Technical Discussion

Flashpoints, Flammables, Combustibles, LEL, and UEL, and Fires

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Fuel, Oxidizer, and Ignition Source

Three ingredients must be present to sustain a fire. There must be a fuel present (something that can burn), an oxidizer, and an ignition source. The oxygen that is in the air can be the oxidizer. Certain other chemicals such as ammonium nitrate, potassium permanganate, and potassium perchlorate can also serve as the oxidizer. The ignition source might be a nearby fire or sparks generated by friction or from static electricity.

For example, consider a pool of gasoline spilled on the ground. The gasoline evaporates forming vapor above the gasoline pool. The warmer the temperature, the faster the gasoline evaporates. The vapor given off forms an ignitable mixture with the air. An ignition source is necessary for a fire to occur.

What is a Flashpoint?

The flashpoint is the minimum temperature of a liquid at which sufficient vapor is given off to form an ignitable mixture with air.

For example, heptane, which is a major component of gasoline, has a flash point of 25°F and a boiling point of 209°F. It is a liquid at ordinary temperatures. At temperatures of 25°F and higher, enough vapors are given off from heptane that the vapors can ignite in air. If the temperature is less than 25°F, not enough vapors are given off for heptane to ignite in air; the liquid would have to be heated up (for example, heat from a nearby fire) for the vapor to ignite. It is the vapor given off of the evaporating liquid which burns, not the liquid itself. Incidentally, gasoline contains components besides heptane, some of which have much lower flashpoints than heptane (otherwise the fuel would not ignite in vehicles on a very cold day).

Note that the flashpoint refers to mixtures of fuel in air, not mixtures that have been enriched with oxygen or purged with an inert gas such as nitrogen.

Can gases or solids have flashpoints? By definition, a flash point is associated with liquids which give off vapors. A fuel which is a gas at room temperature might be a liquid at a very low temperature. That liquid can have a flash point. Similarly, the solid if heated can melt and the liquid formed can have a flash point. Some solids can also give off vapors which burn. Another thing that can happen is that some chemicals will decompose when heated, and the decomposition vapors can form an ignitable mixture with air.

For example, butane is a colorless gas at room temperature. It’s boiling point is 31°F. At temperatures below 31°F, butane is a liquid but that liquid still has a vapor pressure. The flash point of butane is −76°F. Another example is naphthalene which is a solid at room temperature. The melting point and the flash point of naphthalene is about 174°F. Mercury thiocyanate is a solid which decomposes on heating and has a flash point of about 250°F.

Scientists determine flashpoints by very specific test methods. More than one method is available. Flashpoints can also be calculated from other physical property data. If the material is a liquid at room temperature and does not decompose on heating a precise temperature is usually obtained, and usually there is not much disagreement between scientists. If the material decomposes on heating, there can be much disagreement. AristaTek Inc. has reviewed published flash points from a number of different sources and where there is disagreement has listed a more conservative temperature (i.e., a lower flash point) in the PEAC tool.

Flammable vs Combustible? Flammable vs Inflammable?

The words "flammable liquid" and "combustible liquid" have very specific meanings in the context of fire prevention and suppression, as defined by the Code of the National Fire Protection Association, Washington D.C. A flammable liquid has a flash point of 100°F or less; if the flashpoint is above 100°F it is a combustible liquid.

This definition is different from ordinary common speech. In ordinary speech, the words "combustible" and "inflammable" are used to mean a material that can burn or support combustion. Some people are thrown off by the prefix "in" ("inflammable") and think that "inflammable" means "not flammable" which is incorrect.

Obviously, solids and gases can also burn. The material does not have to be a liquid. Sometimes the designation "flammable gas" is used for a chemical which is stored as a gas and has a flash point less than 100°F.

National Fire Protection Association Classifications for Flammable and Combustible Liquids

The NFPA divides flammable and combustible liquids into classes based on flashpoint and boiling point, as shown in table 1

Table 1: NFPA Classifications

Class	Flashpoint and Boiling Point
I A Flammable Liquid	Flashpoint 73°F or less and boiling point 100°F or less
I B Flammable Liquid	Flashpoint 73°F or less and boiling point over 100°F
I C Flammable Liquid	Flashpoint over 73°F but 100°F or less
II Combustible Liquid	Flashpoint between 100°F and 140°F
III A Combustible Liquid	Flashpoint between 140°F and 200°F
III B Combustible Liquid	Flashpoint above 200°F

Note that the boiling point is specified only in the I A and I B classifications.

The I A Flammable Liquid is the most dangerous of all flammable and combustible liquids.

Why choose 73°F and 100°F as the demarcation point? The NFPA considers 73°F as normal room temperature and 100°F as the upper limit of normal outdoor ambient temperature in all but the hottest climates. Temperatures inside closed vehicles or buildings or containers left out in the sun can be much greater than 100°F even though the ambient temperature is less than 100°F.

LEL and UEL

LEL means "lower explosive limit" and UEL means "upper explosive limit". The number is expressed in percent, and means the volume percent of vapor (or gas) in air. For example, pentane has a LEL of 1.50% and a UEL of 7.8%. Its flash point is −57°F. It has a boiling point of 97°F. The NFPA classifies pentane as a Class I A Flammable Liquid. If the volume percent of pentane in air is less than 1.5%, the mixture is considered too lean to ignite. If the volume percent of pentane in air is greater than 7.8%, the mixture is too reach to ignite (not enough oxygen). The actual ignition will take place with explosive violence especially if the concentration of pentane in air is somewhat midway between the UEL and LEL numbers.

The 1.5% concentration of pentane in air is equivalent to 15,000 parts per million (ppm) concentration. The 7.8% conentration is equivalent to 78,000 ppm.

The LEL and UEL percentages are for mixtures of the pure gas or vapor in air. If the mixture is enriched with oxygen, the spread between these two numbers will be greater, perhaps much greater. In other words, the LEL will be less than 1.5% and the UEL will be greater than 7.8%. The same is true if other oxidizers are present.

Toxicity

Many flammable and combustible vapors and gases are also toxic by inhalation. However, some are not toxic. Examples of non-toxic gases are methane, ethane, and propylene. Does this mean that these gases are safe to breathe? No, because other factors must be considered. Fire protection codes recommend that concentrations not exceed 10% of LEL. The National Institute for Occupational Safety and Health (NIOSH) also sets Immediately Dangerous to Life and Health (IDLH) concentrations at 10% of LEL unless there are overriding toxicity considerations in which case the IDLH concentration would be lower. For methane, the LEL is 5%. Ten percent (10%) of LEL is 0.5%, or 5000 ppm. The LEL for ethane is 2.9%; 10% of LEL is 2900 ppm. The LEL for propylene is 2%; 10% of LEL is 2000 ppm. Another consideration is whether there is enough oxygen. Normal air contains 20.9% by volume. If the oxygen is partially replaced by other gases or vapors, the oxygen concentration will drop. This is important in confined space entry.

The U.S. Department of Energy (DOE) has established TEEL concentrations for many chemicals based on toxicity. TEEL is an acronym for Temporary Emergency Exposure Limit. TEEL numbers are developed by the Subcommittee on Consequence Assessment and Protective Actions (SCAPA), under the U.S. Department of Energy (DOE). When the numbers were originally published (up through revision #18 published in January 2001) the LEL was not considered. TEEL concentrations of 500,000 ppm were published for methane, ethane, propylene, and certain other flammable gases. These concentrations were well above the LEL. A 500,000 ppm concentration in air means that the oxygen concentration would be only 10.45%. AristaTek Inc. chose not to list TEEL concentrations in the PEAC tool if the TEEL concentration was greater than the LEL. In January 2002, the DOE came out with its 19th revision for TEELs. This revision considers the LEL, but sets the TEEL at the LEL instead of 10% of LEL. Thus, for example, the TEEL for ethane (TEEL-1, TEEL-2, and TEEL-3) is set at 30,000 ppm (the DOE used 3% and not 2.9% as the LEL). Emergency responders need to be aware that there is not a uniform answer as to what is safe and that they need to check a number of different sources.

Auto Ignition Temperature

If the temperature is hot enough, many organic materials can ignite and burn in the absence of an ignition source. We are talking about temperatures on the order of say 500 to 1000ºF. The temperature at which ignition takes place is the auto ignition point or auto ignition temperature. For the pentane example, the auto ignition temperature is approximately 500ºF. This temperature is not a precise temperature such as boiling point as there are a number of variables that influence whether a chemical will self-ignite.

Even in the absence of air many chemicals especially organic chemicals and chemicals containing nitrogen will decompose if the chemical is heated to a high enough temperature. The decomposition of combustible materials in the absence of air is called pyrolysis. The products of decomposition may include hydrogen, carbon monoxide, methane, ethane, char, soot, hydrogen sulfide, hydrogen chloride, organic acids, water, and other substances.

What Is In That Smoke When a Chemical Burns?

Imagine that a drum originally containing methanol has spilled its contents on the ground. Another name for methanol is methyl alcohol. Methanol has a flash point of 52ºF and a boiling point of 147ºF, and is classified as a I B Flammable Liquid. The methanol catches fire. What is in the gases given off as methanol burns?

A chemist might tell you methanol burns forming carbon dioxide and water. The chemist would be right. He may even write out a chemical equation,

$$CH_3OH + O_2 \rightarrow CO_2 + 2H_2O$$

Here, CH_3OH is the chemical formula for methanol, O_2 represents oxygen from the air, CO_2 represents carbon dioxide, and H_2O represents water.

Methanol is a normally a clean burning fuel. So are natural gas, methane, propane, butane, pentane, and ethanol. When burned, they produce carbon dioxide and water without smoke. Notice the word, "normally". If a pool of methanol on the ground catches fire, there will be some smoke. The burning is not 100% efficient. There may also be some combustible material in the ground which partially burns. The smoke consists of some unburned carbon which makes up the methanol and ground debris plus a some carbon monoxide. If the temperatures in the flame get hot enough (above about 2300ºF), a small amount of the nitrogen in the air could even react with the air oxygen forming nitric oxide.

Let's look at another example. Consider boxes containing containers of moth crystals stored in a warehouse for eventual sale in retail stores. The moth crystals are p-dichlorobenzene (para-dichlorobenzene). The PEAC tool shows p-dichlorobenzene to be a solid with a melting point of 127ºF, a flash point of 150ºF, a boiling point of 345ºF, and a chemical formula of C6H4(Cl)2. The chemical formula can also be written a number of different ways, but the important thing is that p-dichlorobenzene contains carbon (C), hydrogen (H), and chlorine (Cl). A molecule of p-dichlorobenzene contains 6 atoms of carbon, 4 atoms of hydrogen, and two atoms of chlorine. Now what happens if these containers burn. The gases formed will be carbon dioxide, water, and hydrogen chloride. The hydrogen chloride will react (absorb) in water forming hydrochloric acid. Hydrogen chloride is a toxic gas. The Emergency Response Planning Guideline level 2 (EPRG-2) for hydrogen chloride is 20 ppm; the Immediately Dangerous to Life and Health (IDLH) value is 50 ppm. ERPG-2 is defined as the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. A chemist might write out a chemical equation for the burning of p-dichlorobenzene as

$C_6H_4Cl_2 + (13/2)\ O_2 \rightarrow 6CO_2 + H_2O + 2HCl$

Again, the burning probably will not be clean. There will be some carbon soot, possibly some HOCl, carbon monoxide (CO), maybe some chloromethane and other chlorinated hydrocarbons, and possibly very small amounts of dioxins and furans. There could be small amounts of nitric oxide forming from reaction of air nitrogen with air oxygen.

The chemical formula gives a clue what gas will be given off if the chemical is burned. For example, if the element sulfur (S) is in the chemical formula of a combustible chemical, the sulfur will convert to sulfur dioxide on burning. If the burning is not clean, some sulfur monoxide, hydrogen sulfide, carbonyl sulfide, methyl mercaptan (a foul-smelling gas), thiophene (another foul smelling gas) may also be formed. If chlorine (Cl) is also present in the same chemical, some other chlorine/sulfur gases may form. The gases given off during burning are toxic, irritating, and foul smelling.

What if the chemical is not combustible and contains sulfur (S) or chlorine (Cl), but other things are burning? Many things can happen to the chemical depending upon the chemical itself and the dynamics of the fire. Information about the chemical's melting point, boiling point, and whether it will decompose on heating is useful. For example, sodium chloride (table salt), calcium sulfate, mercuric chloride, and mercury sulfate are not combustible. Sodium chloride and calcium sulfate are inert and have very high boiling points (e.g. 2575^{o}F for sodium chloride) and would probably stay behind in the ash unless there was an explosion or the fire dynamics were so turbulent or very hot which would result in the chemical being dispersed in the air as a fine dust. However, mercuric chloride has a boiling point of 576^{o}F. Mercury sulfate decomposes on heating.

In a fire, the mercury would be in the gas as elemental mercury or mercuric chloride, both of which are very toxic by inhalation and by skin absorption. Even if the boiling point temperature is not reached, the chemicals will have a certain vapor pressure corresponding to a given temperature, and will give off gaseous vapors or fumes. If the chemical has "Hg" as part of the chemical furmula, it contains mercury; this mercury can be expected to come off as a toxic gas in a fire.

Organic chemicals containing chlorine (Cl), Bromine (Br), or Fluorine (F) can be expected to produce hydrogen chloride (HCl), hydrogen bromide (HBr), or hydrogen fluoride (HF) in a fire. All are toxic chemicals. Many plastic materials including plastic foam in building and furniture contain chlorine as part of the chemical structure and can be expected to produce hydrogen chloride in a fire. Fire retardants which contain bromine as part of the chemical structure may render a material fire resistant or even be used to put out a small fire, but even these retardants will be overwhelmed in a large fire such as a burning home or business, and some of the bromine convert to toxic hydrogen bromide. Carbon tetrachloride (CCl_4) was once widely used in the dry cleaning industry because of its fire resistant properties; it was later banned for this use in the 1960's because it was found to cause cancer. In a fire, some of the chemical may volatilize unchanged as gaseous carbon tetrachloride, hydrogen chloride will form, and depending upon the burning conditions, some of the chemical can be converted to the deadly gas phosgene. Phosgene is a chemical warfare agent.

Firefighters entering a burning building where chemicals are stored or fighting a transportation accident fire need to know what these chemicals are. Very toxic chemicals can be produced in the fire, much more toxic than the original chemical.