

**FIRE CHEMISTRY**  
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## DEFINITIONS

**Ambient:** The surrounding atmospheric conditions of temperature and pressure.

**Atom:** The basic particle of chemical composition.

**Atomic Number:** The number of protons in an atom.

**British Thermal Unit:** The amount of heat required to raise the temperature of one pound of water one degree Fahrenheit.

**Calorie:** The amount of heat required to raise the temperature of one gram of water one degree centigrade.

**Catalyst:** A substance which, when present in a chemical reaction, affects the rate of the reaction, but is itself not permanently changed.

**Chemical Heat Energy:** Heat energy released by a chemical reaction.

**Combustion:** Rapid oxidation at or above ignition temperature, accompanied by heat and light.

**Compound:** A substance composed of more than one element.

**Contaminant:** Foreign material not normally found in a substance.

**Electrical Heat Energy:** Heat Energy produced by the movement of electrons within a substance.

**Electron:** A subatomic particle which has practically no mass, but carries a negative electrical charge.

**Element:** A substance composed of only one type of atom.

**Endothermic Reaction:** A chemical reaction in which the substances formed have more energy than the reacting materials (Energy Absorbed).

**Exothermic Reaction:** A chemical reaction in which the substances formed have less energy than the reacting materials (Energy Released).

**Fire Point:** The minimum temperature to which a substance must be heated in order to form sufficient flammable vapors, which will ignite and continue to burn when an outside ignition source is applied.

**Flammable vs. Combustible Liquids:** The flash point of a flammable liquid is below 100°F. The flash point of a combustible liquid is above 100°F.

**Flammable Limit vs. Flammable Range:** The flammable limits are the lowest and highest percentage of a vapor in air that will form a combustible mixture at a specific temperature and pressure (usually 70°F and 14.7 psi). The flammable range is the spread between the upper and lower flammable limits.

**Flash Point:** The minimum temperature to which a substance must be heated in order to form sufficient flammable vapors which will ignite when an outside ignition source is applied, but not continue to burn after heat source is removed.

**Fuel (Reducing) Agent:** A substance capable of producing flammable vapors.

**Heterogeneous:** A mixture in which the components are not intimately and uniformly mixed.

**Homogenous:** A mixture in which the components are intimately and uniformly mixed.

**Ignition Temperature:** The minimum temperature to which a substance must be heated in order to cause self-sustained combustion, independent of any outside ignition source.

**Inhibitors:** A substance which may be added to an unstable material to prevent a vigorous reaction.

**Latent Heat:** The heat liberated or absorbed by a substance in passing between liquid and gaseous phases (latent heat of vaporization), or between solid and liquid phases (latent heat of fusion).

**Mechanical Heat Energy:** Heat energy caused by friction, compression, concussion, or other mechanical means.

**Molecule:** Combined group of atoms.

**Molecular Weight:** The sum of the weight of the atoms in the molecule.

**Neutron:** A subatomic particle in the nucleus which has no electrical charge, but does have appreciable mass.

**Nuclear Heat Energy:** Heat energy released from the nucleus of an atom.

**Nucleus:** The core of the atom which is composed of protons and neutrons.

**Oxidizing Agent:** A substance capable of providing electrons for an oxidation reaction.

**Proton:** A subatomic particle which has a positive electrical charge and appreciable mass.

**Pyrolysis:** Chemical decomposition caused by heat.

**Specific Gravity:** The ratio of the weight of a solid or a liquid substance to the weight of an equal volume of water.

**Specific Heat:** The number of B.T.U.s required to raise one pound of a substance one degree Fahrenheit. (Also measured in calories.)

**Vapor Density:** The ratio of the weight of a gaseous substance to the weight of an equal volume of air at standard temperature and pressure.

**Vapor Pressure:** The pressure exerted by vapors from a substance in a closed container at a point of equilibrium.

## **MATTER AND ENERGY**

Chemistry for firemen can deal with but two things; matter and energy. Matter is that which has weight and occupies space. In other words, it is all the material in the world; the air we breathe, buildings we live in, water we drink, etc.

Matter or materials are divided into three classes according to their condition and state: liquid, solid and gas. For example, water as we drink it is a liquid. By reducing its temperature, it becomes a solid and, on the other hand, if we raise its temperature high enough the liquid becomes steam and passes off into the air in a state of gas.

All the changes or phenomenon exhibited by matter may be divided into two categories; physical phenomenon and chemical phenomenon. Physical phenomenon are those in which the composition is not changed or altered. Examples include; the fall of a rock, the vibration of a tuning fork, and all phenomenon of motion. Chemical phenomenon are those in which a change in composition takes place. Examples include; the rusting of iron, the souring of milk, and the burning of a candle.

No destruction of matter is possible. When a substance disappears as in the boiling of water or the burning of a candle, this is because it is changed into an invisible form (gas) and not because it has been destroyed. In its new form, it still has the properties of weight and "impenetrability" which prove it to be matter. Matter is often referred to as a substance, and is identified by physical properties such as density, conductivity, solubility, melting point, boiling point, hardness, color, etc.

The sciences of both physics and chemistry lead to the conclusion that all bodies are made up of minute particles which are never in actual contact with each other and are always in motion. Atoms are the basic unit of all elements and are composed of elementary particles called protons, neutrons, and electrons. Protons and neutrons form the nucleus of the atom, which accounts for the majority of the atom's mass. The number of protons contained in the atom is also known as the atomic number. The number of protons (which carry a positive electrical charge), and electrons (which carry a negative electrical charge) will be equal; (Neutrons carry no electrical charge.) Electrons are in motion around the nucleus in shells or orbits. The number of electrons contained in the outermost shell or orbit will determine the way an atom will react with other atoms.

Atoms will seek to react with each other to form stable molecules. A molecule is the smallest particle of a substance that can exist in a free state. In any given substance, all the constituent particles are alike and of the same composition as the substance. These particles are called molecules. A physical change can go no further than the molecule, and hence, does not affect the nature of the substance. A chemical change is an alteration of the substance, and hence, must consist of the dissolution of old molecules and the formation of new ones.

In solids, the molecules are close together and the mutual attraction is great. In liquids, the molecules are farther apart and the mutual attraction is, therefore, less and they have greater freedom of motion. In gases, the molecules are so far apart that the attraction between them is negligible and they scatter about freely.

Energy is the ability or capacity to do work. Matter in motion possesses energy and is shown by the fact that a strong stream of water from a fire hose played against a burning building frequently breaks off parts of wooden buildings and that is work. There are many kinds of energy such as electrical, chemical, heat, nuclear, and mechanical.

## **HEAT**

Heat is a condition of "motion in matter" caused by the rapid movement of its molecules. When we heat a body, the molecules that are already in motion are speeded up; the greater the speed of the molecules, the higher the temperature of the body. Rub two pieces of wood or two pieces of iron together, and they become heated. Heat in this instance being produced by the vibration of molecules set in motion by friction. Pound a piece of iron or other metal with a hammer in one spot. The continuous pounding has set up molecular motion causing the iron or metal to heat, this time by percussion. An air compressor in a service station is started. In a short while, the cylinder walls of the compressor give off heat due to a greater molecular motion by compression. Thus, heat may be generated by work done in overcoming friction, in percussion, and in compression.

Heat is also produced by many materials when they undergo chemical changes. In this class of materials are fuels such as coal, oil, coke, natural gas, kerosene, and gasoline. When these fuels unite with oxygen, heat is produced by the increased molecular motion due to oxidation caused by the union of the fuel and oxygen.

A load is applied on an electric circuit. The current passing through the wire must overcome resistance which sets the molecules in rapid motion and causes heat. If the resistance of the wire is great enough, it will first become red, then white, and, if the load applied on the circuit is great enough, the material of the wire will liquefy. Heat is produced by electrical energy passing through material.

From the foregoing, it can be seen that anything that sets the molecules of a material into motion produces heat in the material. There are four general categories of heat energy and they include: Chemical heat energy, Electrical heat energy, Mechanical heat energy, and Nuclear heat energy.

### **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 discharge of thousands of volts from either earth to cloud, or from cloud to earth.

### **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.

## **TEMPERATURE**

Heat is a form of energy and temperature is the measure of that energy. When a body feels hot to the touch we are accustomed to say that it has a "high temperature"; when it feels cold, we say it has a "low temperature". Thus, the word temperature is used to denote the condition of hotness or coldness of the body whose state is being described.

Different materials have different abilities for absorbing and giving up heat. Take a piece of iron and wood that has been heated to the same temperature; the iron will feel very warm to the touch while the wood will not. The heat in the piece of iron will transfer to the hand until the temperature of the iron and the hand are the same. Heat always flows from a body of higher temperature to one of lower temperature.

Thermometers are used to measure temperature. The two most common temperature scales are centigrade and Fahrenheit. On the centigrade scale, the boiling point of water is 100 degrees and the freezing point of water is 0 degrees. On the Fahrenheit scale, the boiling point of water is 212 degrees and the freezing point of water is 32 degrees. The following formulas can be used to convert centigrade to Fahrenheit and vice versa:

$$C^{\circ} = (F^{\circ} - 32) \times 5/9$$

$$F^{\circ} = (C^{\circ} \times 9/5) + 32$$

## **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 ore 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.

### **FIRE SPREAD**

Fire spread can be accounted for by radiation, conduction and convection and in the manners listed below:

1. From floor to floor of the same building through:
  - a. Unprotected floor openings, such as those for elevators, stairs, dumb waiters, beltways, chutes, pipes and through light wells
  - b. Fires burning through floors
  - c. Fires burning through protection provided for vertical openings
  - d. External windows or other wall openings
  - e. Smoke passing into upper floors and smoke explosions resulting from smoke accumulation
2. From building to building (adjoining) through:
  - a. Unprotected wall openings
  - b. Failure of fire doors or other protective coverings for wall openings
  - c. Lack of parapets
  - d. Flashing over or around parapets and igniting combustible walls, roofs, roof coverings, monitors or penthouses
  - e. Passing around the ends of fire walls
  - f. Exposure of openings in walls at angles to each other
  - g. Heat passing through walls, especially at points where timbers are connected to them

- h. Smoke passing through wall openings and smoke explosions resulting from smoke accumulation
  - i. Failure of walls through explosion, upsetting by fall of imbedded structural members or other causes
3. From building to building (not adjoining) through:
- a. Flammable roofings
  - b. Combustible cornices
  - c. Overhanging roofs
  - d. Unprotected wall openings
  - e. Permanent or temporary openings through which sparks or brands can pass
  - f. Combustible exterior walls
  - g. Combustible monitors and penthouses
  - h. Combustible additions, passages or other structures

Radiated heat from fires in individual bodies, under still air conditions, has ignited combustible building trim as much as five hundred feet distant from the fire. In conflagrations the "hot blast" (invisible heat) traveling ahead of the fire may ignite combustible material as far away as several thousand feet.

## **EXPANSION AND CONTRACTION DUE TO HEAT**

Heat applied to any material causes a more violent vibration of the molecules of that material; each molecule requires a little more space for its vibrations. The size or volume of the material is increased in proportion to the amount of heat applied, but there is no increase of weight. When heat is removed from a material and allowed to cool by natural or other causes, the vibration of the molecules is slowed down and the volume of the material decreases.

A useful application of expansion is in thermostats and fire detecting devices, while the expansion of steel girders at a fire is an example of a manner in which it proves damaging. Take a small strip of steel and rivet to it a small strip of zinc. Place this bar over a flame with the steel side next to the flame and notice the action of the bar. This is an example of the method used in thermostats controlling heating systems. If a pipe line was laid across a field in the spring of the year or when it was cool, by the middle of summer it would look like the trail of a snake from the expansion of the metal due to the heat absorbed from the sun's rays and from the temperature of the water. Provision must therefore be made to take care of this expansion and contraction by the insertion of expansion joints at certain points in the pipe line. If this were not done the line would break. Solids expand in every direction when heated, but all solids do not expand or contract the same amount when heated or cooled to the same extent.

There are three kinds of expansion a body may undergo; linear expansion, superficial expansion, and cubical expansion. Linear expansion refers to an increase in length, superficial expansion refers to an increase in surface area, and cubical expansion refers to an increase in volume.

A steel beam in a building is heated throughout to a uniform temperature so that all faces have expanded the same amount and the beam is still straight. A stream of water is applied to one face so that this face is cooled. Immediately upon being cooled it contracts and has a tendency of being shorter than the heated side. This will apply to any metal beam as well as concrete. This phenomena is even noticeable on building fronts that are heated and then suddenly cooled by a fire stream. The contraction may hardly be perceptible, while on the other hand it may be so great as to cause the walls to collapse.

Liquids expand more rapidly than solids, but not so rapidly as gases. All the fluids expand when heated, some more than others. Liquids being practically incompressible when heated in closed vessels will result in bulging and ruptures unless provision is made to take care of this enormous expansion (see explosions).

### **Melting Point**

Melting point is the temperature at which a solid is changed to a liquid. Heat diminishes the cohesion of the molecules of a substance. The melting point is of great importance in regard to fire hazards since the commencement of melting is accompanied by:

Sublimates - from solid to gas without liquid (i.e. dry ice).

Accumulation of heat in the melting substance.

The substance is brought nearer to its flashing and ignition point.

Its affinity for oxygen is increased.

Heat may generate flammable explosive vapors in melted bodies as fats, oils, resins, lacquers and varnishes.

Molten substances froth up readily when further heated and then easily take fire.

Molten substances of a metallic nature readily form with water an explosive gas (oxyhydrogen gas) and this increases the chance of explosion.

The molten state considerably heightens the fire hazard and may even, in certain materials, heighten explosive potential.

### **Boiling Point**

The boiling point is the temperature at which a substance changes from a liquid to a gas. Because the molecules of a liquid are always in motion, some of these molecules continually escape into the atmosphere. In a closed container, the escaping molecules and those molecules reentering the liquid reach a point of equilibrium which is called vapor pressure. As a liquid is heated, the vapor pressure increases. When the vapor pressure equals atmospheric pressure, the liquid is said to boil. The boiling of liquids increases the fire hazard, the degree of danger becoming greater in proportion as the boiling point is lower. Should this occur with varnishes, lacquers, resins, mineral oils, tar dissolved fats or fatty oils, the danger of fire will be great. Substances like ether, benzene, benzol, and carbon disulfide that boil and liberate vapor under a very small accumulation of heat are, as a rule, very flammable and may easily form explosive mixtures.

### **Specific Heat**

A substance will absorb heat as it changes from solid to liquid, or liquid to gas. Conversely, a substance will liberate heat as it goes from gas to liquid or liquid to solid. As a substance melts, a certain amount of heat is required above and beyond that necessary to raise the substance to its melting point. This amount of heat is called the latent heat of fusion. Also, the amount of heat required to convert a liquid to a gas once the boiling point has been reached is called the latent heat of vaporization. From a firefighting aspect, specific heat is the measure of the heat absorbing capacity of a substance. Water is taken to have a value of 1. One pound of water will absorb 970.3 B.T.U.s of heat if completely converted to steam (due to the latent heat of vaporization).

## **COMBUSTION**

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. Most fires involve a fuel that is chemically combined with the oxygen normally found in atmospheric air. Atmospheric air contains 21 percent oxygen, 78 percent nitrogen, and 1 percent of other gases. Substances such as chlorine gas and its compounds will also sustain combustion. Other substances, such as organic peroxides, are composed in such a way that they contain both fuel and oxidizer molecules within the compound allowing them to burn in the absence of oxygen.

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.

The initiation of combustion requires the conversion of fuel into the gaseous state by heating. Fuel may be found in any of three states of matter: solid, liquid, or gas. 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. Combustion starts as an endothermic reaction and proceeds to an exothermic reaction. The rate of this reaction doubles for every 18°F rise of temperature.

## **CHARACTERISTICS OF FIRE BEHAVIOR**

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 fire fighting 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.

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.

The solubility of a liquid fuel in water is an important factor. Hydrocarbon liquids as a rule will not mix with water (immiscible). Alcohols and polar solvents mix with water (miscible) 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 alcohols (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 with volatile liquids and with 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.

The second phase in initiating combustion is the mixture of the fuel vapor with an oxidizer (air). 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 70°F (21°C).

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

Fire burns in two basic modes--flaming and/or surface combustion. The flaming mode of combustion is represented by the fire tetrahedron (a four sided figure) with the four sides representing fuel, temperature, oxygen, and the uninhibited chemical chain reaction. The surface or smoldering mode of combustion is represented by the fire triangle with the three sides representing fuel, temperature, and oxygen.

The fuel segment of both theories is any solid, liquid, or gas that can combine with oxygen in the chemical reaction known as oxidation. Temperature is the measure of the molecular activity within a substance. A fuel with a sufficiently high temperature will ignite if an oxidizing agent is present. Combustion will continue as long as enough energy or heat is present. Under most conditions, the oxidizing agent will be the oxygen in air, but the term helps explain how some materials that release their own oxygen during combustion, such as sodium nitrate and potassium chlorate, which can burn in an oxygen-free atmosphere. While scientists only partially understand what happens in a chemical chain reaction, they do know that heating produces vapors that contain substances that will combine with oxygen and burn.

A self-sustaining combustion reaction of solids and liquids depends on radiative feedback. This is radiant heat providing energy for continued vaporization. When sufficient heat is present to maintain or increase this feedback, the fire will remain constant or will grow depending on the heat produced. When heat is fed back to the fuel, this is known as a positive heat balance. If heat is dissipated faster than it is generated, a negative heat balance is created. A positive heat balance is required to maintain combustion.

## **PHASES OF A FIRE**

Fires may start at any time of the day or night if the hazard exists. If the fire happens when the area is occupied, the chances are that it will be discovered and controlled in the beginning phase. But if it occurs when the building is closed and deserted, the fire may go undetected until it has gained major proportions. The condition of a fire in a closed building is one of chief importance for ventilation.

When fire is confined in a building or room, a situation develops that requires carefully calculated and executed ventilation procedures if further damage is to be prevented and danger reduced. This type of fire can best be understood by an investigation of its three progressive stages.

A firefighter may be confronted by one or all of the following phases of fire at any time; therefore, a working knowledge of these phases is important for understanding of ventilation procedures.

### **Incipient Phase**

In the first phase, the oxygen content in the air has not been significantly reduced and the fire is producing water vapor ( $H_2O$ ), carbon dioxide ( $CO_2$ ), perhaps a small quantity of sulfur dioxide ( $SO_2$ ), carbon monoxide ( $CO$ ), 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  $1,000^{\circ}F$  ( $537^{\circ}C$ ), yet the temperature in the room at this stage may be only slightly increased.

### **Free-Burning Phase**

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 uppermost 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 superheated air can sear the lungs. At this point, the temperature in the upper regions can exceed  $1,300^{\circ}F$  ( $700^{\circ}C$ ). 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**

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 1,000<sup>o</sup> (537<sup>o</sup>C). 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.

### **Backdraft Or Smoke Explosion**

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.

With rising heat and high fuel concentrations, a backdraft can occur with explosive force when oxygen is introduced into the area.

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 rushes 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 (CO<sub>2</sub>), or carbon monoxide (CO), 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:

- . Smoke under pressure
- . Black smoke becoming dense gray yellow
- . Confinement and excessive heat with little or no visible flame
- . Smoke leaves the building in puffs or at intervals
- . Smoke-stained windows
- . Muffled sounds
- . 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.

### **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 the 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. When they reach this point, simultaneous ignition occurs and the area becomes fully involved in fire.

## **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, and smoke.

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 due to 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.

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.

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.

## **SPONTANEOUS IGNITION**

Spontaneous ignition is the proceeding without constraint by internal impulse, energy or natural law; to kindle or set on fire. Under this heading are generally classed all cases of quick or slow oxidation or combustion brought about by chemical, electrical, biological (bacterial) or physical processes (vibration, pressure, shock or friction) only, without the assistance of extraneous sources of heat (flame, hot or glowing bodies). If the heat generated in slow oxidation is not allowed to escape, it accumulates until it is sufficient to reach the ignition temperature of the substance and it bursts into flame. The substance appears to burn without having been "set on fire."

Slow oxidation cannot occur without the presence of oxygen (air). A large supply of oxygen will allow the heat from oxidation to be dissipated. Spontaneous heating occurs when sufficient oxygen is present for oxidation, but insufficient to dissipate the heat produced. Many instances of spontaneous ignition are preceded by spontaneous heating as a prelude; others occur suddenly and explosively, without this preliminary, so that they might be regarded as cases of spontaneous explosion. The latter, which one might term "acute" cases, are of a more dangerous general character than such as are preceded by gradual spontaneous heating and might on that account be classed as chronic.

Spontaneous heating or spontaneous ignition has been observed to occur with the following substances:

Coal, lignite, coke, briquettes, lampblack, carbonized peat;

Wood, sawdust, dye-woods, wood charcoal, cork dust, insulating materials, leather;

Paints, varnishes, resins, lacquers, oils, fats, lacquered substances, oilcloth;

Fire lighter, matches, gas-purifying materials, soda residues, slag heaps;

Metallic powders, drill turnings, burnt lime, carbides, carriers of oxygen;

Nitric acid, nitro compounds and sulphur compounds;

Artificial manures, stall manure, fish guano, superphosphates;

Hay, clover, grass, malt, malt clums, cereal grains, bran, hops, tobacco, seeds, concentrated fodder and mixtures of same;

Wool, cotton, silk, flax, hemp, jute, tow, rope;

Oil rags, greasy cloth, polishing rags, polishing discs (buffing wheels), articles of clothing in a greasy and dusty condition.

## **EXPLOSIONS AND EXPLOSIVE SUBSTANCES**

"Explosive" is applied, in a chemical sense, to such solid or liquid substances as possess the faculty, under certain circumstances, of undergoing instantaneous decomposition, extending throughout their entire mass and accompanied by a considerable disengagement of heat, the substances at the same time being partly or wholly converted into gaseous decomposition products. Solid and liquid explosives represent gases or vapors condensed into the smallest possible space or area in the liquid or solid form. The substances used in the arts for blasting are termed "explosives" or "blasting materials." The phenomenon of explosion is a sudden and enormous expansion of gases and vapors liberated from a previous condition of chemical combination.

Certain gases or vapors are also termed explosive, but this is a quality they mostly do not possess so long as they are pure, unmixed and under ordinary pressure. They only acquire it on being mixed with air, other gases, vapors, floating particles of solid dust, in certain proportions by volume or when they are liquefied, solidified or in any way exposed to high pressure, in which latter event they may, even in an unmixed condition give rise to violent explosions (gas or dust explosions).

Little is known of the actual character of the solid and liquid explosive substances at the moment of explosion - almost every one of them behave differently and require a different inciting cause: One needs to be struck, rubbed or subjected to percussion; another has to be heated, a third brought into contact with a flame or spark; another requires to be compressed or packed; some must be in a dry state, others damp and others again frozen before they can be brought to explode. Some will not go off unless in an impure condition or mixed with other perhaps entirely harmless substances.

### **B.L.E.V.E.**

A dangerous condition (boiling liquid, expanding vapor explosion, or bleve) can happen when a liquefied gas container is heated. Gases are liquified by compression at various pressures. If these pressurized containers are heated, the liquid in the tank will boil and the internal pressure of the tank will increase. A pressure relief valve will attempt to relieve this pressure. If this process continues, the pressure relief valve may not be able to vent the excess pressure and an explosion can occur. Because the gases are already under pressure, the potential for explosion is great. If flame impinges on the vapor portion of the tank, the container itself will lose integrity and fail.

A boiler is said to have "exploded" (or bleved) when the walls of the vessel have suffered disruption to such an extent that a sudden equalization of pressure between the inside and outside of the vessel occurs. Strictly speaking, such an occurrence should not be called an explosion. It should be noted that any liquid in a closed container can B.L.E.V.E.

## **DUST EXPLOSIONS**

When a combustible solid is subdivided by a grinding or rubbing process, the minute particles produced may mix into the surrounding air to act chemically and physically as a heavy, flammable vapor or gas.

The burning rate and explosion tendency of combustible solid dusts is in direct proportion to the dust particle size. The finer the dust, the more the tendency it has to remain in suspension in air and mix evenly just as heavy vapor will mix in air. Just as is the case with combustible gas and vapor concentrations in air, combustible dusts have a lower explosion limit (LEL) below which concentration combustion or explosion cannot occur. Combustible dusts also have an upper explosion limit (UEL) above which combustion or rapid explosion is unlikely to occur.

### **Requisite Conditions for Dust Explosions**

In order for a dust explosion to occur, four conditions must be satisfied simultaneously:

1. A combustible solid in a finely divided state must be dispersed in an oxidizing medium- usually oxygen in air.
2. The concentration of the dust in air must be within the explosible range.
3. An external source of ignition of sufficient energy and duration to initiate the explosive chain reaction for that dust must be present.
4. The chemical reaction must occur in a confined space.

The rapid chemical reaction, or flash fire, characteristic of explosions will occur if only the first three conditions are satisfied. However, the rapid buildup of excessive pressures, inherent in the working definition of dust explosions, will result only when the reaction occurs in an enclosed space.

Dust explosions will occur in the case of the following substances when mixed with the proper proportions of air if any source of ignition is present:

Carbon of almost every kind (except purified wood charcoal), alfalfa, aluminum, bark, bran, bronze, celluloid, chaff, charcoal, coal, cork, cotton, dextrine, drugs, feathers, flour, grain, lampblack, leather, magnesium, malt, naphthalene, paper pyroxylin plastics, resins, spice, starch, sugar, sulphur, tow, wood, wool, zinc.

Dust explosions that occur during fire fighting may be classified as follows:

1. Explosions caused by the full stream of water (high pressure) striking settled or static dust in various parts of the building. The water forces the dust cloud on the flames and an explosion results.
2. Explosions that occur when firemen attempt to remove dust or powdered products from bins or other enclosures. When in the form of a cloud, these materials readily ignite upon coming in contact with flame.
3. Explosions caused by the falling of floors or the dropping of the bottom of storage bins.
4. Explosions that result from the chemical reaction between water and dust.

## **FIRE EXTINGUISHMENT**

The extinguishment of fire is based on an interruption of one or more of the essential elements in the combustion process. Concerning 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 By 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. Looking at fuel types and vapor production, we find that solid fuels and liquid fuels with high flash points can be extinguished by cooling. Low flash point 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 of water 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. The addition of a cooling capability is required if extinguishment of smoldering materials is desired.

### **Classification Of Fires And Extinguishment Methods**

#### **Class A Fires**

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, temperature reduction, and breaking the chemical chain reaction.

#### **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 E Fires**

Fires involving radioactive material.