Introduction to Fire & Safety Engineering

Semester VII

Course Code: 2CHOE26

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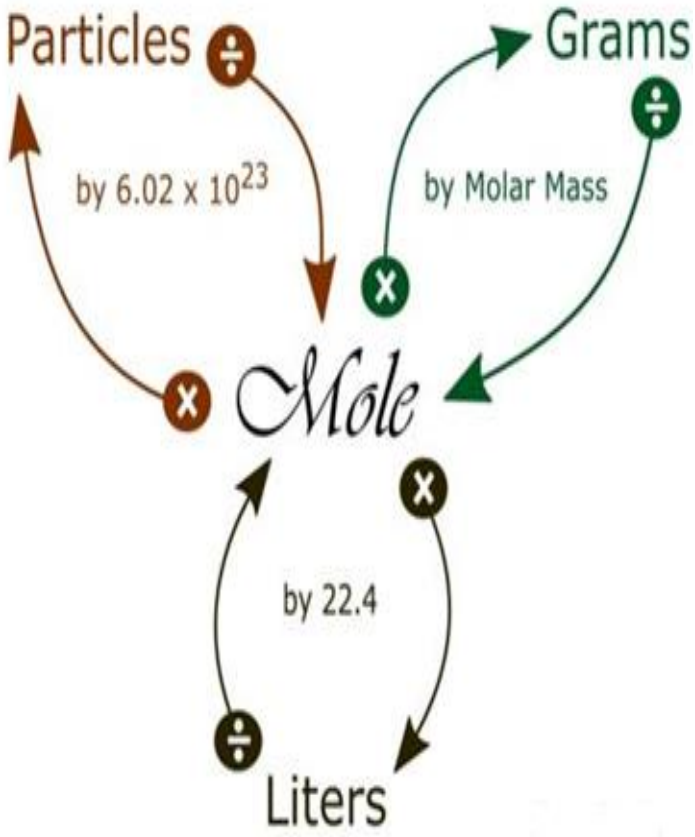
UNIT 3: Chemistry of Fire

Matter around us

- All matter around us is made up with either with elements, molecules, compounds or mixtures.
- Air is a mixture of nitrogen, oxygen, carbon dioxide, vapors and other rare gases.
- It also contains oxides of sulphur and nitrogen, dust, silica and carbon particles etc. which can be physically or chemically separated.
- As we know that there are three states of matter: Solid, Liquid and Gas
- For the purpose of fire fighting one has to gain the knowledge and understanding about the different states of matters and their properties.
- The properties of converting petrol from liquid to vapors can be effectively used in an internal combustion engines.
- Generally combustible matter around us may be natural or manmade comprises carbon, hydrogen, nitrogen, oxygen and some metals (Mg & Al) in vide variety.
- When right condition is achieved, elements, compounds or mixtures can react chemically with each other and give out products of reactions.
- Combustion is a reaction of a fuel with oxygen in presence of heat or energy.

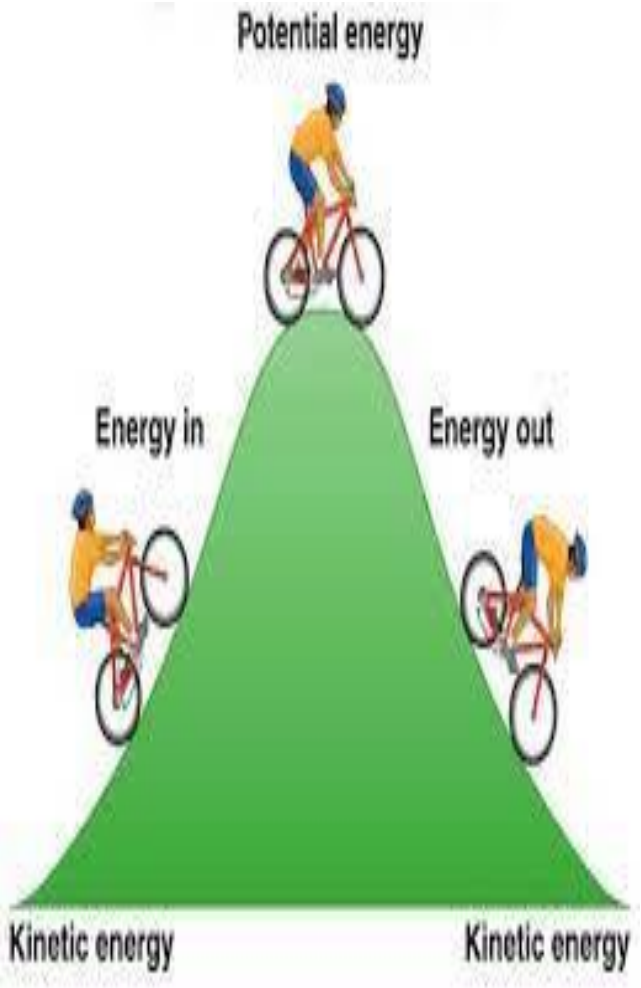
Avogadro's hypothesis

- This is a very basic but very important concept.
- The value of Avogadro's number is $N_A = 6.022 \times 10^{23}$
- The hypothesis says, "Equal volume of gases will occupy the same number of molecules at equal pressure and temperature"
- At STP (273 K and 1 atm) weight equivalent to the molecular weight will occupy 22.4 L volume and it will have 6.022×10^{23} of molecules.
- For e.g. At STP, 32 g O_2, 44 g CO_2, 28 g N_2 will occupy 22.4 L volume and they will have 6.022×10^{23} of molecules.
- This is basic fundamental which is very useful for the fire computation related to heat and energy calculation to determine the intensity of fire.
- Stoichiometric relation is another important concept which every fire fighter must know.

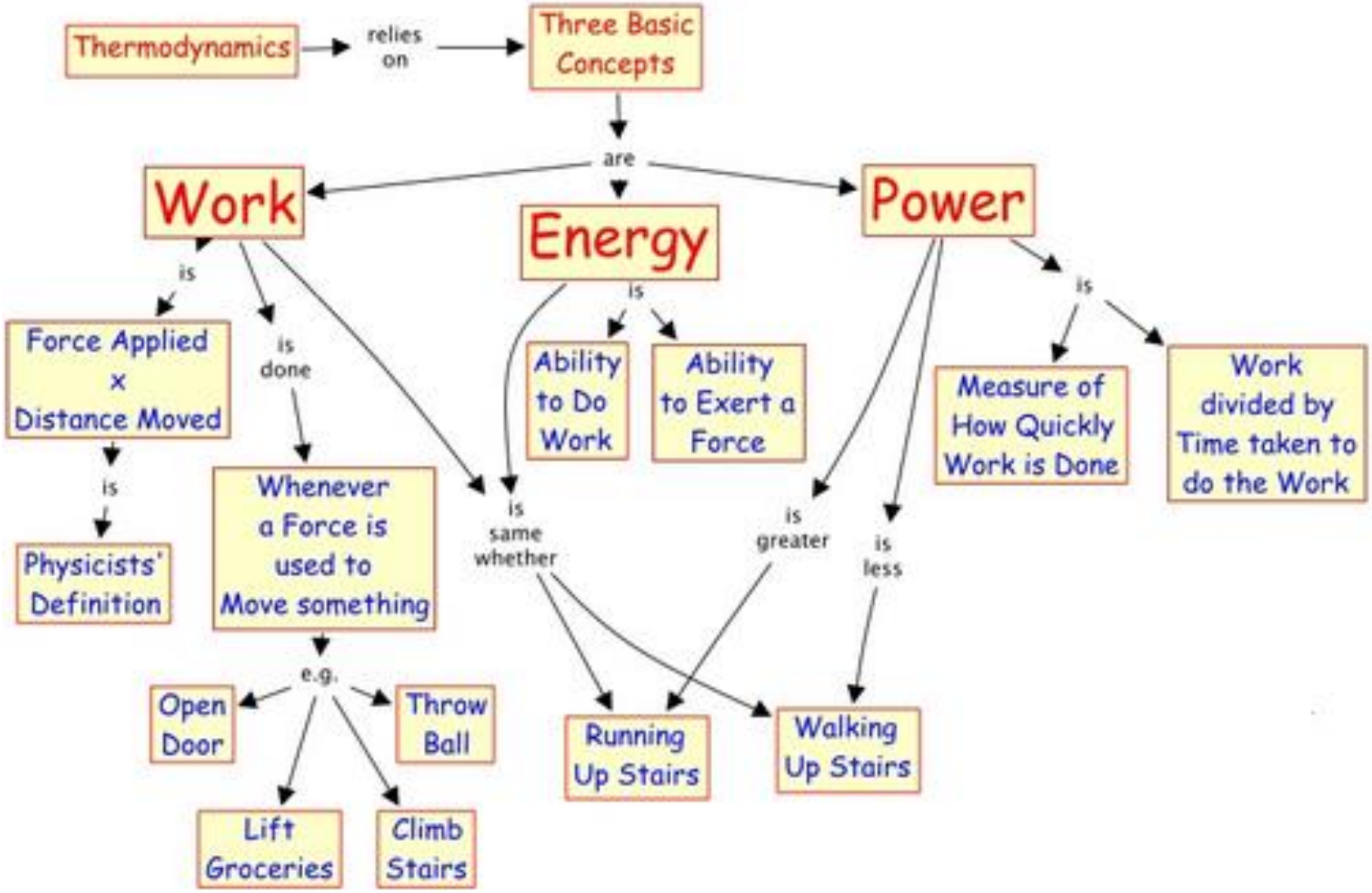


Work vs Energy

- All the combustion reactions are connected to the Thermodynamics laws which is useful to understand the chemistry of fire.
- The first law of Thermodynamics is all about the conservation of energy.
- Energy is the ability to do the work.
- Work is actually done when a force moves through a distance.
- Work done is equal to the converted energy.
- When work is done, energy is converted into different types.
- Mainly Kinetic and Potential energy are the most important to calculate the work and with the help of it one can estimate the intensity of fire and due to it, what is the damage level during any fire accident.



Work, Energy and Power Chart



Energy in chemical reactions

- In any chemical reaction, energy will be either absorbed which is called endothermic reaction or released which is called exothermic reaction.
- All the combustion reactions will release the energy in the form of heat or light.
- Minimum energy is required for any reaction which is known as Activation Energy.
- A fire fighter must have the knowledge about the different types of heats.
  - Heat of Reaction ΔH
  - Heat of Combustion ΔH_c
  - Heat of formation ΔH_f
- Heat capacity (C_p & C_v) is also one of the most important concept for fire and safety.
- C_p values of gases depend on their temperature and this is important for fire calculations at higher temperatures.
- Hence any person involved in fire fighting must know about the chemical reaction going on during the fire incidents.

Oxidation and Reduction

- There are many reactions in chemistry, but the fire process is an oxidation reaction.
- It means, in this reaction, oxygen is added to the substance and nature of the substance will change itself.
- Fire is also a chemical reaction in which the elements present in a fuel react with oxygen of air and will be converted in the combustion product.

$$C + O_2 \rightarrow CO_2$$

$$H_2 + ½\ O_2 \rightarrow H_2O$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + Heat$$

- In some cases, oxygen for the combustion reaction is present in some fuels itself such as nitrates, chlorates of metals like sodium, potassium where the rate of combustion will be very high. E.g. explosives, fireworks etc.
- Hence in combustion reactions an oxidizing and reducing agents react together and produce heat energy and combustion products which are less reactive in nature.
- The term oxidation-reduction are also applied to the oxidation state and transfer of electrons. Oxidation involves loss of electron and reduction involves gain of electron.

Chemical chain reaction in fire

- Fire does not take place in a single step but in multiple steps which sums up as the overall reaction and it is a chain reaction.
- Many changes take place at these different stages and finally it reaches to the completion of the reaction.
- In the case of fire, the stages occur in the visible flame region in a chain.
- For the continuity of this chain reaction, the most essential part is the sustainability of the flame.
- If this chain reaction is interrupted at any stage, the fire will get terminated as the fire triangle will be lost.
- The reaction will involve the activation energy after getting it, the reactant molecules will go through sub-molecular particles like atoms, unstable sub-atomic particles, ions and free radicals and they will react with each other to give new products.
- Thus there will be a chain of formation and consumption of these particles to sustain the process till the completion of reaction.
- This steps will be occurring in the flame region.

- There are different steps in fire as given below:
- Initiation of chain > Propagation of chain > Branching of chain > Termination of chain.
- Except the initiation, there are multiple parallel or series of other steps.
- Polymerization is also a chain reaction but very easy and well known example of chain reaction is fire.
- To terminate or stop a combustion reaction, one of the three elements of the fire triangle must be removed.
- Without sufficient heat, a fire cannot begin and it cannot continue.
- Heat can be removed by the application of a substance which reduces the amount of heat available to the fire reaction.
- We must consider the seven sides of the fire: front, rear, both sides, top, bottom, and interior.
- Fires cannot be considered under control until all seven sides are addressed.

What is the most common cause of death in fire?

- The majority of fire-related deaths are caused by smoke inhalation of the toxic gases produced by fires.
- The majority of fires that kill or injure children are residential fires.
- The killing fumes - smoke is more deadlier than fire.
- Fire and smoke are a deadly duo.
- In addition to producing smoke, fire can lower down the oxygen levels, either by consuming the oxygen or by displacing it with other gases.
- Actual flames and burns only account for about 30 % of fire-related deaths and injuries.
- Most indoor fire deaths are caused by smoke inhalation.
- The best defence against a fire is to be prepared.
- **Alpha, Bravo, Charlie, Delta** terms are used to designate the sides of a structure. “Alpha” side is the front, the “Bravo” side is the left, “Charlie” is the back and “Delta” is the right side of the structure.

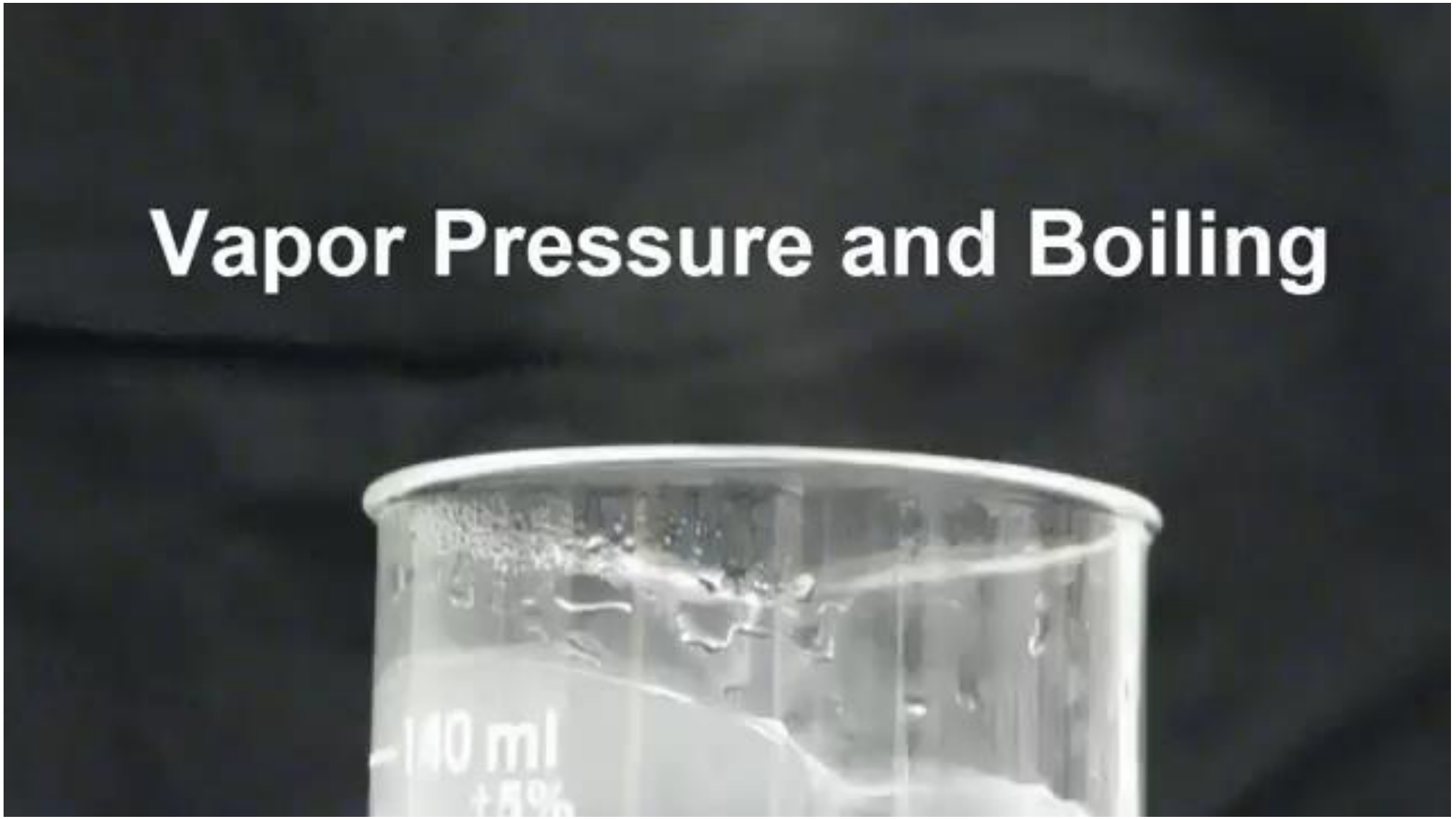
Reducing atmosphere

- If the fire occurs at a closed place where the ventilation is limited i.e. where the oxygen supply is less, the combustion or oxidation process will not sustain for long time.
- The product of incomplete combustion such as carbon monoxide will be formed.
- If air becomes available, the reaction will continue and reaches to completion.
- This can be possible if air is allowed to enter by breaking a window pane or doors of that closed place.
- But this can lead to the phenomenon called backdraft or a sudden transformation into a major fire.
- In the cases of major fire, the fire fighters generally try to create reducing atmosphere in the open compartment by disconnecting the oxygen supply from air by covering that area with gases like carbon dioxide.

Vapor Pressure of Liquids

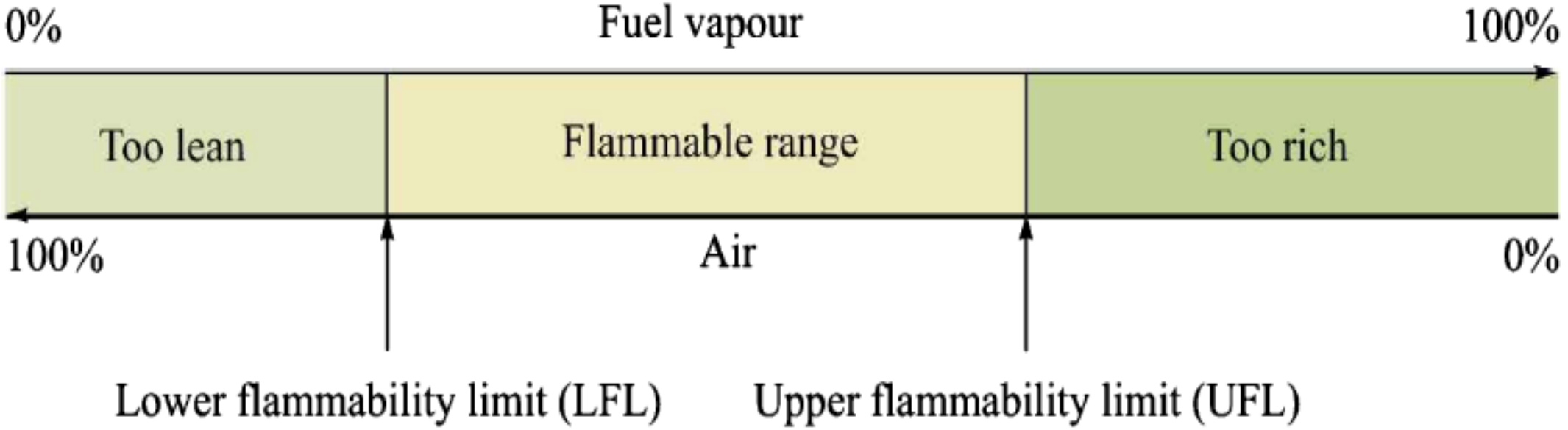
- The pressure exerted by the vapor molecules just above the surface is called vapor pressure of the liquid.
- The rate of vaporization and quantum of vapor generated depend on the nature of the liquid and the heat supplied to the liquid.
- The temperature at which the vapor pressure becomes equals to the atmospheric pressure above the liquid surface is called boiling point of the liquid.
- If the liquid is boiled in a covered vessel, the equilibrium between the liquid and vapors will be established.
- If pure liquid is taken then the vapor pressure at equilibrium will be called saturated vapor pressure (SVP).
- For the mixture of liquids, it is called partial vapor pressure which is being expressed as a product of vapor pressure of pure liquid and the mole fractions of the components assuming that the mixture behaves like an ideal solution.
- **pi = Xi x Pi**, Xi=mole fraction of component, pi=partial pressure of component, Pi=partial vapor pressure of pure component

Vapor Pressure and Boling

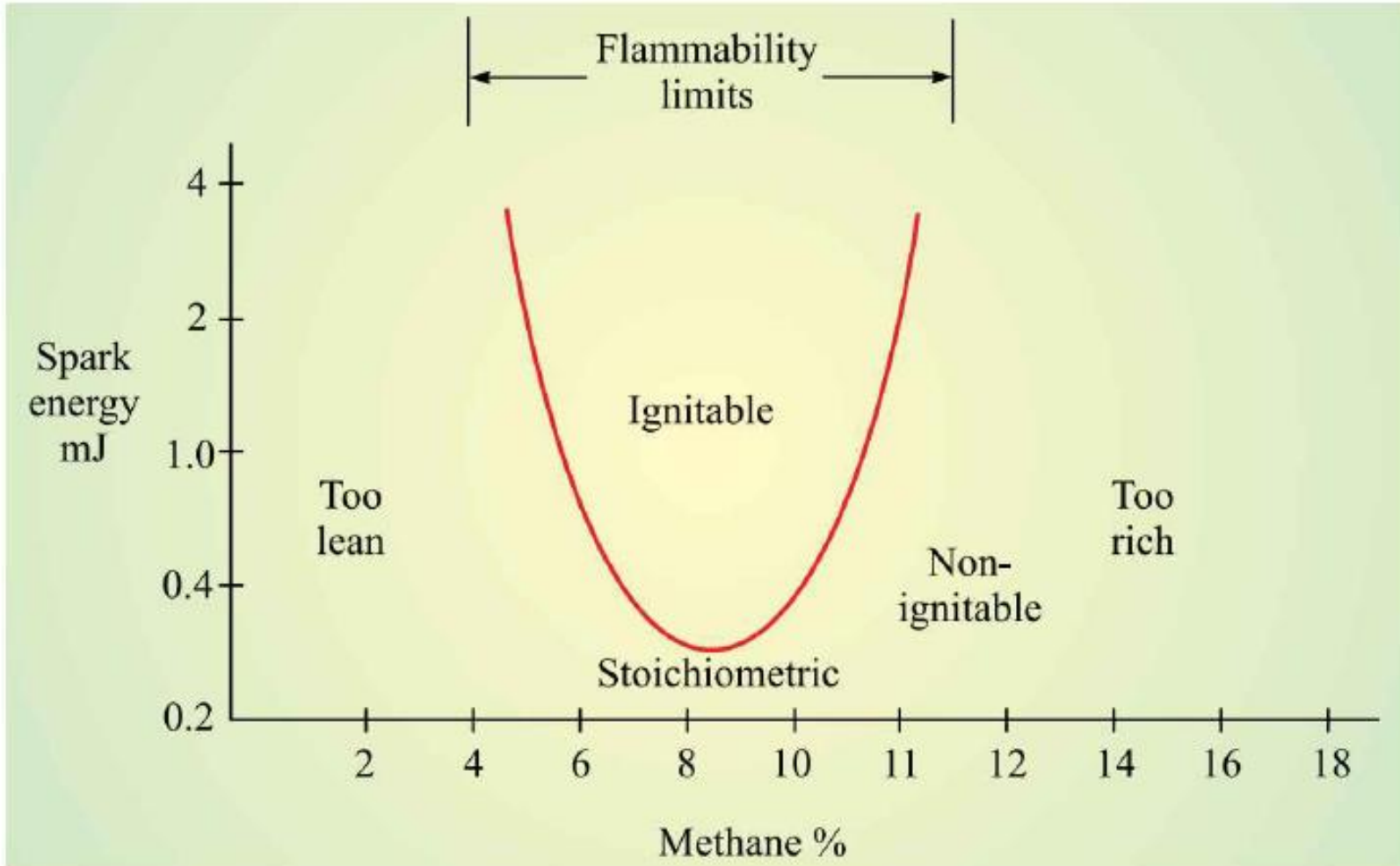


Flammability Limits and Flammable Range

- Flammable limits are defined as the minimum concentration range in which a flammable substance can produce a fire or explosion when an ignition source (such as a spark or open flame) is present.
- The concentration is generally expressed as percent fuel by volume.
- This is also known as Lower Flammability Limit (LFL).
- There is also an upper maximum concentration limit above which the fuel concentration will be so high that the oxidant will be inadequate and will stop the propagation of fire.
- This is also known as Upper Flammability Limit (UFL).
- The range of the concentrations between LFL and UFL is called Flammable Range.
- Flammable range of a fuel widen with increase in temperature.
- LFL is immune to pressure except at very low pressures.
- UFL increases with increase in pressure above atmospheric but not sensitive to sub-atmospheric pressures.



- Remember, this diagram doesn't represent any stoichiometry relation of combustion reaction.
- Flammability ranges of fuels indicate that fuel-air mixture may permit flame propagation over a band of fuel vapor-air concentrations.
- However, remember that not all the concentrations within the range may be equally easy to ignite.



Effects of pressure and temperature on flammability of methane at atmospheric pressure and 26°C

Estimating Lower flammability Limit (LFL)

- Generally fuels are the mixtures of more than one components.
- The flammability limits can be determined by experiments.
- To estimate the flammability limits, Le Chatelier's rule is being used.
- LFL (or UFL) of a fuel mixture is the reciprocal of the sum of reciprocals of the LFL (or UFL) of the components weighted by their respective mole fractions.
- Different other methods are also reported in different books.
- The terms Flammability limits and Explosive limits are generally used as synonyms but they are not same.
- Flammability limits also depend on the type of atmosphere (for example, limits are much wider in oxygen than in air), the pressure, and the temperature of atmosphere.
- Explosion limits usually refer to the range of pressure and temperature for which an explosive reaction at a fixed composition mixture is possible.

$$LFL = \frac{1}{\left[\sum_i^n y_i \left(\frac{1}{LFL_i}\right)\right]}$$

$$UFL = \frac{1}{\left[\sum_i^n y_i \left(\frac{1}{UFL_i}\right)\right]}$$

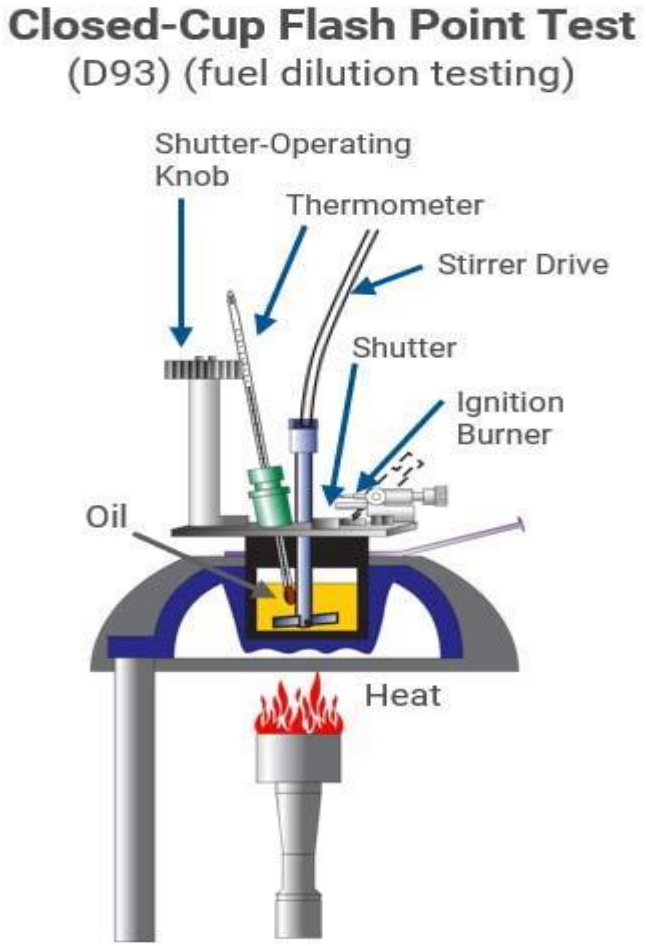
Flash Point

- Flash point is the lowest temperature at which a liquid can gives off vapour to form an ignitable mixture in air near the surface of the liquid.
- The lower the flash point, the easier it is to ignite the material.
- At flash point the momentary flashes will be observed but it will not catch fire.
- Flash point is a warning for fire, i.e. if any fuel reaches at flashes, one should understand that the situation is near to fire and the heating of that solvent or fuel should be stopped.
- At flash point, more vapour may not be produced rapidly enough to sustain combustion and hence, the fire is mostly not sustained.
- It is used to measure how volatile a liquid is and the level of risk it could pose.
- Flash and fire points are measured by heating a liquid to specific temperatures under controlled conditions and then applying a flame with the use of an apparatus called Flash/Fire point apparatus.
- There may be Open or Closed cup apparatus used.
- Closed cup apparatus is more accurate than the open cup apparatus.

Fire Point

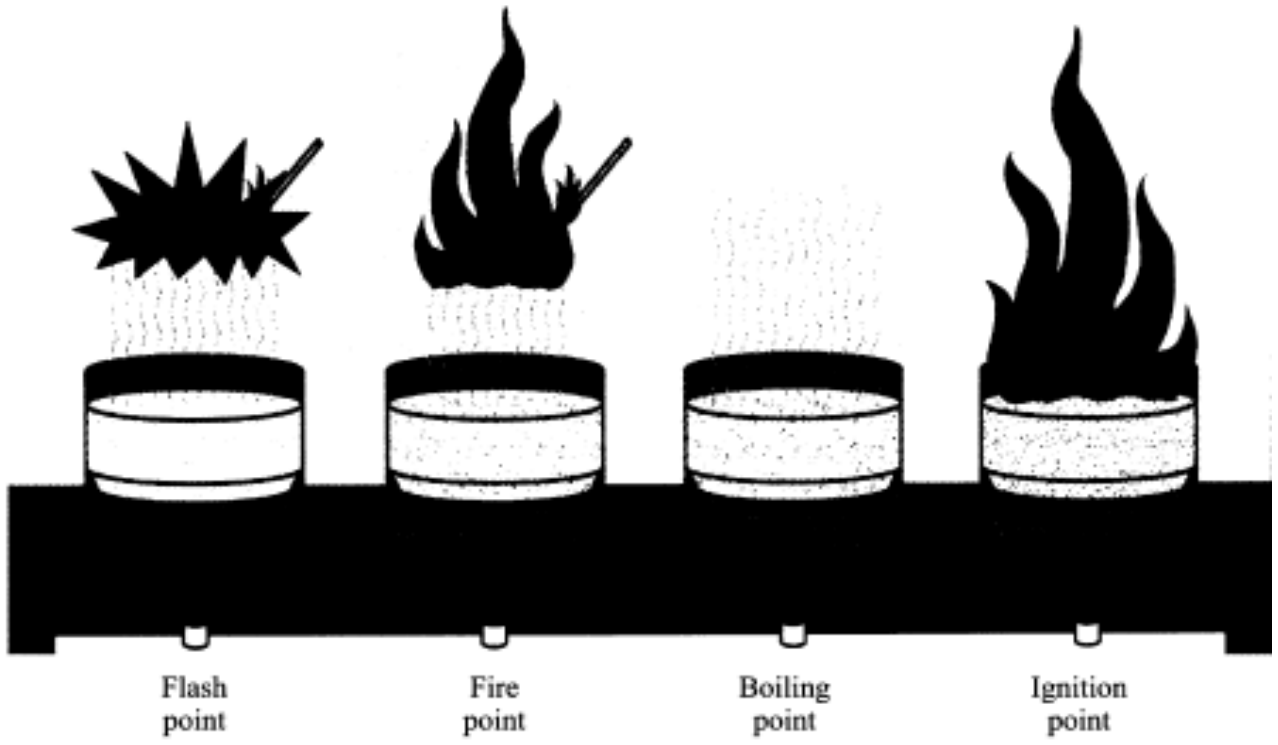
- In terms of fire and safety, fire point refers to the temperature at or above the flash point, at which a flammable liquid produces enough vapour to ignite by spark or flame and burn for at least five seconds.
- The fire point is usually 10°C more than the flash point of a liquid.
- Fire point is higher than the flash point, because at the flash point more vapour may not be produced fast enough to sustain combustion.
- The unit of flash and fire point is degree Celsius.
- Once the flammable liquid reaches at fire point, then further spread of fire will be rapid and may become dangerous in nature.
- Fire point is also used to measure how volatile a liquid is and the level of risk it could pose when comes in contact with heat and air.
- Pensky Martens, Abels, Cleveland are the names of some Flash/Fire point apparatus.
- Before working on fire fighting, the fire fighter must have the knowledge of flash and fire points of liquids.

Closed and Open cup Flash/Fire Point Apparatus



Ignition or Auto-ignition or Spontaneous Temperature

- Ignition or Auto-ignition or Spontaneous ignition point is the temperature at which a material can self-ignite and no pilot ignition source is required.
- The factors on which it depends are:
  - Chemical and physical properties of material
  - Size of the test sample
  - Test method and apparatus used
  - Size and material of test vessel
  - Strength of the heat source
  - Oxygen concentration
- The auto-Ignition temperature derived by any method is not necessarily representative of the minimum temperature at which a material will self-ignite in air.



Ignition Energy

- Ignition is the process of providing the energy that is required to initiate a combustion process.
- A substance must be heated to its ignition point before it can start burning.
- The Minimum Ignition Energy (MIE) is the lowest energy required to ignite the flammable material in air or oxygen.
- It is a measure of how sensitive an explosive dust or powder is to electrical spark ignition.
- It is also defined as the minimum amount of energy released at a point in a combustible mixture that caused flame propagation away from the point, under specified test conditions.
- Ignition point of a substance is essentially constant.
- A finely divided substance is more readily ignited than a massive one. e.g. sawdust can ignite more rapidly than a log of wood.
- Similarly, the vapors of a volatile fuel such as gasoline are more readily ignited than the fuel in bulk form.

Manufacture, Storage and Import of Hazardous Chemical Rules 1989

In India, the Manufacture, Storage and Import of Hazardous Chemical Rules, 1989 has the following classifications for flammable chemicals:

(i) **Flammable gases:** Gases which at 20°C and at standard pressure of 101.3 KPa are
   (a) ignitable when in a mixture of 13% or less by volume with air, or;
   (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limits.

(ii) **Extremely flammable liquids:** Chemicals which have flash point lower than or equal to 23°C and boiling point less than 35°C.

(iii) **Very highly flammable liquids:** Chemicals which have a flash point lower than or equal to 23°C and initial boiling point higher than 35°C.

(iv) **Highly flammable liquids:** Chemicals which have a flash point lower than or equal to 60°C but higher than 23°C.

(v) **Flammable liquids:** Chemicals which have a flash point higher than 60°C but lower than 90°C.

Further, the Petroleum Act, 1934 classifies petroleum products as

(i) 'Petroleum Class A' means petroleum having a flash point below 23°C.

(ii) 'Petroleum Class B' means petroleum having flash point of 23°C and above but below 65°C.

(iii) 'Petroleum Class C' means petroleum having a flash-point of 65°C and above but below 93°C.

Rapid, Spontaneous and Explosive Combustion

- **Rapid combustion** is when a substance bursts in a short span of time, the combustion of the substance is almost complete and a large amount of heat and light is produced. For example, LPG in a gas stove, oxyhydrogen flame used for welding, etc. Rapid combustion often occurs in the form of Fire.
- In **Spontaneous combustion**, a substance catches fire as soon as its temperature reaches the ignition temperature. For example, White Phosphorus catches fire at room temperature of 35 degree Celsius and above without being introduced to any source of heat. The type of combustion in which material suddenly bursts into flames even without the application of heat is called spontaneous combustion.
- **Explosive combustion** is a type of combustion reaction that takes place suddenly with the evolution of heat light and sound. During an explosion a large amount of gas is evolved which gets liberated suddenly, for example when a cracker is ignited it suddenly reacts and bursts. A cracker can also explode when pressure is applied to it.

Thank You