

Chapter 6

Fires and Explosions

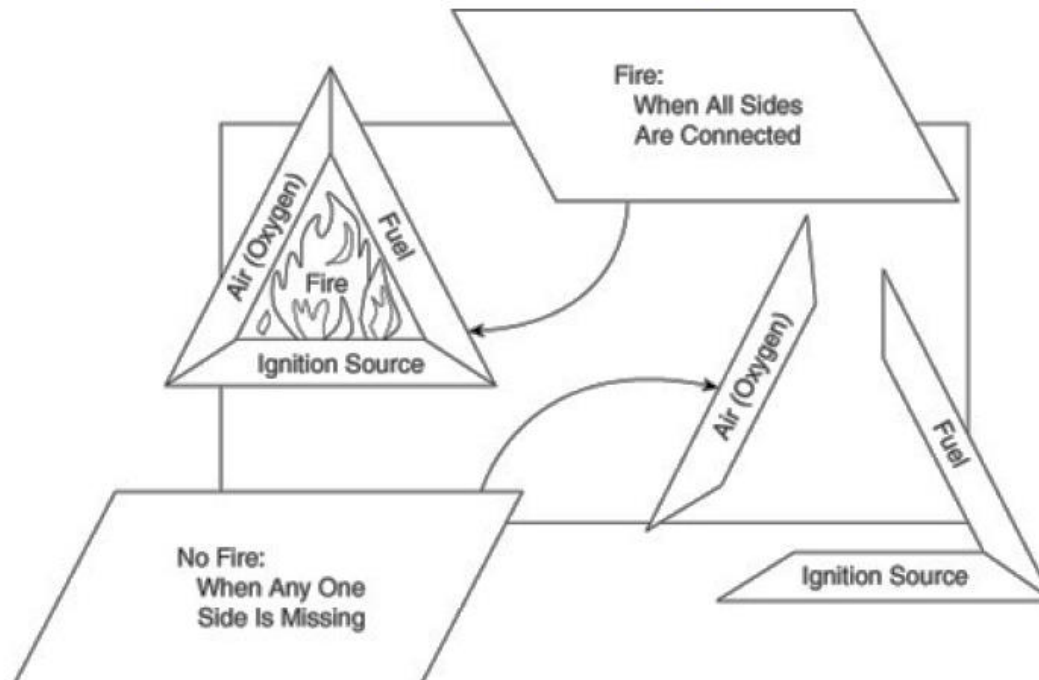


Introduction

- ▶ Chemicals present a substantial hazard in the form of fires and explosions
 - combustion of one gallon of toluene destroy an ordinary chemistry laboratory
- Three most common accidents are **fires, explosions**, and **toxic releases**
- Prevent accidents engineers must be familiar
 - The fire and explosion properties of materials,
 - The nature of the fire and explosion process
 - Procedures to reduce fire and explosion hazards
- Topics, emphasizing definitions and calculation methods for estimating the magnitude and consequences of fires and explosions

The Fire Triangle

- ▶ Essential elements for combustion are fuel, an oxidizer, and an ignition source
- ▶ Elements are illustrated by the **fire triangle**



The Fire Triangle

- ▶ Fire, or burning, is the rapid **exothermic** oxidation of an ignited fuel
- ▶ Combustion always occurs in the **vapor phase**
- ▶ Ignition source are present at the necessary levels, burning will occur
- ▶ Fire will not occur if
 - (1) **fuel** is not present or is not present in **sufficient quantities**,
 - (2) an **oxidizer** is not present or is not present in **sufficient quantities**
 - (3) the **ignition** source is not energetic enough to **initiate** the fire
- In past controlling fires was reduction in ignition sources
- Current practice is to prevent fires by continuing to eliminate ignition sources while focusing efforts strongly on preventing flammable mixtures.

The Fire Triangle

- ▶ Various fuels, oxidizers, and ignition sources common in the chemical industry are

Fuels

- ▶ Liquids: gasoline, acetone, ether, pentane
- ▶ Solids: plastics, wood dust, fibers, metal particles
- ▶ Gases: acetylene, propane, carbon monoxide, hydrogen

Oxidizers

- ▶ Gases: oxygen, fluorine, chlorine
- ▶ Liquids: hydrogen peroxide, nitric acid, perchloric acid
- ▶ Solids: metal peroxides, ammonium nitrite

Ignition sources

- ▶ Sparks, flames, static electricity, heat

Distinction between **Fires and Explosions**

- ▶ Distinction between fires and explosions is **the rate of energy release**
- ▶ Fires release energy **slowly**,
- ▶ whereas explosions release **energy rapidly**
 - order of microseconds
- ▶ Fires can also result from explosions, and explosions can result from fires
- ▶ **Combustion or fire:** Chemical reaction in which a substance combines with an oxidant and releases energy
- ▶ **Ignition:** Flammable mixture coming in contact with a source of ignition gas reaching a temperature high enough to cause the gas to autoignite.

Definitions

Autoignition temperature (AIT): Adequate energy is available in the environment to provide an ignition source.

Flash point (FP): lowest temperature at which it gives off enough vapor to form an ignitable mixture with air

- ▶ At the flash point the vapor will burn but only briefly
- ▶ Inadequate vapor is produced to maintain combustion
 - The open-cup flash point is a few degrees higher than the closed-cup

Fire point: The fire point is the lowest temperature at which vapor above a liquid will continue to burn once ignited

Flammability limits: Vapor-air mixtures will ignite and burn only over a well specified range of compositions

Definitions

- ▶ Mixture will **not burn** when the composition is lower than the **lower flammable limit** (LFL)
- ▶ The mixture is **also not combustible** when the composition is too rich, **upper flammable limit** (UFL)
- ▶ Units are volume percent fuel (percentage of fuel plus air)
- ▶ Lower explosion limit (LEL) and upper explosion limit (UEL) are used interchangeably with LFL and UFL

Explosion: An explosion is a rapid expansion of gases resulting in a rapidly moving pressure or shock wave.

- The expansion can be mechanical
- it can be the result of a rapid chemical reaction.
- Explosion damage is caused by the pressure or shock wave

Mechanical explosion: containing high-pressure non reactive gas

Definitions

Deflagration: An explosion in which the reaction front moves at a speed less than the speed of sound in the unreacted medium.

Detonation: An explosion in which the reaction front moves at a speed greater than the speed of sound in the unreacted medium

Confined explosion: An explosion occurring within a vessel or a building, extensive damage

Unconfined explosion:

- Unconfined explosions occur in the open.
- The gas is dispersed and mixed with air until it comes in contact with an ignition source.
- Unconfined explosions are rarer

Definitions

Boiling-liquid expanding-vapor explosion (BLEVE):

- ▶ Vessel contains a liquid at a temperature above its atmospheric pressure boiling point ruptures
- ▶ Explosive vaporization of a large fraction of the vessel contents, possibly followed by combustion or explosion of the vaporized cloud if it is combustible

Dust explosion: This explosion results from the rapid combustion of fine solid particles

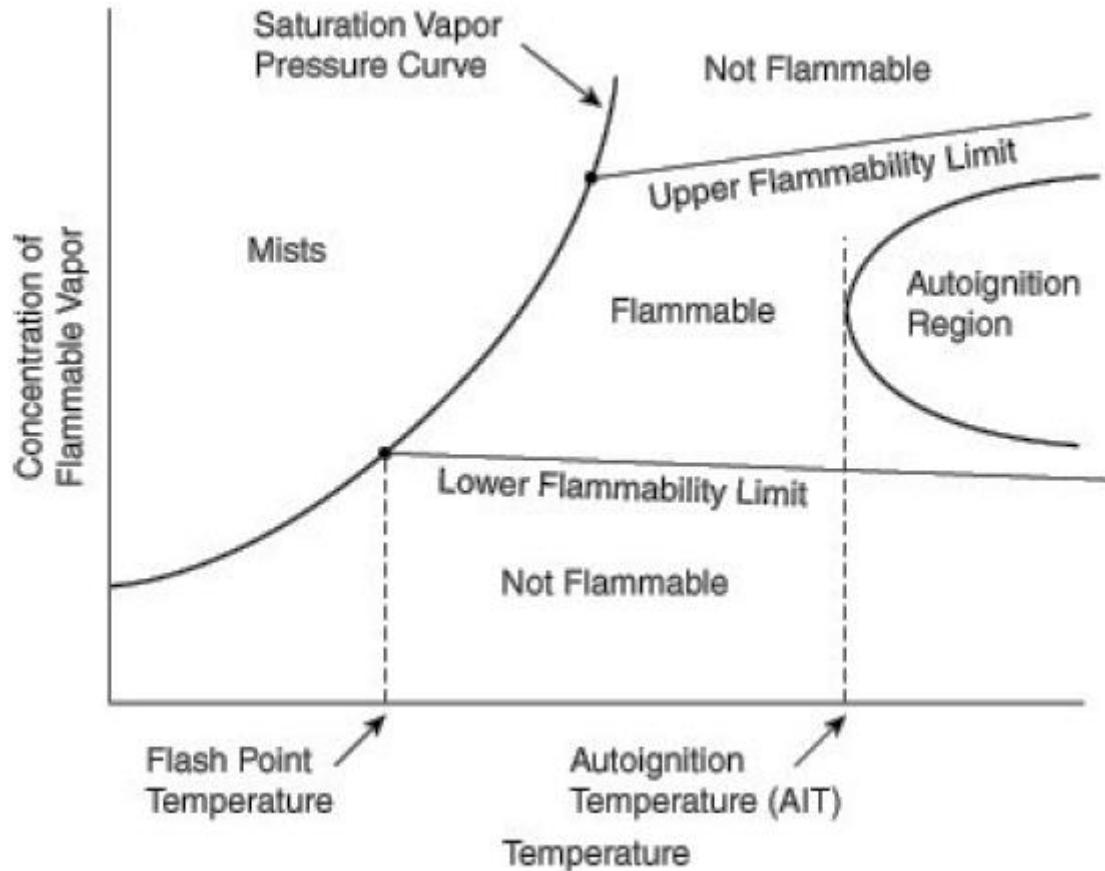
- metals such as iron and aluminium flammable when reduced to a fine powder

Shock wave:

- An abrupt pressure wave moving through a gas
- A shock wave in open air is followed by a strong wind
- the combination of shock wave and wind is called a **blast wave**. process is mostly **adiabatic**.

Overpressure: The pressure on an object as a result of an impacting shock wave.

Relationships between various flammability properties.



Flammability Characteristics of Liquids and Vapors

Liquids: The flash point temperature

$$T_f \text{ is } T_f = a + \frac{b(c/T_b)^2 e^{-c/T_b}}{(1 - e^{-c/T_b})^2} \text{ temperature (K),}$$

a , b , and c are constants provided

Flash points for multicomponent mixtures:

Methanol has a flash point of 54°F, and its vapor pressure at this temperature is 62 mm Hg. What is the flash point of a solution containing 75% methanol and 25% water by weight?

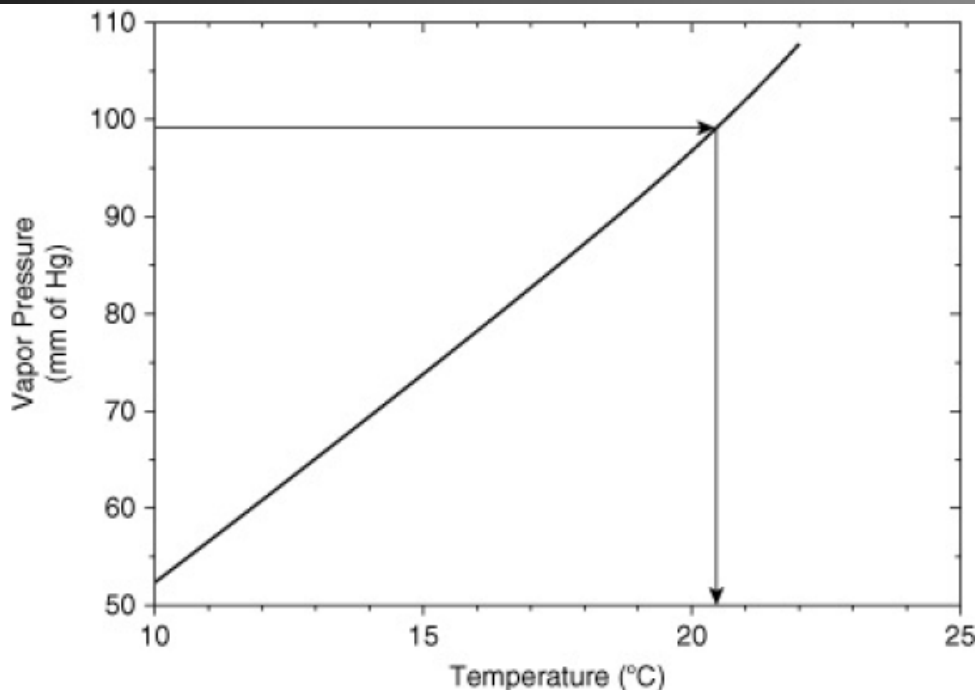
	Pounds	Molecular weight	Moles	Mole fraction
Water	25	18	1.39	0.37
Methanol	75	32	<u>2.34</u>	<u>0.63</u>
			3.73	1.00

Solution: for
methanol

$$p = xP^{\text{sat}}$$

$$P^{\text{sat}} = p/x = 62/0.63 = 98.4 \text{ mm Hg}$$

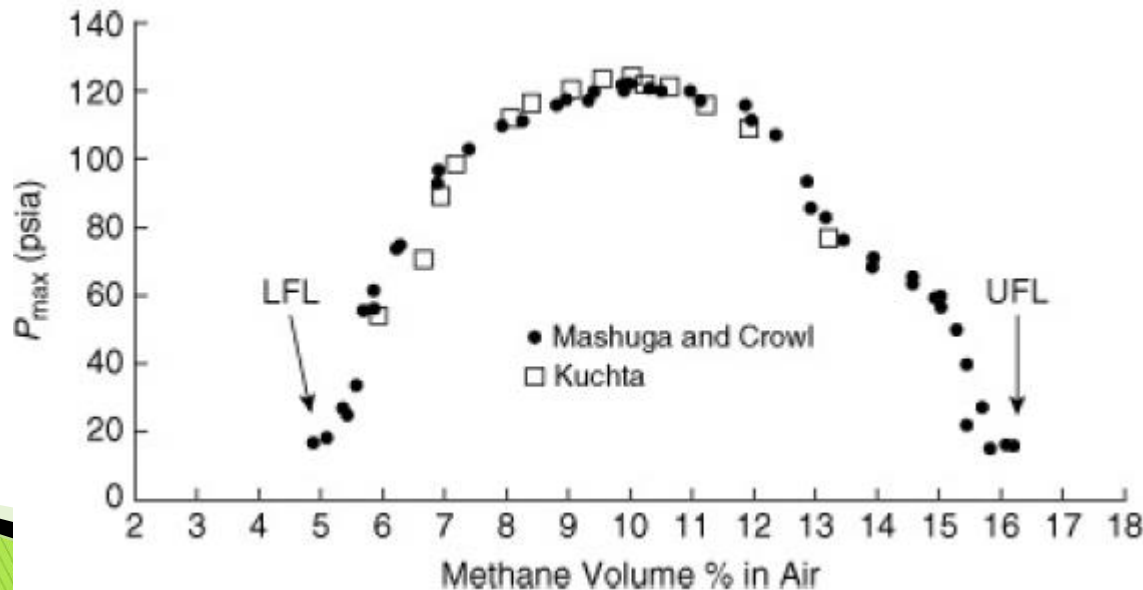
- ▶ Using a graph of the vapor pressure versus temperature, shown in Figure ,
- ▶ the flash point of the solution is 20.5°C,



Flammability Characteristics

Gases and Vapors: Flammability limits for vapors are determined experimentally in a specially designed closed vessel apparatus

- Vapor-air mixtures of known concentration are added and then ignited
- The maximum explosion pressure is measured



Flammability Characteristics

Vapor Mixtures

- ▶ LFLs and UFLs for mixtures are needed
- ▶ These mixture limits are computed using the Le Chatelier equation:

$$\text{LFL}_{\text{mix}} = \frac{1}{\sum_{i=1}^n \frac{y_i}{\text{LFL}_i}}$$

y_i is the mole fraction of component i on a combustible basis

n is the number of combustible species.

UFL_i is the upper flammable limit for component i

$$\text{UFL}_{\text{mix}} = \frac{1}{\sum_{i=1}^n \frac{y_i}{\text{UFL}_i}}$$

Le Chatelier's equation is empirically derived

Vapor Mixtures

What are the LFL and UFL of a gas mixture composed of 0.8% hexane, 2.0% methane, and 0.5% ethylene by volume

Solution:

	Volume %	Mole fraction on combustible basis	LFL _i (vol. %)	UFL _i (vol. %)
Hexane	0.8	0.24	1.2	7.5
Methane	2.0	0.61	5.0	15
Ethylene	0.5	0.15	2.7	36.0
Total combustibles	3.3			

$$\begin{aligned} \text{LFL}_{\text{mix}} &= \frac{1}{\sum_{i=1}^n \frac{y_i}{\text{LFL}_i}} \\ &= \frac{1}{\frac{0.24}{1.2} + \frac{0.61}{5.0} + \frac{0.15}{2.7}} \end{aligned}$$

$$= 1/0.378 = 2.65 \text{ by volume total combustibles.}$$

$$\begin{aligned} \text{UFL}_{\text{mix}} &= \frac{1}{\sum_{i=1}^n \frac{y_i}{\text{UFL}_i}} \\ &= \frac{1}{\frac{0.24}{7.5} + \frac{0.61}{15} + \frac{0.15}{36.0}} \end{aligned}$$

$$= 13.0 \text{ by volume total combustibles.}$$

Because the mixture contains 3.3% total combustibles, it is flammable.

Flammability Limit Dependence on Temperature

In general, the flammability range increases with temperature

$$\text{LFL}_T = \text{LFL}_{25} - \frac{0.75}{\Delta H_c}(T - 25)$$

$$\text{UFL}_T = \text{UFL}_{25} + \frac{0.75}{\Delta H_c}(T - 25)$$

ΔH_c is the net heat of combustion (kcal/mole)

T is the temperature ($^{\circ}\text{C}$)

Flammability Limit Dependence on Pressure

Pressure has **little effect** on the LFL except at very low pressures (<50 mm Hg absolute)

$$\text{UFL}_P = \text{UFL} + 20.6(\log P + 1)$$

P (megapascals absolute) and

UFL (volume % of fuel plus air at 1 atm).

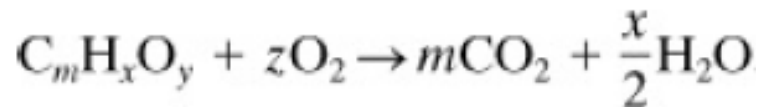
Estimating Flammability Limits

- ▶ **Experimental** determination is always recommended
- ▶ Flammability limits without experimental data
- ▶ Many **hydrocarbon vapors** the LFL and the UFL are a function of the **stoichiometric concentration** (C_{st}) of fuel

$$\text{LFL} = 0.55C_{st} \qquad \text{UFL} = 3.50C_{st}$$

C_{st} is volume % fuel in fuel plus air

Determined using the general combustion reaction



$$z = m + \frac{x}{4} - \frac{y}{2}$$

$$C_{st} = \frac{\text{moles fuel}}{\text{moles fuel} + \text{moles air}} \times 100 = \frac{100}{1 + \left(\frac{z}{0.21}\right)}$$

Estimating Flammability Limits

Substituting z

$$\text{LFL} = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1}$$

$$\text{UFL} = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1}$$

Flammability limits as a function of the **heat of combustion** of the fuel

$$\text{LFL} = \frac{-3.42}{\Delta H_c} + 0.569\Delta H_c + 0.0538\Delta H_c^2 + 1.80,$$

$$\text{UFL} = 6.30\Delta H_c + 0.567\Delta H_c^2 + 23.5,$$

ΔH_c is the heat of combustion for the fuel (in 103 kJ/mol).

Flammability Limits in Pure Oxygen

- ▶ Flammable limits in pure oxygen are frequently useful for designing systems
- ▶ Prevent fires, combustion in pure oxygen also exhibits a lower oxygen limit (LOL) and an upper oxygen limit (UOL),

$$UOL = \frac{UFL[100 - C_{UOL}(100 - UFL_O)]}{UFL_O + UFL(1 - C_{UOL})}$$

- ▶ UOL is the upper oxygen limit (vol. % fuel in oxygen),
- ▶ UFL is the upper flammable limit (vol. % fuel in air),
- ▶ UFL_O is the oxygen concentration at the upper flammable limit (vol. % oxygen in air),
- ▶ C_{UOL} is a fitting constant

Limiting Oxygen Concentration and Inerting

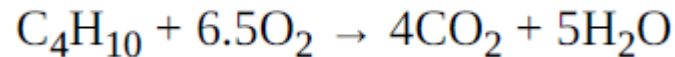
- ▶ Explosions and fires can be prevented by reducing the oxygen
- ▶ Limiting oxygen concentration (LOC)
- ▶ LOC has also been called the minimum oxygen concentration (MOC),
- ▶ Maximum safe oxygen concentration (MSOC)

Problem: Estimate the LOC for butane (C_4H_{10})

Solution

The LFL for butane is 1.8% by volume.

From the stoichiometry



$$LOC = \left(\frac{\text{moles fuel}}{\text{total moles}} \right) \left(\frac{\text{moles } O_2}{\text{moles fuel}} \right) = LFL \left(\frac{\text{moles } O_2}{\text{moles fuel}} \right)$$

$$\begin{aligned} LOC &= \left(1.8 \frac{\text{moles fuel}}{\text{total moles}} \right) \left(\frac{6.5 \text{ moles } O_2}{1.0 \text{ moles fuel}} \right) \\ &= 11.7 \text{ vol. } \% O_2. \end{aligned}$$

Inerting

- ▶ The combustion of butane is preventable by adding **nitrogen, carbon dioxide, or even water vapor** until the oxygen concentration is below 11.7%.
- ▶ The addition of water, however, is not recommended because any condition that condenses water would move the oxygen concentration back into the flammable region
- ▶ LOC can be estimated using the equation

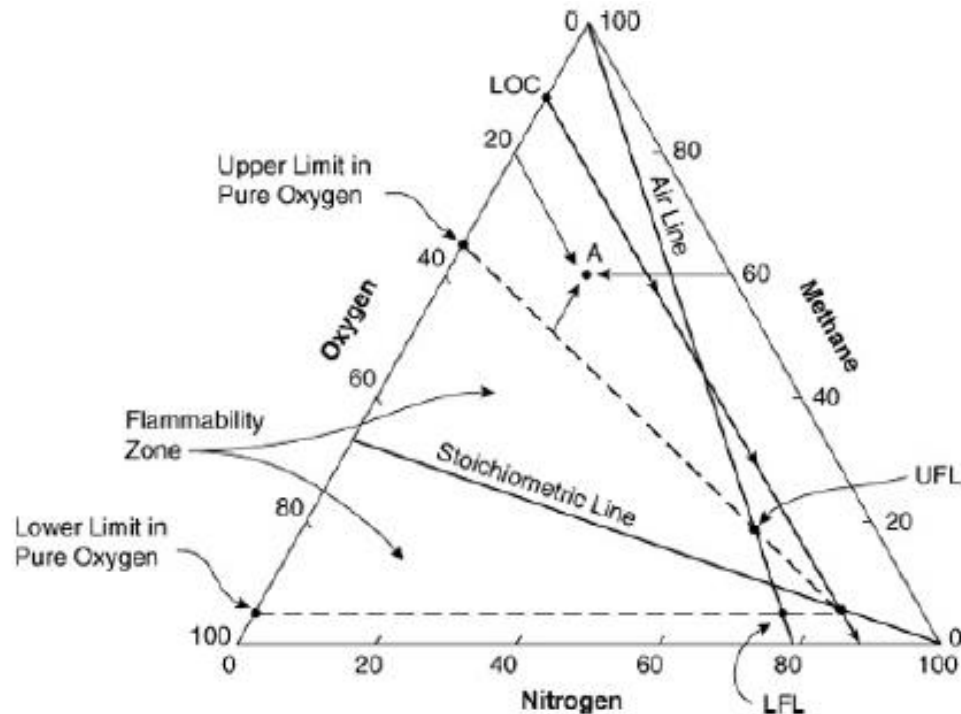
$$\text{LOC} = z (\text{LFL}),$$

$$\text{LOC} = \left(\frac{\text{LFL} - C_{\text{LOC}}\text{UFL}}{1 - C_{\text{LOC}}} \right) \left(\frac{\text{UFL}_0}{\text{UFL}} \right)$$

- ▶ C_{LOC} is a fitting constant

Flammability Diagram

- ▶ Each apex of the triangle represents either 100% fuel, oxygen, or nitrogen
- ▶ Point A represents a mixture composed of 60% methane, 20% oxygen, and 20% nitrogen.
- ▶ The zone enclosed by the dashed line represents flammable mixture



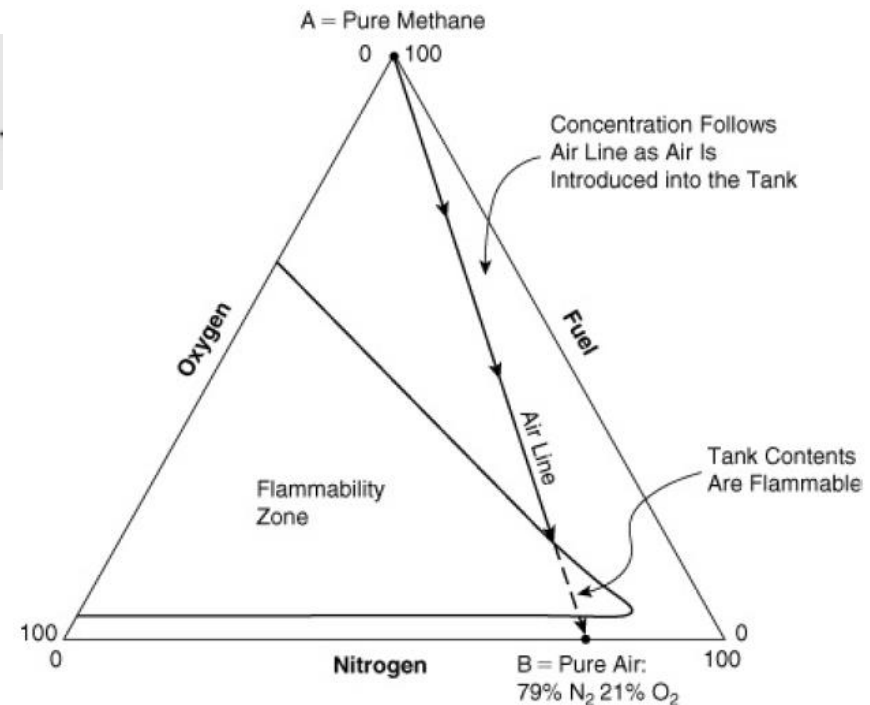
Flammability Diagram

- ▶ The air line represents all possible combinations of fuel plus air.
- ▶ The air line extends from the point where fuel is 0%, oxygen is 21%, and nitrogen is 79% to the point where fuel is 100%, oxygen is 0%, and nitrogen is 0%.

$$\text{Fuel \%} = -\left(\frac{100}{79}\right) \times \text{nitrogen \%} + 100.$$

Fuel + zO₂ → combustion products,

$$\text{Fuel \%} = \frac{100 - \text{Nitrogen \%}}{(1 + z)}$$



Ignition Energy

- ▶ The minimum ignition energy (MIE) is the minimum energy input required to initiate combustion.
- ▶ All flammable materials (including dusts) have MIEs.
- ▶ The MIE depends on the specific chemical or mixture, concentration, pressure, and temperature.
 - The MIE decreases with an increase in pressure
 - The MIE of dusts is at energy levels somewhat higher than combustible gases
 - An increase in nitrogen concentration increases MIE

Chemical	Minimum ignition energy (mJ)
Acetylene	0.020
Benzene	0.225
1,3-Butadiene	0.125
<i>n</i> -Butane	0.260
Cyclohexane	0.223

Autoignition

- ▶ Temperature at which the vapor ignites spontaneously from the energy of the environment.
- ▶ Sometimes called spontaneous ignition temperature (SIT)
- ▶ Function of the concentration of vapor, volume of vapor, pressure of the system, presence of catalytic material, and flow conditions.


▶

Compound	Autoignition temperature^d °C
<i>Paraffin hydrocarbons</i>	
Methane	600
Ethane	515
Propane	450
Butane	405
Isobutane	460
Pentane	260
Isopentane	420
Neopentane	450
Hexane	234

Auto-Oxidation

- ▶ Process of slow oxidation with accompanying evolution of heat,
- ▶ sometimes leading to auto-ignition if the energy is not removed **from the system**.
- ▶ Liquids with relatively **low volatility** are particularly susceptible to this problem.
- ▶ Liquids with high volatility are less susceptible to autoignition because they **self-cool** as a result of evaporation

Examples

- ▶ Oils on a rag in a warm storage area,
 - ▶ insulation on a steam pipe saturated with certain polymers,
 - ▶ Filter aid saturated with certain polymers
- 

Adiabatic Compression

- ▶ Additional means of ignition is adiabatic compression
- ▶ Gasoline and air in an automobile cylinder will ignite if the vapors are compressed to an adiabatic temperature that exceeds the autoignition temperature
- ▶ accidents have been caused by flammable vapors being sucked into the intake of air compressors
- ▶ Adiabatic temperature increase for an ideal gas is computed from the thermodynamic adiabatic compression equation

$$T_f = T_i \left(\frac{P_f}{P_i} \right)^{(\gamma-1)/\gamma}$$

T_f is the final absolute temperature,

T_i is the initial absolute temperature,

P_f is the final absolute pressure,

P_i is the initial absolute pressure, and

$\gamma = C_p/C_v$.

Ignition Sources

- The sources of ignition are numerous; consequently it is impossible to identify and eliminate them all
- prevent a fire or explosion by ignition from an unidentified source
- Combinations of sources must also be investigated
- The goal is to eliminate or minimize ignition sources

Electrical (wiring of motors)	23%
Smoking	18%
Friction (bearings or broken parts)	10%
Overheated materials (abnormally high temperatures)	8%
Hot surfaces (heat from boilers, lamps, etc.)	7%
Burner flames (improper use of torches, etc.)	7%
Combustion sparks (sparks and embers)	5%

Sprays and Mists

- ▶ Static electricity is generated when mists or sprays pass through orifices.
- ▶ A charge may accumulate and discharge in a spark.
- ▶ If flammable vapors are present, explosion will occur.
- ▶ Mists and sprays also affect flammability limits.
- ▶ For suspensions with drop diameters less than 0.01 mm, the LFL is virtually the same as the substance in vapor form
- ▶ Mists with drop diameters between 0.01 mm and 0.2 mm the LFL decreases as the drop diameter increases
- ▶ Sprays have drop diameters between 0.6 mm and 1.5 mm, flame propagation is impossible

Explosions

- ▶ Explosion behavior is difficult to characterize
- ▶ An explosion results from the rapid release of energy
- ▶ Damage from explosion caused by dissipating energy
- ▶ A pressure wave propagating called a **blast wave** because the pressure wave is followed by a strong wind
- ▶ highly explosive materials, such as TNT,

Detonation and Deflagration

- ▶ Damage effects from an explosion
- ▶ Difference whether reaction front propagates above or below the speed of sound
- ▶ Sound or sonic velocity is a function of temperature only and has a value of 344 m/s (1129 ft/s) at 20°C
- ▶ Detonation, resulting in a reaction front and leading shock wave that propagates above the sonic velocity.

Explosions

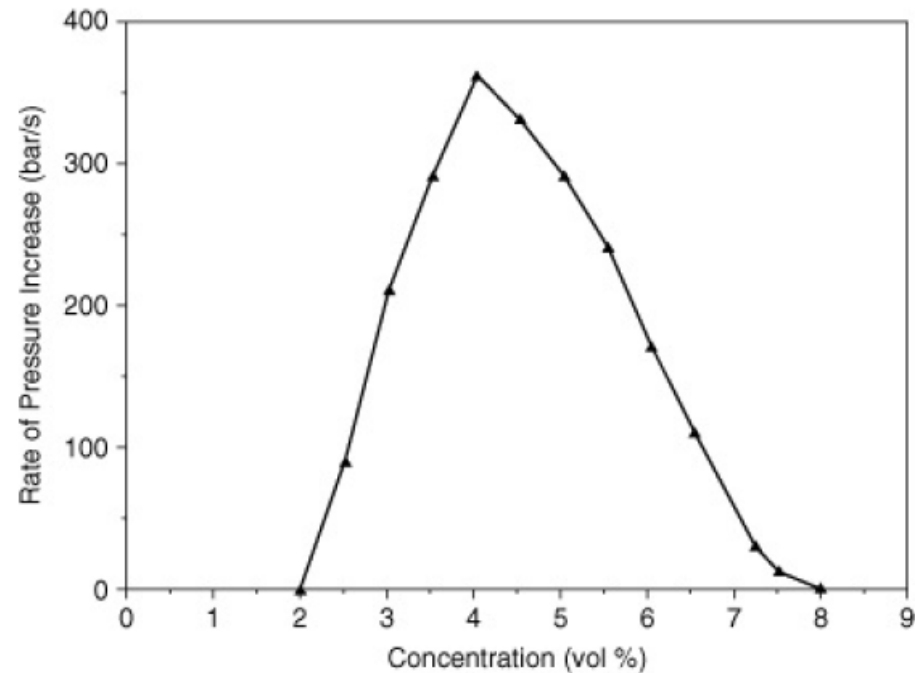
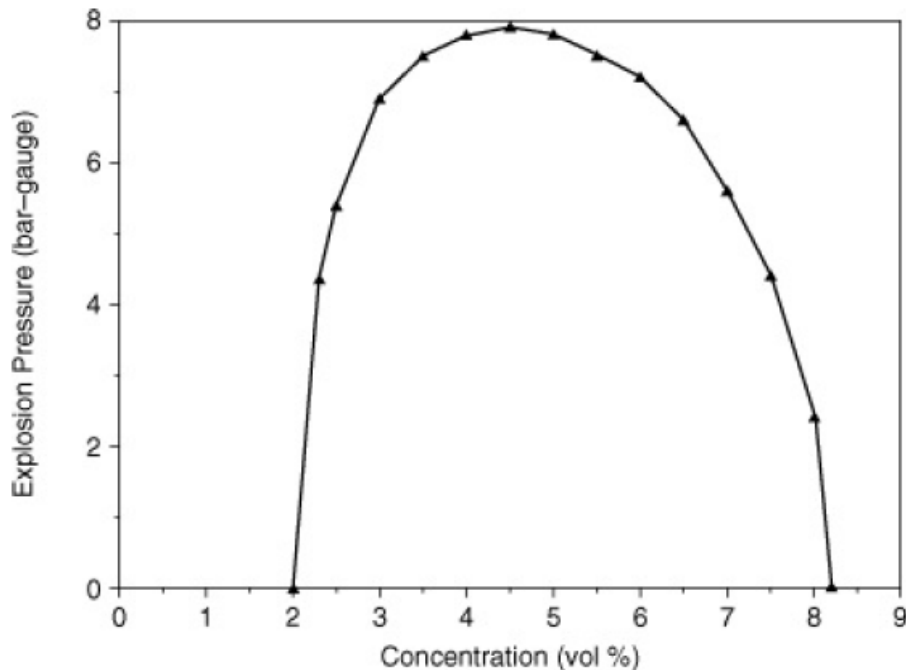
- ▶ Deflagration processes are relatively slow, speed less than the sonic velocity

Confined Explosions

- ▶ A confined explosion occurs in a confined space, such as a vessel or a building
- ▶ confined explosion scenarios involve explosive vapors and explosive dusts
- ▶ Explosion is function of several experimentally characteristics
- ▶ Characteristics depend on the explosive material used and include flammability or explosive limits, the rate of pressure rise after the flammable mixture is ignited, and the maximum pressure after ignition

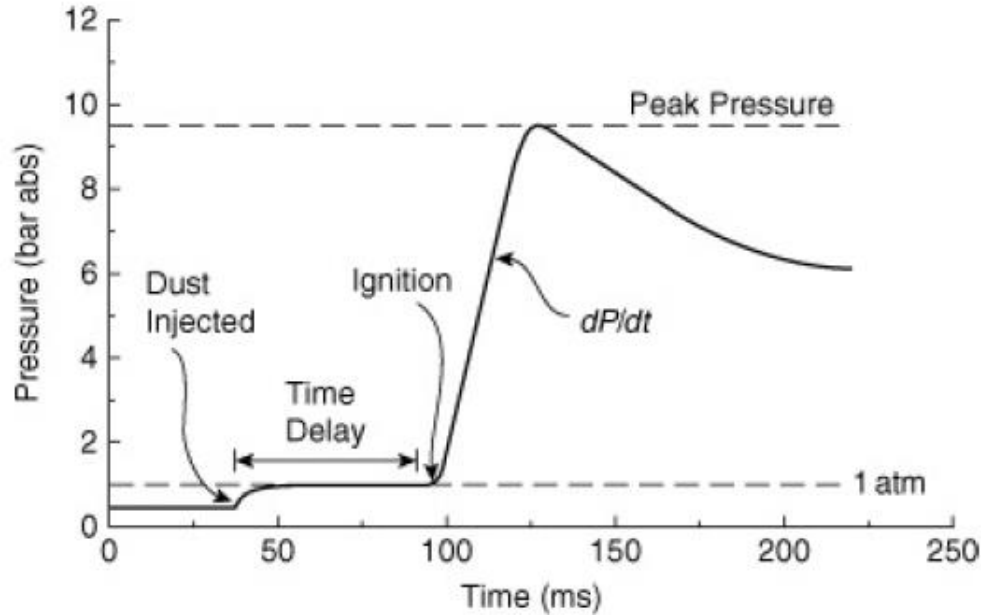
Explosions

- ▶ Pressure rate and maximum explosion pressure as a function of vapor concentration.
- ▶ The maximum pressure rate does not necessarily occur at the maximum pressure.



Explosions

- ▶ Pressure data from dust explosion device



- ▶ **Explosion Characteristics**

$$(dP/dt)_{\max} V^{1/3} = \text{constant} = K_G$$

$$(dP/dt)_{\max} V^{1/3} = K_{St}$$

K_G and K_{St} are the deflagration indexes for gas and dust, respectively

TNT Equivalency

- ▶ known energy of a combustible fuel to an equivalent mass of TNT

$$m_{\text{TNT}} = \frac{\eta m \Delta H_c}{E_{\text{TNT}}}$$

- m_{TNT} is the equivalent mass of TNT (mass),
 - η is the empirical explosion efficiency (unitless),
 - m is the mass of hydrocarbon (mass),
 - ΔH_c is the energy of explosion of the flammable gas (energy/mass), and
 - E_{TNT} is the energy of explosion of TNT
- ▶ Typical value for the energy of explosion of TNT is
1120 cal/g = 4686 kJ/kg = 2016 Btu/lb

TNT Equivalency

$$z_e = \frac{r}{m_{\text{TNT}}^{1/3}}$$

m_{TNT} , and the distance from the ground-zero point of the explosion, denoted r .

Example: One kilogram of TNT is exploded. Compute the overpressure at a distance of 30 m from the explosion.

Solution

The value of the scaling parameter is determined

$$\begin{aligned} z_e &= \frac{r}{m_{\text{TNT}}^{1/3}} \\ &= \frac{30 \text{ m}}{(1.0 \text{ kg})^{1/3}} = 30 \text{ m kg}^{-1/3} \end{aligned}$$

$$p_s = \frac{p_o}{p_a}$$

- ▶ p_s is the scaled overpressure (unit less),
- ▶ p_o is the peak side-on overpressure, and
- ▶ p_a is the ambient pressure

Energy of Chemical Explosions

- ▶ Chemical explosion is generated by the rapid expansion of gases at the explosion site.
- ▶ This expansion can be caused by two mechanisms:
 - (1) thermal heating of the reaction products and
 - (2) the change in the total number of moles by reaction.
- Change in the number of moles is small
- Almost all the blast energy must be due to thermal energy
- Heat of combustion is used, but the reaction energy can be easily computed using standard heats of formation

Energy of Mechanical Explosions

- ▶ Energy is obtained from the energy content of the contained substance
- ▶ Failure of a tire full of compressed air
- ▶ Four methods are used to estimate the energy of explosion for a pressurized gas:
 - Brode's equation
 - isentropic expansion
 - isothermal expansion
 - thermodynamic availability
- Brode's method: Energy required to raise the pressure of the gas at constant volume

$$E = \frac{(P_2 - P_1)V}{\gamma - 1}$$

- ▶ **Isentropic expansion:** method assumes that the gas expands **isentropically** from its initial to final state

$$E = \left(\frac{P_2 V}{\gamma - 1} \right) \left[1 - \left(\frac{P_1}{P_2} \right)^{(\gamma-1)\gamma} \right]$$

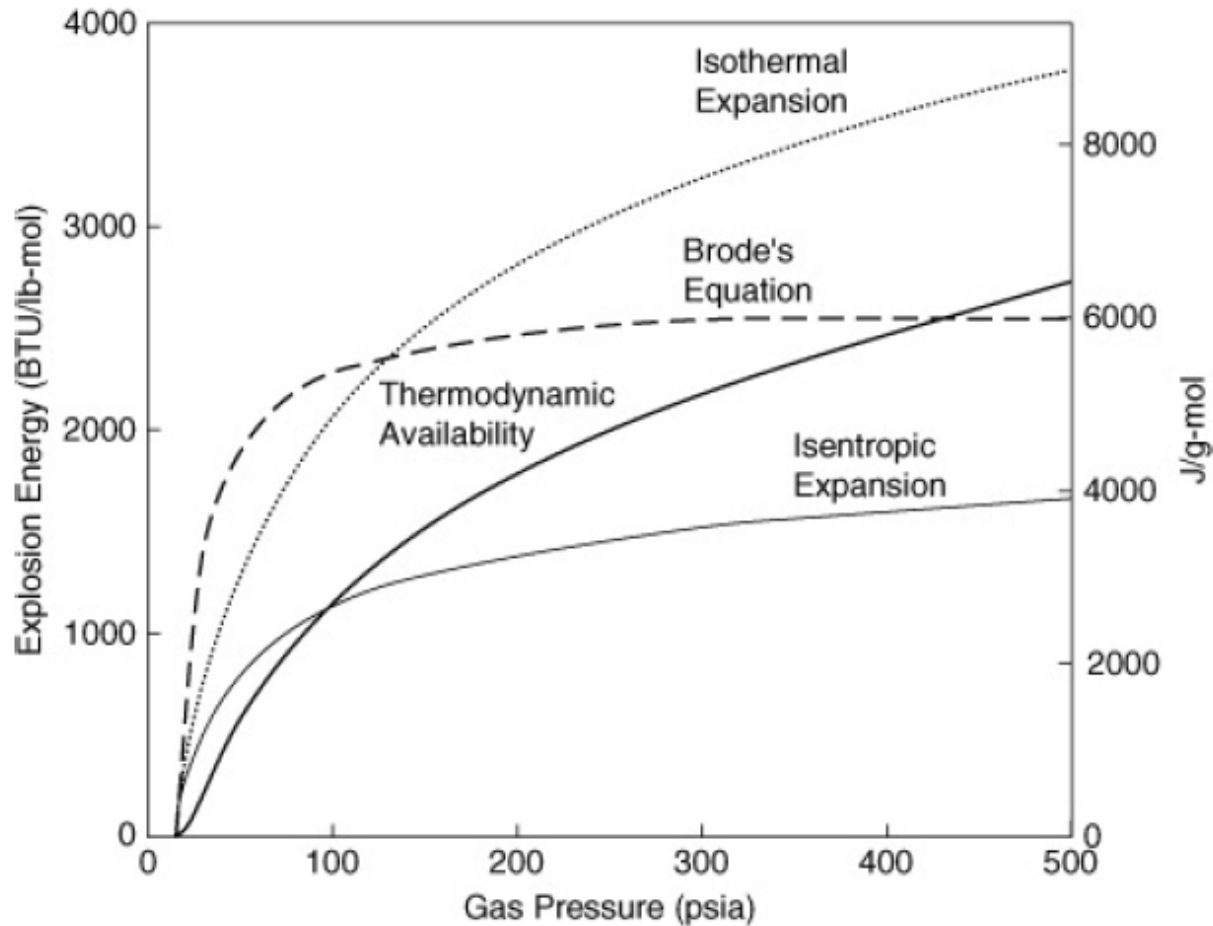
- ▶ **Isothermal expansion:** case assumes that the gas expands **isothermally**

$$E = R_g T_1 \ln \left(\frac{P_2}{P_1} \right) = P_2 V \ln \left(\frac{P_2}{P_1} \right)$$

- ▶ **Thermodynamic availability:** maximum mechanical energy extractable from a material as it comes into equilibrium with the environment

$$E = P_2 V \left[\ln \left(\frac{P_2}{P_1} \right) - \left(1 - \frac{P_1}{P_2} \right) \right]$$

Energy of explosion for a compressed inert gas



Vapor Cloud Explosions

- ▶ The most dangerous and destructive explosions in the chemical process industries
- ▶ These explosions occur in a sequence of steps:
 - Sudden release of a large quantity of flammable vapor (vessel, containing a superheated and pressurized liquid, ruptures),
 - Dispersion of the vapor throughout the plant site while mixing with air,
 - Ignition of the resulting vapor cloud.

Case: The accident at Flixborough, England VCE.

A sudden failure of a 20-inch cyclohexane line between reactors led to vaporization of an estimated 30 tons of cyclohexane. unknown source 45 seconds after the release.

The entire plant site was leveled and 28 people were killed.

Vapor Cloud Explosions

▶ Qualitative studies

- (1) the ignition probability increases as the size of the vapor cloud increases,
- (2) vapor cloud fires are more common than explosions,
- (3) the explosion efficiency is usually small (approximately 2%)
- (4) turbulent mixing of vapor and air and ignition of the cloud

▶ Methods that are used to prevent

- ✓ VCEs include keeping low inventories of volatile, flammable
- ✓ Process conditions that minimize flashing
- ✓ Analyzers to detect leaks at low concentrations
- ✓ Installing automated block valves to shut systems down while the spill is in the incipient stage of development.

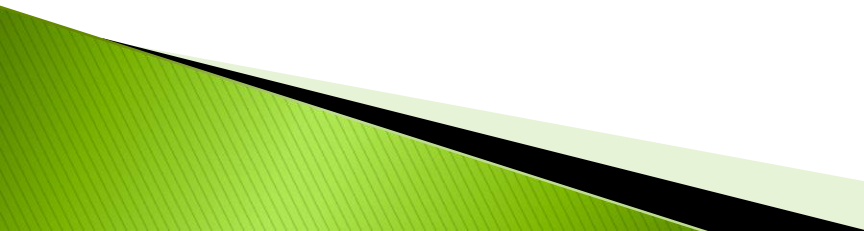
Boiling-Liquid Expanding-Vapor

- ▶ BLEVEs are caused by the **sudden failure** of the container as a result of any cause (commonly is caused by fire)
- ▶ A BLEVE occurs when a tank containing a liquid held above its atmospheric pressure **boiling point ruptures**, materials are flammable, a VCE might result;
- ▶ Toxic, a large area might be **subjected to toxic materials**
- ▶ For either situation the energy released by the BLEVE, in considerable damage.
- ▶ boiling and burning liquid behaves as a **rocket fuel**, propelling vessel parts for great distances
- ▶ Only a fraction of **the liquid vaporizes**
- ▶ the amount depends on the physical and thermodynamic conditions

Boiling-Liquid Expanding-Vapor

Most **common type** of BLEVE is caused by **fire**

The steps are as follows:

- A fire develops adjacent to a tank containing a liquid.
 - The fire heats the walls of the tank.
 - The tank walls below liquid level are cooled by the liquid, increasing the liquid temperature and the pressure in the tank.
 - If the flames reach the tank walls or roof where there is only vapor and no liquid to remove the heat, the tank metal temperature rises until the tank loses its structural strength.
 - The tank ruptures, explosively vaporizing its contents
- 

Thanks