Chapter 4
Chemical Properties and Hazardous Materials Behavior

Lesson Goal

After completing this lesson, the student shall be able to describe the physical properties of hazardous materials and describe the General Hazardous Materials Behavior Model.

Objectives

Upon successful completion of this lesson, the student shall be able to:

1. Discuss the three states of matter. [NFPA® 472, 5.2.3(a)(vii, ix)]
2. Discuss the flammability of various hazardous materials. [NFPA® 472, 5.2.3(a)(iv-vii)]
3. Describe vapor pressure. [NFPA® 472, 5.2.3(a)(xiv)]
4. Explain boiling point. [NFPA® 472, 5.2.3(a)(i)]
5. Define melting point, freezing point, and sublimation.
6. Describe vapor density. [NFPA® 472, 5.2.3(a)(xiii)]
7. Define solubility and miscibility. [NFPA® 472, 5.2.3(a)(xv)]
8. Discuss specific gravity. [NFPA® 472, 5.2.3(a)(xi)]
9. Define persistence. [NFPA® 472, 5.2.3(a)(viii)]
10. Define reactivity and describe the reactivity triangle. [NFPA® 472, 5.2.3(a)(ii)]
11. Describe the General Hazardous Materials Behavior Model. [NFPA® 472, 5.2.1.4, 5.2.3(2-6), 5.2.4(2), 5.2.4(4)]

Estimated Total Time: 4 hours 30 minutes

Classroom teaching/written evaluation: 4 hours 30 minutes

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Section I: Introduction to Chapter 4

I. INTRODUCTION TO CHAPTER 4

A. Lesson Goal
   1. Chapter 4 lesson goal — After completing this lesson, the student shall be able to describe the physical properties of hazardous materials and describe the General Hazardous Materials Behavior Model.

B. Objectives
   1. Discuss the three states of matter.
   2. Discuss the flammability of various hazardous materials.
   3. Describe vapor pressure.
   4. Explain boiling point.
   5. Define melting point, freezing point, and sublimation.
   6. Describe vapor density.
   7. Define solubility and miscibility.
   8. Discuss specific gravity.
   10. Define reactivity and describe the reactivity triangle.

Section II: States of Matter

II. STATES OF MATTER

pp. 193-194 Objective 1 — Discuss the three states of matter.

A. State of Matter
   1. Gas
      a. Fluid that has neither independent shape nor volume
      b. Tends to expand indefinitely
c. If hazardous material, will be present in air
d. Potentially presents a breathing/inhalation hazard
e. May present contact hazard
f. Difficult, if not impossible, to contain for mitigation purposes
g. Will move according to prevailing wind and air movement
h. Compressed gases will expand rapidly when released, potentially threatening large areas

2. Liquid
   a. Fluid that has no independent shape but does have a specific volume
   b. Flows in accordance with laws of gravity
c. Will flow or pool according to surface contours and topography
d. May give off vapors that become inhalation hazards
e. Primarily splash or contact hazard

3. Solid
   a. Substance that has both a specific shape and volume
   b. May be moved by exterior forces, but will typically remain in place unless acted upon

Review Question: Describe the three states of matter. 
See pages 193-194 of the manual for answers.

Section III: Flammability 15 min.

III. FLAMMABILITY
pp. 194-199 Objective 2 — Discuss the flammability of various hazardous materials.

A. Flammability
   1. Majority of hazardous materials are flammable; can cause damage to life and property when they ignite, burn, or explode
   2. Depends on several properties
   3. Flash point
      a. Minimum temperature at which liquid or volatile solid gives off sufficient vapors to form ignitable mixture with air near surface
      b. Vapors will flash but will not continue to burn
      c. Liquids do not burn, but the vapors they produce do

Ask Students: What is fire point? How is it different from flash point?

Briefly discuss answers with students. Explain that fire point is the temperature at which enough vapors are given off to support continuous burning. The fire point is usually only slightly higher than the flash point.
4. Autoignition temperature
   a. Minimum temperature to which the fuel in air must be heated to initiate self-sustained combustion without initiation from an independent ignition source
   b. The point at which a fuel spontaneously ignites
   c. Considerably higher than flash and fire points

5. Flammable, explosive, or combustible range
   a. Percentage of gas or vapor concentration in air that will burn or explode if ignited
   b. Lower explosive limit (LEL) – Lowest concentration that will produce a flash of fire when an ignition source is present
   c. Upper explosive limit (UEL) – Highest concentration that will produce a flash of fire when an ignition source is present

Review Question: Define lower explosive limit (LEL) and upper explosive limit (UEL).
See page 198 of the manual for answers.

Section IV: Vapor Pressure

IV. VAPOR PRESSURE
   pp. 200-201 Objective 3 — Describe vapor pressure.

   A. Vapor Pressure
      1. Pressure exerted by a saturated vapor above its own liquid in a closed container
      2. Can be viewed as the measure of the tendency of a substance to evaporate
      3. Expressed in terms of pounds per square inch (psi), kilopascals (kPa), bars, or in millimeters of mercury (mmHg) or atmospheres (atm)
      4. The higher the temperature of the substance, the higher the vapor pressure will be
      5. Vapor pressures reported on SDSs in mmHg are usually very low
      6. The lower the boiling point of a substance, the higher its vapor pressure will be

Section V: Boiling Point

V. BOILING POINT
   pp. 202 Objective 4 — Explain boiling point.

   A. Boiling Point
      1. Temperature at which the vapor pressure of a liquid is equal to or greater than atmospheric pressure
      2. Usually expressed in degrees Fahrenheit (Celsius) at sea level air pressure
      3. Boiling liquid expanding vapor explosion (BLEVE)
a. Can occur when a liquid within a container is heated, causing the material inside to boil or vaporize
b. If resulting increase in internal vapor pressure exceeds vessel’s ability to relieve the excess pressure, it can cause the container to fail catastrophically
c. As vapor is released, it expands rapidly and ignites, sending flames and pieces of tank flying in a tremendous explosion

**Review Question:** What is a BLEVE?
See page 202 of the manual for answers.

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**Section VI: Melting Point/Freezing Point/Sublimation**

**VI. MELTING POINT/FREEZING POINT/SUBLIMATION**

pp. 202-203  Objective 5 — Define melting point, freezing point, and sublimation.

A. **Melting Point/Freezing Point/Sublimation**

1. Melting point – Temperature at which a solid substance changes to a liquid state at normal atmospheric pressure
2. Freezing point – Temperature at which liquid becomes solid at normal atmospheric pressure
3. Sublimation – Change directly from solid to gas without going into a liquid state in between

**Section VII: Vapor Density**

**VII. VAPOR DENSITY**

*p. 204 Objective 6 — Describe vapor density.*

**A. Vapor Density**

1. Weight of a given volume of pure vapor or gas compared to the weight of an equal volume of dry air at the same temperature and pressure
2. Vapor density less than 1 indicates a vapor lighter than air
3. Vapor density greater than 1 indicates a vapor heavier than air
4. Lighter materials tend to rise and dissipate
5. Heavier vapors and gases likely to concentrate in low places where they may create fire or health hazards

**Review Question:** What are some of the chemicals that have a vapor density lighter than air?

*See page 204 of the manual for answers.*

**Ask Students:** How does knowing the vapor density of a material help during a hazardous materials incident?

Briefly discuss answers with students. Explain that while the spread of vapors cannot be predicted exactly from the vapor density, knowing the vapor density of a material gives a general idea of what to expect from a specific gas.

**Section VIII: Solubility/Miscibility**

**VIII. SOLUBILITY/MISCIBILITY**

*pp. 205 Objective 7 — Define solubility and miscibility.*

**A. Solubility/Miscibility**

1. Solubility
   a. Percentage of a material (by weight) that will dissolve in water at ambient temperature
   b. Affects whether the substance mixes with water
   c. Can be useful in determining spill cleanup methods and extinguishing agents
      i. Non-water-soluble liquids such as hydrocarbons do not mix with water
      ii. Water-soluble liquids such as polar solvents mix easily with water

**Ask Students:** What are some examples of hydrocarbons and polar solvents?
Briefly discuss answers with students. Gasoline, diesel, fuel, and pentane are examples of hydrocarbons; alcohol, methanol, and methyl ethyl ketone are examples of polar solvents.

d. Important contributor in symptom development
   i. Irritants that are water-soluble usually cause upper respiratory tract irritation
   ii. Partially water-soluble chemicals penetrate into the lower respiratory system

2. Miscibility – Degree or readiness to which two or more gases or liquids are able to mix with or dissolve into each other

**Section IX: Specific Gravity**

**IX. SPECIFIC GRAVITY**

pp. 205-207 Objective 8 — Discuss specific gravity.

A. Specific Gravity
   1. Ratio of the density of a material to the density of some standard material at standard conditions of pressure and temperature
   2. Example – Weight of substance compared to the weight of an equal volume of water
   3. Solubility plays important role – Highly soluble materials will mix or dissolve more completely in water

**Section X: Persistence**

**X. PERSISTENCE**

pp. 207 Objective 9 — Define persistence.

A. Persistence
   1. Ability to remain in the environment

**Section XI: Reactivity**

**XI. REACTIVITY**

pp. 207-211 Objective 10 — Define reactivity and describe the reactivity triangle.

A. Reactivity
   1. Relative ability to undergo a chemical reaction with another material
   2. Results
      a. Pressure buildup
      b. Temperature increase
      c. Formation of noxious, toxic, or corrosive byproducts
3. Reactive materials – Commonly react vigorously or violently with air, water, heat, light, each other, or other materials

4. Reactivity triangle
   a. Explains the basic components of many chemical reactions
   b. Oxidizing agent
      i. Provides oxygen necessary for the chemical reaction
      ii. Strong oxidizers – Materials that encourage a strong reaction from reducing agents
      iii. Greater concentrations will burn hotter, faster, and brighter
   c. Reducing agent
      i. Acts as fuel source
      ii. Combines with oxygen in such a way that energy is released
      iii. Oxidation-reduction reactions can be extremely violent and dangerous
      iv. Some are more volatile than others
   d. Activation energy source
      i. Necessary amount depends on particular reaction
      ii. Can be in the form of added heat from an external source
      iii. If low, reactions happen easily

5. Polymerization
   a. Chemical reaction in which a catalyst causes simple molecules to combine to form long chain molecules
   b. Materials that may undergo violent polymerization if subjected to heat or contamination are designated with a P in the blue and yellow sections of the ERG

6. Inhibitors
   a. Materials that are added to products that easily polymerize in order to control or prevent an undesired reaction
   b. May be time-sensitive
   c. Shipments may become extremely unstable if delayed during transport or involved in accidents

Section XII: General Hazardous Materials Behavior Model

XII. GENERAL HAZARDOUS MATERIALS BEHAVIOR MODEL


A. General Hazardous Materials Behavior Model
   1. Definition of hazardous materials – Things that can escape from their containers and hurt or harm the things that they touch
   2. Explains that hazardous materials incidents have common elements
      a. Material or materials presenting hazards to people, the environment, or property
b. Container or containers that have failed or have the potential to fail
C. Exposure or potential exposure to people, the environment, and/or property

3. Helps first responders predict the course of an incident, thereby enabling them to limit the effects of a hazardous material

4. Defensive-mode action that is concerned with potential haz mat emergencies involving containers

5. First responders must calmly assess the situation at hand and then identify the appropriate response depending on answers to the following questions:
   a. How long will the harmful exposure exist?
   b. What has stressed or is stressing the container?
   c. How will the stressed container and its material behave?
   d. What are the harmful effects of the container materials?

6. Hazardous materials incidents generally follow the same sequence
   a. Stress
   b. Breach
   c. Release
   d. Dispersion/Engulf
   e. Exposure/Contact
   f. Harm

B. Stress
   1. Classified as stimulus causing strain, pressure, or deformity
   2. Causes almost ¼ of all reported haz mat incidents
   3. Evaluation
      a. Type of container
      b. Type and amount of stress
      c. Potential duration
   4. May involve single factor or several stressors acting simultaneously
   5. May be readily visible or not directly observed; may need to be predicted
   6. Prevention – Reducing or eliminating stress
   7. Common stressors
      a. Thermal
         i. Excessive heat or cold causing intolerable expansion, contraction, weakening, or consumption of the container and its parts
         ii. May simultaneously increase internal pressure and reduce container shell integrity
         iii. May result from heating or cooling of container
         iv. Clues – Observation of flame impingement, operation of a relief device, changing environmental conditions
      b. Chemical
i. Uncontrolled reactions/interactions of contents in the container and the container itself, resulting in a sudden or long-term deterioration of the container

ii. Reactions involving two chemicals into the same container can cause excessive heat and/or pressure

iii. May be the result of corrosive action or other chemical attack

iv. Clues – Visible corrosion or other degradation of container surfaces

C. Mechanical

i. Physical application of energy resulting in container/attachment damage

ii. May change the shape of the container, reduce the thickness of the container surface, crack or produce gouges, unfasten or disengage valves and piping, or penetrate the container wall

iii. Causes – Collision, impact, or internal over-pressure

iv. Clues – Physical damage, mechanism of injury, operation of relief devices

C. Breach

1. Occurs when container is stressed beyond limits of recovery

2. Happens differently according to container types and variety of other factors

3. Dependent on the type of container and stress applied

4. Extent varies with container construction and type of stress

5. Major factor in planning offensive product control operations


6. Types of breaches

a. Disintegration

i. Container suffers loss of integrity

ii. Occurs in containers that are made of a brittle material

b. Runaway cracking

i. Crack develops in a container as a result of some type of damage, which continues to grow rapidly, breaking the container into two or more relatively large pieces

ii. Associated with closed containers such as drums, tank cars, or cylinders

iii. Commonly associated with BLEVEs

c. Attachments (closures) open or break

i. Occurs when attachments are subjected to stress, leading to a total failure of a container

ii. Evaluating – Consider entire system and effect of failure at given point

d. Puncture — Caused by mechanical stress coming into contact with a container

e. Split or tear

i. Examples – Welded seam on a tank or drum fails or seam on a bag of fertilizer rips
ii. Caused by mechanical or thermal stressors

Review Question: Describe several types of breaches.
See pages 216-217 of the manual for answers.

D. Release
1. When container fails, three things may release – Product, energy, or container
2. Can occur quickly or over an extended time period
3. Classifications
   a. Detonation
      i. Instantaneous and explosive release of stored chemical energy of a hazardous material
      ii. Results include fragmentation, disintegration, or shattering of container, extreme overpressure, and considerable heat release
      iii. Duration can be measured in hundredths or thousandths of a second
   b. Violent rupture
      i. Immediate release of chemical or mechanical energy caused by runaway cracks
      ii. Results – Ballistic behavior of container and contents and/or localized projection of container pieces/parts and hazardous material
      iii. Occurs within a timeframe of one second or less
   c. Rapid relief
      i. Fast release of pressurized hazardous material through properly operating safety devices
      ii. Caused by damaged valves, piping, or attachments or holes in the container
      iii. May occur in a period of several seconds to several minutes
   d. Spill/leak
      i. Slow release of a hazardous material under atmospheric or head pressure through holes, rips, tears, or usual openings/attachments
      ii. Can occur in a period of several minutes to several days

E. Dispersion Patterns/Engulfment
1. Depends on type of release as well as physical and chemical laws
2. Product may release in form of solid, liquid, or gas/vapor
3. May also release mechanical, thermal, or chemical energy and ionizing radiation
4. Path of product, energy, and container travel depends on form and physical characteristics
5. Pattern may be predicted
6. Distribution occurs according to five factors:
   a. Physical/chemical properties
   b. Prevailing weather conditions
   c. Local topography
d. Duration of the release

e. Control efforts of responders

7. Shape and size of pattern depends on how material emerges from container

**Review Question:** What are the classifications of releases?
*See pages 217-218 of the manual for answers.*

8. Dispersion patterns

a. Hemispheric
   i. Semicircular or dome-shaped pattern of airborne hazardous material that is still partially in contact with ground or water
   ii. Generally results from a rapid release of energy
   iii. Energy generally travels outward in all directions from the point of release
   iv. Dispersion of energy is affected by terrain and cloud cover
   v. Energy release may propel the hazardous material and container parts

b. Cloud
   i. Ball-shaped pattern of the airborne hazardous material where the material has collectively risen above the ground or water
   ii. Can occur to gases, vapors, and finely divided solids that are released quickly
   iii. Can be transformed into a plume by terrain and/or wind effects

c. Plume
   i. Irregularly shaped pattern of an airborne hazardous material where wind and/or topography influence the downrange course from the point of release
   ii. Dispersion is affected by vapor density, terrain, and wind speed and direction
   iii. When all of the material is released at one time, the concentration of gas or vapor in the cloud or plume decreases over time
   iv. In an ongoing release, concentration increases over time until the leak is stopped or all of the product has been exhausted, then it decreases

d. Cone
   i. Triangular-shaped pattern of a hazardous material with a point source at the breach and a wide base downrange
   ii. May be directed and may project solid, liquid, or gaseous material in a three-dimensional cone-shaped dispersion

e. Stream
   i. Surface-following pattern of liquid hazardous material that is affected by gravity and topographical contours
   ii. Liquid releases flow downslope whenever there is a gradient away from the point of release

f. Pool
   i. Three-dimensional, slow-flowing liquid dispersion
   ii. Liquids assume the shape of their container and pool in low areas
iii. As liquid level rises above confinement provided by the terrain, the substance flows outward from the point of release

g. Irregular — Irregular or indiscriminate deposit of a hazardous material

9. Can be estimated for pre-incident surveys using computer software
   a. CAMEO (Computer-Aided Management of Emergency Operations)
   b. ALOHA (Area Locations of Hazardous Atmospheres)
   c. HPAC (Hazard Prediction and Assessment Capability)

**Review Question:** Describe each of the dispersion patterns. 
*See pages 219-222 of the manual for answers.*

F. **Exposure/Contact**

1. Types of exposures
   a. People – Includes responders and others in the path of a hazardous material
   b. Environment
      i. Air, water, ground, and life forms other than humans
      ii. Potential effect varies with location in which product is released and its characteristics
   c. Property – Things threatened directly by the product or the energy liberated at the time of release

2. Contacts are associated with the following general timeframes:
   a. Immediate
      i. Milliseconds, seconds
      ii. Examples: Deflagration, explosion, or detonation
   b. Short-term
      i. Minutes, hours
      ii. Example: Gas or vapor cloud
   c. Medium-term
      i. Days, weeks, months
      ii. Example: Lingering pesticide
   d. Long-term
      i. Years, generations
      ii. Example: Permanent radioactive source

G. **Harm**

1. Injury or damage caused by exposure to a hazardous material
2. Health and physical hazards that could cause harm in a hazardous materials incident
   a. Thermal
   b. Mechanical
   c. Poisonous
d. Corrosive
e. Asphyxiation
f. Radiation
g. Biological

**Review Question:** What types of exposures should be considered in hazard and risk assessment? See page 224 of the manual for answers.

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**Section XIII: Summary and Review**  
15 min.

XIII. SUMMARY AND REVIEW

A. Chapter Summary

1. First responders need the ability to predict how a hazardous material will behave when it escapes its container.
2. The behavior is often determined by the material’s physical properties.

B. Review Questions

1. Describe the three states of matter. (193-194)
2. What is flash point?
3. Define lower explosive limit (LEL) and upper explosive limit (UEL). (198)
4. What is a BLEVE? (202)
5. What are some of the chemicals that have a vapor density lighter than air? (204)
6. What are the six portions of the GEBMO? (214-215)
7. Describe several types of breaches. (216-217)
8. What are the classifications of releases? (217-218)
9. Describe each of the dispersion patterns. (219-222)
10. What types of exposures should be considered in hazard and risk assessment? (224)