

FIRE BEHAVIOR AND CHEMISTRY

FIRE BEHAVIOR

Effective fire control and extinguishment requires a basic understanding of the chemical and physical nature of fire. This includes information describing sources of heat energy, composition and characteristics of fuels, and environmental conditions necessary to sustain the combustion process.

ANATOMY OF FIRE

Combustion is the self-sustaining process of rapid oxidation of a fuel being reduced by an oxidizing agent along with the evolution of heat and light. Fires are defined by their physical characteristics. They may vary from very slow oxidation, as in rusting, to very fast oxidation, such as detonations and explosions. Somewhere between these extremes are the two most common reactions concerning firefighters: smoldering fires and flaming or free-burning fires.

For many years, the “fire triangle” (oxygen, fuel, and heat) was used to teach the components of fire. While this simple example is useful, it is not technically correct. For combustion to occur, four components are necessary:

- • **Oxygen (oxidizing agent)**
- • **Fuel**
- • **Heat**
- • **Self sustained chemical reaction (also referred to as the chain reaction)**

These components can be graphically described as the “fire tetrahedron”. Each component of the tetrahedron must be in place for combustion to occur. This concept is extremely important to fire suppression personnel. Remove any one of the four components and combustion will not occur. If ignition has already occurred, the fire is extinguished when one of the components is removed from the reaction.

OXIDIZING AGENTS

Oxidizing agents are those materials that yield oxygen or other oxidizing gases during the course of a chemical reaction. Oxidizers are not themselves combustibles, but they support combustion when combined with a fuel. While oxygen is the most common oxidizer, other substances fall into this category.

Common oxidizers include:

Bromates	Bromine	Chlorates	Chlorine
Flourine	Iodine	Nitrates	Nitric Acid
Nitrites	Perchlorates	Peroxides	Permanganates

Most fires involve a fuel that is chemically combined with the oxygen normally found in atmospheric air. Atmospheric air contains 21 percent oxygen, 79 percent nitrogen and 1 percent of other gases.

FUEL

Fuel is the material or substance being oxidized or burned in the combustion process. In scientific terms, the fuel in a combustion reaction is known as the “reducing agent”. Most common fuels contain carbon along with combinations of hydrogen and oxygen. These fuels can be further broken down into hydrocarbon-based fuels (such as gasoline, fuel oil, and plastics) and cellulose-based materials (such as wood and paper).

Fuel may be found in any of three (3) states of matter:

- • **Solid**
- • **Liquid**
- • **Gas**

The initiation of combustion requires the conversion of fuel into the gaseous state by heating. Fuel gases are evolved from solid fuels by pyrolysis. This is defined as the chemical decomposition of a substance through the action of heat. Fuel gases are evolved from liquids by vaporization. This process is the same as boiling water or evaporation of a pan of water in sunlight. In both cases, heat caused the liquid to vaporize. No heat input is required with gaseous fuels and this places considerable restraints on the control and extinguishment of gas fuel fires.

- • **Solid Fuels**

Solid fuels have definite shape and size. One primary consideration with solid fuels is the surface area of the material in relation to its mass. The larger the surface area for a given mass, the more rapid the heating of the material and increase in the speed of pyrolysis. The physical position of a solid fuel is also of great concern to firefighting personnel. If the solid fuel is in a vertical position, fire spread will be more rapid than if it is in a horizontal position. This is due to increased heat transfer through convection and direct flame contact in addition to conduction and radiation.

<i>Temperature</i>	<i>PYROLYSIS Reaction</i>
392 ⁰ F acetic (200 ⁰ C)	Production of water vapor, carbon dioxide, formic and acids
392 ⁰ -536 ⁰ F	Less water vapor - some carbon monoxide - still

primarily an	(200 ⁰ -280 ⁰ C)	endothermic reaction (absorbing heat)
	536 ⁰ -932 ⁰ F	Exothermic reaction (giving off heat) with flammable vapors and particulates; some secondary reaction from charcoal formed
	(280 ⁰ -500 ⁰ C)	
action	Over 932 ⁰ F	Residue primarily charcoal with notable catalytic
	(500 ⁰ C)	

- • **Liquid Fuels**

Liquid fuels have physical properties that increase the difficulty of extinguishment and hazard to personnel. Liquids will assume the shape of their container. When a spill occurs, the liquid will assume the shape of the ground (flat) and will flow and accumulate in low areas.

The density of liquids in relation to water is known as **specific gravity**. Water is given a value of one. Liquids with a specific gravity less than one are lighter than water, while those with a specific gravity greater than one are heavier than water. It is interesting to note that most flammable liquids have a specific gravity of less than one, therefore they would float on top of water.

The solubility of a liquid fuel in water is an important factor. Hydrocarbon liquids as a rule will not mix with water. Alcohol and polar solvents mix with water and if large volumes of water are used, they may be diluted to the point where they will not burn. Consideration must be given to which extinguishing agents are effective on hydrocarbons (insoluble) and which affect porous solvents and alcohol (soluble).

The volatility or ease with which the liquid gives off vapor influences fire control objectives. The density of gas or vapor in relation to air is of concern to volatile liquids and with gas fuels.

- • **Gas Fuels**

Gases tend to assume the shape of their container but have no specific volume. If the vapor density of a gas is such that it is less dense than air (air is given a value of one), it will rise and tend to dissipate. If a gas or vapor is heavier than air, it will tend to hug the ground and travel as directed by terrain and wind.

An easy way to remember those gases that are lighter than air is the acronym "HA HA MICEN", where:

- H = Hydrogen
- A = Anhydrous Ammonia

H = Helium
A = Acetylene
M = Methane
I = Illuminating Gas
C = Carbon Monoxide
E = Ethylene
N = Nitrogen

This is a significant property for evaluating exposures and where hazmat gas and vapor will travel.

The mixture of the fuel vapor and air must be within the flammable range. The upper and lower limits of concentration of vapor in air will allow flame propagation when contacted by a source of ignition.

The flammable range varies with the fuel and with the ambient temperature. Usually the flammable range is given for temperatures of 70⁰F (21⁰C).

EXAMPLES OF FLAMMABLE RANGES

<u>Fuel</u>	<u>Lower Limit</u>	<u>Upper Limit</u>
Gasoline Vapor	1.4	7.6
Methane (natural gas)	5.0	17.0
Propane	2.2	9.5
Hydrogen	4.0	75.0
Acetylene	2.5	100.0

When the proper fuel vapor/air mixture has been achieved, it must be raised to its ignition temperature.

HEAT

Heat is a form of energy that may be described as a condition of matter in motion caused by the movement of molecules. All matter contains some heat regardless of how low the temperature is because molecules are constantly moving all the time. When a body of matter is heated, the speed of the molecules increases, thus the temperature increases. Anything that sets the molecules of a material in motion produces heat in that material. There are four (4) general categories of heat energy and they include:

- • Chemical Heat Energy
 - • Electrical Heat Energy
 - • Mechanical Heat Energy
 - • Nuclear Heat Energy
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- • **Chemical Heat Energy**

Heat of Combustion - The amount of heat generated by the combustion (oxidation) process.

Spontaneous Heating - The heating of an organic substance without the addition of external heat. Spontaneous heating occurs most frequently where sufficient air is not present to dissipate the heat produced. The speed of a heating reaction doubles with each 18° F (8° C) temperature increase.

Heat of Decomposition - The release of heat from decomposing compounds. These compounds may be unstable and release their heat very quickly or they may detonate.

Heat of Solution - The heat released by the mixture of matter in a liquid. Some acids, when dissolved, give off sufficient heat to pose exposure problems to nearby combustibles.

- • **Electrical Heat Energy**

Resistance Heating - The heat generated by passing an electrical force through a conductor such as a wire or an appliance.

Dielectric Heating - The heating that results from the action of either pulsating direct current, or alternating current at high frequency on a non-conductive material.

Induction Heating - The heating of materials resulting from an alternating current flow causing a magnetic field influence.

Leakage Current Heating - The heat resulting from imperfect or improperly insulated electrical materials. This is particularly evident where the insulation is required to handle high voltage or loads near maximum capacity.

Heat from Arcing - Heat released either as a high-temperature arc or as molten material from the conductor.

Static Electricity Heating - Heat released as an arc between oppositely charged surfaces. Static electricity can be generated by the contact and separation of charged surfaces or by fluids flowing through pipes.

Heat Generated by Lightning - The heat generated by the discharged of thousands of volts from either earth to cloud, cloud to cloud or from cloud to ground.

- • **Mechanical Heat Energy**

Frictional Heat - The heat generated by the movement between two objects in contact with each other.

Friction Sparks - The heat generated in the form of sparks from solid objects striking each other. Most often at least one of the objects is metal.

Heat of Compression - The heat generated by the forced reduction of a gaseous volume. Diesel engines ignite fuel vapor without a spark plug by the use of this principle.

- • **Nuclear Heat Energy**

Nuclear Fission and Fusion - The heat generated by either the splitting or combining of atoms.

PHASES OF FIRE

The burning process occurs in clearly defined stages. By recognizing the different phases (or stages), a fire fighter can better understand the process of burning and fighting the fire at different levels and with different tactics and tools. Each phase (or stage) is characterized by differences in room temperature and atmospheric composition.

A firefighter may be confronted by one or all of the following three phases (or stages) of fire at any time:

- • **Incipient Phase (Growth Stage)**

In the first phase, the oxygen content in the air has not been significantly reduced and the fire is producing water vapor, carbon dioxide, perhaps a small quantity of sulfur dioxide, carbon monoxide and other gases. Some heat is being generated, and the amount will increase with the progress of the fire. The fire may be producing a flame temperature well above 1,000⁰F (537⁰C), yet the temperature in the room at this stage may be only slightly increased.

- • **Free-Burning Phase (Fully Developed Stage)**

The second phase of burning encompasses all of the free-burning activities of the fire. During this phase, oxygen-rich air is drawn into the flame as convection (the rise of heated gases) carries the heat to the upper most regions of the confined area. The heated gases spread out laterally from the top downward, forcing the cooler air to seek lower levels, and eventually igniting all the combustible material in the upper levels of the room. This heated air is one of the reasons that firefighters are taught to keep low and use protective breathing equipment. One breath of this super-heated air can sear the lungs. At this point,

the temperature in the upper regions can exceed 1,300⁰F (700⁰C). As the fire progresses through the latter stages of this phase, it continues to consume the free oxygen until it reaches the point where there is insufficient oxygen to react with the fuel. The fire is then reduced to the smoldering phase and needs only a supply of oxygen to burn rapidly or explode.

- • **Smoldering Phase (Decay Stage)**

In the third phase, flame may cease to exist if the area of confinement is sufficiently airtight. In this instance, burning is reduced to glowing embers. The room becomes completely filled with dense smoke and gases to the extent that it is forced from all cracks under pressure. The fire will continue to smolder, and the room will completely fill with dense smoke and gases of combustion at a temperature of well over 1,000⁰F (537⁰C). The intense heat will have vaporized the lighter fuel fractions such as hydrogen and methane from the combustible material in the room. These fuel gases will be added to those produced by the fire and will further increase the hazard to the firefighter and create the possibility of a backdraft.

TIME TEMPERATURE CURVE

The demarcations between the three phases can be identified by a “time temperature curve”. During the incipient (or growth) phase of a fire, shown below as the upward curve, the time can vary depending on the type of fuel, the size of the room, and the amount of oxygen supplying the fire. Flashover occurs at the end of the incipient (or growth) phase and start of the free burning (or fully developed) stage. Backdraft can occur in the smoldering (or decay) phase.

FLASHOVER

Flashover occurs when a room or other area becomes heated to the point where flames flash over the entire surface or area. Originally, it was believed that flashover was caused by combustible gases released during the early stages of fire. It was thought that these gases collected at the ceiling level and mixed with air until they reached their flammable range, then suddenly ignited causing flashover. It is now believed that while this may occur, it precedes flashover. The cause of flashover is not attributed to the excessive build-up of heat from the fire itself. As the fire continues to burn, all the contents of the fire area are gradually heated to their ignition temperatures, through “thermal radiation feedback”. When they reach this point, simultaneous ignition occurs and the area becomes fully involved in fire.

BACKDRAFT

Firefighters responding to a confined fire that is late in the free-burning phase or in the smoldering phase risk causing a backdraft or smoke explosion if the science of fire is not considered in opening the structure.

In the smoldering phase of a fire, burning is incomplete because not enough oxygen is available to sustain the fire. However, the heat from the free-burning phase remains, and the unburned carbon particles and other flammable products of combustion are just waiting to burst into rapid, almost instantaneous combustion when more oxygen is supplied. Proper ventilation releases smoke and the hot unburned gases from the upper areas of the room or structure. Improper ventilation at this time supplies the dangerous missing link -- oxygen. As soon as the needed oxygen rises in, the stalled combustion resumes, and it can be devastating in its speed, truly qualifying as an explosion.

Combustion is related to oxidation, and oxidation is a chemical reaction in which oxygen combines with other elements. Carbon is a naturally abundant element present in wood, among other things. When wood burns, carbon combines with oxygen to form carbon dioxide, or carbon monoxide, depending on the availability of oxygen. When oxygen is no longer available, free carbon is released in the smoke. A warning sign of possible backdraft is dense, black (carbon-filled) smoke.

The following characteristics may indicate a backdraft or smoke explosion condition:

1. Smoke under pressure
2. Black smoke becoming dense gray yellow
3. Confinement and excessive heat
4. Little or no visible flame
5. Smoke leaves the building in puffs or at intervals
6. Smoke-stained windows
7. Muffled sounds
8. Sudden rapid movement of air inward when opening is made

This type of condition can be made less dangerous by proper ventilation. If the building is opened at the highest point involved, the heated gases and smoke will be released, reducing the possibility of an explosion.

HEAT TRANSFER

Heat can travel throughout a burning building by one or more of three methods, commonly referred to as **conduction, convection and radiation**. Since the existence of heat within a substance is caused by molecular action, the greater the molecular activity, the more intense the heat. A number of natural laws of physics are involved in the transmission of heat. One is called the Law of Heat Flow. It specifies that heat tends to flow from a hot substance to a cold substance. The colder of two bodies in contact will absorb heat until both objects are the same temperature.

• • Conduction

Heat may be conducted from one body to another by direct contact of the two bodies or by an intervening heat-conducting medium. The amount of heat that will be transferred and its rate of travel depends upon the conductivity of the material through which the

heat is passing. Not all materials have the same heat conductivity. Aluminum, copper and iron are good conductors. Fibrous materials, such as felt, cloth and paper are poor conductors.

Liquids and gases are poor conductors of heat because of the movement of their molecules. Air is a relatively poor conductor. Certain solid materials when shredded into fibers and packed into batts, make good insulation because the material itself is a poor conductor and there are air pockets within the batting. Double building walls that contain an air space provide additional insulation.

- • **Convection**

Convection is the transfer of heat by the movement of air or liquid. When water is heated in a glass container, the movement within the vessel can be observed through the glass. If some sawdust is added to the water, the movement is more apparent. As the water is heated, it expands and grows lighter, hence, the upward movement. In the same manner, air becomes heated near a steam radiator by conduction. It expands, becomes lighter and moves upward. As the heated air moves upward, cooler air takes its place at the lower levels. When liquids and gases are heated, they begin to move within themselves. This movement is different from the molecular motion discussed in conduction of heat and is known as heat transfer by convection.

Heated air in a building will expand and rise. For this reason, fire spread by convection is mostly in an upward direction, although air currents can carry heat in any direction. Convected currents are generally the cause of heat movement from floor to floor, from room to room and from area to area. The spread of fire through corridors, up stairwells and elevator shafts, between walls and through attics is mostly caused by the convection of heat currents and has more influence upon the positions for fire attack and ventilation than either radiation or conduction.

Another form of heat transfer by convection is direct flame contact. When a substance is heated to the point where flammable vapors are given off, these vapors may be ignited, creating a flame. As other flammable materials come in contact with the burning vapors, or flame, they may be heated to a temperature where they too, will ignite and burn.

- • **Radiation**

The warmth of the sun is felt soon after it rises. When the sun sets, the earth begins to cool with similar rapidity. We carry an umbrella to shade our bodies from the heat of the sun. A spray of water between a firefighter and a fire will lessen the heat reaching the firefighter. Although air is a poor conductor, it is obvious that heat can travel where matter does not exist. This method of heat transmission is known as radiation of heat waves. Heat and light waves are similar in nature, but they differ in length per cycle. Heat waves are longer than light waves and they are sometimes called infrared rays. Radiated heat will travel through space until it reaches an opaque object. As the object is exposed to heat radiation, it will in return radiate heat from its surface. Radiated heat is one of the major sources of fire spread, and its importance demands immediate attention at points where radiation exposure is severe.

PRODUCTS OF COMBUSTION

When a material (fuel) burns, it undergoes a chemical change. None of the elements making up the material are destroyed in the process, but all of the matter is transformed into another form or state. Although dispersed, the products of combustion equal in weight and volume that of the fuel before it was burned. When a fuel burns there are four products of combustion:

- • Fire gases
- • Flame
- • Heat
- • Smoke

The smoke encountered at most fires consists of a mixture of oxygen, nitrogen, carbon dioxide, carbon monoxide gases, finely divided carbon particles (soot), and a miscellaneous assortment of products that have been released from the material involved.

Heat is a form of energy that is measured in degrees of temperature to signify its intensity. In this sense, heat is the product of combustion that is responsible for the spread of fire. In a physiological sense, it is the direct cause of burns and other forms of personal injury. Injuries caused by heat include dehydration, heat exhaustion and injury to the respiratory tract, in addition to burns.

Flame is the visible, luminous body of a burning gas. When a burning gas is mixed with the proper amounts of oxygen, the flame becomes hotter and less luminous. This loss of luminosity is because of a more complete combustion of the carbon. For these reasons, flame is considered to be a product of combustion. Heat, smoke and gas, however, can develop in certain types of smoldering fires without evidence of flame.

Some materials give off more smoke than others. Liquid fuels generally give off dense black smoke. Oils, tar, paint, varnish, molasses, sugar, rubber, sulfur and many plastics, also generally give off a dense smoke in large quantities.

FIRE EXTINGUISHMENT THEORY

The extinguishment of fire is based on an interruption of one or more of the essential elements in the combustion process. With flaming combustion the fire may be extinguished by reducing temperature, eliminating fuel or oxygen, or by stopping the uninhibited chemical chain reaction. If a fire is in the smoldering mode of combustion, only three extinguishment options exist: reduction of temperature, elimination of fuel or oxygen.

- • **Extinguishment of Temperature Reduction**

One of the most common methods of extinguishment is by cooling with water. The process of extinguishment by cooling is dependent on cooling the fuel to a point where it

does not produce sufficient vapor to burn. If we look at fuel types and vapor production, we find that solid fuels and liquid fuels with high flash points can be extinguished by cooling. Low flashpoint liquids and flammable gases cannot be extinguished by cooling with water as vapor production cannot be sufficiently reduced. Reduction of temperature is dependent on the application of an adequate flow in proper form to establish a negative heat balance.

- • **Extinguishment by Fuel Removal**

In some cases, a fire is effectively extinguished by removing the fuel source. This may be accomplished by stopping the flow of liquid or gaseous fuel or by removing solid fuel in the path of the fire. Another method of fuel removal is to allow the fire to burn until all fuel is consumed.

- • **Extinguishment by Oxygen Dilution**

The method of extinguishment by oxygen dilution is the reduction of the oxygen concentration to the fire area. This can be accomplished by introducing an inert gas into the fire or by separating the oxygen from the fuel. This method of extinguishment will not work on self-oxidizing materials or on certain metals as they are oxidized by carbon dioxide or nitrogen, the two most common extinguishing agents.

- • **Extinguishment by Chemical flame Inhibition**

Some extinguishing agents, such as dry chemicals and halons, interrupt the flame producing chemical reaction, resulting in rapid extinguishment. This method of extinguishment is effective only on gas and liquid fuels as they cannot burn in the smoldering mode of combustion. If extinguishment of smoldering materials is desired, the addition of cooling capability is required.

CLASSIFICATION OF FIRES AND EXTINGUISHMENT METHODS

- • **Class A Fire** - Fires involving ordinary combustible materials, such as wood, cloth, paper, rubber and many plastics.

Water is used in a cooling or quenching effect to reduce the temperature of the burning material below its ignition temperature.

- • **Class B Fires** - Fires involving flammable liquids, greases and gases.

The smothering or blanketing effect of oxygen exclusion is most effective. Other extinguishing methods include removal of fuel and temperature reduction.

- • **Class C Fires** - Fires involving energized electrical equipment.

This fire can sometimes be controlled by a non-conducting extinguishing agent. The

safest procedure is always to attempt to de-energize high voltage circuits and treat as a Class A or B fire depending upon the fuel involved.

- • **Class D Fires** - Fires involving combustible metals, such as magnesium, titanium, zirconium, sodium and potassium.

The extremely high temperature of some burning metals makes water and other common extinguishing agents ineffective. There is no agent available that will effectively control fires in all combustible metals. Special extinguishing agents are available for control of fire in each of the metals and are marked specifically for that metal.

- • **Class K Fires** - Class K is a new classification of fire as of 1998 and involves fires in combustible cooking fuels such as vegetable or animal fats.

Its fuels are similar to Class B fuels but involve high temperature cooking oils and therefore have special characteristics. Class K agents are usually wet chemicals, water-based solutions of potassium carbonate-based chemical, potassium acetate-based chemical, or potassium citrate-based chemical or a combination. These agents are usually used in fixed systems, but some extinguishers are available.

DEFINITIONS: The following are some terms used to define and describe fire activity.

BOILING POINT - The temperature of a substance where the rate of evaporation exceeds the rate of condensation.

BRITISH THERMAL UNIT (BTU) - The amount of heat needed to raise the temperature of one pound of water one degree F.

CALORIE - The amount of heat needed to raise the temperature of one gram of water one degree Centigrade.

CENTIGRADE (Celsius) - On the Centigrade scale, zero is the melting point of ice; 100 degrees is the boiling point of water.

ENDOTHERMIC HEAT REACTION - A chemical reaction where a substance absorbs heat energy.

EXOTHERMIC HEAT REACTION - A chemical reaction where a substance gives off heat energy.

FAHRENHEIT - On the Fahrenheit scale, 32 degrees is the melting point of ice; 212 degrees is the boiling point of water.

FIRE POINT - The temperature at which a liquid fuel will produce vapors sufficient to support combustion once ignited. The fire point is usually a few degrees above the flash point.

FLAMMABLE OR EXPLOSIVE LIMITS - The percentage of a substance in air that will burn once it is ignited. Most substances have an upper (too rich) and a lower (too lean) flammable limit.

FLASH POINT - The minimum temperature at which a liquid fuel gives off sufficient vapors to form an ignitable mixture with the air near the surface. At this temperature, the ignited vapors will flash, but will not continue to burn.

HEAT - The form of energy that raises temperature. Heat is measured by the amount of work it does.

IGNITION TEMPERATURE - The minimum temperature to which a fuel in air must be heated in order to start self-sustained combustion independent of the heating source.

OXIDATION - The complex chemical reaction of organic material with oxygen or other oxidizing agents in the formation of more stable compounds.