# FIRE BEHAVIOR AND CHEMISTRY OF FIRE

**OBJECTIVE:**
- To familiarize the firefighter with the process of combustion & the effects of fire propagation as it relates to firefighting operations.

**CONTENTS:**
- An explanation of principles of fire behavior, the phases of fire, methods of heat transfer, the classifications of fires and the theory of extinguishment

**SOURCE:**
- Essentials of Fire Fighting (Third and Fourth Editions) – International Fire Service Training Association

**FDNY REFERENCE:**

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People first learn about fire as children. They know that fire consumes fuel, needs air, and gives off heat and light. Normally, that degree of understanding is all that one needs. Firefighters, however, have to take their understanding of this process a step or two further. In particular, they have to know more about the chemical process that goes on, the methods of heat transfer a fire can use, the makeup and nature of the fuels, and the environment the fire needs. It is this knowledge that arms the firefighter to fight fire and win.

Fire is actually a by-product of a larger process called combustion. Fire and combustion are two words used interchangeably by most people; however, firefighters should understand the difference. Combustion is the self-sustaining process of rapid oxidation of a fuel, which produces heat and light. Fire is the result of a rapid combustion reaction.

**IMPORTANT TERMS**

*Flammable or explosive limits* – The percentage of a substance (vapor) 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 can be measured by the amount of work it does; for example, the amount of heat needed to make a column of mercury expand inside a glass thermometer.

*Ignition temperature* – The minimum temperature to which a fuel in air must be heated to start self-sustained combustion without a separate ignition source.

**HEAT TRANSFER**

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 at the same temperature. Heat can travel throughout a burning building by on or more of three methods: conduction, convection, and radiation. The following sections describe how this transfer takes place.
Conduction

Heat may be conducted from one body to another by direct contact of the two bodies or by an intervening heat-conducting minimum. An example of this type of heat transfer is a basement fire that heats pipes enough to ignite the wood inside walls several rooms away (See Figure 1-1). The amount of heat that will be transferred and its rate of travel depend 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; however, fibrous materials, such as felt, cloth, and paper, are poor conductors.

![Figure 1-1](image_url)

Liquids and gas are poor conductors of heat because of the movement of their molecules, and air is a relatively poor conductor. This factor is why double building walls and storm windows that contain an airspace provide additional insulation from outside air temperatures. Certain solid materials, such as fiberglass, 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.

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 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, as air near a steam radiator becomes heated 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 responsible for heat transfer by convection.
Heated air in a building will expand and rise (See Figure 1-2). For this reason, fire spread by convection is mostly in an upward direction; however, air currents can carry heat in any direction. Convection 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 caused mostly by the convection of heat currents. If the convecting heat encounters a ceiling or other barrier that keeps it from rising, it will spread out laterally (sideways) along the ceiling. If it runs out of ceiling space, it will travel down the wall toward the floor, being pushed by more heated air that is rising behind it. Convected heat encountering a ceiling is commonly referred to as mushrooming. Convection has more influence upon the positions for fire attack and ventilation than either radiation or conduction.

Although often mistakenly thought to be a separate form of heat transfer, direct flame contact is actually a form of convective heat transfer. 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

Although air is a poor conductor, it is obvious that heat can travel where matter does not exist. The warmth of the sun reaches us even though it is not in direct contact with us (conduction), nor is it heating up gases that travel to us (convection). 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 infra-red waves. Radiated heat will travel through space until it reaches an opaque object (See Figure 1-3). 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 to exposures, and its importance as a source of fire spread demands immediate attention at location where radiation exposure is severe.

Figure 1-3

PRINCIPLES OF FIRE BEHAVIOR

Fire Tetrahedron

For many years, the fire triangle (oxygen, fuel, and heat) was used to teach the components of fire (Figure 1-5). 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
These components can be graphically described as the fire tetrahedron (Figure 1-4). Each component of the tetrahedron must be in place for combustion to occur. This concept is extremely important to students of fire suppression, prevention, and investigation. 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.

Fuel may be found in any of three states of matter; solid, liquid, or gas. Only gases burn. The initiation of combustion of a liquid or solid fuel require their conversion into a gaseous state by heating. Fuel gases are evolved from solid fuels by pyrolysis. Pyrolysis is the chemical decomposition of a substance through the action of heat (Figure 1-5).

Fuel gases are evolved from liquids by vaporization. This process is the same for water evaporating by boiling or water in a container evaporating in sunlight. In both cases, heat causes the liquid to vaporize. Generally, the vaporization process of liquid fuels requires less heat input than does the pyrolysis process for solid fuels. This places considerable restraints on the control and extinguishment of liquid fuel fires because their reignition is much more likely.

Gaseous fuels can be the most dangerous, because they are already in the natural state required for ignition. No pyrolysis or vaporization will be needed to ready the fuel. These fuels are also the most difficult to contain.

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Figure 1-4
Figure 1-5

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Chapter Two
CHEMISTRY OF FIRE

Figure 1-5
PHASES OF FIRE

Fires may start at any time of the day or night if a hazard exists. If the fire happens when the area is occupied and/or protected by automatic suppression and detection systems, chances are that it will be discovered and controlled in the beginning (incipient) phase. If the fire occurs when the building is closed, deserted, and without fixed protection systems, the fire may go undetected until it has gained major headway. The phase of a fire in a closed building is of chief importance when determining ventilation requirements.

Fire in a confined room or building has two particularly important characteristics. The first characteristic is that there is a limited amount of oxygen. This differs from an outside fire, where the oxygen supply is unlimited. The second characteristic is that the fire gases that are given off are trapped inside the structure and build up, unlike outdoors where they can dissipate. When fire is confined in a building or room, the situation requires carefully thought-out and executed ventilation procedures if further damage is to be prevented and danger reduced. Fire confined to a building or room can be best understood by an investigation of its three main progressive phases: incipient, steady-state burning, and hot smoldering. A firefighter may be confronted by one or all of the phases of fire at any time, therefore, a working knowledge of these phases is important for understanding ventilation procedures. Firefighters must also be aware of the variety of potentially hazardous conditions that may be intertwined within the three main phases. These hazards include rollover, flashover, and backdraft.

Incipient Phase

The incipient phase is the earliest phase of a fire beginning with the actual ignition. The fire is limited to the original materials of ignition (Figure 1-6). In the incipient phase, the oxygen content in the air has not been significantly reduced, and the fire is producing water vapor (H2O), carbon dioxide (CO2), perhaps a small quantity of sulfur dioxide (SO2), carbon monoxide (CO), and other gases. Some heat is being generated, and the amount will increase as the fire progresses. The fire may be producing a flame temperature well above 1,000°F (537°C), yet the temperature in the room at this stage may be only slightly increased.
Rollover

Rollover, sometimes referred to as flameover, takes place when unburned combustible gases released during the incipient or early steady-state phase accumulate at the ceiling level (Figure 1-7). These superheated gases are pushed, under pressure, away from the fire area and into uninvolved areas where they mix with oxygen. When their flammable range is reached, they ignite and a fire front develops, expanding very rapidly and rolling over the ceiling (Figure 1-8). This is one of the reasons firefighters must stay low when advancing hoselines. Rollover differs from flashover in that only the gases are burning and not the contents of the room. The rollover will continue until its fuel is eliminated. This is done by extinguishing the main body of fire. The rollover will cease when the fire itself stops producing the flammable gases that are feeding the rollover.

Figure 1-7

Steady-State Burning Phase

For purposes of simplicity, the steady-state burning phase (sometimes referred to as the free-burning phase) can generally be considered the phase of the fire where sufficient oxygen and fuel are available for fire growth and open burning to a point where total involvement is possible. During the early portions of this phase, oxygen rich air is drawn into the flame, as convection (the rise of heated gases) carries the heat to the uppermost regions of the confined area (Figure 1-9).
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 early portion of the steady-state burning phase is often called the flame-spread phase. The presence of this heated air is one of the reasons firefighters are taught to keep low and use protective breathing equipment. One breath of this superheated air can sear the lungs. At this point, the temperature in the upper regions can exceed 1,300°F (700°C).

If conditions are perfect, and they rarely are, the fire may achieve what is commonly referred to as “clear burning.” Clear burning is accompanied by high temperatures and complete combustion. Little or no smoke is given off. This fire is usually seen only when very clean fuels, such as methanol-based race car fuels, burn.

Thermal columns will normally occur with rapid air movements upward from the base of the fire. As the fire progresses (in a confined space) through the latter portions of the steady-state burning phase, the fire 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, but this fire needs only a fresh supply of oxygen to burn rapidly.

**Flashover**

Flashover occurs when flames flash over the entire surface of a room or area (Figure 1-10). The actual cause of flashover is attributed to the buildup 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. When they reach their ignition point, simultaneous ignition occurs, and the area becomes fully involved in fire. This actual ignition is almost instantaneous and can be quite dramatic. A flashover can usually be avoided by directing water toward the ceiling level and the room contents to cool materials below their ignition temperatures.
Hot Smoldering Phase

After the steady-state burning phase, flames may cease to exist if the area of confinement is sufficiently airtight. In this instance, burning is reduced to glowing embers (Figure 1-11). As the flames die down, the room becomes completely filled with dense smoke and gases. Air pressure from gases being given off may build to the extent that smoke and gases are forced through small cracks. Room temperatures in excess of 1,000°F (370°C) are possible. The intense heat will have liberated the lighter fuel fractions, such as methane, from the combustible material in the room. These fuel gases will be added produced by the fire and will further increase the hazard to the firefighter and create the possibility of a backdraft if air is improperly introduced into the room. If air is not introduced into the room, the fire will eventually burn out, leaving totally incinerated contents.

Backdraft

Firefighters responding to a confined fire that is late in the steady-state burning phase or in the hot smoldering phase risk causing a backdraft (also known as a smoke explosion) if the science of fire is not considered in opening the structure.

In the hot-smoldering phase of a fire, burning is incomplete because of insufficient oxygen to sustain the fire. However, the heat from the steady state burning phase remains, and the carbon particles and other flammable products of combustion are available for instantaneous combustion when more oxygen is supplied (Figure 1-12). Improper ventilation, such as opening a door or breaking a window, supplies the dangerous missing link — oxygen. As soon as the needed oxygen rushes in, the stalled combustion resumes; it can be devastating in its speed, truly qualifying as an explosion (Figure 1-13). Backdraft can be the most hazardous condition a firefighter will ever face.
Combustion is oxidation, and oxidation is a chemical reaction in which oxygen combines with other elements. Carbon is a naturally abundant element present in wood and most plastics, among other things. When the wood burns, carbon combines with oxygen to form carbon dioxide (CO2) or carbon monoxide (CO), depending on the availability of oxygen. When enough oxygen is no longer available, large quantities of free carbon are released in the smoke. Thus a warning sign of possible backdraft is dense, black (carbon-filed) smoke.

The following characteristics may indicate the potential for a backdraft to occur:

- Pressurized smoke exiting small openings
- Black smoke becoming dense gray yellow
- Confinement and excessive heat
- Little or no visible flame
- Smoke leaving the building in puffs or at intervals
- Smoke-stained windows
- Muffled sounds
- Sudden rapid movement of air inward when opening is made

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

**THERMAL LAYERING OF GASES**

The thermal layering of gases is the tendency of gases to form into layers, according to temperature.

Other terms sometimes used to describe this layering of gases by heat are heat stratification and thermal balance. The hottest gases tend to be in the top layer, while the cooler ones form the bottom layer. Smoke is a heated mixture of air, gases, and particles, and it rises. If a hole is made in the roof, the smoke will rise from the building or room to the outside.
Thermal layering is critical to fire fighting activities. As long as the hottest air and gases are allowed to rise the lower levels will be safer for firefighters (Figure 1-14). This normal layering of the hottest gases to the top and out the ventilation opening can be disrupted if water is improperly applied.

If water is improperly applied to the fire area and the area is not ventilated, the water will cool and condense, the steam generated by the initial fire attack. This reaction causes the smoke and steam to circulate within all levels of the fire area. This swirling of smoke and steam is the result of disrupted normal thermal layering (Figure 1-15). This process is sometimes referred to as disrupting the thermal balance or creating a thermal imbalance. Many firefighters have been needlessly burned when thermal layering was disrupted. Once the normal layering is disrupted, forced ventilation procedures must be used to clear the area.
PRODUCTS OF COMBUSTION

Incomplete combustion, of course, also leaves behind some unburned or charred school. 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 material is transformed into another form or state. For example, when a piece of paper burns, the gases and moisture contained within the paper are liberated. The remaining solids take on the appearance of carbonized, charred flakes. Although it was once thought that the weight of various byproducts was the same as the original weight of the fuel, it is now known that a tiny amount of fuel is indeed converted into energy, so the by-products weigh slightly less than the fuel did.

When a fuel burns, there are four products of combustion: heat, light, smoke, and fire gases (Figure 1-16). Heat is a form of energy that is measured in degrees of temperature to signify its intensity. Heat is the product of combustion that is responsible for the spread of fire. It is also the direct cause of burns, dehydration, heat exhaustion, and injury to the respiratory tract.

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. The loss of luminosity is caused by a more complete combustion of the carbon. For these reasons, flame is considered to be a product of combustion. Of course, it is not present in those types of combustion, such as smoldering fires, that does not produce flame.

The smoke encountered at most fires consists of a mixture of oxygen, nitrogen, carbon dioxide, carbon monoxide, finely divided carbon particles (soot), and a miscellaneous assortment of products that have been released from the material involved. The contents of the smoke will vary depending on the exact material that is burning; some materials give off more smoke than others. Liquid fuels generally give off dense, black smoke. Oil, tar, paint, varnish, rubber, sulfur, and many plastics also give off dense smoke.
FIRE EXTINGUISHMENT THEORY

The extinguishment of fire is carried out by limiting or interrupting 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 elimination of oxygen.

Extinguishment By Temperature Reduction

One of the most common methods of extinguishment is by cooling with water (Figure 1-17). This process of extinguishment is dependent on reducing the temperature of the fuel to a point where it does not produce sufficient vapor to burn. Solid fuels and liquid fuels with high flash points can be extinguished by cooling. Fires involving low flash point liquids and flammable gases cannot be extinguished by cooling with water, because 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 (Figure 1-18). Removal of the fuel sources 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

Reducing the oxygen content in an area also puts out the fire (Figure 1-19). Reduction of the oxygen content can be done by flooding an area with an inert gas, such as carbon dioxide, which displaces the oxygen; or the oxygen can be reduced by separating the fuel from the air such as by blanketing it with foam. Of course, neither of these methods work on those rare fuels that are self-oxidizing.

Extinguishment By Chemical Flame Inhibition

Some extinguishing agents, such as dry chemical and halogenated hydrocarbons (Halons), interrupt the flame-producing chemical reaction and stop flaming (Figure 1-20). This method of extinguishment is effective on gas and liquid fuels, because they must flame to burn. Smoldering fires are not easily extinguished by this method because the moment the Halon is shut off, air once again has access to the smoldering fuel and it continues to burn. Cooling is the only practical way to extinguish a smoldering fire.
CLASSIFICATION OF FIRES AND EXTINGUISHMENT METHODS

Class A Fires

Class A fires are 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. The addition of Class A foams (sometimes referred to as wet water) may enhance water’s ability to extinguish Class A fires, particularly those that are deep seated in bulk materials. This is because the Class A foam agent reduces the water’s surface tension, allowing it to penetrate more easily into piles of the material.

Class B Fires

Class B fires involve flammable and combustible liquids and gases such as gasoline, oil, lacquers, paints, mineral spirits, and alcohol. The smothering or blanketing effect on oxygen exclusion is most effective for extinguishment. Other extinguishing methods include removal of fuel and temperature reduction when possible.
Class C Fires

Fires involving energized electrical equipment are Class C fires. Household appliances, computers, transformers, and overhead transmission lines are examples of these. These fires can sometimes be controlled by a nonconductive extinguishing agent such as Halon, dry chemical, or carbon dioxide. The safest extinguishment procedure is to first deenergize high voltage circuits and then to treat the fire as Class A or Class B fire depending upon the fuel involved.

Class D Fires

Class D fires involve combustible metals such as aluminum, magnesium, titanium, zirconium, sodium, and potassium. These materials are particularly hazardous in their powdered form. Proper airborne concentrations of metal dusts can cause powerful explosions given a suitable ignition source. The extremely high temperature of some burning metals makes water and other common extinguishing agents ineffective. There is no single 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. These agents are used to cover up the burning material and smother the fire.