can create toxic salt byproducts. Diluting acids and bases with water is usually not effective unless there is only a great deal of water and a small amount of acid or base. Remember to “follow the alphabet”:

A to W -------- acid to water
G to W -------- base to water
U to W -------- unknown to water

Activities
Reactivity

Questions

1. What is one example of an air-reactive chemical?

2. What are some examples of water-reactive chemicals?

Definition

Reactivity is the ability of a material to undergo a chemical reaction. Unreactive materials are stable. Reactive materials can explode, combust, or spontaneously ignite when mixed with another substance. Chemicals can be either water or air reactive.

Water reactive materials are those that react when exposed to water. For example, sodium metal is extremely water reactive. Sodium metal may be found in chemical laboratories and illegal drug labs. A finger-sized chunk of sodium metal will explode like a small stick of dynamite when placed in water. Sodium metal is generally manufactured and shipped in dry form in small metal cans. Once removed from the can it is stored immersed in mineral oil or kerosene.

Air reactive materials are those that react when exposed to air. White and yellow phosphorous spontaneously ignite in air and are normally shipped and stored under water. Lithium hydride is another air reactive material. As mentioned earlier, a related term—pyrophoric—is used to describe a material (liquid or solid) that spontaneously ignites in air at or below 130°F.

Activity
Compressed Gases

Questions

1. Can you identify several common types of compressed gases that are used in industries in your response area?

2. Are these examples flammable, nonflammable, or poisonous gases?

3. Do any of these gases have more than one hazardous property?

4. Why is propane sold for use in five gallon home barbecue tanks as a liquid? Why not just as a gas?

Definition

Compared with other states of matter, gases are the least dense. They have no “shape” and they take on the volume of the container in which they exist. For purposes of storage and transportation, gases are often compressed to reduce the amount of space they occupy. Gases can be compressed by increasing the pressure applied to the gas and forcing it into a smaller volume.

Some gases are also liquefied by decreasing their temperatures to further reduce their volumes. Certain gases that are liquefied are classified as cryogenic because of their extremely low boiling points. The figure below illustrates the categories of these gases.
Compressed gases are defined by the DOT as having, in the container, an absolute pressure exceeding 40 psi at 70°F. Other specifications are also used. While this may not be immediately important in an emergency response situation, these measurements may appear in references, transportation documents, or facility documents.

Pressure may be measured in psia (pounds per square inch absolute) or psig (pounds per square inch gauge). These measures are related. If psig = 0 in a cylinder, the pressure in the cylinder is equal to the pressure in the atmosphere outside the cylinder. Atmospheric pressure is 14.7 psi at sea level. Absolute pressure (psia) is the pressure in the cylinder, as read on the gauge (psig) plus atmospheric pressure (14.7 psi).

\[
\text{psia} = \text{psig} + 14.7
\]

Like other measurements, various systems of measure may be used for pressure:

\[
14.7 \text{ psi} = 1 \text{ atmosphere (atm)} = 760 \text{ mm Hg}
\]

Some gases, such as oxygen, may be stored and transported either as compressed gases or as liquefied gases, as shown in the figure on the next page.

**Activity**
IN THE Pressurized, gaseous state, molecules are compressed but relatively far apart (as compared to a liquefied gas).

Containers are never completely filled with liquefied gases, at least 15% of container space is left empty – this empty space is immediately occupied by gas from the liquefied product.

In the liquefied state, molecules are further compressed.

Oxygen as a Compressed Gas and a Liquefied Gas.
Liquefied Gases

Questions

1. What is the vapor pressure of propane?

2. Approximately how much pressure is in a five-gallon home barbecue tank of propane?

Liquefied gases are those that are kept under pressure and at cool temperatures. The critical temperature and pressure of a gas refer to the temperature and pressure needed to liquefy the gas. A gas cannot be liquefied by pressure alone if it is above its critical temperature. For example, the critical temperature for carbon dioxide (CO₂) is 88°F. Above 88°F, carbon dioxide cannot be liquefied, regardless of the amount of pressure applied. The critical pressure is the pressure required to liquefy a gas when it is at its critical temperature. Again, using the carbon dioxide example, the critical pressure at 88°F is 73 atmospheres (or 1,070 psia).

Home propane tanks have a pressure relief device set at 375 psi to release the internal pressure should these tanks be subjected to a fire. Their working pressure is 240 psi and test pressure is 480 psi.

The relationship between pressure, temperature, and volume can be illustrated by discussing how methane is liquefied. Cooling methane (or any other gas) below its boiling point will change its state from gaseous to liquid. Since the boiling point for methane is -258°F, it is not possible to liquefy it at ordinary temperatures. As stated above, it is also possible to compress the gas by increasing the pressure. The critical temperature of methane is -116.5°F. So, at room temperature (80°F), pressure alone will not be enough to compress methane to liquid form; it must also be cooled. By increasing the pressure and decreasing the temperature, the volume occupied by the gas is greatly decreased.

Cryogenic Gases

Cryogenic gases such as liquefied oxygen, nitrogen, and natural gas (LNG) are in widespread use. A liquefied gas is defined by the DOT as “cryogenic” if its boiling point is
below -130°F (-90°C) at 1 atmosphere of pressure. Other authorities use a boiling point below -238°F (-150°C) to define cryogens. Regardless of the definition used, these liquefied gases are always extremely cold.

Even anhydrous ammonia which has a boiling point of -28°F is extremely cold when released under pressure. The DOT does not consider it “cryogenic” but as with other materials having low boiling points, exposure to skin can cause frostbite.

True DOT cryogenic gases are stored and transported in special insulated containers. (These materials have such low boiling points that it is virtually impossible to prevent them from slowly boiling away, even when they are housed in specially designed containers.) Their containers typically have safety relief devices that vent the vapor produced by boiling liquid. Unlike other compressed gases, strategies for controlling releases or for minimizing the effect of impinging flames must take into consideration the extreme coldness of the material. For example, a container of LNG cannot be cooled using hose streams because the water is warmer than the LNG; although, in the event of direct flame impingement upon the container, application of water to the container may absorb heat. Likewise, application of water may freeze safety relief devices. It is also important to remember that the extremely cold temperatures of cryogenic gases can freeze flesh with contact of very short duration.

Finally, it is important to remember that cryogenic gases are heavier than air when released from their container due to their extreme cold. When warmed to atmospheric temperature they will then either rise or fall depending upon their vapor density. They can displace air when spilled or released in unventilated spaces or in large amounts, posing a potential hazard of asphyxiation from air displacement.

Expansion Ratio

A hazard common to all compressed gases is the potential for expansion when warmed or no longer under pressure. Container failure and large releases of such gases may result. For example, a tank car carrying 11,000 gallons of
compressed material can release hundreds of thousands of cubic feet of vapor or gas through a breach in the container. This is a particular concern with liquefied gases. The expansion ratio or vapor-to-liquid ratio refers to the comparison of the volume of the gas to its liquefied form. LNG has an expansion ratio of 600 to 1; liquefied petroleum gas (LPG) has an expansion ratio of 250 to 1. In other words, one cubic foot of LNG will expand to 600 cubic feet of methane gas, and one cubic foot of LPG will expand to 250 times that volume when the propane-butane mixture changes from liquid to gas.

**BLEVE**

Flammable gases that are transported or stored in their liquefied form (especially those liquefied by pressure alone) are particularly hazardous because there exists the potential for a boiling liquid expanding vapor explosion (BLEVE). This is the term for the uncontrolled fire and explosion of vapor as it escapes from a ruptured container of liquefied flammable gas. BLEVEs occur when a contained liquid is heated to well above its boiling point (at normal atmospheric pressure) and the container breaks apart. This may occur when a container is exposed to fire. The liquid inside begins to boil and vaporize. The vapor is vented from the relief valve and the level of liquid begins to drop. As this occurs, the flames begin to impinge on the vapor space of the tank. Though the effect of the impinging flames is initially minimized by the presence of liquid in the tank—which helps to absorb the heat—there is less liquid in the tank to prevent the container from becoming heated. As heat and pressure build, the container weakens and may eventually rupture, resulting in a BLEVE.

**Activity**
Ignition Temperature

Questions

1. Have you ever seen documents that note a chemical’s maximum safe storage temperature (MSST) or self accelerating decomposition temperature? If so, where?

2. MSST and SADT data is usually associated with which class of chemicals?

Definition

Ignition temperature (also called autoignition temperature) is the temperature at which a material’s vapors start to burn without a flame or other ignition source present. These vapors are consumed in fire as rapidly as they are formed. Many flammable solids have ignition temperatures greater than 400°F, much higher than flash points for flammable liquids. One notable exception is phosphorus (white or yellow) with an ignition temperature of 86°F. Books have an autoignition temperature of 451°F.

MSST
Above the MSST (maximum safe storage temperature) a chemical may become unstable, spontaneously igniting and rupturing its container. Typically such materials are stored in a refrigerated cabinet.

SADT
Above the SADT (self accelerating decomposition temperature) a chemical will become unstable and can rupture its container and ignite violently. Typically such materials are stored in a refrigerated cabinet.
Toxic Byproducts of Combustion

Questions

1. What are some common toxic byproducts of combustion?

2. Have you ever been exposed to toxic byproducts?

How Byproducts are Created

Burning, or combustion, involves breaking down materials such as plastics into new byproducts of combustion that are often toxic and very hazardous. Byproducts include but are certainly not limited to carbon monoxide, vinyl chloride and hydrochloric acid. Considering the toxic nature of most combustion byproducts, the statement “every fire is a hazardous materials incident” rings true.

Fire departments must recognize potential hazards from byproducts and take steps to protect their members, including providing storage areas for fire turnout gear away from sleeping and eating areas and separate washing facilities to clean that gear.
Viscosity

Questions

1. What liquids are extremely viscous?

2. What are some examples of liquids that are less viscous?

Definition

Viscosity refers to the ability of a liquid to pour. Liquids with a low viscosity (water) pour easily. Liquids with a high viscosity (molasses or thick motor oil) are thick and pour slowly. Typically, many liquids with a high viscosity need to be warmed up in order to be pumped from one location to another (e.g., bunker C oil, used to fuel many large commercial ships).

Activity
Radiation

Questions

1. Where might you find radioactive materials in your response area?

2. When might you find yourself exposed to radiation?

Definition

Radioactivity is related to the ability of certain materials to emit energy as a result of changes to the nucleus or center of their atoms leading to instability. Unstable radioactive atoms have extra energy in the nucleus. These unstable atoms naturally seek to get rid of their excess energy and return to a stable state by emitting alpha or beta particles or gamma rays from the nucleus. The amount of time that it takes for half of the atoms in a sample to decay in this way is called the half-life of the material.

When particles of energy emitted from the atom collide with matter they cause the matter to ionize, thus changing the atomic makeup of the matter. When these changes occur in atoms that make up living matter, such as the body’s cells, damage can result. Radiation can cause damage by 1) disrupting cell division, or 2) forming a hydrogen peroxide-like chemical inside the body. Radioactive materials may have other hazardous properties; for example, they may also be corrosive or toxic.

Types of Radiation

Alpha particles travel only a short distance from their source (about 4 inches) and can be stopped by a thin film of water or a sheet of paper. These are the largest radioactive particles. Since alpha particles cannot penetrate the outer layer of skin, they present little hazard to the skin or to the body through skin penetration. They are, however, extremely hazardous if allowed to enter the body through the mouth, lungs or eyes. The use of positive pressure self-contained breathing apparatus prevents exposure to this respiratory hazard.
Beta particles penetrate further than alpha particles, in part, because they have higher energy levels than alpha particles. Beta particles can travel in air about 30 feet from their source. They can penetrate through about 1.5 inches of wood and about 0.1 to 0.5 inches of human skin. The penetration of skin by beta particles can cause serious skin burns, and is particularly hazardous to the eyes. Like alpha particles, beta particles can cause serious damage if internal exposure occurs. Barriers such as the walls of a room or a thin piece of metal will effectively stop beta particles.

Structural fire fighting gear should not be relied on to provide protection against beta radiation. Positive-pressure self-contained breathing apparatus should be worn and appropriate decontamination should be performed to prevent inhalation or ingestion of beta-emitting particles.

Gamma rays and x-rays have higher energy and penetrate farther than alpha or beta particles. Both gamma and x-rays are electromagnetic waves that have no electrical charge. X-rays and gamma rays are stopped only with dense shielding, such as several inches of lead or several feet of concrete. At any incident involving radioactive materials, proceed under the assumption that gamma rays are involved. In fact, there are few sources of pure alpha or beta radiation; most radioactive elements emit both particles and gamma rays. Gamma rays and x-rays (like the other forms of radiation) can cause damage to the genetic material of the cells. Like materials contaminated with other types of radiation, gamma-emitting materials may cause a great deal of damage if inhaled or ingested. The difference between gamma and x-rays is that gamma rays originate inside the nucleus and x-rays originate outside the nucleus. However, both ionize an atom by directly interacting with electrons.

Neutron Particles

Neutrons are particles normally contained in the nucleus of an atom. They can be released through certain manufacturing processes, such as nuclear fission (splitting an atomic nucleus). Neutrons are considerably larger than beta particles but have only one-fourth the mass of alpha particles. Because they can penetrate even thick lead shields,
they can be extremely damaging to humans. However, neutron radiation is very rare since it is generally emitted only when atomic weapons are detonated.

Minimizing Exposure

The dose of radiation absorbed by an exposed individual depends on four factors: the type of radiation; the length of exposure (time); the distance from the source; and the presence of shielding. By doubling the distance from the source, an individual can quarter the amount of radiation exposure. Distance is the most effective means of reducing exposure. Finally, exposure is limited by minimizing the amount of time spent near the source of radiation. You can also shield yourself from some types of radiation by placing objects between yourself and the radioactive source.

Contamination occurs when radioactive material (usually in dust or liquid form) becomes attached to something, such as clothing, skin, or equipment. The presence of this radioactive material results in the contaminated object having detectable levels of radiation, and can lead to additional exposure through secondary contamination. Secondary contamination occurs when contaminated materials leave the restricted area of maximum hazard and contaminate persons or equipment in the Cold Zone. However, once something is properly decontaminated, it no longer presents a hazard.

The dose of radiation is measured in rad (radiation absorbed dose). Rad is estimated by multiplying another measurement, rem (radiation equivalent man), by a “quality factor” unique to each type of radiation. Some radiation detection devices measure in rem.

Permissible occupational doses of ionizing radiation can be found in the Code of Federal Regulations, part 1910.96 of Title 29 (29 CFR 1910.96). The exposure limits differ according to the part of body exposed. For example, for whole body irradiation the annual and quarterly total weighted dose should not exceed three rem per quarter or five rem per year. “Sieverts” is another term you may encounter referring to radiation measurement.
There are no specific limits for acceptable radiation exposures in emergency conditions. The National Council on Radiation Protection and Measurements, however, suggests that 100 rems whole body and 300 rems to the extremities are acceptable in the case of lifesaving actions. Because this is a somewhat complicated risk to assess, it is essential that the Technicians consult with a health professional trained specifically in the effects of radiation.

When responding to an incident with a suspected radiation hazard, do not ignore the fact that other hazards may be present. Check for unknown dangers as soon as you arrive at the scene.

Activity
Chemical Structures (Optional)

A basic understanding of what makes up chemicals and how they react will allow Technicians to make better use of information provided in references and other sources. This is only a basic overview of the subject and should serve as a foundation for continuing education in this area. Technicians who would like a more in-depth discussion of the concepts presented in this unit should refer to basic chemistry textbooks.

With experience, Technicians will remember the more unique characteristics of some chemicals, such as the strong potential for chlorine to react with other chemicals, or the water reactivity of potassium. By knowing that chemicals in the same group in the Periodic Table will have similar properties, Technicians may also predict the chemical behavior of related elements.

Elements and Groups of Elements

Elements

An element is a substance made up of only one kind of atom. Atoms are the smallest units of matter that cannot be divided into smaller pieces and still maintain their chemical and physical properties. The atoms of elements are the building blocks of all matter.

For example, chlorine is an element. Chlorine gas consists of only chlorine atoms. This yellow-green gas with a strong, sharp odor and a bitter taste is involved in many hazardous materials incidents each year. In addition to its serious health effects, chlorine supports combustion and reacts violently with many other materials.

Chemical Symbols

Chemical symbols are one or two letters, usually the first letters of the chemical’s English or Latin name.
For example, chlorine is abbreviated using Cl, its chemical symbol. The first letter of the chemical symbol is always capitalized; if there is a second letter, it is not capitalized. Chemical symbols are never followed by a period. Abbreviations for some of the elements discussed in this unit are listed in the table below.

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<tr>
<th>ELEMENT</th>
<th>SYMBOL</th>
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<tr>
<td>Phosphorus</td>
<td>P</td>
<td>Radon</td>
<td>Rn</td>
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</table>

Some Elements and Their Symbols

The Periodic Table

All matter is made up of only one or a combination of different elements. These elements are systematically arranged in the Periodic Table, shown on the following pages. The Periodic Table is a system for organizing elements according to their chemical properties, size, and weight. Each box in the Periodic Table is reserved for a separate element. The abbreviation, or chemical symbol in each box represents a specific element. The number associated with each element of the Periodic Table is its atomic number. The atomic number is the number of protons in the nucleus of a particular element. The concept of atomic number is illustrated on the Periodic Table. Change the atomic number (number of protons) of an element, and it
becomes a different element. Each element has its own number. Hydrogen, for example, has one proton; carbon has six.

There are 18 groups arranged in columns in the Periodic Table. All members of a group have similar characteristics or properties. So, knowing how one element in a group reacts can provide an idea of how another member of that group may react. For example, chlorine is located in the second column from the right, which represents Group VIIA, known as the halogens. The halogen group includes fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). In their elemental form, the members of this group are strong oxidizing agents and react violently with many chemicals. In high concentrations, they are corrosive to many substances, including metals and body tissues, such as the skin, eyes, and respiratory system. The corrosive action of halogens is related to their strong tendency to react with other chemicals. In addition, they become strong acids in the presence of moisture.

The members of Group IA, at the far left of the Periodic Table, are known as the alkali metals. These include lithium (Li), sodium (Na), and potassium (K). The members of this group all react violently with water to form hydrogen gas and bases (also called alkalis).

Group IIA, known as the alkaline earth metals, includes beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). These elements also react with water to form bases.

On the far right of the Periodic Table is Group VIIIA, often referred to as the noble gases. This group includes helium (He), neon (Ne), argon (Ar), and radon (Rn). These elements are sometimes referred to as the “inert gases” because of their very low tendency to undergo chemical reactions with other elements. Helium, neon, and argon are found in some industries, usually as gases stored in high pressure cylinders. Although these gases will not burn and are not reactive, they still present a hazard. Their high pressure containers can become explosion hazards in a fire. They may become projectiles if the valve on the top of the cylinder is broken off. Except for helium, the noble gases are heavier than air and will displace oxygen.
### Alkali Metals

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### Module 5: Practical Chemistry
Combining Atoms

Atomic Structure

Atoms consist of protons, neutrons, and electrons. Protons and neutrons are particles in the center, or nucleus, of the atom. The atomic number (shown on the Periodic Table) equals the number of protons in the nucleus. Generally, it also represents the number of electrons. Electrons orbit around this center in pathways called “orbits” or “shells” and are in constant motion. The shells of every atom have set capacities to accommodate electrons and are layered around one another to hold all the electrons of the atom.

The capacity of each shell varies. The first shell can hold only two electrons, the second shell can hold up to eight. Other shells may have larger capacities, but they are filled in a way that keeps the atoms the most stable. Regardless of the element, the outermost shell holds no more than eight electrons.

The outermost shell of an atom is the most important because it accounts for the chemical properties of that atom. An atom is most stable when its outermost shell is filled with all the electrons it can accommodate.
The first shell of an atom is full with two electrons. Hydrogen (H), which has only one electron in its shell, is very unstable. Helium (He), with two electrons, has a full shell and is very stable.

![Hydrogen and Helium diagrams]

Atoms with more than two electrons have a second shell. The second shell is full when it contains eight electrons. Fluorine (F) has only seven electrons in its outermost shell, so it has a strong tendency to combine with other atoms to become more stable.

![Fluorine diagram]

All members of the halogen group are one electron short of a full outer shell. So, as a halogen, chlorine also has a strong tendency to combine with another element in order to become stable.

You can determine the number of electrons in the outermost shell of an atom by the position of that element in the
Periodic Table. For example, “Group VII” above the vertical column of the halogen group indicates that there are seven electrons in the outermost shell of the atoms of elements in this group. An atom of lithium (Li), sodium (Na), or potassium (K) in Group I has only one electron in its outermost shell. This is an important characteristic to remember when discussing how atoms combine.

**Molecules and Compounds**

A **molecule** is a unit of matter formed by the chemical combination of two or more atoms from different elements. Combining chlorine (Cl) with hydrogen (H) to form hydrochloric acid (HCl) is an example of atoms bonding to form a **molecule**. Molecules are groups of atoms bonded together so tightly that they act as one particle, in the same way that individual pieces of metal are bound together to form a single machine. In the case of chlorine gas, the atoms naturally combine in groups of two to form a chlorine molecule, Cl2. This form is more stable than one chlorine atom alone. Other examples of elements whose molecules are made up of two atoms are: hydrogen (H2), oxygen (O2), and nitrogen (N2).

A **compound** is a pure substance composed of two or more different elements combined in fixed proportions. A well known compound is water, which in pure form is composed entirely of water molecules (H2O). Another compound is table salt, which is composed entirely of sodium chloride (NaCl) molecules.

Compounds should not be confused with **mixtures**. Mixtures are not the result of chemical bonding; rather, they consist of separate elements or compounds that are mixed together. For example, coal is mixed with water in a slurry for transportation via pipelines. As with all mixtures, a slurry can be broken down into its original components by physically separating the components, in this case, coal and water.

Mixtures are **solutions** when a **solute** (for example, sugar) is dissolved in a **solvent** (such as water). Like all mixtures, each component of a solution retains its own chemical properties.
**Formulas for Molecules**

**Chemical formulas** are a shorthand way of expressing the composition of molecules and the way they react with one another. Hydrochloric acid, the chemical combination of hydrogen and chlorine, is abbreviated HCl representing its chemical formula for hydrochloric acid. In this case, there is one atom of hydrogen and one atom of chlorine in every molecule of hydrochloric acid. If there is more than one of the same atom in a molecule, the number is represented by a subscript after the symbol for that atom, as in the chemical formula for sulfuric acid, H₂SO₄. In sulfuric acid, there are two atoms of hydrogen, one atom of sulfur and four atoms of oxygen in every molecule of sulfuric acid.

The chemical formula for hydrochloric acid (HCl) indicates that the acid can pose several hazards in a fire. In addition to the hazards posed by the acid itself, there may be hazards resulting from combustion involving HCl. For example, if material burns in the presence of HCl and oxygen, water and highly toxic chlorine gas will be produced. This is illustrated by the following chemical reaction:

\[
\text{hydrochloric acid (HCl)} + \text{oxygen (O}_2\text{)} + \text{energy (from fire)} \rightarrow \text{water vapor (H}_2\text{O)} + \text{chlorine gas (Cl}_2\text{)}
\]

As the bonds that hold molecules together are broken, the elements break free and bond in a different way to form different molecules. (Actually, chemicals rarely react completely. In this example, there may be additional HClO, hypochlorous acid, and there is usually some hydrochloric acid and oxygen left over at the end of the reaction.) The arrow indicating the direction of the reaction above points in both directions. This means that the reactions depicted by the formula can occur in either direction. Thus, using water to extinguish a fire involving chlorine gas will result in the formation of hydrochloric acid.

**Activity**
The Making of Molecules

Chemical formulas illustrate chemical combinations. Conversely, how do molecules break apart and form completely new molecules? The capacity for chemicals to break apart and form new molecules is called bonding. Chemicals combine by either ionic or covalent bonding. Ionic bonds are formed when two atoms exchange electrons, as in the bonding of sodium (Na) and chlorine (Cl) to form table salt. Sodium (Na) gives the one electron in its outer shell to the chlorine (Cl) atom which needs one electron to fill its outer shell. As a general rule, elements in Groups I and II form ionic bonds by giving up electrons whereas elements in Groups VI and VII form ionic bonds by accepting electrons.

Since electrons carry a negative charge, the atom that receives the electron will be slightly negative, in this case, Cl-. The atom that gives up the electron will carry a slightly positive charge, here, Na+. This results in an uneven distribution of the charge, or polarity in the molecule. The two (or more) atoms are held together by the attraction of the opposite electrical charges.

An atom (or molecule) that receives one or more electrons becomes a negative ion, and one that loses one or more electrons becomes a positive ion. The formation of ions gives rise to the term “ionic.” This formation of ions is the principle underlying some detection equipment, as will be discussed later. Salts, such as NaCl (sodium chloride), KBr (potassium bromide), and NaI (sodium iodide), are the products of reactions between positive and negative ions.

Like many molecules with ionic bonds, sodium chloride (NaCl) is easily dissolved in water. Water is a polar molecule, having an uneven distribution of charges among the two hydrogen and one oxygen atoms. When polar (ionic) solids dissolve in water, the ions separate from each other. The ions with the positive charge, Na+, line up with the negative parts of the water molecules, and the negative ions, Cl-, line up with the positive parts of the water molecules. Solubility among ionic (as well as covalent) compounds varies, so references must be consulted when solubility information is needed.
Covalent bonds are those formed when electrons are shared between two atoms in a molecule. Pure hydrocarbons (molecules with only hydrogen and carbon, such as gasoline and other petroleum products), are formed with covalent bonds. When placed in solution, these atoms do not separate as ions do, rather they stay together as a unit. As discussed previously, hydrocarbons are nonpolar, with their positive and negative charges spread throughout the molecule. These compounds are usually sparingly soluble or insoluble in water. Exceptions to this are usually oxygen- and nitrogen-containing solvents.

Predicting How Chemicals Combine

You can predict how likely it is for an element to form a bond based on that element’s position in the Periodic Table. The tendency to bond with other elements is the chemical reactivity of the element. All members of the halogen group have outer shells that are one electron short of being full. A full shell makes the atom stable, and atoms seek this stability. This is the reason that chlorine, fluorine and the other members of the halogen group are very reactive. This instability is due to the strong tendency to bond with other elements in order to gain an electron.

The elements in the far right column of the Periodic Table all have full outermost shells. These inert gases rarely combine, or react, with other elements. An industrial application of this property is “heliarc welding” in which an inert gas is used to keep the oxygen in air away from the hot weld zone, making it possible to weld materials that would normally oxidize or burn at the welding temperature.

On the far left of the Periodic Table is the alkali metals group. Each member of the alkali metals group (Group IA) has only one electron in its outer shell and has a strong tendency to empty and eliminate this shell by giving up the one electron it contains. The next inside shell (which is already complete) becomes the outer shell.

Each of the elements in the next group to the right, the alkaline earth metals (Group IIA) has two electrons in its
outer shell. Each Group IIA member is also reactive, though not as reactive as the members of Group IA.

Technicians must be aware that elements in Groups IA, IIA, VIA, and VIIA of the Periodic Table are the most chemically reactive. The elements in these groups have a strong tendency to bond with other elements and compounds to satisfy their need for a full outer shell.

**The Energy of Bonding**

Chemical reactivity, the potential to form bonds, is important to Technicians because energy (usually in the form of heat) is a component of every chemical reaction. Reactions that require or absorb heat from their surroundings are called **endothermic** reactions. Most chemical cold packs use the endothermic reaction of ammonium nitrate and water to provide cooling.

Reactions that give off heat are called **exothermic** reactions. An explosion is an obvious example of an exothermic reaction. What is not as obvious is the way molecules are breaking apart and reforming in an explosive chemical reaction. For example, ammonium nitrate (NH₄NO₃) mixed with fuel oil (ANFO) is commonly used as a blasting agent in construction. The ammonium nitrate molecule is unstable and contains more oxygen than is required for its own combustion. When this mixture is heated, the weaker bonds of the ammonium nitrate molecule are broken and the nitrogen atoms reform bonds. Hydrogen will form water with some of the oxygen and some of the oxygen will be left over to burn the fuel oil. Common explosives do not rely on oxygen from the air, but carry oxygen in their molecular makeup. The reaction involving ANFO is illustrated in the following equation:

\[
\text{ammonium nitrate (NH}_4\text{NO}_3\text{) + fuel oil (carbon compound) + heat (energy) } \rightarrow \text{nitrogen gas (N}_2\text{) + carbon dioxide (CO}_2\text{) + water (H}_2\text{O) + energy}
\]

**Influencing Chemical Reactions**

In the above equation a certain amount of energy is required to start the breakdown of ammonium nitrate. In the construction industry, detonators such as trinitrotoluene caps
(TNT) are placed with bulk amounts of ANFO mixtures to supply the energy to begin this chemical reaction. Dynamite is also sometimes used. The intense heat supplied by the detonation speeds the reaction.

Besides temperature, the rate of chemical reactions can be influenced by:
- Concentration and total amount of materials involved
- Pressure
- Catalysts

In addition to changing the rate of the reaction, these factors may also change the nature of the reaction. That is, the actual products of the reaction may be different.

For example, in the above reaction involving ammonium nitrate and fuel oil, carbon dioxide (CO₂) is produced. In fact, carbon dioxide (CO₂) is the result of virtually any reaction involving the combustion of carbon-containing compounds. Fire fighters are aware that carbon monoxide (CO) can be formed in the combustion of wood, gasoline, or other carbon-containing compounds representing a change in the nature of the reaction.

This occurs because the concentration of the chemicals undergoing reaction changes. The reason that carbon monoxide is produced in fires involving fuel oil and other carbon-containing compounds is that incomplete combustion occurs. This is the result of an environment rich in the carbon-containing fuel or limited in the amount of oxygen available for the reaction. In such an environment, there is not enough oxygen to react with all of the available carbon. Thus, carbon monoxide (CO) and soot (carbon alone) are among the products of the combustion.

In a hazardous materials incident, it is important to know all the potential products that may result from combustion or other reactions. Resources, such as the Material Safety Data Sheet (MSDS) for a given material, can provide information about products of combustion.

This section, however, emphasizes those factors that can influence the rate of the reaction.
Effects of Temperature

An increase in temperature almost always results in an increase in the rate of a chemical reaction. Most reactions do not occur spontaneously, but require energy in the “system” to begin. This energy is often referred to as energy of activation. Heat supplies this energy. Heat increases the speed of molecules and thereby increases the likelihood that they will collide. When collision occurs, electrons can be exchanged or shared, resulting in a chemical reaction.

Conversely, cooling reacting materials (or the container holding them) minimizes or slows this reaction.

Effects of Concentration and Reactant Quantities

The concentration of reactants determines, to a greater extent, the probability that the atoms or molecules of reactants will come into contact with one another. Again, contact often results in a chemical reaction taking place.

The concentration of oxygen in an environment provides an example of the effect of concentration on the rate of a reaction. In an oxygen-rich environment, materials burn at a much faster rate than in an atmosphere of air, which normally has an oxygen concentration of 21%. In fact, some materials that are not combustible in air, such as flame retardant materials, burn readily in an oxygen-enriched atmosphere. Of course, limiting the amount of available oxygen by smothering the burning material slows and eventually stops most reactions.

Effects of Pressure

Pressure decreases the distance between reacting atoms or molecules, thereby increasing the likelihood of collision. There is a direct relationship between pressure and temperature. This relationship can be illustrated by observing a gas in a closed container. As the temperature of the gas is increased, the molecules of the gas speed up and strike the walls of the container with greater force, thereby increasing pressure in the container. Likewise, as the pressure inside the container increases, the number of collisions also
increases, resulting in an increase in the amount of friction heat generated.

**Effects of Catalysts**

A catalyst increases or decreases the rate of a reaction without being consumed or altered at the end of the reaction. **Catalysts** are substances that speed reactions, while **inhibitors** are used for substances that prevent or slow reactions.

As previously discussed, a specific amount of energy is required to initiate and sustain the reaction. Catalysts speed reactions by providing a pathway for the reaction that requires less energy. Catalysts can either take part in the reaction, or can provide a surface for the reaction. For example, hydrogen and oxygen gases mix to form water very slowly at room temperature. The reaction occurs at a much faster rate when metals such as nickel, copper, and silver are present.

The mixed metal oxide bed of a car’s catalytic converter acts in a similar manner, promoting the oxidation of carbon monoxide (CO) and fuel to produce the less hazardous carbon dioxide (CO2) and water (H2O). Since the surface of the oxide bed is destroyed by lead, unleaded fuel must be used with this catalyst.

**Carbon-Containing Compounds**

**Question**

*Why is it important to know about organic chemistry?*

So far, this unit has dealt mainly with **inorganic** compounds (those that do not contain carbon). **Organic** compounds always contain **carbon**. Usually, they also contain hydrogen. Compounds primarily made up of hydrogen and carbon are referred to as **hydrocarbons**. Organic compounds may also contain nitrogen, oxygen, and many other elements. Though organic chemicals were originally
thought to be available only from nature, many synthetic organic compounds are now manufactured, including pesticides, plastics, and explosives.

Carbon-containing compounds can be made up of short chains of carbon, long and complex chains of carbons with many branches, or rings of carbon atoms. This is due to carbon’s ability to easily link with itself and other atoms and molecules. Carbon (Group IV) has four electrons in its outermost shell. It requires a great deal of energy to either give up or receive four electrons, so carbon atoms bond by sharing electrons with other atoms. Because it has four electrons, each carbon atom can share with as many as four other atoms or molecules. It is because of this ability of each carbon atom to make four covalent bonds that there are over one million organic compounds.

Fire fighters are already very familiar with many aspects of the chemistry of hydrocarbons since these compounds are flammable or combustible. This section will provide basic information regarding the structure and the chemical properties of hydrocarbons so that Technicians will be better equipped to evaluate the hazards posed by incidents involving these compounds.

**Carbon Bonds**

The following reaction illustrates a propane fire which is a reaction between hydrocarbon propane (C\textsubscript{3}H\textsubscript{8}) and oxygen (O\textsubscript{2}) from air. If the propane were completely consumed in this chemical reaction of combustion, the equation would be:

\[
\text{propane (C}_3\text{H}_8) + \text{oxygen (O}_2) \rightarrow \text{carbon dioxide (CO}_2\text{) + water vapor (H}_2\text{O) + heat (energy)}
\]

Propane is a carbon containing compound. One way to represent the propane molecule is:

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]
Each dash between a C and an H represents a covalent bond. Again, each single carbon atom has the unique ability to form four bonds. In the case of propane, each carbon atom has a single bond with another atom (either hydrogen or carbon). This is referred to as a saturated hydrocarbon.

**Saturated Hydrocarbons**

Saturated hydrocarbons consist of molecules that contain *more* than twice as many hydrogen atoms as carbon atoms. In fact, for all saturated hydrocarbon molecules, the number of hydrogen atoms in any molecule is equal to twice the number of carbons in the molecule plus two. So, the hydrocarbon propane, having three carbons, has exactly eight hydrogen atoms in each molecule. Saturated hydrocarbons are called *alkanes*. A generic alkane is represented by the formula $C_nH_{2n+2}$, where $n$ represents the number of carbon atoms in the hydrocarbon. Their chemical names begin with a Greek prefix representing the number of carbon atoms in the molecule.
Methane $\text{CH}_4$

Ethane $\text{C}_2\text{H}_6$

Propane $\text{C}_3\text{H}_8$

Butane $\text{C}_4\text{H}_{10}$

Pentane $\text{C}_5\text{H}_{12}$

Hexane $\text{C}_6\text{H}_{14}$
Unsaturated Hydrocarbons

Alkenes

When a hydrocarbon has two or more carbons sharing two covalent bonds, called a double covalent bond, it is called an unsaturated hydrocarbon. The other carbons in the hydrocarbon may have single, double, or triple bonds. Hydrocarbons that have one or more double bonds are called alkenes. A double bond is very unstable, therefore, for the hazardous materials Technician, an incident involving heat exposure with a molecule that contains a double is very dangerous. The generic formula for an alkene is \( C_nH_{2n} \), where \( n \) represents the number of carbon atoms. Representations of the first three members of this family are:

- **Ethylene** \( C_2H_4 \)
  
  ![Ethylene Structure](image)

- **Propylene** \( C_3H_6 \)
  
  ![Propylene Structure](image)

- **1-Butene** \( C_4H_8 \)
  
  ![1-Butene Structure](image)

Note that a double bond uses two of the four electrons of a carbon atom, leaving only two other electrons to share, so it can form only two more covalent bonds. A double bond is counted as two bonds. In the diagrams above, each carbon has four bonds, but the end carbon (with double bonds) bonds with only two hydrogens and the adjacent carbon bonds with only one hydrogen and one other carbon.
Like the members of the alkane family, the ending of the name of the compound, in this case “-ene”, indicates the family to which it belongs. The prefix indicates the number of carbons in the molecule. It is important to keep in mind that this naming system does not apply to trade names such as kerosene. Kerosene, like gasoline, is actually a mixture of hydrocarbons.

**Alkynes**

Another type of unsaturated hydrocarbon is that which includes hydrocarbons with a triple bond shared by two carbon atoms. The generic formula is $C_n\text{H}_{2n-2}$ where $n$ equals the number of carbon atoms in the chain. The only member of this family, the **alkyne** family, that is likely to be of concern to Technicians is acetylene (C$_2$H$_2$):

$$\text{H} \quad \equiv \quad \text{C} \equiv \text{C} \quad \text{H}$$

A triple bond is counted as three bonds. Acetylene and other members of this family are unstable. Shock or heat can cause them to spontaneously burn or explode. Acetylene may also explode if compressed to greater than 30 pounds per square inch. To ship acetylene safely, it is stored in steel cylinders filled with a porous solid saturated with acetone. The acetylene is not forced in the cylinder at high pressure, but is slowly pumped in where it dissolves in acetone.

All of these families, the alkanes, alkenes, and alkynes, are grouped together as **aliphatic hydrocarbons**. Almost all of the members of these families are configured in straight chains or straight chains with branches.

**Aromatic Hydrocarbons**

Aromatic hydrocarbons are a special class of hydrocarbons that contain benzene or related ring structures in their molecules. **All aromatic hydrocarbons have alternating double and single bonds in ring form.**
The alternating double and single bond is known as a resonant bond. A resonant bond is very stable, and difficult to break, even in fire conditions. The stability of a resonant bond resists oxidation, therefore, resulting in a very sooty smoke. Benzene is the simplest of the aromatic hydrocarbons. It contains six carbon atoms, like hexane and 1-hexene, but the atoms are arranged in a circle and bonded together by resonant bonds.

Benzene has special properties that make it particularly toxic. Many members of this group pose health hazards, even in low concentrations. These materials may affect the brain, other parts of the nervous system, and the liver. Benzene is also a known human carcinogen.

**General Properties of Hydrocarbons**

The number of bonds between carbon atoms gives an indication of the reactivity of the chemical. In general, the more double and triple bonds, the more unstable the hydrocarbon compound. So, saturated hydrocarbons are more resistant to burning than unsaturated hydrocarbons. When double and triple bonds are broken, they tend to react more readily with other chemicals to form hydrocarbon derivatives.

In addition to the number of bonds, an important factor influencing the properties of a hydrocarbon is the number of carbons in the hydrocarbon chain. As the number of carbons increases, the physical state of the hydrocarbon
changes. Substances with chains of one to four carbons are usually gases; chains of five to sixteen carbons are usually liquids; and seventeen or more carbons in a chain are usually found as solids.

The flash point generally increases as the number of carbons increase. Boiling points also increase with the number of carbons in the compound. This characteristic is the basis for the process of petroleum refining.

### Flash Points

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### Hydrocarbon Derivatives

Because of the bonding flexibility of a carbon atom, hydrocarbons often serve as a basic structure for the formation of hydrocarbon derivatives. Replacing hydrogen or carbon atoms in a chain or ring with another element or molecule forms hydrocarbon derivatives. The additional element or molecule is often referred to as the functional group. These additions to basic hydrocarbons determine the chemical and physical characteristics of the hydrocarbon derivatives that are formed. Because these derivatives are so numerous, they will be discussed briefly as groups of derivatives:

- Halogenated hydrocarbons
- Alcohols
- Ethers
- Organic peroxides
- Amines
- Nitro-containing hydrocarbons
- Carbonyls: ketones and aldehydes
- Carboxylic acids: esters and amides
Each of these groups or families can be recognized by the presence of a specific functional group. Recognition of these functional groups in the name of the derivative or its chemical formula will increase your awareness of the potential dangers presented by the substance. It is vitally important to keep in mind that these chemicals are classified by DOT according to their predominant hazard. There are likely to be other hazards associated with the material. For example, since these are hydrocarbon derivatives, each family member is likely to be flammable, or at least combustible. However, some are toxic and pose greater health hazards than fire hazards.

**Halogenated Hydrocarbons**

Members of this group of hydrocarbon derivatives are formed when a halogen is added to a hydrocarbon chain. The primary halogens that are used to form these hydrocarbon derivatives are chlorine, fluorine, bromine, and iodine—for example, methyl dichloride, CH₂Cl₂; trichloroethane, C₂H₃Cl₃; methyl dibromide, CH₂Br₂; or, vinyl chloride, C₂H₃Cl.

Some of the halogenated hydrocarbons are combustible, while others do not burn. In fact, some of these compounds, such as carbon tetrachloride and 1, 2 dibromoethane, have been used as fire extinguishing agents. The primary danger of these compounds lies in their toxicity. All of them affect the central nervous system. Some can lead to convulsions, and others can depress the brain’s ability to stimulate breathing. Chronic exposure can lead to permanent nerve, liver, or kidney damage.

While some of the halogenated hydrocarbons do not burn, all of them can decompose in a fire, resulting in the production of toxic vapors. For example, chlorinated hydrocarbons can produce phosgene gas (COCl₂) when broken.
down by combustion. Vapors of most of halogenated hydrocarbons are heavier than air and tend to accumulate in low areas. Entering such an area without positive-pressure self-contained breathing apparatus could result in asphyxiation.

**Alcohols**

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

Methyl, ethyl, and isopropyl alcohols have widespread use. Adding a functional group that is referred to as a hydroxyl group, \( \text{OH} \) (one oxygen and one hydrogen), to a hydrocarbon forms an alcohol. Adding a hydroxyl group makes the hydrocarbon more water soluble. The degree of solubility among alcohols depends on the number of carbons in the chain. The longer the chain, the greater the carbon content and the less soluble the alcohol.

Alcohols can produce very hot fires because they have a great affinity for oxygen before and during a fire. They tend to oxidize when in storage, thus becoming more acidic.

The toxicities of alcohols vary, but overexposure to the vapors of any alcohol is likely to cause sleepiness and unconsciousness, depending on concentration and length of exposure. The alcohols can be toxic by inhalation and ingestion. With the exception of methyl alcohol (methanol, \( \text{CH}_3\text{OH} \)), they are not well absorbed through the skin. Methyl alcohol is particularly toxic and may cause blindness, particularly when ingested or inhaled. Ethyl alcohol (ethanol, \( \text{C}_2\text{H}_5\text{OH} \)) is less toxic, and many people are familiar with the central nervous system effects resulting from the ingestion of alcoholic beverages.

Phenol (carbolic acid, \( \text{C}_6\text{H}_5\text{OH} \)) is an aromatic alcohol (a benzene ring with an \( \text{OH} \) in place of an \( \text{H} \)). Phenol has very different properties than other alcohols. It acts as a
strong acid, although this is not characteristic of alcohols. Phenol and its chemical relatives destroy skin tissue, making them extremely hazardous. As it is readily absorbable, phenol destroys one layer of tissue after another as it penetrates through the skin. Such penetration through skin and underlying tissues often occurs without warning pain and can result in massive tissue destruction. Skin exposure greater than 64 square inches is generally considered fatal.

**Ethers**

**Diethyl Ether**  
\[ \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \]

Ethers are a group of hydrocarbon derivatives which have oxygen between two hydrocarbon groups (either chains or rings).

Some ethers are highly volatile and will result in extremely hot fires. Many of them have low boiling points and low flash points. Over time, ethers tend to react with oxygen in the atmosphere to form unstable peroxides.

**Organic Peroxides**

**Ethyl Peroxide**  
\[ \text{C}_2\text{H}_5\text{O}_2\text{C}_2\text{H}_5 \]

Organic peroxides (like their inorganic counterparts) contain the peroxide functional group (O-O). The single bond between two oxygen atoms is weak, and little energy is required to break a peroxide molecule apart. In fact, at temperatures unique to each organic peroxide, breaking the oxygen bonds in some of the molecules of a sample generates enough heat energy to continue the reaction of all the
molecules of organic peroxide in the sample. This is known as the **Self-Accelerating Decomposition Temperature**. Once this temperature is reached, the reaction cannot be reversed. Because organic peroxides are by nature highly unstable, they must be inhibited or diluted. Peroxides are extremely reactive, especially with body tissue. Their instability makes organic peroxides *serious* fire and explosion hazards. Containers holding these materials have been known to explode with the force of a powerful bomb. Another example of the danger of organic peroxides is that posed by old containers of ether in laboratories, including clandestine drug labs. With time and exposure to air, stored ethyl ether will spontaneously form small amounts of peroxides. As the peroxides build up, the bottle becomes a shock-sensitive explosive, requiring special care in removal and disposal. Two oxygen atoms between two hydrocarbon groups is the typical chemical formula for an organic peroxide, i.e. dimethyl peroxide, CH$_3$O$_2$CH$_3$; methyl ethyl peroxide, CH$_3$O$_2$C$_2$H$_5$; and dipropyl peroxide, (C$_3$H$_7$)$_2$O$_2$. As can be seen, organic peroxides can easily be confused with ethers.

### Amines

![Ethylamine chemical structure](image)

**Ethylamine** $\text{C}_2\text{H}_5\text{NH}_2$

(UN #1036 or #2270)

The amines are hydrocarbons that have a nitrogen hydrogen (NH$_2$) added to them. NH$_2$ is called an **amine group**. Amines are colorless to yellow flammable liquids that smell like ammonia or rotten fish. They tend to vaporize very readily due to their low boiling points.

Many amines are very toxic. Several amines with four or more carbon atoms are absorbed through the skin. Once absorbed into the body they may cause kidney and liver damage, particularly at a high level or with prolonged exposure. They act like corrosives when they come in
contact with skin, ulcerating the tissue. The amines are the “organic bases”, with pH readings around 12. Inhalation injuries are also a potential danger. Also, some aromatic amines are human carcinogens.

Amines are recognized in their chemical formulas by a nitrogen atom, two hydrogen atoms, and a hydrocarbon; or one nitrogen atom, one hydrogen, and two hydrocarbon groups; or one nitrogen atom and three hydrocarbon groups. For example, methyl amine, CH₃NH₂; dimethyl amine CH₃NHCH₃; trimethyl amine, CH₃N(CH₃)₂; diethyl amine (C₂H₅)₂NH; and butyl amine C₄H₉NH₂.

**Nitro-containing Hydrocarbons**

![Trinitrotoluene (TNT)](https://example.com/tnt.png)

Organic compounds containing nitro groups (NO₂) are explosives. Like the peroxide group, the oxygen atoms in this group are held together by a single bond.

Organic compounds containing nitro groups can be very toxic. Exposure to vapors from some compounds can produce dilation of blood vessels, resulting in a dramatic drop in blood pressure. The same effects are seen with the nitroglycerine preparation used in medications.

The NO₂ group in their chemical formulas defines nitro compounds. For example, nitro methane, CH₃NO₂; nitro ethane, C₂H₅NO₂; and picric acid, C₆H₂OH(NO₂)₃.
Carbonyls

The carbonyls include two different families of hydrocarbon derivatives:

- Ketones
- Aldehydes

These families are similar in that the members of each family contain a carbonyl group. A carbonyl group is a carbon atom linked to an oxygen atom by means of a double covalent bond (C=O). The carbonyl group is polar, although not to the extent of a hydroxyl group. The degree of polarity still requires the application of foam that is U.L. listed for controlling flammable vapors and fire suppression for molecules that contain a carbonyl group. Similar to alcohols, most foams that are listed for polar solvent application are applied at a 6% concentration.

The difference in the hydrocarbon chain between these families is the position of the carbonyl group. In ketones, the carbonyl group is always attached to an inside carbon, never an end carbon. In aldehydes, the carbonyl group always involves an end carbon, never an inside carbon. The carbonyls are very flammable and can be toxic, but each family has its own specific dangers.

Ketones

![Acetone Structure](UN #1090)

Ketones can form peroxides, although they do not form peroxides as readily as ethers. Some ketones can polymerize. Many are highly volatile and can have anesthetic or narcotic effects on the nervous system. Also, some may cause kidney and liver damage upon repeated exposures.

Smaller ketones are water soluble. Similar to alcohols, the longer the hydrocarbon chains, the less soluble the ketone. Two systems of nomenclature are common with ketones,
along with common names. In the name acetone, CH₃COCH₃, the “acet” identifies the two-methyl groups and the “one” identifies the carbonyl group. Another method of naming acetone is dimethyl ketone. A third method identifies the molecule as 2-propanone. This nomenclature system identifies and names the longest hydrocarbon chain, and then the “one” is added to identify the ketone. Another example is methyl ethyl ketone, MEK, or CH₃COC₂H₅. MEK is also commonly named 2-butanone.

**Aldehydes**

Aldehydes, like ketones, can form peroxides. Some can also polymerize. While aldehydes are more chemically reactive than ketones, they do not form peroxides as readily as ethers. Aldehydes are very irritating to mucous membranes, including those of the lungs and eyes. High level, short-term exposure may result in lung damage. Repeated exposures, even at relatively low levels, can cause lung, liver and kidney damage. The smallest member of the group, formaldehyde, has produced cancer in rats, but has not been shown to cause cancer in humans.

Chemical formulas for aldehydes always have the “CHO” at the end of the formula, similar to the structure. By convention, the aldehyde group is always indicated by “CHO” in order to avoid any confusion with a hydroxyl group (OH), for example, acetaldehyde, CH₃CHO and propionaldehyde, C₂H₅CHO. Another nomenclature system uses the suffix “al” to identify an aldehyde. For example, a synonym for formaldehyde is methanal; a synonym for acetaldehyde is ethanal; and a synonym for propionaldehyde is propanal.
Carboxylic Acids

A carbon with an = O and an OH attached is referred to as a **carboxyl group**. Carboxylic acids have a carboxyl group on an *end* carbon.

Carboxylic acids are made commercially by oxidizing alcohols. Like carbonyls, these organic acids are flammable and toxic. Their toxicity, however, is not necessarily related to their acidity. In fact, they tend to be much less corrosive than inorganic acids. Carboxylic acids can form salts just as inorganic acids can. The sodium salt of acetic acid (CH\(_3\)CO\(_2\)Na) is called sodium acetate.

The chemical formulas for carboxylic acids are noted by the COOH at the end of the formula or the hydrogen may appear at the front of the formula. Some examples of organic acid formulas are formic acid, HCOOH; propionic acid, C\(_2\)H\(_5\)COOH (HC\(_2\)H\(_5\)CO\(_2\)); butyric acid, C\(_3\)H\(_7\)COOH (HC\(_3\)H\(_7\)CO\(_2\)); and benzoic acid, C\(_6\)H\(_5\)COOH.

In addition to corrosive properties, carboxylic acids present a combustibility hazard. Most carboxylic acids are water soluble.

**Esters**

Esters are formed by the chemical combination of an organic acid and an alcohol. Esters are readily converted back to their respective acids and alcohols by the addition of water molecules (the process of hydrolysis). Esters are commonly used in the flavor and fragrance industries, and may be sweet smelling, like the odor of fruits. They are also used as solvents in many other industries, including the manufacture of varnishes and plastics. They are volatile.
and can produce central nervous system effects such as dizziness and disorientation. Their toxicities vary from slight to high.

Esters are not easily recognized by their names alone, because the term “ester” does not appear in the name of any member of the family. A way of recognizing an ester by the name of a chemical is to drop the “ic” or “oic” suffix of a carboxylic acid and add the suffix “ate”. Some examples of the members of the ester family include formates, acetates, acrylates, and benzoates.

Chemical formulas for esters are often confused with chemical formulas for ketones and organic peroxides. The key for ester recognition by formulas is the identification of the CO₂ between two hydrocarbon groups, for example, methyl acetate, CH₃CO₂CH₃; methyl acrylate, C₂H₃CO₂CH₃; and methyl benzoate, C₆H₅CO₂CH₃.

**Amides**

Amides are similar to esters; they are formed however, by the chemical combination of an acid and an amine, instead of an acid and an alcohol. They are used to make water repellants and lubricants. Amides are readily converted back to their respective acids by hydrolysis. The properties of amides are generally the same as those of their respective acids and amines. Acetamide, illustrated above, is the product of a reaction of acetic acid and ammonia. Amides are usually solids at room temperature. During a fire, they form toxic and irritating gases.

"Amides are often named after their component acids. The suffix "oic" or "ic" of the acid is replaced with "amide." For example, acetamide is formed from acetic acid. Amide chemical formulas end with CONH₂. Other examples are benzamide (C₆H₅CONH₂) and formamide (HCOONH₂)."
Application Exercises
Application Exercise

You will need:

• Descriptions of several very short incident scenarios incorporating hazardous materials that could be used at a processing or manufacturing facility in your local area

• Use at least four or five chemicals that clearly illustrate the properties discussed in this module (e.g., vapor pressure, corrosivity, radioactivity, water reactivity).
• Use the same “facility” or “process” in each scenario but vary the conditions. For example, in some scenarios include fire, rain, high temperatures, winds, or other factors that influence chemical and physical properties.

• Several copies of the North American Emergency Response Guidebook

• Several copies of the NIOSH Pocket Guide to Chemical Hazards

• Additional reference books and other resource material normally used within the department

• Twenty-five copies of the questions on the following page

Preparation:

This exercise is intended to help students understand how chemical and physical properties of hazardous materials can determine their response tactics in the field.

Divide the class into five groups. Give each group a North American Emergency Response Guidebook, a NIOSH Pocket Guide to Chemical Hazards, access to the other reference materials, and five copies of the tables and questions on the following pages. Assign a scenario to each group. Tell the groups to read their scenarios and complete the tables and questions. After about an hour, reconvene the class and discuss each group’s responses to the questions.

As an alternative to an in-class exercise, you may choose to conduct a site visit to a local facility that uses a variety of chemicals. If so, take resource materials and the questions and tables on the following pages. Allow the students to research the chemicals they find at the site and discuss possible scenarios and response actions.
Application Exercise

Read the scenario you have been given. Using all your resources, research the chemical and answer the following questions.

1. Complete the following table for the chemicals described in your scenario. (Properties may not apply to all chemicals.)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>State (solid, liquid, gas)</th>
<th>Vapor Pressure</th>
<th>Vapor Density</th>
<th>Flash Point</th>
<th>Specific Gravity</th>
<th>Solubility</th>
<th>pH</th>
<th>Other Reactivity</th>
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</table>

2. What are the primary hazards posed by the chemical and physical properties of these hazardous materials?

______________________________________________________________________________
______________________________________________________________________________
______________________________________________________________________________
______________________________________________________________________________

3. How do the conditions at the scene affect the chemical and physical properties of each material?

______________________________________________________________________________
______________________________________________________________________________
______________________________________________________________________________
______________________________________________________________________________
4. From what you know about the hazardous material, its physical and chemical properties, and the conditions on-site, how would you assess the risks and benefits of taking offensive action in this scenario?

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Risk</th>
<th>Benefit</th>
<th>Assessment (action taken)</th>
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</table>
Action Statement
Action Statement

You have just completed the fifth module of the Hazardous Materials Technician course. The topics included:

- The physical and chemical properties of hazardous materials
- Chemical structures
- Combining atoms

Knowing how you respond to emergencies in your first due areas, would you change your actions or habits based on the information covered in this module? Listed below are some suggested actions. Some you may already do, and others may not fit your work environment. If there are actions you have not done in the past, do you think you will begin doing them as a result of this training?

As a result of this training I will:

1. More carefully analyze the chemical and physical properties of chemicals suspected to be present at a hazardous materials incident
2. Evaluate the effect of weather, temperature, and other conditions on the properties of hazardous materials at an incident
3. Take additional courses in atomic and molecular structures and chemical bonding
4. Take additional courses in practical chemistry
5. (Create my own action statement)
Appendix A

Activities
Sublimation Demonstration Activity 1
(Optional)

Instructor Notes

Place a small piece of dry ice in a plastic pan and set it on a table so the students can see it. Use leather gloves to handle the dry ice. Place the pan on a table so it is visible to the students. Check the ice periodically. Eventually it will evaporate without melting.

Student Questions

1. Sublimation is the process by which a solid becomes a vapor without passing through a liquid state. Why do some solids sublime and others do not?

2. List at least two other substances that sublime.
Vapor Pressure Demonstration Activity 2

Instructor Notes

Demonstrate evaporation rates using water and acetone. Prepare one cup of water, a pint of acetone, and two aluminum pans.

1. Place one teaspoon of water in an aluminum pan.

2. Place one teaspoon of acetone in an aluminum pan.

Student Questions

1. If you have equal amounts of water and acetone, which will evaporate faster, and why?

2. How would an increase in room temperature affect the evaporation rates?
Vapor Pressure Activity 3 (Optional)

Instructor Notes

Purchase common, relatively nonhazardous solvents (e.g. acetone, gasoline, kerosene, toluene, motor oil, cooking oil), over the counter at a hardware or grocery store. Obtain only small amounts and familiarize yourself thoroughly with their hazards before using them.

Divide students into small groups and provide at least three reference materials for each group (e.g. NIOSH Pocket Guide, SAX, CAMEO). Provide disposable gloves and safety glasses for each student, obtain a fire extinguisher and provide adequate ventilation so fumes do not accumulate in the training room or throughout the building. Direct students to nearest eye-wash and provide sink for handwashing when the exercise is over. Give each group 65mm glass watch dishes (two each) and a dozen or so 5 milliliter disposable pipettes. Provide paper towels, water and garbage cans for cleanup. Protect tabletops with aluminum foil.

Have the students follow the instructions below:

Student Instructions and Questions

Place one to two drops of each material you have been given on your watch glasses and observe how fast the materials evaporate. Clean watch glasses between samples.

Look up the vapor pressure for each substance in your references. Compare these vapor pressures to your own observations. This will help validate the concept of VP and the quality of the information you are providing by observing the concepts firsthand.

1. How fast would a liquid puddle of anhydrous ammonia evaporate from the watch glass?

2. What pressure would normally be found inside an anhydrous ammonia cylinder?

3. What would happen to the pressure inside the anhydrous ammonia cylinder if the outside temperature were to rise?

4. Occasionally you may find different values for the vapor pressure of a chemical in different reference materials. Why?
Vapor Density Demonstration Activity 4

Instructor Notes

The purpose of this demonstration is to show how gases and vapors that are heavier than air will pool in low areas, and to demonstrate the effect of air turbulence on gases and vapors.

Obtain the following materials:

- Five pounds of dry ice
- Several gallons of warm tap water
- Two large plastic containers or basins
- Table
- Tarps, chairs, candles (optional)

Handle the dry ice with leather gloves and eye protection. Place the dry ice in a basin. Slowly pour warm tap water over the dry ice and note the path the vapors follow. Students should be able to predict areas where the vapors of carbon dioxide and water will pool near the ground. Cover the chairs with the tarp so that the dry ice vapors follow a path to the ground. You can make this demonstration more interesting by constructing an irregular terrain with a tarp and chairs. Place candles on the chairs at different levels. The candles will be extinguished by vapors as they flow to the ground.

When sufficient vapors have accumulated, ask a participant to walk through the vapors to show how they move. The vapor should continue to disperse until it is no longer visible.

Student Questions

1. What are the effects of various weather conditions (such as high winds) on gases that are heavier than air?

2. How would a gas or vapor that is lighter than air, such as methane or hydrogen, act in this situation? What effect would air turbulence have on its dispersion?
**Vapor Density Activity 5**

**Student Instructions**

Using available reference sources, research the vapor densities of the chemicals listed below. If the vapor density is not given, refer to the molecular weight. Predict whether the material will rise or sink in air.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>VD</th>
<th>MW</th>
<th>Reference Source</th>
<th>Rise or Sink</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td></td>
<td>16</td>
<td></td>
<td></td>
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<tr>
<td>Acetylene</td>
<td></td>
<td>26</td>
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<tr>
<td>Propane</td>
<td></td>
<td>44</td>
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<tr>
<td>Hydrogen fluoride</td>
<td></td>
<td>20</td>
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<tr>
<td>Arsine</td>
<td></td>
<td>78</td>
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<tr>
<td>Carbon dioxide</td>
<td></td>
<td>44</td>
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<tr>
<td>Ammonia (Anhydrous)</td>
<td></td>
<td>17</td>
<td></td>
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<tr>
<td>Carbon monoxide</td>
<td></td>
<td>28</td>
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<tr>
<td>Chlorine</td>
<td></td>
<td>71</td>
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<tr>
<td>Hydrogen sulfide</td>
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<td>34</td>
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Flash Point Demonstration Activity 6

Instructor Notes

Obtain the following:

- One pint of acetone
- Disposable pipettes
- Fire Extinguisher
- Small aluminum baking pan
- Tongs for holding the pan
- Matches
- Tongs for holding the matches at least six inches away from your hand
- Eye protection
- Fire fighter gloves

Place approximately five milliliters of acetone in the pan. Hold the pan securely in the air in front of you with the pair of tongs. Wear fire fighter gloves and safety glasses. Take precautions so that if you drop the pan, the acetone will not damage the floor.

Light a match in another pair of tongs and slowly lower it into the vapor space above the liquid acetone. The acetone should flash and burn in the pan. Little or no smoke should be produced. Let the acetone burn off completely. Allow the pan to cool before placing it on any surface.

It should take less than 30 seconds for five milliliters of acetone to burn.

Student Questions

1. What is the flash point of acetone?

2. Why did it burn when lit?

3. Research the flash points of the solvents provided by your instructor and rank them in order of flammability. Use the table on the following page.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Flash Point</th>
<th>Reference Source</th>
<th>Highest Flammability Rank = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tbody>
</table>
**Flash Point Activity 7**

**Instructor Notes**

Divide the class into small groups. Caution the students that they will be igniting flammable liquids, and to appoint one of their group as Safety Officer. The Safety Officer should not allow the exercise to begin until the group takes the proper precautions. Provide each with the following materials:

- Safety glasses
- Aluminum foil to protect the tabletops
- Squirt bottle with water
- Watch glasses
- Matches
- Samples of solvents (the same ones used in the VP exercise)
- Disposable pipettes
- Garbage cans

Have the students follow the instructions below.

**Student Instructions and Questions**

Place one to two drops of a solvent onto the watch glass. Before the solvent evaporates, hold a match in a pair of tongs, light the match, and slowly bring it toward the watch glass at table level.

If the match does not ignite the liquid even when placed directly in it, the material probably has a flash point above 200°F.

If the match lights the liquid before coming into contact with it, the material probably has a flash point less than 100°F.

1. How did the results you observed compare with the flash points you researched in the reference materials?

2. What is the flash point for methane?
Concentration in Water Demonstration Activity 8

Instructor Notes

The purpose of this demonstration is to visually illustrate the size of one part of liquid per million. Obtain the following:

- One two-liter soda bottle
- Food coloring

Fill the two-liter pop bottle with water. Place one drop of food coloring into the soda bottle.

Student Questions

One drop of a liquid chemical into a two-liter container of water is approximately how many ppm?
Concentration in Air Demonstration Activity 9

Instructor Notes

The purpose of this demonstration is to visually illustrate the size of one part of gas per million. Obtain the following:

- Ammonia inhalant ampules or small amount of ammonia cleaning solution

Break an ampule or place a small amount of ammonia cleaning solution on a paper towel and have the students smell it. Most people can detect ammonia below two ppm; the nose is very sensitive to ammonia.

Student Question

Estimate the size of the room you are in (cubic feet). Approximately how large would a 100 ppm sample of gas be?
**Flammable Limits Demonstration Activity 10**

**Instructor Notes**

*Place a drop or two of acetone into a pan and ignite a match at least three feet from the pan.*

**Student Questions**

1. Is acetone flammable?

2. What is the flashpoint?

3. Based on the demonstration conducted by your instructor, why didn’t the acetone vapors create an explosion in the room?

4. How much acetone would it take to blow up your classroom?
Flammable Limits Demonstration Activity 11

Instructor Notes

**WARNING:** The following demonstration involves creating an explosive mixture of acetone vapors in a confined container and purposely igniting those vapors. An explosion will occur, with risks including flying debris, flames, and loud noise. Do not substitute any material for acetone or use any container other than that which is recommended! Take appropriate safety precautions, do outside and wear personnel protective equipment at all times.

Prepare an LEL/UEL test container. Obtain a one-gallon open-top plastic container. Cut a one-inch hole in both the center of the lid and on the side of the container, in the middle as shown below. The container should be made of relatively pliable plastic to help absorb the energy of an explosion by flexing with the buildup of internal pressure. Most containers made of clear plastic are too brittle and should not be used. More pliable containers, (e.g., Tupperware™ or Rubbermaid™) will not shatter. Do not use a five-gallon water cooler jug; the acetone will degrade the plastic, weaken it and increase the potential for container failure. If you see that the acetone is degrading your container, discard it.

Obtain two containers, one to practice the demonstration prior to training.

![Lid with hole](image)
![Jug with hole](image)

Obtain the additional following materials:
- Eye protection
- Fire fighter gloves
- Gloves
- Matches
- Acetone
To perform the demonstration:

1. **Don eye protection and fire fighter gloves.**
2. **Position the container so that the holes are facing away from both you and the class.**
3. **Place approximately five milliliters of acetone into the container and close the lid. Move the can of acetone at least twelve feet away from the container.**
4. **Light a match and hold it with the tongs. The tongs should hold the match at least six inches from your hand.**
5. **Slowly approach the hole in the container from the side. **Do not stand in front of the hole on the side or above the hole in the lid.**
6. **If the match reaches a concentration of acetone between the LEL and UEL, a flash will occur. (This will probably happen just as the match reaches the hole in the container or as soon as it is inserted.)**
7. **Option: Wrap a small plastic doll in tyvek or other chemical protective material and place it in the bottom of the container. Often the flash will melt the material, illustrating that CPC does not offer flash protection.**

*Have the students look up the flammable ranges for acetone in their reference material.*

**Student Questions**

1. What is the flammable range for acetone?

2. What type of personal protective equipment would protect you from this type of reaction in an incident involving a large acetone spill?
Flammable Limits Demonstration Activity 12

Instructor Notes

Repeat the Flammable Limits Demonstration 10. This time, use a combustible gas indicator to monitor the level of combustible vapors in the container. (You may need to introduce the basic capabilities of the CGI meter to the students prior to demonstrating it.)

Check vapor levels with the CGI:
• Prior to adding the acetone
• After adding a small amount
• After adding a bit more
• After adding enough to reach the LEL

Once you’ve reached the LEL in the container, try igniting it again.

Student Questions

1. What does the CGI measure?

2. When does the CGI alarm sound?

3. What happens when the CGI detects the LEL?

4. What does a reading of 100% indicate?
Specific Gravity Demonstration Activity 13

Instructor Notes

To demonstrate specific gravity:

1. Fill a clear plastic cup 1/2 full with water. (To make the water easier to see, add food coloring.)

2. Add about 1/4 cup of cooking oil to the water to illustrate how the oil floats on top.

Student Questions

1. Is the specific gravity of cooking oil greater than or less than 1?

2. How does the specific gravity of gasoline affect your control technique in case of a gasoline spill?

3. What are examples of other liquids with a specific gravity less than one?
Specific Gravity Demonstration Activity 14

Instructor Notes

1. Fill a clear plastic cup 1/2 full with water. (To make the water easier to see, add food coloring.)

2. Slowly add about 1/4 cup of dishwasher rinse solution (i.e. Jet Dry) to the water. Most brands will sink.

Student Questions

1. Is the specific gravity of dishwasher rinse solution greater than or less than 1?

2. How does the specific gravity of a liquid affect your control technique in case of a spill in a body of water?

3. What are examples of other liquids with a specific gravity greater than 1?
Specific Gravity Activity 15

Instructor Notes

Divide the class into small groups and instruct them to use a variety of reference sources to determine the specific gravity of the chemicals listed below.

Student Instructions

Using available reference sources, research the specific gravities for the chemicals listed below. Predict whether the material will sink or float in water, or if it will mix.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Specific Gravity</th>
<th>Reference Source</th>
<th>Float, Sink, or Mix?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naptha (coal tar)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Carbon disulfide</td>
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<tr>
<td>Diazinon®</td>
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<td></td>
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<tr>
<td>Octane</td>
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<td></td>
<td></td>
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<tr>
<td>Nicotine</td>
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<td></td>
<td></td>
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<tr>
<td>Propyl alcohol</td>
<td></td>
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<td></td>
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<tr>
<td>Triethylamine</td>
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<td></td>
<td></td>
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<tr>
<td>Hydrogen peroxide</td>
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<tr>
<td>Kerosene</td>
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</tbody>
</table>
**Solubility Demonstration Activity 16**

**Instructor Notes**

To demonstrate solubility, mix a tablespoon of sugar or salt in a cup of room temperature water until the sugar/salt dissolves.

**Student Notes**

1. What would happen if the water were warmer?

2. What would happen if you gradually added more sugar or salt?
Solubility Activity 17

Instructor Notes

Obtain the following materials for each group of students:

- One test tube rack
- Six to twelve test tubes (depending on the number of samples provided to the students)
- One metal test tube holder
- Twelve disposable five milliliter pipettes
- Aluminum foil to protect the tabletops
- Safety glasses for each student
- Disposable gloves
- Garbage cans
- Indelible marking pens to write on the glass test tubes
- Empty milk containers for used empty test tubes (identify as WASTE GLASS)
- Empty containers for used solvents (identify as FLAMMABLE LIQUIDS)
- About one cup of water per group of students
- Solvent samples used for the flash point activity

Have the students follow the instructions below.

Student Instructions

1. Research the solubility and specific gravity of the samples your instructor has provided.

2. Predict the solubility of each sample.

3. Write the name of each sample on a separate test tube.

4. Place about one inch of water in each test tube.

5. Hold the marked test tube with water in the metal test tube holder.

6. Slowly add about one-half inch of the sample liquid to the water, starting with one drop at a time. Point the test tube away from yourself and others in the room.

7. Shake the test tube slightly to try and mix the water and sample together.

8. Dispose of the flammable solvents into the waste container marked FLAMMABLE LIQUIDS. Do not put any chlorinated solvents in this waste.
Record the results of this exercise on the table below.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility</th>
<th>Specific Gravity</th>
<th>Reference Source</th>
<th>Observation (Did solvent mix?)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tbody>
</table>
Oxidation Case Study Activity 18

Henderson, Nevada (1988)

A series of explosions on May 4, 1988 totally destroyed a chemical plant in a desert area just outside of Henderson, Nevada. The explosions were large enough to register on a seismograph located at the California Institute of Technology, 215 miles away. Two employees were killed, 350 workers and local residents were injured, and 17,000 people were evacuated from their homes. At the time of the explosion, the plant had about 130 employees and was producing 40 million pounds of ammonium perchlorate per year for use as an oxidizer in rocket engine fuel.

The manufacturing process took place in a series of buildings described as the brine plant, the chlorate building, the process building, a crystallizer room, a large dryer building, a smaller dryer building attached to the process building called the batch house, and a blender building. Sodium chloride was mixed with water in the brine plant. Electrolytic cells in the chlorate building oxidized the sodium chloride to sodium chlorate and then oxidized the sodium chlorate to sodium perchlorate. Next, in the process building, the sodium perchlorate was reacted with ammonium chloride to produce ammonium perchlorate. The ammonium chloride was produced on the site in the process building by reacting ammonia with hydrochloric acid. In the final steps, the ammonium perchlorate was crystallized from the water solution, filtered, dried, and packaged. This work took place in the crystallizer room, the large dryer building, the batch house, and the blender building.

At the time of the accident, about 8.5 million pounds of ammonium perchlorate were stored in polyethylene barrels and aluminum tote bins in a number of locations in the plant. It is estimated that 700 polyethylene barrels, each holding 250 pounds of ammonium perchlorate (a total of 180,000 pounds) were stored outside, adjacent to the batch house. Another 7,780 full barrels (about 2 million pounds) were stacked near buildings on asphalt pavement. In addition, approximately 1,275 aluminum tote bins holding about 5,000 pounds each (totaling over 6 million pounds) were stored on asphalt pavement in several locations, near buildings on the plant property.

The initial fire, when discovered, had engulfed a heated, rotating steel cylinder used to dry ammonium perchlorate crystals. Insulation around this cylinder (which was contaminated with ammonium perchlorate) was burning. Three fire hoses were manned at this time. Employees who fought the fire stated that about a dozen polyethylene barrels in the building containing ammonium perchlorate caught fire. Four of these barrels contained a mixture of trash and floor sweepings made up of ammonium perchlorate and various combustible materials. The fire spread to the walls of the building, which were made of fiberglass-plastic corrugated sheets contaminated with ammonium perchlorate dust. At about 11:45 a.m., the fire hoses lost all water pressure and workers ran from the building.

The first small explosion occurred at 11:51 a.m., shortly after the workers ran from the batch house. The cause was thought to be fire that reached a 5,000 pound closed aluminum bin of ammonium perchlorate. This first explosion was equivalent to about half a ton of TNT. It
started a fire in the large dryer building. At this time, several hundred polyethylene barrels, each containing 250 pounds of ammonium perchlorate, were observed to be burning outside the batch house. The plant apparently had no fire alarm system or other means of notifying employees to evacuate. There were no telephones in the process buildings and no means of communication between these work areas and the front office.

A fireball from the first explosion spread the fire to the large dryer building. It is also possible that the fire was spread by ammonium perchlorate that had spilled on and washed into the asphalt pavement around the plant over the years. At 11:53 a.m. and 11:57 a.m., two huge explosions occurred. These destroyed the chemical plant, leveled a nearby plant, ruptured the 16-inch gas line running under the plant, and caused property damage up to 12 miles away. The first of these two explosions was equivalent to 108 tons of TNT and the second, 235 tons of TNT.

The Clark County Fire Dispatcher received the first call from the front office of the chemical plant at 11:51 a.m., about the time of the first small explosion. The 11:57 a.m. explosion damaged fire vehicles and injured fire fighters on their way to the scene. Small explosions continued to occur. The Clark County and the Henderson City Fire Departments set up a command post about two miles from the plant and decided not to send personnel into the area until the fire had burned itself out.

Questions

1. Using a variety of reference sources, research the hazards of ammonium perchlorate.

2. What factors contributed to this disaster?
Oxidation Demonstration Activity 19

Instructor Notes

Obtain the following materials:

- Small road flare
- Matches
- Large bucket of water

Conduct this activity outside:

1. Using appropriate safety precautions, light a standard road flare. (Hint: Duct tape the road flare to the end of a pole. This will keep it further from your body as you hold it.)

2. Try to extinguish the flare in a bucket of water. Depending upon the brand of road flare, it will probably continue to burn for some time even under water.

Student Question

Why does a road flare continue to burn under water?
Rapid Hazard Identification Activity 20

Instructor Notes

Divide the class into small groups and provide the following materials to each group:

- One test tube rack
- Six to twelve test tubes (depending on the number of samples provided to the students)
- One metal test tube holder
- Twelve disposable plastic five ml pipettes
- Plastic table covers
- Safety glasses for each student
- Disposable nitrile gloves
- Garbage cans with plastic liners
- Indelible marking pens to write on the glass test tubes
- Empty plastic milk containers for used empty test tubes (identify as WASTE GLASS)
- Empty containers for used solvents (identify as FLAMMABLE LIQUIDS)
- About one cup of water per group of students
- Solvent samples, used for the flash point activity
- Acid and base samples used for pH activity
- pH paper or indicator strips
- Potassium iodide (KI) strips or oxidizer test strips
- 3N hydrochloric acid in 125 - 250 ml flip spout plastic bottles
- One watch dish
- Book of matches or cigarette lighter
- Hair pins

Student Notes

1. Place a small amount of the unknown product on a watch dish and observe it. Note characteristics such as odor, color, viscosity, and evaporation rate.

2. Using the same unknown product on the watch dish in step one, test for an oxidizer by placing one drop of 3N hydrochloric acid on a potassium iodide (KI) test indicator strip. Slowly move the wet end of the KI test indicator strip over the unknown product without actually touching the product with the KI test indicator strip. Note any color change to the strip. If there is no change, slowly place the wet end of the strip onto the unknown product and note any color change. If the product is an oxidizer, the KI test indicator strip will change color from white to a dark blue or black within a few seconds. Wait a few seconds and add a few drops of the 3N hydrochloric acid to the unknown on the watch dish and observe any reactions.
3. Other reactions may be noted, such as:
   - White fumes, which may indicate ammonia, amines, hydrazine, and other nitrogen containing molecules
   - Boiling, which may indicate a hydroxide
   - Strong effervescence, which may indicate a reactive metal or cyanide salt
   - A change in color of the KI paper (to yellow), indicating an iodide salt or acid

4. Pour approximately one-half inch of water into a test tube. Add a few drops of unknown liquid or a pea size amount of unknown solid material. If the unknown solid effervesces, use extreme caution and do not cap the test tube. Observe and note the reaction. For example, did the unknown float, sink, dissolve, effervescce, react violently, change color, or form an emulsion (become milky)? Did the test tube become hot or cold? An unknown liquid that floats may be a hydrocarbon. An unknown liquid that sinks may be a halogenated hydrocarbon, carbon disulfide (rotten egg odor). An unknown liquid that dissolves may be a polar solvent or acid. A solid that dissolves could indicate an oxysalt, a soap, sugar, or a type of salt. An unknown solid that effervesces could be a reactive metal, a carbide or a cyanide salt. A violent reaction from an unknown solid can indicate reactive metal or sodium bicarbonate. An exothermic reaction could be the result of several different types of salts, including hydroxides. An endothermic reaction indicates an ammonium salt or nitrate salt.

5. Use the water results of the water solubility test to determine and classify the pH of the unknown.

6. Clean the watch dish and place a small amount of an unknown liquid or solid on the watch dish. Bend a hair pin into a loop and burn off any plastic coating on the hair pin with the lighter or match. Then place the hot loop into the unknown, at which point, burn the unknown on the hot hair pin. If any kind of popping sound is noted, do not go any further and assume the unknown has explosive potential. If no reaction is noted with the hair pin, light a match and slowly bring the match to the unknown on the watch dish. Note at what point the unknown ignites on the watch dish or does nothing.

Conduct each of the above tests on several of the materials used to demonstrate other physical and chemical properties. A considerable amount of knowledge about an unknown material can be gained through conducting each of the tests listed above. An unknown can be broadly categorized as either an oxidizer or not, acid or base, organic or inorganic, water reactive, etc. Once the properties have been identified, the proper tactical procedures can be implemented.
Polymerization Demonstration Activity 21

Instructor Notes

Obtain the following materials:

- A spray can of expanding foam from the hardware store (the kind that is used to fill in around door jams or cracks in foundations)

- A clear plastic cup

Spray some of the foam mixture into a clear plastic cup and let the students watch as it expands and hardens.

Student Question

In the demonstration conducted by your instructor, why did the foam expand?
pH Activity 22

Instructor Notes

The purpose of this activity is to familiarize students with the use of pH paper and the pH of common materials. This activity also allows you to demonstrate dilution and its effect on pH, and how neutralizing a chemical releases heat.

Obtain the following materials:

- One container of pH paper
- Access to water, including one quart per table
- 1/4 cup of muriatic acid, available at most hardware stores (about 30% Hcl)
- One pound of baking soda
- A small sample of acetone
- Thermometer with a range of at least 0°C to 110°C
- Four beakers or glass jars with capacities of at least four cups
- Safety glasses for each student
- Disposable gloves
- Eyewash bottles or nearby sink w/eyewash
- Garbage cans
- Paper towels
- Sink for hand washing after the exercise

Prepare these samples (enough for each group of students) and number them one through five. The students will only need a few drops of each.
1. Tap water
2. Vinegar
3. Muriatic acid
4. Acetone
5. Water with a small amount of lye added

Warning: Safety glasses and gloves are to be worn at all times. Eyeglasses are acceptable only if they have side shields. If any exposure occurs, rinse the exposed area with large amounts of water.

Demonstrate to the students how to use the pH paper and how to read the scale on the pH container. Make sure they understand that most pH paper is only accurate to about 1-2 pH units, which is adequate for most field response operations.
Student Instructions and Questions

Measure the pH of the five samples your instructor has prepared. Rank each sample according to pH and level of hazard. Note your reading on the table below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Level of Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muriatic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinegar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water with a small amount of Drano added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soda pop</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coffee</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soap solutions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other liquids found in training area</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Measure the pH of several common household items and note the readings on the table above.

1. How can you measure the pH of a dry powder?

2. If a material has a neutral pH, is it harmless?
Strength Activity 23

Instructor Notes

*Obtain the following materials:*

- Two plastic buckets about half full with water
- pH papers
- Vinegar
- Muriatic acid
- Stirrer

Student Instructions

1. Measure the pH of the water in each bucket. Readings should be the same.
2. At each measurement, place pieces of pH paper in front of each bucket as a visual record of the exercise.
3. Add equal amounts of vinegar to one bucket and muriatic acid to the other bucket (about 1/3 cup each).
4. Stir the contents of the buckets and measure the pH of each.

Student Questions

1. What are your readings?

2. Why are the muriatic readings lower when equal amounts of vinegar and acid were added?

3. What did you observe when only a small amount of an acid was added to a large amount of water (1/3 of a cup of acid into a bucket of water)?

4. How many gallons of water would it take to change the pH of a solution from 4 to 5? From 4 to 6? From 4 to 7?

Keep both of the buckets in place for the following activities.
Neutralization Activity 24

Instructor Notes

Explain that fire departments do not neutralize large acid spills because it is very difficult to do safely. The following activity demonstrates why.

Obtain the following materials:
• Baking soda
• Tablespoons

Distribute tablespoons and baking soda to each group of students.

Student Instructions and Questions

1. Place one tablespoon of baking soda into each of the buckets. Stir the buckets and observe the results.

   What was the reaction in the vinegar solution?

   What was the reaction in the muriatic acid solution?

2. Keep the pieces of pH paper visible in front of each bucket. Continue to add baking soda, one tablespoon at a time to each bucket until the solutions are close to a pH of 7, or slightly above. Allow the baking soda time to react after each addition. Stir and measure the pH every time.

   Which requires more baking soda for neutralizing—the vinegar or the muriatic acid?

   Once the two buckets are between a pH of 7 and 9 you can dispose of them in the sanitary sewer.

3. What hazards did you observe during the previous exercise?
Heat of Neutralization Activity 25

Instructor Notes

Obtain the following materials:
- Quart glass jars or beakers
- Additional pans/buckets for overflow
- Baking soda
- Thermometer

Have the students follow the instructions below.

Student Instructions and Questions

1. Place one cup of water in a one quart glass jar or beaker. Measure the temperature and pH of the water.

2. Pour one cup of muriatic acid into a glass jar. Measure the pH of the acid. (It should be around 0-1.)

3. Add the muriatic acid to the water slowly and carefully. Stir and record the temperature change as you add the muriatic acid.

   What happens to the temperature of the solution?

4. Measure the pH of the solution. The pH should be around 0-1.

   Why is the pH of this solution essentially unchanged?

5. For the next step, put the quart sized glass jar or beaker into a second pan or bucket to act as secondary containment in the event it bubbles or spills over.

6. Slowly add baking soda to this solution, one tablespoon at a time, stirring during the process.

7. Measure the temperature of the solution as it is being neutralized.

   What happens to the temperature?
8. Continue to add baking soda to the solution until the pH is between 7 and 9. Continue to check the temperature until you reach this point.

   How does the change in temperature compare to the temperature change in the dilution method?

9. Based on your observations, which method of bringing the pH of an acid to 7 would be most effective in the event of skin contamination?

10. What do you think would happen if a strong base, such as potassium hydroxide, were used to neutralize a concentrated solution of hydrochloric acid?

11. Dispose of the solution by flushing it down a sanitary sewer.
Newton, Massachusetts Case Study Activity 26

On October 25, 1993, an explosion occurred at the industrial facility of the H.C. Starck Company in Newton, Massachusetts. The company is a metal manufacturing facility. Operations include the heating of 55-gallon drums of metallic sodium, in its solid form. After it’s heated, the liquefied sodium is pumped out, and the drum cooled. The top of the drum is then cut off, and the drum containing the sodium residue is taken to a masonry enclosure called the “hood room.” There, the residue is reheated to a liquid state and ignited; the burning sodium is then allowed to fully oxidize. When the drum has cooled, water is introduced by means of spray nozzles, and the drum is washed, then removed for disposal.

During the afternoon on the day of the explosion, a 55-gallon barrel was placed in a drum heater with the intent to liquefy and pump out the 400 pounds of metallic sodium contained within it. Due to a mathematical error, however, only 300 pounds were actually removed, leaving 100 pounds of sodium—in its solid form—at the bottom of the drum.

Despite the fact that the normal amount of residue that remains in a drum ranges between four to ten pounds, a supervisor authorized the burning of the 100 pounds of metallic sodium remaining in the drum. (Under standard procedures, a drum containing more than four to ten pounds of residue is inerted with argon, stored, and then shipped for disposal).

Five minutes into the burn of the residue, the excessive amount of what had become liquid sodium overflowed the drum, spilling into a wet pan located under the drum. The pan had allegedly become wet during a washdown that was performed earlier. Metallic sodium, when burning, reacts violently with water. The chemical reaction between the water and the highly reactive metallic sodium resulted in an explosion which blew employees across the hood room.

Employees summoned the Newton Fire Department. Newton’s fire personnel had trained at the plant on previous occasions, and responded to a number of small fires there. In those previous instances, fire fighters extinguished the metal fires with salts that are kept on the premises for that purpose.

Entering the hood room, fire fighters encountered dense smoke which prevented them from seeing that water had built up on the floor. Fire fighters began to shovel salts onto the fire. At one point a shovel was placed on the floor and became wet. When this shovel was used to apply more salt to the molten sodium in the barrel, the sodium exploded. The heat of this second explosion was so intense it melted fire fighter protective clothing. Eleven fire fighters were injured.

As a result of this incident, the plant has discontinued the practice of burning residue sodium. All drums removed from the process heaters shall be inerted with argon gas and returned to the originator for processing.
Questions

1. Fire fighters had trained at this plant in the past and were familiar with the effects of sodium and water. Neverless, a second explosion occurred. Could it have been prevented? If so, how?

2. List some facilities in your jurisdiction that may use or store sodium metal. How would you respond to a similar incident at these locations?
Compressed Gas Activity 27

Instructor Notes

Obtain an SCBA cylinder for demonstration to the class. Release air from the cylinder, then ask the questions below.

Student Questions

1. Your SCBA cylinder is one of your most valuable pieces of equipment. What would happen to it if it were left in a fire and exposed to intense heat.

2. What happens when you release air from your SCBA cylinder quickly?
Shreveport, Louisiana Case Study Activity 28

Shreveport, Louisiana, September 1984

In response to reports of an ammonia odor, maintenance personnel in a cold storage warehouse attempt to repair a leaking valve in one room of the building’s refrigeration system. Anhydrous ammonia is used as the refrigerant, and the room is normally kept at 12°F. At the time repair work begins, the temperature in the room is about 50°F. Although the faulty section of the refrigeration unit is shut down, the concentration of ammonia increases, causing discomfort and irritation to the workers who are wearing only filter masks. The fire department is contacted. First arriving fire fighters correctly identify the situation as a hazardous materials incident and request assistance from the hazardous materials response team. While waiting for the hazardous materials team to arrive, fire fighters attempt to disperse the ammonia with a water fog. Warehouse employees inform emergency responders that the leak has been isolated and that only residual gas remains in the room. Wearing fully encapsulating, vapor-protective suits, two members of the hazardous materials team enter the room in order to replace the leaking valve.

A spark from a forklift used in the repair process touches off a sudden explosion. The force of the blast raises the building’s roof about one foot and severely damages interior walls. Although combustible products in the vicinity of the leak were removed, other combustibles in adjacent areas of the building catch fire. The two hazardous materials team members are severely burned when their protective clothing ignites. One team member dies within 36 hours; the other is admitted to the hospital in critical condition.

1. What hazards are presented by anhydrous ammonia?

2. Given that anhydrous ammonia presents a relatively low fire hazard, how could an explosion occur?

3. What effect did the increasing temperature in the room with the leaking valve have on the incident?

This case study was summarized from a report prepared by the National Fire Protection Association under an agreement with the Federal Emergency Management Agency/United States Fire Administration and the National Bureau of Standards/Center for Fire Research.
4. Many refrigeration units that previously used ammonia and freon have been modified to use different refrigerating gases. How do these new gases impact fire fighting?
Verbal Quiz Activity 29

Review the initial questions posed to the students at the start of this unit. Ask the students to answer these questions in a discussion or small group format. Have them not only give you the correct answer, but explain all of their answers in detail including the use of the practical chemistry terminology they have just covered. Allow 30 minutes for a thorough review of these questions and the physical chemistry terms mentioned.

1. Which is more flammable—gasoline or diesel fuel?

2. Which is more flammable—methyl ethyl ketone or toluene?

3. Will ammonia vapors tend to rise or sink in air?

4. Why is propane found as both a gas and liquid in five-gallon propane bottles? What is the typical pressure in those bottles? How does this compare to an industrial sized tank of propane?

5. How can you evaluate whether a material will readily evaporate quickly, posing a potential inhalation or flammable threat?

6. Why doesn’t grease dissolve in water? Why does soap dissolve in water, and dissolve grease?

7. What is the definition of “flash point?”
8. When can you be sure that hazards involving an acid have been effectively controlled?

9. What three precautions can reduce exposure from a radioactive source? Which is most effective?
Radiation Demonstration Activity 30

Instructor Notes

Obtain the following materials:

- Radiation survey meter
- Check sources

The purpose of this activity is to demonstrate some fundamental principles of radiation, using a meter designed to detect radiation.

1. Turn on the audio function if your meter has one. If not, you may need to move around the room so the students can see the meter readout.

2. Using the check source, take readings with the meter at varying distances (0’, 1’, 2’, etc.) This demonstrates the effectiveness of using distance to protect yourself from radiation.

3. Use additional check sources to illustrate the differences between alpha, beta and gamma radiation. These sources should be available from your radiation survey instrument manufacturer.

Using the check source and items in the classroom (e.g. disposable gloves, turnout gear, a piece of paper, fire fighter helmet) demonstrate the principle of shielding as a method of protecting yourself from radiation.

Student Questions

1. Identify facilities in your local area where a radiation incident could occur. Are you equipped to handle it?

2. List the local, state, and federal government agencies you should contact in case of a radiation incident.
Using the reference sources available, complete the blank spaces in the table below.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Chemical</th>
<th>Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diethylamine</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td></td>
<td>Flammable, irritating, possible carcinogen</td>
</tr>
<tr>
<td>(CH₃)₂CO</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrous Oxide</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td></td>
<td>Corrosive</td>
</tr>
<tr>
<td>Cl₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyl Chloride</td>
<td>Flammable, frostbite</td>
</tr>
<tr>
<td>Sn</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Iodine</td>
<td>Irritating</td>
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<tr>
<td></td>
<td>Sulfuric Acid</td>
<td>Corrosive</td>
</tr>
<tr>
<td>HNO₃</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>Combustible, irritating</td>
</tr>
<tr>
<td>Si</td>
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</tr>
</tbody>
</table>
### Atomic Structure Activity 32

Fill in the blanks.

<table>
<thead>
<tr>
<th>Element name</th>
<th>Symbol</th>
<th>Atomic number</th>
<th># of protons</th>
<th># of neutrons</th>
<th>Mass number</th>
<th># of electrons</th>
<th># of electrons in outer shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hydrogen</td>
<td>H</td>
<td>11</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td></td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Carbon</td>
<td>C</td>
<td>6</td>
<td>6</td>
<td></td>
<td>35</td>
<td>8</td>
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</tr>
<tr>
<td>4.</td>
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<td>26</td>
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<td>32</td>
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<td>6.</td>
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<td>7.</td>
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<td></td>
<td>26</td>
<td></td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Calcium</td>
<td>C</td>
<td>29</td>
<td>29</td>
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<td></td>
</tr>
<tr>
<td>9.</td>
<td></td>
<td></td>
<td>29</td>
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<td></td>
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</tr>
<tr>
<td>10.</td>
<td></td>
<td></td>
<td>29</td>
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</tr>
</tbody>
</table>
**Hydrocarbon Activity 33**

Name the molecule, write the molecular formula, determine the hydrocarbon family, and the type of bond that identifies the family.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Formula</th>
<th>HC family</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
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</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
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<td><img src="image6" alt="Structure 6" /></td>
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<tr>
<td><img src="image7" alt="Structure 7" /></td>
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</tr>
</tbody>
</table>

---
Draw the structure, write the formula, determine the hydrocarbon family, and the type of bond that identifies the family.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Formula</th>
<th>HC family</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Butadiene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Propylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c-Butane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Octane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Propyne</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Draw the structure, name the molecule, determine the hydrocarbon family, and the type of bond that identifies the family.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Formula</th>
<th>HC family</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c-C\textsubscript{6}H\textsubscript{12}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{2}H\textsubscript{4}</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td>C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}</td>
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</tr>
<tr>
<td></td>
<td>n-C\textsubscript{5}H\textsubscript{10}</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{2}H\textsubscript{2}</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{7}H\textsubscript{16}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c-C\textsubscript{6}H\textsubscript{12}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3}CHCH\textsubscript{3}CH\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{6}H\textsubscript{6}</td>
<td></td>
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</tbody>
</table>
**Hydrocarbon Derivatives Activity 34**

Name the molecule, write the molecular formula, and determine the functional group.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Formula</th>
<th>Functional group</th>
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</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
</tr>
<tr>
<td>H</td>
<td>C–C–Cl</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C–O–C–H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C–O</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C–O–O–C–H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C–C–N</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C–C–O</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C–C–O</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
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<tr>
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<td>C–C–O</td>
<td>H</td>
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<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C–C–O</td>
<td>H</td>
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</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
</tbody>
</table>
Draw the structure, write the formula, and determine the functional group.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Formula</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetaldehyde</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methanoic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyl acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Formamide</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Propanone</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dipropyl peroxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isopropyl alcohol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyl acrylate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trichloroethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitromethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Draw the structure, name the molecule, and determine the functional group.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Formula</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)Br</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_3)CO(_2)(_2)H(_5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_2)O(_2)CH(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_5)CONH(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)H(_5)OC(_2)H(_5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)H(_5)NO(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-C(_4)H(_9)OCH(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C(_2)H(_2))(_2)O(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_2)OH(NO(_2))(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_4)H(_9)OH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_5)CO(_2)CH(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix B

Additional Chemical Information
Chemical Properties: Definitions and Relationships
Implications for Field Application

**Flash Point**: Minimum temperature of a liquid that generates enough vapor to form an ignitable mixture above the liquid.

**Lower Explosive Level (LEL)**: Minimum liquid concentration of vapor in air that can ignite, given a source of ignition.

These measurements are obtained at 68°F/20°C. If the ambient temperature is greater than the flash point of a product, then the vapor above the product could be within the explosive range. Possible sources of ignition include: catalytic converters, 100°F; light switches (sparks), 800-1000°F; and flares, 100°F.

**Vapor Pressure**: The ability of a solid or liquid to move into a gaseous state (vaporize).

**Boiling Point**: The temperature at which the vapor pressure of the solid or liquid is equal to (1) atmosphere (760 mm Hg).

Vapor pressure and boiling point have an inverse relationship: the higher the vapor pressure the lower the boiling point and vice versa. For example, toluene has a vapor pressure of 20 mm Hg and boiling point of 239°F; conversely carbon disulfide has a vapor pressure of 297 mm Hg and a boiling point of 116°F.

**Vapor Density**: The tendency of a gas or vapor to rise or fall in air. Air has a vapor density of 1.0.

**Molecular Weight**: The total of the atomic weights for each of the atoms making up a substance. The estimated molecular weight of air is 29.

Vapor density is usually given a value of <1 or >1, indicating whether the product will rise or fall in air. Whereas, comparing the molecular weights of two products allows you to determine just how much heavier than air a product is, or rather, gives you a more specific vapor density. This helps in determining how well the product mixes with air and what type of ventilation set-up would be appropriate.

Some rules of thumb of vapor density:

1. If >1 but <2 and not a liquid, the product will mix well with air and generally be found at waist level.
2. If >2 but <3, the product does not mix readily with air and will generally be found at knee level.
3. If >3, the product will not mix with air and must be exhausted from the area.
4. Naturally occurring gases mix readily with air.

**Solubility**: The degree to which one substance mixes with another.

**Specific Gravity**: The weight of a solid or liquid in comparison to an equal volume of water. Water is assigned a specific gravity of 1.0.

Solubility indicates the amount of a substance that mixes with water, while the specific gravity indicates whether the remainder of the product will sink or float in water. This information can guide you in your selection of a vapor suppression agent, water or foam.
## Properties of Eleven Commonly Released Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Form</th>
<th>Boiling Point</th>
<th>Vapor Pressure</th>
<th>Vapor Density</th>
<th>Specific Gravity</th>
<th>Solubility (% by volume) [See page 26]</th>
<th>Flash Point</th>
<th>Ignition Temp.</th>
<th>Flammable Range (% by volume)</th>
<th>Odor Threshold†</th>
<th>Exposure Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous Ammonia</td>
<td>Gas</td>
<td>-28° F</td>
<td>8.5 atm @ 20° C</td>
<td>0.6</td>
<td>0.68</td>
<td>Appreciable 51%</td>
<td>1204° F</td>
<td>1562° F</td>
<td>16-25%</td>
<td>46-55 ppm</td>
<td>25 ppm</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Gas</td>
<td>-29° F</td>
<td>6.3 atm @ 20° C</td>
<td>2.49</td>
<td>1.468</td>
<td>Slight 0.7%</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.3-5 ppm</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Gasoline</td>
<td>Liquid</td>
<td>100-399° F</td>
<td>NA</td>
<td>3.0-4.0</td>
<td>0.7-0.8</td>
<td>Immiscible</td>
<td>-45° F</td>
<td>536-836° F</td>
<td>1.5-7.6%</td>
<td>0.005-10 ppm</td>
<td>300 ppm</td>
</tr>
<tr>
<td>Hydrochloric Acid (37%)</td>
<td>Liquid</td>
<td>227° F</td>
<td>190 mm Hg @ 20° C</td>
<td>1.27</td>
<td>1.18</td>
<td>Appreciable 62%</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1-5 ppm</td>
<td>5 ppm (c)</td>
</tr>
<tr>
<td>Methyl Alcohol</td>
<td>Liquid</td>
<td>148° F</td>
<td>97 mm Hg @ 20° C</td>
<td>1.1</td>
<td>0.8</td>
<td>Miscible 52° F</td>
<td>725° F</td>
<td>6.7-36.5%</td>
<td>NA</td>
<td>100 ppm</td>
<td>200 ppm</td>
</tr>
<tr>
<td>Methyl Chloride</td>
<td>Gas</td>
<td>-12° F</td>
<td>4.8 atm @ 20° C</td>
<td>1.74</td>
<td>1</td>
<td>Immiscible</td>
<td>-50° F</td>
<td>1170° F</td>
<td>7.6-19%</td>
<td>10-100 ppm</td>
<td>25000 ppm</td>
</tr>
<tr>
<td>Nitric Acid (60-68%)</td>
<td>Liquid</td>
<td>251° F</td>
<td>62 mm Hg @ 20° C</td>
<td>2 to 3</td>
<td>1.41</td>
<td>Complete NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>2 ppm</td>
<td>CA</td>
</tr>
<tr>
<td>PCBs</td>
<td>Liquid</td>
<td>527-725° F</td>
<td>&lt; 1 mm Hg @ 20° C</td>
<td>NA</td>
<td>1.5</td>
<td>Negligible ca 0.01 ppm</td>
<td>284-392° F</td>
<td>NA</td>
<td>NA</td>
<td>0.5 mg/m³</td>
<td>CA</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>Solid</td>
<td>2534° F</td>
<td>1 mm Hg @ 739° C</td>
<td>NA</td>
<td>2.13</td>
<td>Appreciable 50%</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>2 mg/m³</td>
<td>250 mg/m³</td>
</tr>
<tr>
<td>Sulfuric Acid (93 to 98%)</td>
<td>Liquid</td>
<td>518° F</td>
<td>&lt; 3 mm Hg @ 25° C</td>
<td>3.4</td>
<td>1.84</td>
<td>Complete NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1 mg/m³</td>
<td>80 mg/m³</td>
</tr>
<tr>
<td>Toluene</td>
<td>Liquid</td>
<td>232° F</td>
<td>22 mm Hg @ 20° C</td>
<td>3.14</td>
<td>0.86</td>
<td>Negligible 0.05 gm/100 gm</td>
<td>40° F</td>
<td>997° F</td>
<td>1.3-7.1%</td>
<td>0.17-4.0 ppm</td>
<td>100 ppm</td>
</tr>
</tbody>
</table>

CA = Carcinogen † From "Odor Thresholds in Air as Compared to Threshold Limit Values" by Charles Billings and Linda Jones. AIH Journal, June 1981.

Reprinted from: Union Pacific Railroad Company and the United States Environmental Protection Agency Region VII
Selected Terms in Chemistry

Selected Prefixes

meth- (one, e.g., methane has one carbon)
eth- (two, e.g., ethane has two carbons)
prop- (three, e.g., propane has three carbons)
but- (four, e.g., butane has four carbons)
pent- (five, e.g., pentane has five carbons, a pentagon has five sides)
hex- (six, e.g., hexane has six carbons, a hexagon has six sides)
hept- (seven, e.g., heptane has seven carbons, a heptagon has seven sides)
oct- (eight, e.g., octane has eight carbons, an octagon has eight sides)
methyl- (radical of methane)
ethyl- (radical of ethane)
propyl- (radical of propane)
butyl- (radical of butane)

hydroxyl- (an oxygen-hydrogen group, -OH)
carbonyl- (contains a carbon double bonded to an oxygen, C=O)
carboxyl- (contains a carbon double bonded to an oxygen and single bond to a hydroxyl group)

di- (two of something, e.g., in diethyl ether, there are two ethyl radicals—CH₃—in the molecule)
tri- (three of something, e.g., three nitro groups in trinitrotoluene)

Suffixes

-ite (contains oxygen, e.g., sodium nitrite NaNO₂)
-ate (contains extra oxygen, e.g., chlorate ion ClO₃⁻ contains more oxygen than the chlorite ion ClO₂⁻—this does not mean that it is more or less reactive, that depends on the ion)
-per- (contains one extra oxygen, e.g., potassium permagenate KMnO₄, perchloric acid HClO₄)

Chemicals with names that end in -ite or -ate, or that have per- in their names should be treated as potential oxydizers because many of them are.

Other Terms

anhydrous (contains no water, e.g., anhydrous ammonia)
aqueous (in a solution with water)
### Hazardous Materials Chemical Summary

<table>
<thead>
<tr>
<th>Type of Chemical</th>
<th>Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Salts</strong></td>
<td></td>
</tr>
<tr>
<td>Binary Salts (_ide)</td>
<td>Various Hazards</td>
</tr>
<tr>
<td>Binary Oxides</td>
<td>Corrosive Liquid/Flammable</td>
</tr>
<tr>
<td>Peroxides</td>
<td>Corrosive Liquid/Flammable/Oxygen</td>
</tr>
<tr>
<td>Hydroxides</td>
<td>Corrosive Liquid/Flammable</td>
</tr>
<tr>
<td><strong>Hydrocarbon Derivitives</strong></td>
<td></td>
</tr>
<tr>
<td><strong>(Polar)</strong></td>
<td></td>
</tr>
<tr>
<td>Alkyl-Halides</td>
<td>Toxic/Flammable</td>
</tr>
<tr>
<td>Nitros</td>
<td>Explosive</td>
</tr>
<tr>
<td>Amine</td>
<td>Toxic/Flammable</td>
</tr>
<tr>
<td>Ether</td>
<td>Flammable/Anesthetic/May form peroxides</td>
</tr>
<tr>
<td>Organic Peroxides</td>
<td>++Flammable/Explosive</td>
</tr>
<tr>
<td><strong>(Non-Polar)</strong></td>
<td></td>
</tr>
<tr>
<td>Alcohol (_nol)</td>
<td>Flammable/Toxic</td>
</tr>
<tr>
<td>Ketones (_one)</td>
<td>Narcotic/Flammable</td>
</tr>
<tr>
<td>Ester</td>
<td>Flammable/Polymerize</td>
</tr>
<tr>
<td>(Methyl + Ester = Acetate)</td>
<td></td>
</tr>
<tr>
<td>(Vinyl + Ester = Acrylate)</td>
<td></td>
</tr>
<tr>
<td>Aldehydes</td>
<td>Flammable/Toxic</td>
</tr>
<tr>
<td>Organic Acids</td>
<td>Corrosive Liquid/Toxic</td>
</tr>
</tbody>
</table>
Appendix C

Chemistry Resources
References

- Hazmat databases (CAMEO, CCINFO, etc.)
- Maps and diagrams (facility diagrams, preplans, LEPC info, etc.)
- Monitoring equipment (available to your hazmat team)
- Reference manuals (SAX - Dangerous Properties of Industrial Materials; NIOSH Pocket Guide to Chemical Hazards; CHRIS; Railroad Manuals, etc.)
- Technical information centers (CHEMTREC, CANUTEC, SETIQ, local Poison Control Centers)
- Technical information specialists (local industry specialists, chemists, etc.)
- Chemical Manufacturers’ Association (CMA)
  1300 Wilson Blvd.
  Arlington, VA 22209
  800-262-8200
- Texts (Condensed Chem Dictionary, CHRIS, SAX, NIOSH Pocket Guide, etc.)
- Databases (CAMEO, CCINFO, Online resources for MSDSs, etc.)
- Industry trade groups, (CHEMTREC, Chlorine Institute, Pesticide Institute, GATX, etc.)
- A mention about specialists in your response area (industrial chemists, municipal water and waste water chemists, poison control center staff, crime lab chemists, academic chemists, etc.)
Additional Academic Chemistry Instruction

Community and local college courses:
(Discuss your needs with the faculty at the college before enrolling in a course that may not be appropriate.)
Possible course needs: Chem 101, Introductory Chemistry

Computer-based courses:
ActivChemistry from Salamander Interactive (ISBN 0-8053-4594-9)
Additional titles from other publishers are being developed and, an online search may be useful for descriptions and ordering information.

National Fire Academy Chemistry of Hazardous Materials Curriculum texts:
Chemistry of Hazardous Materials; Meyer, Prentice Hall
Hazardous Materials Chemistry for Emergency Responders; Burke, CRC Lewis Publishers
Chemistry: Cliffs Quick Review; Cliffs Notes Inc.
Go to your local community college or university bookstore and look through their chemistry textbooks and lab manuals for one that is written in a style that looks useful to you. New books of high quality are being published every year.