# BACKGROUND

## INTRODUCTION

The NRC requires a fire protection program to be established at each U.S. commercial nuclear power facility. The programs are designed to meet the following objectives:

- Prevent fires from starting.
- Detect rapidly control, and promptly extinguish any fire that does occur.
- Protect structures, systems, and components and provide reasonable assurance that a fire will not prevent shutdown of a facility.
- Assure that a fire will not significantly increase the risk of radioactive releases to the environment.

The NRC monitors licensee actions through its oversight program. The NRC has begun emphasizing risk-informing fire protection requirements and performance-based methods found in NUREG-1520, Standard Review Plan for the Review of a License Application for a Fuel Cycle Facility, and National Fire Protection Association (NFPA) Standard 801. See NFPA Standards and Codes at the end of this section.

Fundamental concepts relevant to fires and include:

- Principles of combustion
- Spontaneous combustion/heating
- Combustible metals
- Flammable and combustible liquids
- Selected industrial gases
- Incompatible chemicals
- Fire stages

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## PRINCIPLES OF COMBUSTION

### Combustion and Oxidation

**Combustion** is defined as the burning of a gas, liquid, or solid in which the fuel is rapidly oxidized, producing heat and often light.  Combustion falls into a class of chemical reactions called oxidation.

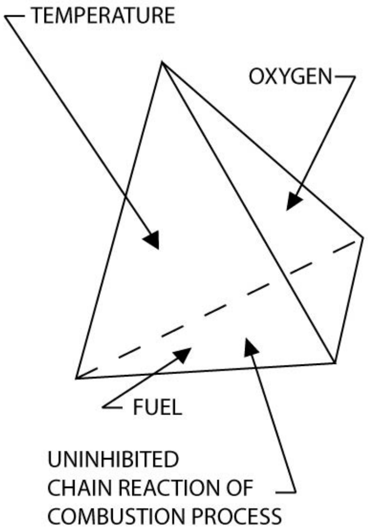
**Oxidation** may be defined as the chemical combination of a substance with oxygen or, more generally, the removal of electrons from an atom or molecule.  Oxidation reactions almost always release heat (exothermic).

### Fire Tetrahedron

Traditionally, there were three distinct elements assumed for combustion: heat, fuel, and oxygen.  Known as the fire triangle, this theory had to be modified as halons became more widely used and better understood.  A fourth element, a chemical chain reaction, was recognized as being part of the combustion process.  Typical fire extinguishment involves either removing the fuel from the fire to limit oxygen to the fire (smothering), or removing the heat (quenching).  Halons usually use low enough concentration to be non-hazardous to the worker or the public.  The halons do not extinguish fire in any of these ways, but instead break up the uninhibited chain reaction or the combustion process.

The tetrahedron of the fire, with its four sides, symbolize fuel, heat, oxygen, and chemical chain reaction.  Theoretically, fire extinguishers put out fire by taking away one or more elements of the fire tetrahedron, as shown in Figure 1.

**Figure 1.  Tetrahedron of the Fire**



## BACKGROUND

### Oxidizing Agent

An **oxidizing agent** (or oxidizer) is a chemical substance that gives up oxygen easily, removes hydrogen from another substance, or attracts electrons.

The most common oxidizing agent is oxygen in the earth's atmosphere. There are many chemical compounds that also act as oxidizing agents. Some of these react with fuels more readily and violently than oxygen. Additional information on the relative hazards and classifications of oxidizing agents may be found in Appendix B, NRC Inspection Procedure 88055. An example of an oxidizing agent used in fuel cycle facilities would be hydroperoxide.

### Fuel

A **fuel** is a material that reacts with the oxidizing agent during combustion. Examples include coal, wood, and gasoline. Examples used in Fuel Cycle Facilities are solvents, wiring and plastics.

### Heat Source

Normally a **heat source**, such as a flame or spark, ignites a mixture of an oxidizing agent and a fuel. There are some fuels that react so readily with oxygen that a heat source is not required for ignition. Ignition for these fuels occurs as a result of spontaneous heating or pyrophoricity. This is known as spontaneous combustion.

### Uninhibited Chain Reaction of Combustion Process

The extinguishing mechanism of the halogenated agents is not completely understood, yet there is definitely a chemical reaction that interferes with the combustion process. The halogen atoms act by removing the active chemical species involved in the flame **chain reaction**.

## SPONTANEOUS COMBUSTION/HEATING

### Spontaneous Combustion

**Spontaneous combustion** is the ignition of a combustible material caused by the accumulation of heat from a runaway oxidation reaction. Fires started by spontaneous combustion are caused by the following mechanisms:

- Spontaneous heating
- Hypergolic reactions
- Pyrophoricity

# BACKGROUND

## Spontaneous Heating

**Spontaneous heating** is the slow oxidation of an element or compound that causes the bulk temperature of the element or compound to rise without the addition of an external heat source. Spontaneous heating may be the result of direct oxidation of hydrocarbons (for example, oils, coal, solvents), or it may occur because of the action of microorganisms in organic materials. An example of spontaneous heating may occur with oily rags in a fuel cycle facility.

## Hypergolic Reaction

A **hypergolic reaction** is defined as a material's ability to spontaneously ignite or explode upon contact with ANY oxidizing agent; for example, a chemical reaction between nitric acid and oil.

## Pyrophoricity

**Pyrophoricity** is a special case of a hypergolic reaction because the oxidizing agent is restricted to atmospheric oxygen.

Pyrophoric substances ignite instantly upon exposure to air (atmospheric oxygen). A pyrophoric substance may be a solid, liquid, or gas. Most materials are not pyrophoric unless they are in a very finely divided state. Most pyrophoric materials are metals. For example plutonium is pyrophoric in finely divided state.

## Hydrocarbons

Some **hydrocarbons** are capable of spontaneous heating and ignition under proper conditions. Spontaneous heating of hydrocarbons usually involves a combustible liquid hydrocarbon in contact with a combustible material. An example of this would be a combustible rag impregnated with oil or solvent. Some solid hydrocarbons, such as coal, can react directly with atmospheric oxygen.

## Ignition Temperature

The **ignition temperature** is defined as the temperature at which an element or compound will catch fire in air (atmospheric oxygen). The ignition temperature of the materials is obviously of concern and varies widely among materials. More stringent controls must be placed on materials that have lower ignition temperatures and those that liberate explosive gases. Material Safety Data Sheets (MSDSs) are a source of information such as ignition temperature, vapor pressure, toxicity, and reactivity.

## Specific Area

The **specific area** of a combustible substance is a measure of the surface area of the materials exposed to an oxidizing atmosphere per gram of materials and is expressed in units of cm2/g. Materials that have a high specific area are more prone to heat and ignite spontaneously.

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Liquid combustibles on fibrous material is an example of a potential fire hazard. This is because the fibers of the material allow the liquid to spread out over a larger surface area thus allowing more contact with oxygen. Therefore, porous combustible materials are more likely to ignite than tightly packed solid materials.

## Moisture Content

**Moisture content** is always a concern, and it is important to keep potentially spontaneously heating compounds as dry as possible. High ambient temperatures magnify moisture problems. As the ambient temperature rises, the rate of spontaneous heat generation will also rise. High ambient temperatures also reduce the rate of heat removal bringing the hydrocarbon closer to ignition temperature.

## COMBUSTIBLE METALS

### General Characteristics

Nearly all metals will burn in air under certain conditions. Some are oxidized rapidly in the presence of air or moisture generating sufficient heat to reach their ignition temperatures. Others oxidize so slowly that heat generated during oxidation is dissipated before the metal becomes hot enough to ignite.

Certain metals—notably magnesium, titanium, sodium, potassium, lithium, zirconium, hafnium, calcium, zinc, plutonium, uranium, and thorium—are referred to as combustible metals because of the ease of ignition when they reach a high specific area ratio (thin sections, fine particles, or molten states). The same metals in massive solid form are comparatively difficult to ignite.

### Combustibility Factors

Some metals (such as aluminum, iron, and steel), which are not normally thought of as combustible, may ignite and burn when in finely divided form. Clean, fine steel wool, for example, may be ignited. Important factors to consider when evaluating metal combustibility are:

- Particle size
- Shape
- Quantity
- Alloy

Combustibility of metallic alloys may differ and vary widely from the combustibility characteristics of the alloys' constituent elements.

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### Properties of Burning Metals

Temperatures produced by burning metals can be higher than temperatures generated by burning flammable liquids. Hot or burning metals may react violently upon contact with other materials, such as oxidizing agents and extinguishing agents used on fires involving ordinary combustibles or flammable liquids. Some metals can continue to burn in carbon dioxide, nitrogen, water, or steam atmospheres in which ordinary combustibles or flammable liquids would be incapable of burning.

Burning titanium produces little smoke, while burning lithium smoke is dense and profuse. Some water-moistened metal powders, such as zirconium, burn with near explosive violence. The same zirconium powder wet with oil will burn quiescently. Sodium melts and flows while burning; calcium does not. Some metals (for example, uranium) acquire an increased tendency to burn after prolonged exposure to moist air, while prolonged exposure to dry air makes it more difficult to ignite.

### Toxicity and Radioactivity Concerns

Some metals (especially heavy metals) can be toxic or fatal if they enter the bloodstream or their smoke fumes are inhaled. Metal fires should not be approached without the proper protective equipment (clothing and respirators).

A few metals, such as thorium, uranium, and plutonium, emit ionizing radiation that can complicate fire fighting and introduce a radioactive contamination problem.

### Melting, Boiling, and Ignition Temperatures of Pure Metals

Table 1 shows the melting, boiling, and ignition temperatures of pure metals in solid form.

## BACKGROUND

**Table 1. Melting, Boiling, and Ignition Temperatures of Pure Metals in Solid (Source: NFPA Handbook, l7th Edition)**

| | Temperature | | | | | |
|---|---|---|---|---|---|---|
| | Melting point | | Boiling point | | Solid metal ignition | |
| Pure metal | °F | °C | °F | °C | °F | °C |
| Aluminum | 1,220 | 660 | 4,445 | 2,452 | 1,832[2, 3] | 5552,[3] |
| Barium | 1,337 | 725 | 2,084 | 1,140 | 347[2] | 175[2] |
| Calcium | 1,548 | 824 | 2,625 | 1,440 | 1,300 | 704 |
| Hafniurn | 4,032 | 2,223 | 9,750 | 5,399 | --- | --- |
| Iron | 2,795 | 1,535 | 5,432 | 3,000 | 1,706[2] | 930[2] |
| Lithium | 367 | 186 | 2,437 | 1,336 | 356 | 180 |
| Magnesium | 1,202 | 650 | 2,030 | 1,110 | 1,153 | 623 |
| Plutonium | 1,184 | 640 | 6,000 | 3,315 | 1,112 | 600 |
| Potassium | 144 | 62 | 1,400 | 760 | 156[2] | 69[2] |
| Sodium | 208 | 98 | 1,616 | 880 | 239[4] | 115[4] |
| Strontium | 1,425 | 774 | 2,102 | 1,150 | 1,328[2] | 720[2] |
| Thorium | 3,353 | 1,845 | 8,132 | 4,500 | 932[2] | 500[2] |
| Titanium | 3,140 | 1,727 | 5,900 | 3,260 | 2,900 | 1,593 |
| Uranium | 2,070 | 1,132 | 6,900 | 3,815 | 6,900[2,5] | 3,815[2,5] |
| Zinc | 786 | 419 | 1,665 | 907 | 1,652[2] | 900[2] |
| Zirconium | 3,326 | 1,830 | 6,470 | 3,577 | 2,552[2] | 1,400[2] |

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1. Variation of test conditions may produce different results
2. Ignition in oxygen
3. Spontaneous ignition in moist air
4. Above indicated temperature
5. Below indicated temperature

# BACKGROUND

## FLAMMABLE AND COMBUSTIBLE LIQUIDS

The NRC has a general approach to preventing a fire by following the guidelines in NFPA 69, Standard on Explosion Prevention Systems. The approach is to limit fuel, limit oxygen to less than 5%, avoid ignition sources, and interrupt combustion reactions (chain inhibitors). The triangle/tetrahedron (Figure 1) illustrates these elements that must be present for a fire to occur. The target for lower flammability limit is less than 25%.

Flammable and combustible liquids vaporize to form flammable mixtures in open containers when heated or spilled. The hazards that exist from these mixtures is largely dependent on the flash point of the liquid, the concentration of the mixture, and the potential of a source of ignition at a temperature sufficient to cause the mixture to burst into flame. See Tables 2 and 3.

### Definitions

**Flammable Liquid**. As defined by OSHA, DOT, and the National Fire Association Standard, NFPA 30, a Class I liquid is one having a flash point below 100°F (37.8 °C) and having a vapor pressure not exceeding 40 psia (2068 mm Hg) at 100°F (37.8 °C).

- ◙ Class I liquids are subdivided as follows:
    - □ Class IA includes those having flash points below 73°F (22.8 °C) and having a boiling point below 100°F (37.8 °C).
    - □ Class IB includes those having flash points below 73°F (22.8 °C) and having a boiling point at or above 100°F (37.8 °C).
    - □ Class IC includes those having flash points at or above 73°F (22.8 °C) and below 100°F (37.8 °C).

**Combustible Liquid**. A liquid having a closed cup flash point at or above 100°F (37.8 °C).

- ◙ Combustible liquids are subdivided as follows:
    - □ Class II liquids include those having flash points at or above 100°F (37.8 °C) and below 140°F (60 °C).
    - □ Class IIIA liquids include those having flash points at or above 140°F (60 °C) and below 200°F (93 °C).
    - □ Class IIIB liquids include those having flash points at or above 200°F (93 °C).

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**Flash Point**. The flash point is the minimum temperature at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid (under controlled conditions).

Although combustible liquids do not ignite as easily as flammable liquids, they must be handled with caution because of their ability to ignite under certain conditions, such as sprays or mists, or at elevated temperatures.

**Lower Flammable Limit (LFL)**. The minimum concentration of vapor in air below which propagation of flame does not occur when in contact with a source of ignition. This is sometimes called the Lower Explosive Limit (LEL).

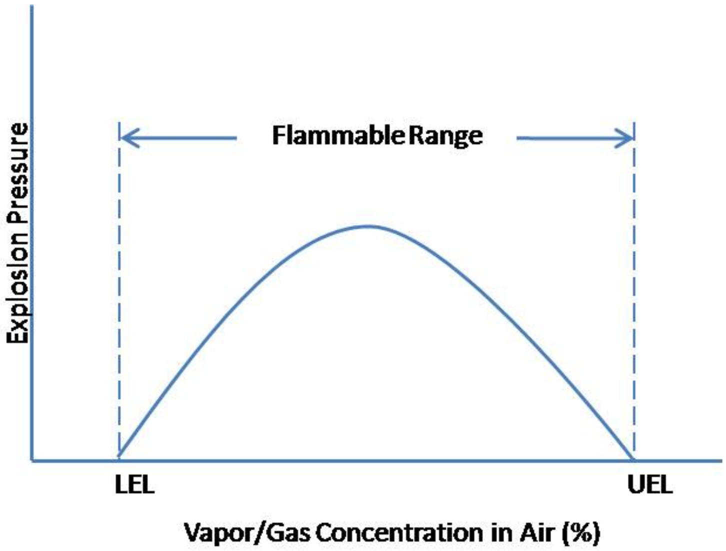
**Upper Flammable Limit (UFL)**. The maximum concentration of vapor or gas in the air above which propagation of flame will not occur. This is sometimes called the Upper Explosive Limit (UEL).

**Flammable Range**. The difference between the lower and upper flammable limits, expressed in percentage of vapor or gas in air by volume. This is also known as the Explosive Range.

**Note:** The LEL/UELs are technically different but sometimes used interchangably for safety purposes. The LEL/UEL provides more conservatism (Figure 2).

**Permissible Exposure Limit (PEL)**. The limits of the vapor according to OSHA standards, expressed in parts of vapor per million parts of contaminated air. The PEL is important because many of these substances present inhalation as well as fire hazards.

Figure 2. Vapor/Gas Concentration in Air (%) (flammable range) - OSHA source



## NFPA Classes

NFPA 30, Flammable and Combustible Liquids Code, is summarized in Table 2.

Table 2. Classes of Flammable and Combustible Liquids

| Class | Flash Point | Sub-Classes |
|---|---|---|
| Class I | Below 100°F | IA Those liquids having flash points below 73°F and having a boiling point below 100°F.<br>IB Those liquids having flash points below 73°F and having a boiling point at or above 100°F.<br>IC Those liquids having flash points at or above 73°F and having a boiling point below 100°F. |
| Class II | At or above 100°F and below 140°F | None |
| Class III | Above 140°F | IIIA Those liquids having flash points at or above 140°F and below 200°F.<br>IIIB Those liquids having flash points at or above 200°F. |

### Table 3: Selected Properties of Some Flammable and Combustible Materials

**Class IA**

| Liquid | | Flash Point (°F) | Boiling Point (°F) | Flammable Limits | | Vapor Density Air=1 | PEL (ppm) |
|---|---|---|---|---|---|---|---|
| | | | | LEL | UEL | | |
| Common Name | Other Names | | | | | | |
| 1-1 Dichloroethylene | Vinylidene chloride | 0 | 99 | 7.3 | 10.0 | 3.4 | - |
| Ethylamine | | <0 | 63 | 3.5 | 14.0 | 1.6 | 10 |
| Ethyl Chloride | Chloroethane | - 58 | 54 | 3.8 | 15.4 | 2.2 | 1000 |
| Ethyl Ether | Ether | - 49 | 95 | 1.9 | 36.0 | 2.6 | 400 |
| Isopentane | | <- 60 | 82 | 1.4 | 7.6 | 2.5 | - |
| Isopropyl Chloride | 2-Chloropropane | - 26 | 97 | 2.8 | 10.7 | 2.7 | - |
| Methyl Formate | | - 2 | 90 | 5.0 | 23.0 | 2.1 | 100 |
| Pentane | | <- 40 | 97 | 1.5 | 7.8 | 2.5 | 1000 |
| Propylene Oxide | | - 35 | 93 | 2.8 | 37.0 | 2.0 | 100 |

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## Class IB

| Liquid | | Flash Point (°F) | Boiling Point (°F) | Flammable Limits | | Vapor Density Air = 1 | PEL (ppm) |
|---|---|---|---|---|---|---|---|
| Common Name | Other Names | | | LEL | UEL | | |
| Acetone | | 0 | 134 | 2.6 | 12.8 | 2.0 | 1000 |
| Benzene | Benzol | 12 | 176 | 1.3 | 7.1 | 28 | 1 |
| Carbon Disulfide | Carbon bisulfide | - 22 | 115 | 1.3 | 50.0 | 2.6 | 20 |
| 1,2- Dichloroethylene | Acetylene dichloride | 43 | 140 | 9.7 | 12.8 | 3.4 | 200 |
| Ethyl Acetate | | 24 | 171 | 2.2 | 11.0 | 3.0 | 400 |
| Ethyl Alcohol | Ethanol,<br>Grain alcohol | 55 | 173 | 3.3 | 19 | 1.6 | 1000 |
| Ethyl Benzene | | 59 | 277 | 1.0 | 6.7 | 3.7 | 100 |
| Gasoline | | - 45 | 100-399 | 1.4 | 7.6 | 3 - 4 | - |
| Hexane | | - 7 | 156 | 1.1 | 7.5 | 3.0 | 500 |
| Methyl Acetate | | 14 | 135 | 3.1 | 16 | 2.6 | 200 |
| Methyl Alcohol | Wood alcohol,<br>Methanol | 52 | 147 | 6.7 | 3.6 | 1.1 | 200 |
| Methyl Ethyl Ketone | MEK, 2-Butanone | 21 | 176 | 1.8 | 10 | 2.5 | 200 |
| Methyl Propyl Ketone | 2-Pentanone | 45 | 216 | 1.5 | 8.2 | 2.9 | 200 |
| VM&P Naphtha | 76 Naphtha | 20 - 45 | 212-320 | 0.9 | 6.0 | 4.2 | - |
| Octane | | 56 | 257 | 1.0 | 6.5 | 3.9 | 500 |
| Propyl Acetate | | 58 | 215 | 2.0 | 8.0 | 3.5 | 200 |
| Isopropyl Acetate | | 40 | 192 | 1.8 | 8.0 | 3.5 | 250 |
| Isopropyl Alcohol | IPA, 2-propanol | 53 | 180 | 2.0 | 12 | 2.1 | 400 |
| Toluene | Toluol | 40 | 232 | 1.2 | 7.1 | 3.1 | 200 |
| Butyl Acetate | | 72 | 260 | 1.7 | 7.6 | 4.0 | Liquid |

**Class IC**

| Liquid | | Flash Point (°F) | Boiling Point (°F) | Flammable Limits | | Vapor Density Air = 1 | PEL (ppm) |
|---|---|---|---|---|---|---|---|
| Common Name | Other Names | | | LEL | UEL | | |
| Isoamyl Acetate | Banana Oil | 77 | 288 | 1.0 | 7.5 | 4.5 | 100 |
| Amyl Alcohol | Pentanol | 91 | 281 | 1.2 | 10 | 3.0 | |
| Butyl | Butanol | 84 | 243 | 1.4 | 11.2 | 2.6 | 100 |
| Methyl Isobutyl Ketone | MIBK, Hexone | 73 | 246 | 1.4 | 7.5 | 3.5 | 100 |
| Naphtha (Petroleum) | Mineral Spirits, Petroleum Ether | 85-110 | 302-399 | 0.8 | 6.0 | 4.2 | - |
| Propyl Alcohol | Propanol | 77 | 208 | 2.1 | 13.5 | 2.1 | 200 |
| Styrene (Monomer) | Vinyl Benzene | 90 | 295 | 1.1 | 6.1 | 3.6 | 100 |
| Turpentine | | 95 | 307-347 | 0.8 | - | - | 100 |
| Xylene | Xylol | 81-115 | 281-291 | 1.1 | 7.0 | 3.7 | 100 |

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## Class II

| Liquid | | Flash Point (°F) | Boiling Point (°F) | Flammable Limits | | Vapor Density Air = 1 | PEL (ppm) |
|---|---|---|---|---|---|---|---|
| Common Name | Other Names | | | LEL | UEL | | |
| Isoamyl | | 109 | 268 | 1.2 | - | 3.0 | 100 |
| Cellosolve Acetate | 2-Ethoxyethyl acetate | 117 | 313 | 1.7 | - | 4.7 | 100 |
| Cyclohexanone | | 111 | 313 | - | - | 3.4 | 50 |
| Fuel Oil # 1 and # 2 | | 100+ | - | - | - | - | - |
| Fuel Oil # 4 | | 110+ | - | - | - | - | - |
| Fuel Oil # 5 | | 130+ | - | - | - | - | - |
| Kerosene | | 110-150 | 180-300 | 0.7 | 5.0 | 4.5 | - |
| Naphtha (coal tar) | | 100-110 | 300-400 | - | - | 4.3 | 100 |
| Naphtha (High Flash) | 100 Naptha Safety Solvent, Stoddard Solvent | 100-110 | 300-400 | 0.8 | 6.0 | >4.2 | 500 |
| Methyl Cellosolve | 2-Methoxyethanol | 115 | 255 | 2.5 | 14.0 | - | 25 |

### Class III

| Liquid | | Flash Point (°F) | Boiling Point (°F) | Flammable Limits | | Vapor Density Air = 1 | PEL (ppm) |
|---|---|---|---|---|---|---|---|
| Common Name | Other Names | | | LEL | UEL | | |
| Aniline | | 158 | 363 | 1.3 | - | 3.2 | 5 |
| Butyl Cellosolve | 2-Butoxyethanol | 160 | 340 | 1.1 | 10.6 | 4.1 | 50 |
| Cellosolve Solvent | 2-Ethozyethanol<br>Cellosolve Solvent | 202 | 275 | 1.8 | 14.0 | 3.1 | 200 |
| Cyclohexanol | | 162 | 322 | - | - | 2.5 | 50 |
| Ethylene Glycol | Glycol | 232 | 387 | 3.2 | - | - | - |
| Furfural | | 140 | 324 | 2.1 | 19.3 | 3.3 | 5 |
| Glycerine | Clycerol | 320 | 554 | - | - | 3.2 | - |
| Isophorone | | 184 | 419 | 0.8 | 3.8 | - | 25 |
| Nitrobenzene | | 190 | 412 | - | - | 4.3 | 1 |

### Non-Flammable Liquids(*)

| Liquid | | Boiling Point (◦F) | PEL (ppm) |
|---|---|---|---|
| Common Name | Other Names | | |
| Carbon Tetrachloride | | 171 | 10 |
| Chloroform | Trichloromethane | 142 | 50 |
| Ethylene Dibromide | 1,2-Dibromoethane | 270 | 20 |
| Methyl Chloroform | 1,1,1-Trichloroethane | 165 | 350 |
| Methylene Chloride | Dichloromethane | 104 | 500 |
| Perchloroethylene | Tetrachloroethylene | 248 | 100 |
| Trichloroethylene | TCE, Trichlor | 190 | 100 |

* Non-flammable under normal conditions.  Unstabilized trichloroethylene can decompose violently in presence of fine aluminum powder.

## BACKGROUND

### Vaporization

Flammable and combustible liquids vaporize to form flammable mixtures when they:

- Are stored in open containers
- Leak
- Spill
- Are heated

The hazard that exists from these mixtures is largely dependent upon the flash point of the liquid, the concentration of the mixture, and the potential source of ignition at a temperature sufficient to cause the mixture to burst into flames.

## INDUSTRIAL GASES

Flammable gases, such as acetylene, butane, ethylene, hydrogen, methylamine and vinyl choride, can burn or explode under certain conditions. The concentration of the gas in air (or in contact with an oxidizing gas) must be between its lower flammable limit and upper flammable limit.

Hydrogen and oxygen are two common gases used for industrial purposes. Understanding the chemical properties and characteristics of these gases is important for accident prevention.

### Hydrogen

Hydrogen is extremely flammable in oxygen or air. The LFL of hydrogen gas in air is 4% and its UFL is 75% (at atmospheric pressure and temperature). This means that hydrogen can be ignited when its concentration in the air is between 4 and 75 percent.

A mixture of 10% to 65% hydrogen by volume in air will explode if ignited. Pure hydrogen burns quietly in air with an almost invisible flame, and when burned with oxygen, a very high temperature may be reached. Hydrogen will burn readily in chlorine gas and, under the proper conditions, will combine with nitrogen to form ammonia.

### Oxygen

Oxygen supports combustion but does not burn. The normal oxygen content in air is 21%. At slightly higher oxygen concentrations, for example 25%, combustible materials, including fabrics, ignite more easily and burn faster. The results of an enriched oxygen atmosphere includes a(n):

- Lowered ignition temperature
- Increased flammable range
- Acceleration of the burning rate

## BACKGROUND

Oxygen readily combines with other elements and compounds with spontaneous ignition in some cases. When oxygen comes in contact with oil, grease, or fuel oils, it may ignite violently.

All possible sources of ignition should be anticipated and eliminated. Ignition sources include:

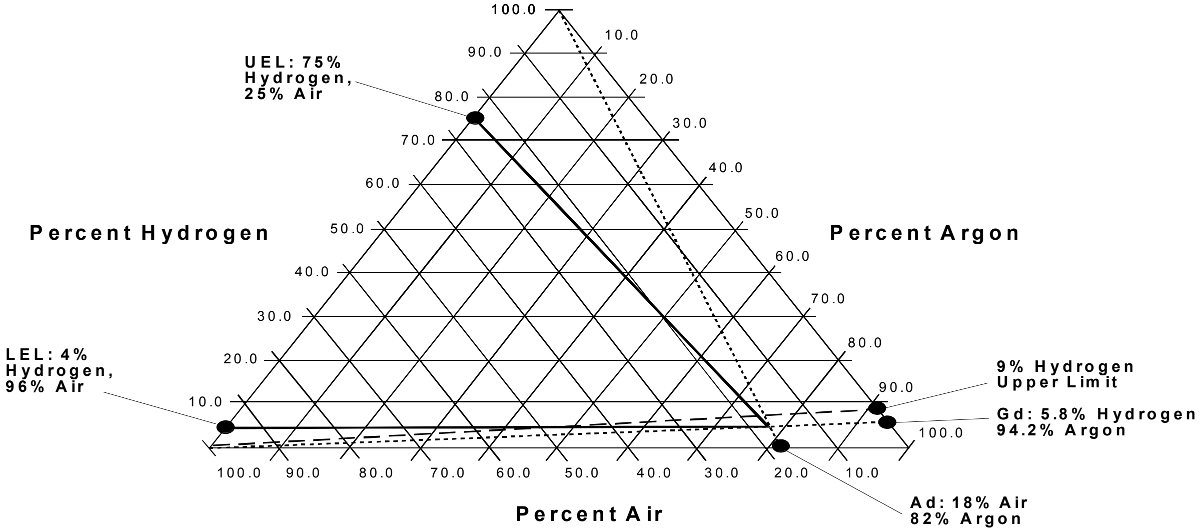
- Electrical equipment
- Portable electric tools and equipment
- Static electricity

### Temperature and Composition

Flammability limits are affected by temperature and by various concentrations of inert diluents, such as argon gas. Increasing the temperature tends to lower the LFL and raise the UFL for hydrogen in air until spontaneous ignition temperature is reached. At this point, the burning occurs with a slow flame. However, this effect is different when hydrogen is diluted with an inert gas. Flammable mixtures of hydrogen in air can be made nonflammable by the addition of argon, provided sufficient controls are placed on the environment in which the mixed gas is used. Different diluents have different levels of inerting efficiency which must be accounted for in evaluating the potential risks for creating explosive mixtures.

The explosiveness of a mixture depends on the gas concentration, temperature, pressure (flammability limit), the container surface conditions and container size. Gas concentrations below or above the LFL and UFL are nonexplosive. Because the flammability limits vary with temperature and gas composition, these variables must be considered when choosing the applicable lower and upper explosive limits. See Figure 3 and Table 4, below.

**Figure 3. Limiting Safe Mixtures of Hydrogen, Argon and Air (Ref: Louis Medard, Accidental Explosions, 1989)**



LEL: Lower Explosive Limit
UEL: Upper Explosive Limit
AD: Limiting safe mixture - % of argon in air
Gd: Limiting safe mixture - % of argon in hydrogen

**Table 4. Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solid (Flammability Limit Data from NFPA 325-1994)**

| Gas | Density at NTP (kg/m3) | Flammability Limits (percentage volume in air at NTP) |
|---|---|---|
| Hydrogen* | 0.0824 | 4.0-75.0 |
| Deuterium* | 0.180 | 5.0-75.0 |
| Methane | 0.668 | 5.0-15.0 |
| Acetylene* | 1.174 | 2.5-100** |
| Ethane | 1.26 | 3.0-12.5 |
| Propane | 1.87 | 2.1-9.5 |
| Isobutane | 2.49 | 1.8-8.4 |
| Dimethyl Ether | 1.95 | 3.4-27.0 |

*Not expected to be routinely used in detectors because of its large flammability range, included for reference only.

**Flammable limit is 82%, but can explode under pressure up to 100%.

Note: Cylinders are generally specified as containing a given number of standard cubic feet (SCF). The inventory may be estimated by using the above densities of the phase with the conversion 0.028 m 3/ft$^3$.

## INCOMPATIBLE CHEMICALS

A wide variety of chemicals react dangerously when mixed with certain other materials. Some of the more widely-used incompatible chemicals are given in Table 5, but the absence of a chemical from this table should not be taken to indicate that it is safe to mix it with any other chemical.

### Chemical Interactions

Human error or equipment malfunction could result in inadvertent chemical interactions and initiate hazardous reactions. To control use of process chemicals, some precautions can be taken that include:

- Sampling of chemical reagents when received
- Control of chemical preparation according to operating procedures
- Use of training personnel to handle chemicals
- Proper storage

**Table 5. Incompatible Chemicals**

| Chemical | Incompatible with |
|---|---|
| acetic acid | chromic acid, ethylene glycol, nitric acid, hydroxyl compounds, perchloric acid, peroxides, permanganates |
| acetone | concentrated sulphuric and nitric acid mixtures |
| acetylene | chlorine, bromine, copper, fluorine, silver, mercury |
| alkali and alkaline earth metals | water, chlorinated hydrocarbons, carbon dioxide, halogens, alcohols, aldehydes, ketones, acids |
| aluminum (powdered) | chlorinated hydrocarbons, halogens, carbon dioxide, organic acids |
| anhydrous ammonia | mercury, chlorine, calcium hypochlorite, iodine, bromine, hydrofluoric acid |
| ammonium nitrate | acids, metal powders, flammable liquids, chlorates, nitrites, sulphur, finely divided organic combustible materials |
| aniline | nitric acid, hydrogen peroxide |
| arsenic compounds | reducing agents |
| azides | acids |

## BACKGROUND

**Table 5. Incompatible Chemicals**

| Chemical | Incompatible with |
|---|---|
| bromine | ammonia, acetylene, butadiene, hydrocarbons, hydrogen, sodium, finely-divided metals, turpentine, other hydrocargons |
| calcium carbide | water alcohol |
| calcium oxide | water |
| carbon, activated | calcium hypochlorite, oxidizing agents |
| chlorates | ammonium salts, acids, metal powders, sulphur, finely divided organic or combustible materials |
| chromic acid | acetic acid, naphthalene, camphor, glycerin, turpentine, alcohols, flammable liquids in general |
| chlorine | see bromine |
| chlorine dioxide | ammonia, methane, phosphine, hydrogen sulphide |
| copper | acetylene, hydrogen peroxide |
| cumene hydroperoxide | acids, organic or inorganic |
| cyanides | acids |
| flammable liquids | ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens |
| hydrocarbons | fluorine, chlorine, bromine, chromic acid, sodium peroxide |
| hydrocyanic acid | nitric acid, alkali |
| hydrofluoric acid | aqueous or anhydrous ammonia |
| hydrogen peroxide | copper, chromium, iron, most metals or their salts, alcohols, acetone, organic materials, aniline, nitromethane, flammable liquids, oxidizing gases |
| hydrogen sulphide | fuming nitric acid, oxidizing gases |
| hypochlorites | acids, activated carbon |
| iodine | acetylene, ammonia (aqueous or anhydrous), hydrogen |
| mercury | acetylene, fulminic acid, ammonia |
| mercuric oxide | sulphur |
| nitrates | sulphuric acid |
| nitric acid (conc.) | acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulphide, flammable liquids, flammable gases |
| oxalic acid | silver, mercury |

**Table 5. Incompatible Chemicals**

| Chemical | Incompatible with |
|---|---|
| perchloric acid | acetic anhydride, bismuth and its alloys, ethanol, paper wood |
| peroxides (organic) | acids, avoid friction or shock |
| phosphorus (white) | air, alkalies, reducing agents, oxygen |
| potassium | carbon tetrachloride, carbon dioxide, water |
| potassium chlorate | acids |
| potassium perchlorate | acids |
| potassium permanganate | glycerin, ethylene glycol, benzaldehyde, sulphuric acid |
| selenides | reducing agents |
| silver | acetylene, oxalic acid, tartaric acid, ammonium compounds, fulminic acid |
| sodium | carbon tetrachloride, carbon dioxide, water |
| sodium nitrate | ammonium salts |
| Sodium nitrite | ammonium salts |
| sodium peroxide | ethanol, methanol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulphide, glycerin, ethylene glycol, ethyl acetate, methyl acetate, furfural |
| sulphides | acids |
| sulphuric acid | potassium chlorate, potassium percholorate, potassium permanganate (or compounds with similar light metals, such as sodium lithium, etc. |
| tellurides | reducing agents |
| zinc powder | sulphur |

## Combustible Loading

Controls for combustible loading within an area must be designed to control combustible loads inherent in the fixtures and equipment as well as any transient combustible loads during operations. The safety function of these administrative controls is to limit the transient combustible material; that is, material temporarily residing within a fire area, to allowable quantities. The quantities must not exceed the design basis for control of combustion. Administrative controls, primarily in the form of procedures, are used to control storage, use of combustible material, and ignition sources. These controls are carried out by training, posting, routine housekeeping, and periodic surveillance.

## BACKGROUND

## FIRE STAGES

Compartment fires are often discussed in terms of growth stages. The growth stages are:

- Ignition
- Growth
- Flashover
- Fully developed fire
- Decay

While many fires will not follow this idealization, it provides a useful framework for the discussion of compartment fires. All fires include an ignition stage but beyond that may fail to grow, or they may be affected by manual or automatic suppression activities before going through all of the stages.

### Growth Stage Definitions

The following are growth stage definitions.

Ignition stage. The period during which the fire begins.

Growth stage. Following ignition, the fire initially grows primarily as a function of the fuel itself, with little or no influence from the compartment. The fire can be described in terms of its rate of energy and combustion product generation. If sufficient fuel and oxygen are available, the fire will continue to grow, causing the temperature in the compartment to rise. Fires with sufficient oxygen for combustion are said to be fuel controlled.

Flashover. Flashover is generally defined as the transition from a growing fire to a fully developed fire in which all combustible items in the compartment are involved in fire. During this transition there are rapid changes in the compartment environment. Flashover is not a precise term, and several variations in definition can be found in fire literature. Most have criteria based on the temperature at which the radiation from the hot gases in the compartment will ignite all of the combustible contents. Gas temperatures of 300°C to 650°C have been associated with the onset of flashover, although temperatures of 500°C to 600°C are more widely used. The ignition of unburnt fuel in the host fire gases, the appearance of flames from openings in a compartment, or the ignition of all of the combustible contents may actually be different phenomena.

Fully developed fire. During this stage, the heat release rate of the fire is the greatest. Frequently during this stage more fuel is pyrolized than can be burned with the oxygen available in the compartment. In this case, the fire is said to be ventilation controlled. If there are openings in the compartment, the unburned fuel will leave the compartment in the gas flow and may burn outside of the compartment. During the fully developed stage, the environment within the compartment has a significant effect on the pyrolysis rate of the burning objects.

Decay stage. Decay occurs as the fuel becomes consumed and the heat release rate declines. The fire may change from ventilation to fuel controlled during this period.

## Browns Ferry Fire

A fire at the Browns Ferry Nuclear Power Plant, on March 22, 1975, was a pivotal event that brought fundamental change to fire protection and its regulation in the U.S. nuclear power industry. The fire started when plant workers in the cable spreading room used a candle to test for air leakage through a non-fire-rated (e.g. polyurethane foam) penetration seal that led to the reactor building. The fire ignited both the seal material and the electrical cables that passed through it, and burned for almost 7 hours before it was extinguished. More than 1600 cables were affected and, of those, 628 were important to safety.

The fire damaged electrical power, plant control systems, and instrumentation cables that impaired the functioning of both the normal and standby reactor cooling systems and affected the plant monitoring capability for the operators. Given the loss of many safety systems, the plant operators had to perform emergency repairs to restore the plant's systems that were needed to place the reactor in a safe shutdown condition.

The investigations that followed the Browns Ferry fire identified significant deficiencies, both in the design of fire protection features at nuclear power plants and in the plant procedures for responding to a fire event. The investigators concluded that the occupant safety and property protection concerns of fire insurance companies did not sufficiently encompass nuclear safety issues. Following the Browns Ferry fire the Commission revised its fire protection regulations to address the identified deficiencies related to the nuclear safety issues.

The NRC issued fire protection guidance shortly after the Browns Ferry fire, and, over the next several years, developed a rule that sets detailed requirements related to fire prevention and detection, fire brigade training and other areas of fire protection. See module 3.0 and Appendix D for a discussion of the Portsmouth Gaseous Diffusion Plant fire.

## NFPA STANDARDS AND CODES

The National Fire Protection Association has a goal of reducing the burden of fire and other hazards by providing and advocating scientifically-based codes and standards to follow in establishing fire protection programs.

## BACKGROUND

### NFPA 35

“Standard for the Manufacture of Organic Coatings,” 1999 Edition. NFPA 35 provides requirements for fire-safe design and operation of facilities that manufacture organic chemical-based coatings such as paints and inks.  The coatings are used for industrial, automotive, marine, transportation, institutional, household, and other purposes.

### NFPA 69

“Standard on Explosion Prevention Systems,” 2002 Edition.  NFPA 69 covers the design, construction, operation, maintenance and testing of systems for the prevention of deflagration explosions by means of the following methods:

- control of oxidant concentration;
- control of combustible concentration;
- explosion suppression;
- deflagration pressure containment; and
- spark extinguishing systems.

### NFPA 801

“Standard for Fire Protection for Facilities Handling Radioactive Materials,” 2003 Edition.  NFPA 801 applies to facilities that handle radioactive materials (except nuclear reactors).  Wherever radioactive materials are handled, processed, or stored, special precautions are needed to reduce the risk of fire or explosion and the severity of contamination from a fire or explosion.

### SUMMARY

An understanding of fire fundamentals and NFPA Standards and Codes is integral to effective oversight of fire protection programs. Essential points to know are:

<u>Principles of combustion</u>.  Combustion is the burning of a gas, liquid, or solid in which fuel is rapidly oxidized, producing heat and often light.  Oxidation is the chemical combination of a substance with oxygen.  Oxidation reactions release heat and are therefore exothermic.  The fire tetrahedron, with its four sides, symbolizes fuel, heat, oxygen and chemical chain reaction.

<u>Spontaneous combustion/heating</u>.  The burning occurs when combustible material ignites from an accumulation of heat from a runaway oxidation reaction.  Fire can be caused by spontaneous heating, a slow oxidation that causes temperature to rise without an additional heat source; a hypergolic reaction, defined as a material’s ability to spontaneously ignite when in contact with any oxidizing agent; or pyrophoricity, a type of hypergolic reaction with oxidizing agent restricted to atmospheric oxygen.

## BACKGROUND

Combustible metals. Some metals will oxidize rapidly and others more slowly. Combustible metals, such as magnesium, titanium, plutonium and uranium, are subject to ignition when they reach a high specific area ratio; i.e., thin sections, fine particles or molten states. When evaluating combustibility, factors to consider are: particle size, shape, quantity, and alloy constituent. Some metals are toxic, particularly heavy metals; some metals emit ionizing radiation that can cause radioactive contamination.

Flammable and combustible liquids. A flammable liquid has a flash point below 100 degrees F and a vapor pressure not exceeding 40 psia. A flash point is the minimum temperature at which a liquid gives off a concentration of vapor to form an ignitable mixture with air. Flammable liquids are defined as Class I. A combustible liquid has a flash point at or above 100 degrees F, and can be either Class II or Class III. An LFL is the % of vapor in air below which a fire can’t occur due to not enough fuel; an UFL is the % of vapor in air above which there isn’t enough air for a fire.

Industrial gases. Flammable gases such as acetylene, butane, and hydrogen can burn or explode under certain conditions. The concentration of gas in air must be between its LFL and UFL. Hydrogen and oxygen are two common gases. Hydrogen is extremely flammable. Oxygen supports combustion but does not burn. However, when oxygen is combined with other elements/compounds, such as oil, grease or fuel, spontaneous ignition can result.

Incompatible chemicals. Some chemicals react dangerously when mixed with other materials. Review Table 3, which shows incompatibility among various chemicals. Chemical interactions. Human error or equipment malfunction can result in a hazardous reaction. Process chemicals must be controlled and stored properly and personnel who handles the chemicals must be trained.

Fire stages. Fires have growth stages, which are: ignition, during which the fire begins; growth, which is a function of the fuel and oxygen; flashover, the transition of a growing fire to a fully developed fire with involvement of all compartments; fully developed fire, when heat release is greatest and fire is said to be ventilation controlled; and finally decay, when fuel becomes consumed and heat release declines.

NFPA codes and standards. NFPA provides codes and standards for fire protection programs to follow. Some of these are NFPA 801, 69, 35, and 805. NFPA 805, which is currently a proposed rule, sets forth requirements for a performance-based standard for fire protection. The NRC has begun emphasizing risk-informing fire protection requirements and performance-based methods.