CHAPTER 3

CHARACTERISTICS, CHEMISTRY, AND PHYSICS OF FIRE

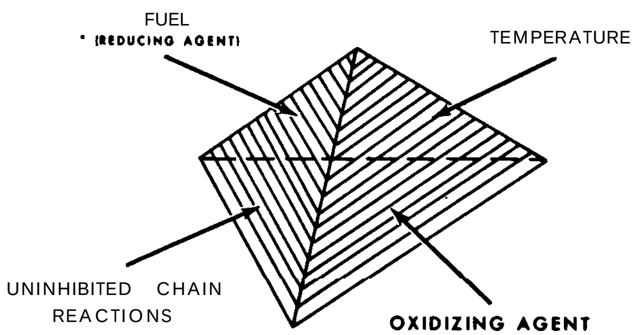
3-1. Introduction

The number of fires caused by uncontrollable natural reactions is minimal in relation to those caused by the carelessness of man and his apathy in acquiring and using the information available on the characteristics, chemistry, and physics of fire. The knowledge of the principles of fire also helps the firefighter in extinguishing those fires that he fails to prevent.

3-2. The Nature of Fire

Previously, the process of chemical oxidation and combustion and that of halting combustion was shown with the familiar fire triangle (fig. 3-1). This two-dimenional triangle aided in explaining the combustion process. Thus, when all the sides of the fire triangle were intact and in proper state and proportion, burning took place. When any one of the sides (factors) was removed, burning was stopped. Before the introduction of the modern knowledge on chemical fire extinguishment, there were only three methods of extinguishing a fire, alined closely with each leg of the fire triangle. Cooling the fire removed the "heat leg"; excluding the oxygen from the fire removed the "oxygen leg"; and separating the fuel from the fire removed the "fuel leg". When chemical extinguishing agents were introduced and successfully used for fire extinguishment, additional information was required to explain the action of the chemical. This new information added another dimension to the diagram. The new diagram is known as the *tetrahedron of fire* (fig. 3-2). It has four triangular surfaces that make up a solid pyramidal form which has depth. Each of the triangular surfaces shows an element necessary to continue combustion. It shows that combustion (fire) is a continuous chemical reaction which changes constantly because of external conditions. Chemical extinguishment agents (potassium and sodium bicarbonate type dry chemicals or vaporizing liquid agents) inhibit the chain reaction of a fire by interfering with or cutting off the conditions necessary for combustion. Thus, all the three parts of the fire triangle may be present, but the chain reactions are prevented (inhibited) by a chemical extinguishment agent (or agents) which puts out the flame.

Figure 3-1. The fire triangle.



(Courtesy Walter M. Haessler, The
Figure 3-2. The tetrahedron of fire.

3-3. Basic Definitions and Properties of Fire

a. *Ignition Temperature.* The ignition temperature of a substance (solid, liquid, or gaseous) is the minimum temperature to which the substance exposed to air must be heated in order to initiate or cause self-sustained combustion. Ignition temperatures of the same substance vary according to the percentage composition of the vapor or gas-air mixture, shape, and size, of space where the ignition occurs, rate and duration of heat, kind and temperature of the ignition source, oxygen concentration, and other effects of materials that may be present. Therefore, given ignition temperatures should be looked upon as approximations.

b. Vapors. Vapors in the process of combustion are the gaseous substance given off by the material that is burning. In burning wood, heat causes the resinous substance in the wood to vaporize. The vapors combine with the oxygen of the air, and the flame from the kindling ignites the combustible vapor-oxygen gas. The heat from the fire heats the wood, which in turn liberates more vapors and thus sustains the fire until the wood is consumed.

c. Vapor Density. Vapor density is the term used to explain the weight of vapors. When speaking of the weight of these vapors, they are usually compared to air, which has a vapor density of 1. Therefore, if a substance has a vapor density of 1.5, it is 1½ times as heavy as air. If it has a vapor density of .5, it weighs only ½ as much as air. Figure 3-3 shows how the density of gasoline vapors can be demonstrated with a small trough, a candle, and a gasoline-soaked rag. A lighted candle (the ignition source) is placed at the lower end of the trough, and the gasoline-soaked rag placed at the upper end. Gasoline vapors are heavier than air and will flow down through the trough to the lighted candle, where they will ignite, and flash back to the rag at the top of the trough, This illustration shows the need for the "No smoking within 100 feet" signs displayed around gasoline storage areas.

d. Flammable or Explosive Limits. In the case of gases or vapors which form flammable mixtures with air (or oxygen), there is a minimum concentration of vapor in air below which flame does not occur when the vapor-air mixture comes in contact with a source of ignition; thus, it is too "lean" to ignite. Most flammable vapors and gases also have a maximum proportion of vapor or gas in air above which flame does not occur (too "rich" to ignite). A few materials, like ethylene oxide, decompose and burn with no oxygen present.

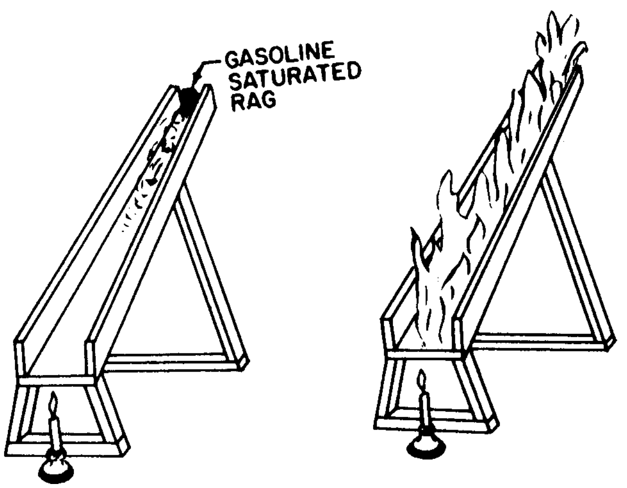


Figure 3-3 Vapor density.

e. *Flammable (Explosive) Range.* The range of combustible vapor or gas-air mixtures between the upper and lower flammable limits is known as the "flammable range" (or "explosive range"). For example, the lower limit of flammability of acrylonitrile at ordinary ambient temperatures is approximately 3 percent vapor in air by volume. The upper limit of flammability is about 17 percent. Thus, all concentrations of acrylonitrile vapor in air falling between 3 and 1'7 percent are in the flammable or explosive range.

f. Flash Point and Fire Point. The flash point of a liquid is the lowest temperature of the liquid at which it gives off vapor sufficient to cause a flammable mixture with the air near the surface of the liquid or within the vessel used. Some solids, such as camphor and naphthalene, change from solid to a vapor at ordinary room temperature and therefore have flash points while still in the solid state. The fire point (the lowest temperature at which a substance continues to burn in air) is usually a few degrees above the flash point.

34. Principles of Fire

a. Ignition and Combustion. Fire or combustion may be described as rapid oxidation with the action (evolution) of heat and light. Oxidation of a material takes place continuously as long as it is exposed to an oxidizing agent, which may be air. At ambient temperatures, oxidation is usually so slow that the process is not noticeable to human senses. Examples of such slow oxidation are the rusting of iron and the yellowing of paper. As temperatures rise above the ambient, the rate of oxidation becomes more rapid and generates heat. When the ignition temperature is reached, flame appears, thus ignition has taken place. Combustion is the continuous burning that follows after ignition.

b. Fire. Actual burning (fire) is a much more complicated chemical reaction than is commonly explained by the "fire triangle" (fig. 3-1) or the more recent "tetrahedron of fire" fig. (3-2). As the temperatures rise above the ambient, pyrolysis takes place. Pyrolysis is the chemical decomposition of matter through the action of heat. It proceeds through the following stages:

(1) Decomposition of combustible material slowly gives off gases, including water vapor. The combustible gases are not ignitible during the early stages of pyrolysis.

(2) Gas evolution continues with some of the gas becoming ignitible. As the temperature increases the gas evolution also increases.

(3) At the ignition temperature the evolved gases are too rich, at first, in carbon dioxide and water vapor to sustain flame very long. However, the heat of the flame starts a secondary pryolysis reaction process and flaming combustion occurs entirely in the gaseous distillate vapor phase. Gas evolution may be so fast that it blankets the fuel surface and excludes air. This prevents the char from burning, retards the penetration of heat, and delays the ignition temperatures in penetrating deeper into the combustible material. As temperatures increase, the char begins to glow, air flows in to support combustion, and the fuel itself burns as well as its decomposition gases. If the released heat is concentrated and sufficient to sustain oxidation, and more heat is generated than lost through conduction, convection, or radiation, a positive heat balance exists. If, however, most or all of the heat generated is lost, there is a negative heat balance and the fire goes out as a match flame in a wind. At the same time, a condition known as feedback may exist. Feedback is generated heat that prepares adjacent combustible material for burning by raising it to ignition temperatures. If the feedback is not adequate, the fire goes out. In addition to heat generation during pyrolysis, the concentration of the oxidizing agent is another factor that determines whether or not ignition and combustion can occur. There appears to be a minimal oxidizing agent concentration for almost all materials below which combustion will not take place. Exceptions to the latter are some combustible solids, such as cellulose nitrate, that contain oxygen in the constituent molecules. This oxygen can be released by heat even if there is no air supply. Thus, pyrolysis reaction may take place without the presence of air. An example is charcoal in coking ovens which continues to oxidize and produce heat with a minimal amount of air.

*c. **Summary of the Principles of Fire.*** The principles of fire may be summarized as follows:

(1) There must be an oxidizing agent, combustible material, and a source of ignition for combustion to take place.

(2) Combustible material must be heated to its ignition temperature before it will burn.

(3) Combustion will continue until-

(a) The combustible material is removed or consumed.

(b) The oxidation agent concentration is lowered below that essential.

(c) The combustible material is cooled below its ignition temperature.

3-5. Heat Energy Sources

Since fire prevention and extinguishment are dependent on the control of heat energy, it is essential that firefighters know the common ways in which heat can be produced. The following discusses briefly the heat energy sources.

a. ***Chemical Heat Energy.*** This source of heat is the result of oxidation, and is of primary concern to fire protection engineers. The following are the different ways heat is produced thorugh the chemical process:

(1) ***Combustion.*** Heat of combustion is the quantity of heat released during the oxidation of a substance (fuel). This is the heat normally utilized by industry and for domestic use, and is measured in terms of British thermal units (BTU). The heat intensity of oxidation (complete or partial) of almost all compounds of carbon, hydrogen, and oxygen depends on the oxygen consumed. Thus, the heat produced by combustion is limited by the air supply.

(2) ***Spontaneous heat.*** Practically all organic substances which are capable of combining with oxygen will oxidize at some critical temperature with evolution of heat if exposed to the atmosphere. The rate of oxidation at normal temperatures is usually slow and the heat which is released is transferred to its surroundings. This keeps the temperature down and prevents ignition. This is not true of all combustible materials. The oxidation of some material generates heat more rapidly than it can dissipate, which results in spontaneous combustion. Enough air must be available to permit oxidation, yet not so much that the heat is carried away by convection as rapidly as it is formed. Oily rags might heat spontaneously in a wastebasket, but would not do so if these rags were hung on a line where air movement is sufficient to remove the heat. Again, a tightly packed bale of rags is not as likely to

cause spontaneous combustion as a loose bale. Because of the many possible combinations of air supply and insulation, no positive prediction can be made as to when material will heat spontaneously. Fire safety engineers should not only be aware of the possibility of spontaneous combustion and fires caused by oily rags, paper, coal piles, and foam rubber, but also be aware that oxidation of agricultural products can produce fires by spontaneous combustion. Grains in large piles or bins and piles of grass (hay) will oxidize to a point of ignition when saturated with a certain amount of moisture. Fires from this source may not be as prevalent on farms as in urban areas where the agricultural products are stored.

(3) ***Decomposition.*** Heat of decomposition is the heat released by the decomposition of compounds such as cellulose nitrate and many commercial and military explosives.

(4) ***Solution.*** Heat of solution is the heat produced when a substance is dissolved in a liquid. Most materials release heat when dissolved. Chemicals, such as concentrated sulfuric acid, produce enough heat when dissolved to be dangerous. The chemicals that react in water and release heat are not combustible, but liberate sufficient heat to ignite combustible material nearby.

b. ***Electrical Heat Energy.*** Electrical heat energy produces heat when an electric current flows through a conductor or when a spark jumps an airgap.

(1) ***Resistance.*** An electric wire or other conductor of electricity offers resistance and thus produces heat. The heat from these causes the oxidation and ignition of nearby combustibles and fire results. Fires of this type are quite common in all areas using electricity as a source of heat and energy.

(2) ***Induction.*** When an alternating current is passed through a wire and induces a current in another wire parallel to it, a form of heat called induction heating is produced if the current-carrying capacity of the second wire is inadequate. Inducted heat is produced by the resistance to the flow of electricity and by molecular friction. An example of the latter is the heat produced in a microwave oven.

(3) ***Dielectric.*** Dielectric heating is that produced when the insulating materials are imperfect and, therefore, allow a leakage of current. This heats the insulating material which may eventually ignite the nearby combustible material.

(4) ***Arcing.*** Heat from arcing occurs when an electric circuit which carries a current is interrupted and the current leaps the gap. The temperatures of arcs are very high and may ignite combustible and flammable material in the area.

(5) ***Static.*** Static electricity (friction electricity) is an electrical charge that accumulates on the surfaces of two materials that have been brought together and then separated. One surface becomes charged positively and the other negatively. If the two objects are not bonded or grounded, they may accumulate sufficient electricity to discharge a spark. 'The spark produces little heat, but it will ignite flammable vapors, gas, and clouds of combustible dust.

(6) ***Lightning.*** Lightning is the discharge of electrical charge on one cloud to an opposite charge on another cloud or on the ground. Lightning develops very high temperatures in any material of high resistance which may be in its path.

c. ***Mechanical Heat Energy.*** Mechanical heat energy, especially friction heat, is responsible for a significant number of fires annually. A few are caused by heat energy released by compression.

(1) ***Friction heat.*** Friction heat is the result of resistance to motion when two solids are rubbed together. The intensity of heat depends upon the amount of mechanical energy transformed to heat and on the rate at which the heat is generated.

(2) ***Heat of compression.*** This is the heat released when a gas is compressed. A useful purpose of ignition by compression is the diesel engine which needs no spark plugs for ignition. A fire may be caused by directing a jet of compressed air into a pipe. The air is converted to heat which ignites an oil film on the inside surface of the pipe fittings.

d. Nuclear Heat Energy. Nuclear heat energy is released from the nucleus of the atom. The nucleus is held together by a great force which can be released by bombardment of the nucleus with particles of energy. The bombardment (fission and fusion) releases the energy in the form of tremendous heat and pressure, and also nuclear radiations. In nuclear fission, energy is released by splitting the nucleus. In nuclear fusion, energy is released by the fusion of two nuclei. Nuclear weapons firefighting procedures are discussed in chapter 6.

3-6. Classes of Fire

Fires are divided into four main classes: class A, class B, class C, and class D fires. These classes are based on the combustion characteristics of the ignited material. In most cases, installation fires are combinations of at least two and sometimes all of these classes.

a. *Class A Fires.* Class A fires are fires in ordinary combustible materials such as bedding, mattresses, dunnage, books, cloth, canvas, wood, and paper. Class A fires must be dealt with by cooling the fire below its ignition temperature. All class A fires leave embers which are likely to rekindle if air comes in contact with them. Therefore, a class A fire must not be considered extinguished until the entire mass has been cooled thoroughly. Smothering is not effective for class A fires because it does not lower the temperature of the burning embers below the surface of the fire.

b. Class B Fires. Class B fires are those which occur in flammable substances such as gasoline, jet fuels, kerosene, oils, paint, turpentine, grease, tar, and other combustible substances which do not leave embers or ashes. Class B fires can be extingusihed by providing a barrier between the burning substance and the air or oxygen necessary for its combustion. Chemical foam and mechanical foam produce such barriers, and are known as "permanent" smothering agents. Carbon dioxide is also a smothering agent, but its effect is only temporary and the application must be renewed if there is any danger of reignition.

c. Class C Fires. Class C fires are fires in live electrical materials. They present an extra hazard to the firefighter, because of the danger of electrical shock. A nonconducting extinguishing agent is essential for fighting class C fires. An additional consideration in fighting class C fires is the fact that it may be quite important to avoid damaging the electrical equipment in the process of extinguishing the fire. Electrical instruments and contacts will be contaminated by any extinguishing agents except gases, The first step in extinguishing a class C fire is to secure the source of power to the circuit or equipment on fire. The preferred agent in fighting class C fires is carbon dioxide or monobromotrifluoromethane, since they give protection against electrical shock and are not likely to injure the equipment. Water fog, although not preferred, may be used; under ordinary conditions it does not transmit electricity to the firefighter (as would a solid stream of water), but it may damage the energized electrical equipment.

d. Class D Fires. Class D fires are those in combustible metals, such as titanium, zirconium, sodium, potassium, etc. The greatest hazard exists when these metals are in the molten state or in finely divided forms of dust, trimmings, or shavings. Ordinary extinguishing agents are ineffective on these metal fires, and they are best controlled by covering with special dry powdered or granular materials which exclude oxygen and which will not react or combine adversely with metal.