# CENTRAL POLYTECHNIC COLLEGE

## THARAMANI, CHENNAI

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## 1122 Diploma in Fire Technology and Safety

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**UNIT 2 BASIC CHEMISTRY AND PHYSICS OF FIRE**

Atomic structure - Elements, compounds - Pure substance and mixture - Physical and chemical changes - Condition for the changes - Energy changes - Effects of heat on matter – Combustion – Temperature - Specific heat capacity – Catalyst –Neutralization – Sublimation - Heat of decomposing - Chemical reaction - Exothermic reaction and endothermic reaction - Transmission of heat - Flash and fire point -Ignition temperature.

## Atomic structure

**Atomic structure** refers to the arrangement and organization of subatomic particles—protons, neutrons, and electrons—that make up an atom.

At its simplest:

- **Nucleus:** The tiny, dense center made of positively charged **protons** and uncharged **neutrons**, which together contain nearly all of the atom's mass.
- **Electron Cloud:** The surrounding region of mostly empty space where negatively charged **electrons** move rapidly in specific energy levels or orbitals, bound to the nucleus by electromagnetic attraction.

In essence, atomic structure defines how these fundamental particles are configured, which determines the physical identity, chemical properties, and behavior of every chemical element.

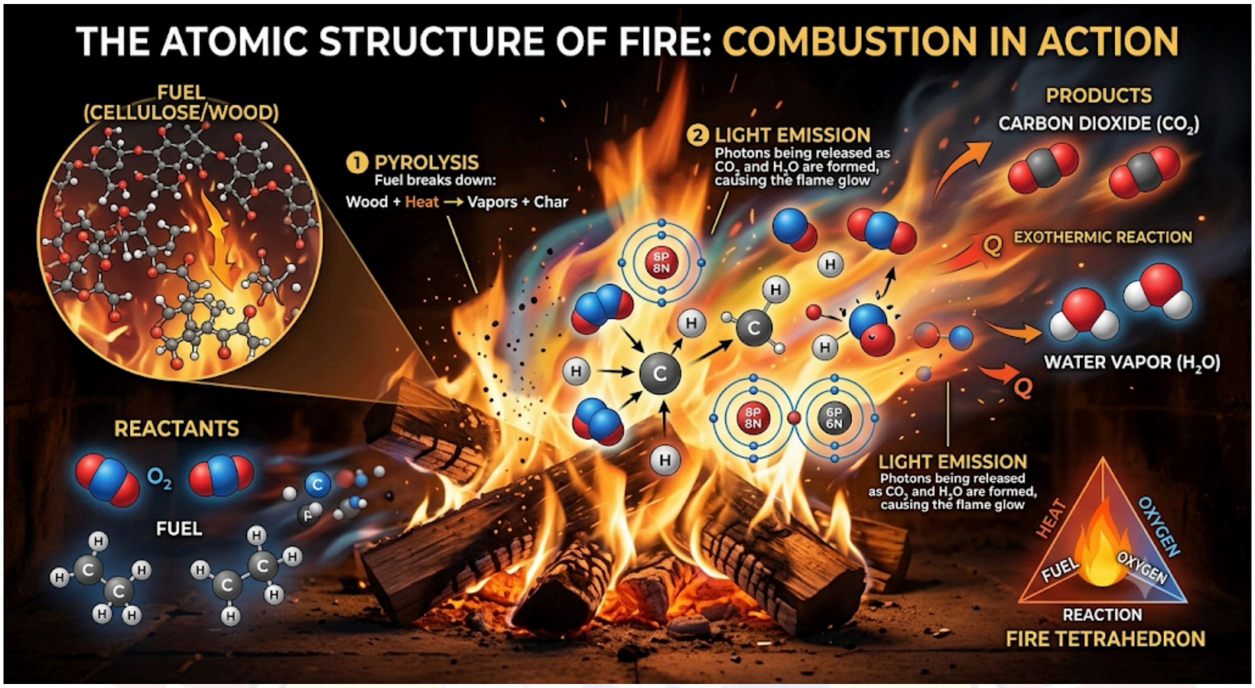
Fire isn't a substance, element, or single molecule, so **it does not have its own atomic structure**.

Instead, fire is an **exothermic chemical reaction in action**—specifically, a rapid process called **combustion**. What you see as a flame is a localized region of hot gases, unburned soot particles, free radicals, and excited molecules releasing energy.

### What Fire Is Made Of (At the Atomic Level)

When fuel (like wood, methane, or candle wax) reacts with oxygen ($\text{O}_2$), thermal energy breaks the chemical bonds holding the fuel together. At any given instant, the flame contains a shifting soup of four main components:

- **Reactants:** Fuel molecules (typically hydrocarbons consisting of carbon and hydrogen atoms) and oxygen gas
- **Free Radicals (Short-Lived Fragments):** High heat splits molecules into extremely reactive, unstable fragments such as hydroxyl radicals , methyl radicals , and dicarbon .
- **Final Products:** Stable output molecules—primarily carbon dioxide  and water vapor
- **Trace Plasma:** At high temperatures, a tiny fraction of gas atoms lose electrons, forming ionized gas (plasma).




__Elements, compounds__

**Elements and compounds are the two pure forms of matter**, defined by how their constituent atoms are combined.

- **Element:** A pure chemical substance consisting of only **one type of atom**. Elements cannot be broken down into simpler substances by any chemical reaction.
    - Examples: Gold ,Oxygen gas , Hydrogen , Carbon .
    -
- **Compound:** A pure chemical substance formed when **two or more different elements** are chemically bonded together in fixed, definite proportions. Compounds can be broken down into their individual elements through chemical reactions.
    - Examples: Water , Carbon Dioxide

fire is an **exothermic chemical reaction in action** (combustion) rather than a static substance, it does not have a single fixed formula. Instead, a fire consists of a dynamic, shifting mixture of **elemental reactants**, **intermediate radical compounds**, and **final product compounds**.

Here is the breakdown of the primary elements and compounds involved in fire:

**1. Elements Involved in Fire**

In chemistry, an element consists of only one type of atom. The elements present in fire exist either as individual unbonded atoms, free radicals, or homonuclear diatomic molecules:

- **Oxygen :** The critical elemental gas required to sustain combustion. It reacts with fuel at high temperatures to oxidize carbon and hydrogen atoms.
- **Carbon :** Present as free carbon atoms, carbon radicals, and microscopic soot particles. Heated unburned carbon soot clusters glow brightly, giving fires their characteristic yellow and orange light.
- **Hydrogen :** Exists as elemental hydrogen gas or short-lived hydrogen radicals formed when fuel molecules break apart under extreme heat.
- **Nitrogen :** Makes up about 78% of the surrounding air. While mostly an inert bystander in fire, at high flame temperatures it reacts with oxygen to form nitrogen oxides .

**2. Compounds Involved in Fire**

A compound consists of two or more different elements chemically bonded together. Fire involves compounds in three main stages:

**A. Reactant Compounds (The Fuels)**

- **Hydrocarbons:** Fuels like methane , propane , and gasoline vapor containing carbon and hydrogen.
- **Cellulose and Lignin :** The primary organic compounds found in wood, paper, and plant matter.

**B. Intermediate Compounds & Free Radicals (Short-Lived)**

During the high-energy reaction, heat breaks down fuel molecules into unstable, highly reactive intermediate compounds and radical fragments:

- **Hydroxyl Radical :** Drives the chain reaction of burning.
- **Carbon Monoxide :** A poisonous intermediate compound produced during incomplete combustion when oxygen is limited.
- **Formaldehyde & Acrolein:** Volatile organic compounds produced when complex fuels incompletely break down (pyrolysis).

**C. Product Compounds (The Outputs)**

When combustion goes to completion, the chemical reaction reorganizes the atoms into stable output compounds:

- **Carbon Dioxide :** The primary carbon-based gaseous product of complete combustion.
- **Water Vapor :** Produced when hydrogen from the fuel combines with oxygen.

**Summary of the Fire Chemical Reaction**

For a simple hydrocarbon fire (like burning natural gas/methane), the elemental rearrangement between compounds looks like this:

$$\underbrace{CH_4}_{\text{Compound (Fuel)}} + \underbrace{2O_2}_{\text{Element (Oxygen)}} \xrightarrow{\text{Heat}} \underbrace{CO_2}_{\text{Compound (Product)}} + \underbrace{2H_2O}_{\text{Compound (Product)}}$$

**<u>Pure substance and mixture</u>**

**Pure Substance:** Matter that has a **constant, uniform chemical composition** and consistent physical and chemical properties throughout. A pure substance consists of only one type of particle (either a single type of atom or a single type of chemical compound) and cannot be separated into simpler components by physical methods like filtering, evaporation, or magnetic separation.

- Types: Elements (e.g., pure Gold , Oxygen gas ) and Compounds (e.g., Pure Water , Table Salt ).

**Mixture:** Matter formed when **two or more pure substances are physically combined** without undergoing a chemical reaction. Because the components are not chemically bonded together, each substance retains its individual chemical identity and properties. Mixtures can be separated back into their original components using physical methods.

- Types:
    - **Homogeneous Mixtures (Solutions):** Uniform in appearance and composition throughout (e.g., Saltwater, Air, Brass).
    - **Heterogeneous Mixtures:** Non-uniform composition where individual components are visibly distinct (e.g., Oil and Water, Salad, Granite).

**Fire is a mixture.**

Specifically, fire is a dynamic, gas-phase **heterogeneous mixture** created during a combustion reaction.

**Why Fire Is a Mixture (and Not a Pure Substance)**

1. **It Contains Multiple Substances:** Fire is not composed of a single element or compound. At any given moment, a flame is composed of a changing combination of:
    - **Reactants:** Fuel molecules (e.g., methane, cellulose, wax) and oxygen gas
    - **Products:** Carbon dioxide , water vapor , and carbon monoxide .
    - **Intermediates:** Free radicals , and unburned soot particles (solid carbon clusters).
2. **Components Are Not Chemically Bonded Together as One:** The gases, radicals, and glowing soot in a flame exist side by side in physical contact, but they are not bonded into a single uniform molecule.
3. **Variable Composition:** The exact makeup of a fire changes depending on the fuel, temperature, and available oxygen. A candle flame, a wood campfire, and a natural gas stove flame all contain different ratios of gases and particles.
4. **It Is Non-Uniform (Heterogeneous):** Different parts of a flame contain different things. The blue base of a flame is rich in short-lived free radicals like while the bright yellow tip contains glowing solid soot particles suspended in hot gas.

<u>**Physical and Chemical changes**</u>

**Physical changes associated with fire:**

Physical changes alter the form, state, or appearance of matter without changing its underlying chemical identity. Before and during a fire, thermal energy causes several key physical transformations:

- **Phase Changes in Fuel (Melting & Vaporization):** Solid or liquid fuels do not burn directly; they must first change into a gas phase.
    - Candle wax melts from a solid to a liquid, travels up the wick, and vaporizes into a gas.
    - Liquid gasoline or alcohol rapidly vaporizes into gas before igniting.
- **Thermal Expansion:** As gases (like air and water vapor) heat up inside and around the flame, they expand rapidly, lowering their density and causing hot gases to rise (convection).
- **Emission of Light & Radiant Heat (Incandescence):** Unburned carbon soot particles in the flame get heated to thousands of degrees and glow yellow/orange, emitting blackbody radiation. Light emission itself is a physical energy release.


**Chemical Changes (Bond Breaking & Rearrangement)**

A chemical change occurs when substances react to break old chemical bonds and form entirely new chemical substances with different properties. Fire is fundamentally a series of rapid oxidation reactions.

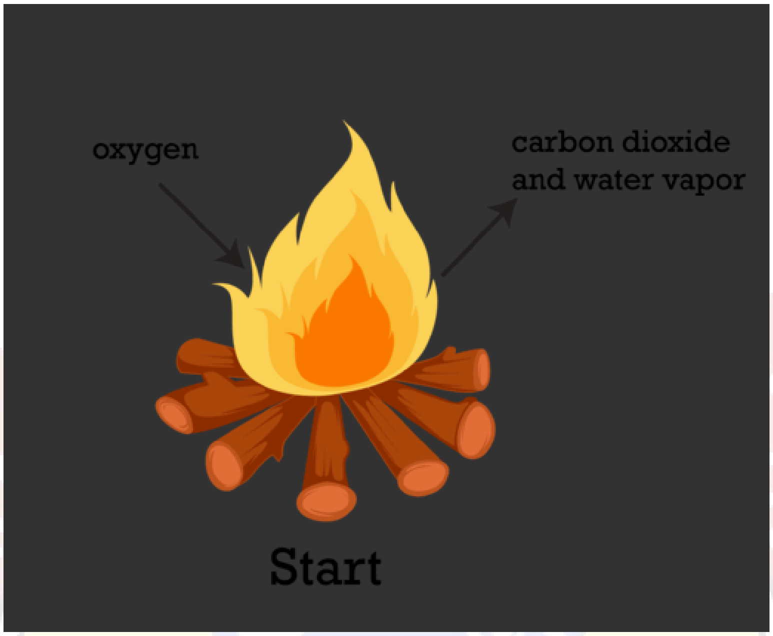
- **Pyrolysis (Thermal Decomposition):** Heavy organic solids (like wood) are broken down by intense heat into smaller, volatile gaseous molecules, char, and tar before even reacting with oxygen.
- **Combustion (Oxidation):** Vaporized fuel molecules react chemically with oxygen gas in air.

$$\text{Fuel (Hydrocarbons)} + \text{Oxygen } (O_2) \xrightarrow{\text{Heat}} \text{Carbon Dioxide } (CO_2$$

**Formation of New Substances:**

- Wood or gas (hydrocarbons) and oxygen gas are consumed.
- Completely new compounds are produced: **carbon dioxide** , **water vapor ,** and toxic **carbon monoxide** during incomplete combustion.

**Irreversibility:** Once the fuel is transformed into ash, smoke, and water vapor, you cannot simply cool them down to get the original wood or gas back.




| Feature | Physical Changes in Fire | Chemical Changes in Fire |
|---|---|---|
| Primary Examples | Melting wax, vaporizing fuel, gas expansion, soot glowing | Pyrolysis of wood, burning methane into CO2 and H2O |
| Chemical Identity | Remains the same (e.g., liquid wax is still wax) | Changes completely (hydrocarbons become CO2 and H2O |
| Reversibility | Often reversible (e.g., wax vapors can re-solidify) | Irreversible (ash and exhaust gases cannot easily reform fuel) |

**Condition for the physical and chemical changes due to fire**

When fire interacts with matter, it triggers a combination of physical changes (alterations in state, form, or appearance without changing chemical identity) and chemical changes (alterations that transform the substance into entirely new chemical products).

Whether these changes occur depends on specific conditions. Here is a breakdown of the conditions required for both:

1. Conditions for Chemical Changes Due to Fire

A chemical change caused by fire is fundamentally a combustion reaction (an oxidation reaction). For this to happen, the conditions must satisfy the classic Fire Tetrahedron:

Presence of Fuel: There must be a combustible material (solid, liquid, or gas) containing elements that can be oxidized, typically carbon and hydrogen.

Presence of an Oxidizer (Oxygen): Generally, a minimum oxygen concentration of about 16% in the air is required to sustain a fire.

Sufficient Heat (Activation Energy): The temperature must reach the material's ignition point to break existing chemical bonds and kickstart the reaction.

Self-Sustaining Chain Reaction: The heat generated by the fire must be enough to keep vaporizing more fuel and reacting with oxygen, maintaining a continuous loop.

What happens chemically?

The original molecules break down and recombine with oxygen. For example, burning wood (cellulose) yields entirely new substances:

$$\text{Cellulose} + O_2 \rightarrow CO_2 + H_2O + \text{Ash} + \text{Heat/Light}$$

2. Conditions for Physical Changes Due to Fire

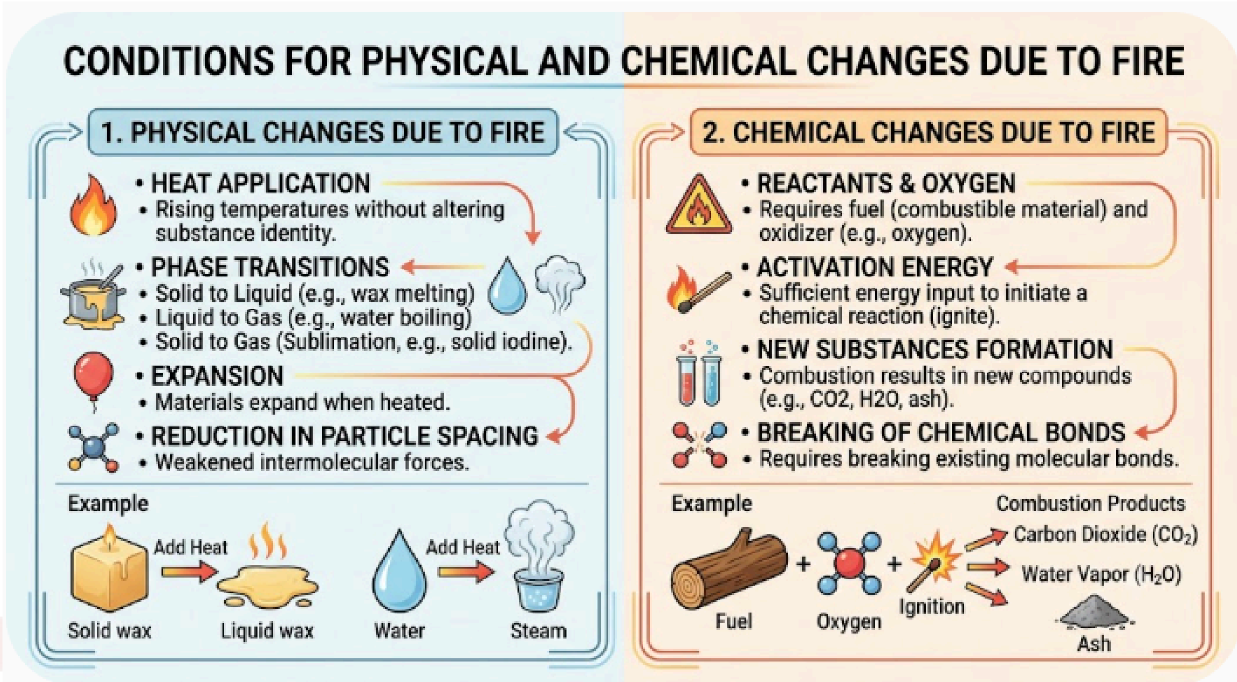
Physical changes often accompany or precede chemical changes. They do not create new substances but alter the physical state of the matter. The primary conditions required are:

Thermal Energy Input (Heat): The temperature must rise enough to increase kinetic energy at the molecular level, forcing phase changes or thermal expansion.

Reaching Specific Phase Transition Points: * Melting: The temperature must reach the material's melting point (e.g., wax melting near a candle flame, or metal warping in an intense fire).

Vaporization/Pyrolysis: Liquids must hit their boiling point. For solids like wood, heat causes pyrolysis—turning the solid into flammable gases before it actually burns.

Thermal Gradients: Rapid or uneven heating causes different parts of a material to expand at different rates, leading to physical fracturing (like glass cracking in a fire).




<u>**Energy changes in fire**</u>

When a fire burns, it is essentially a grand display of energy transformation. Energy cannot be created or destroyed, but fire is incredibly efficient at converting stored potential chemical energy into kinetic, thermal, and electromagnetic energy.

Here is a breakdown of how energy changes and flows during a fire.

1. The Primary Energy Shift: Chemical to Thermal and Radiant Before a fire starts, the energy is "trapped" inside the chemical bonds of the fuel (like wood, gasoline, or wax). This is chemical potential energy.When the ignition temperature is reached, a chemical reaction (combustion) begins. The high-energy bonds in the fuel and oxygen break, and new, lower-energy bonds form to create carbon dioxide  and water . The "leftover" energy from this bond rearrangement is violently released into the surroundings.

[Chemical Potential Energy in Fuel]

|

▼ (Combustion Reaction)

[Thermal Energy (Heat)] + [Radiant Energy (Light)]

Thermal Energy (Heat): The broken bonds release kinetic energy at the molecular level, causing the surrounding molecules to move and vibrate rapidly. We experience this as a rise in temperature.

Radiant Energy (Light): The intense heat excites electrons in the reacting gases and soot particles. As these electrons drop back down to lower energy states, they release energy as electromagnetic radiation—visible light (the flames) and infrared radiation (the heat you feel from a distance).

Thermodynamics: An Exothermic Process

Because a fire releases more energy than it absorbs to get started, it is classified as an exothermic reaction.

Activation Energy : This is the initial spark or heat source required to kickstart the fire. It pushes the fuel over the "energy hill" to break the initial chemical bonds.

Net Energy Release: Once the reaction starts, the energy released by forming and is vastly greater than the activation energy. This surplus heat feeds back into the unburned fuel, making the reaction self-sustaining.

Energy Transfer Mechanisms (How the Heat Moves)

Once chemical energy is converted into thermal energy, that heat immediately begins to move away from the fire to areas of lower temperature via three distinct physical mechanisms:

Conduction

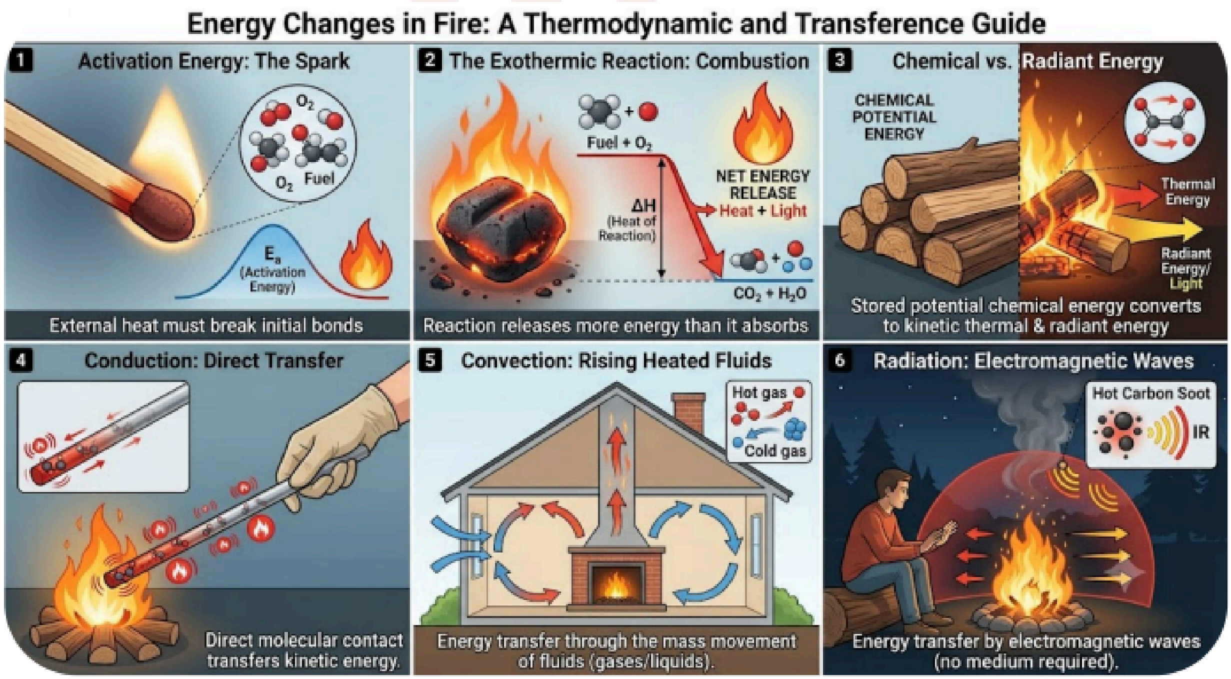
The transfer of thermal energy through direct contact. In a fire, if a metal poker is left in the flames, the rapidly vibrating molecules at the hot end bump into neighboring molecules, passing the kinetic energy down the rod until the handle becomes hot.

Convection

The transfer of heat through the movement of fluids (liquids or gases). As the fire heats the surrounding air, the air expands, becomes less dense, and rises. Cooler, denser air rushes in at the bottom to take its place, creating a convection current that carries thermal energy upward.

Radiation

The transfer of energy via electromagnetic waves. Unlike conduction and convection,radiation does not need a medium (like air or metal) to travel. You can feel the radiant energy of a campfire on your face even if the wind is blowing the hot air (convection) away from you.




## Effects of heat on matter:

When thermal energy (heat) is added to or removed from matter, it alters the behavior of the constituent atoms and molecules. Because heat is essentially the transfer of kinetic energy at a microscopic level, adding heat causes particles to move faster, while removing heat slows them down.

The effects of heat on matter can be broadly categorized into three types: physical changes, chemical changes, and biological changes.

1. Physical Effects of Heat

Physical effects change the state, size, or form of matter without altering its chemical composition.

A. Thermal Expansion and Contraction

As matter absorbs heat, its particles vibrate or move more violently. This pushes the particles slightly further apart, causing the material to expand. Conversely, cooling causes materials to contract.

Solids: Expand slightly (e.g., railway tracks can buckle on hot days, which is why they have expansion joints).

Liquids: Expand more than solids (e.g., mercury or alcohol rising in a thermometer).

Gases: Expand the most because their particles are free to move entirely apart.

B. Change of State (Phase Transitions)

Providing enough heat to a substance can break the intermolecular bonds holding its particles in a specific structure, forcing a phase change.

Note: Removing heat reverses these processes (Freezing, Condensation, and Deposition).

2. Chemical Effects of Heat

Unlike physical changes, heat can also supply the necessary activation energy to break internal chemical bonds, leading to the formation of entirely new substances.

3. Biological Effects of Heat

When matter is part of a living organism, heat alters the complex organic molecules necessary for life.

Summary of Heat's Effect on Particle Behavior

Melting: Solid becomes a liquid (e.g., ice turning to water).

Vaporization/Boiling: Liquid becomes a gas (e.g., water turning to steam).

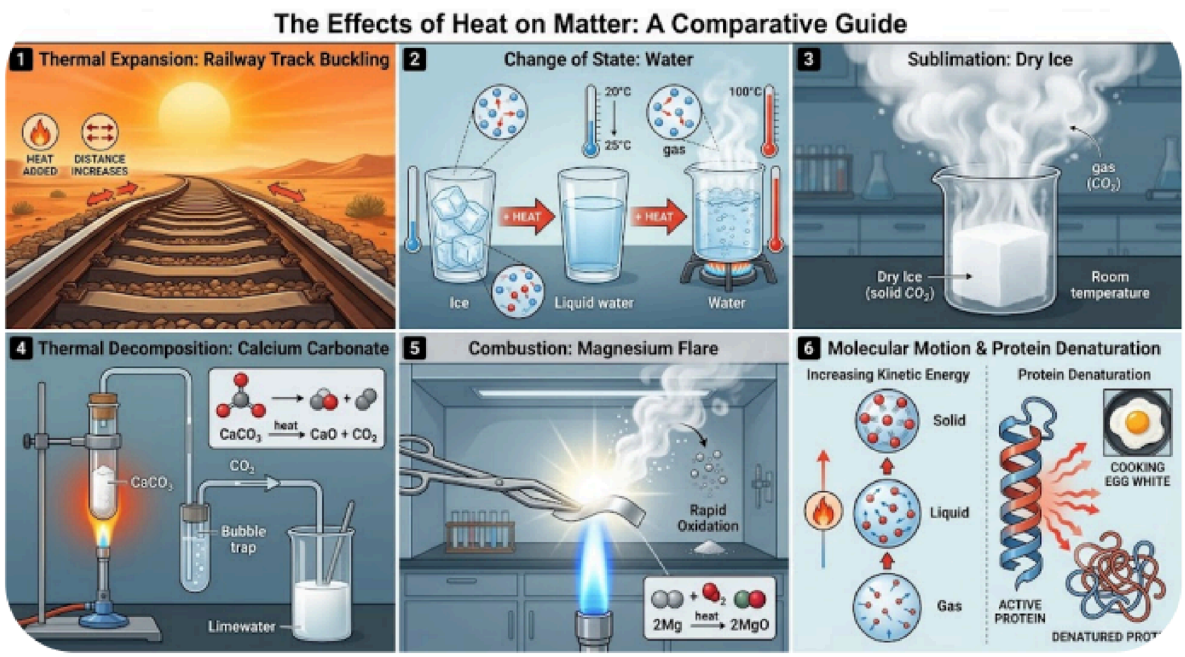
Sublimation: Solid turns directly into a gas without becoming a liquid (e.g., dry ice/frozen carbon dioxide).

Thermal Decomposition: Some compounds break down into simpler substances when heated. For example, heating calcium carbonate (limestone) breaks it down into calcium oxide and carbon dioxide gas:

$$CaCO_3 + Heat \rightarrow CaO + CO_2$$

Combustion (Burning): As seen in fires, heat can cause a substance to rapidly react with oxygen, releasing more heat and light while turning the original fuel into ash, carbon dioxide, and water vapor.

Accelerating Reactions: In general, heating a chemical mixture causes particles to collide more frequently and with greater force, significantly speeding up the rate of most chemical reactions.




## Combustion

In fire engineering, **combustion** isn't just "something catching fire"—it is defined as a complex, self-sustaining, exothermic chemical reaction between a fuel and an oxidant (usually oxygen), accompanied by the evolution of heat and light.

Understanding combustion is the bedrock of fire engineering because it dictates how fires start, spread, and how they can be effectively controlled or extinguished.

**The Fire Tetrahedron**

For decades, the "Fire Triangle" (Fuel, Oxygen, Heat) was the standard model. However, fire engineering recognizes the **Fire Tetrahedron**, which adds a critical fourth element: the **uninhibited chain reaction**.

- **Fuel:** The material being oxidized. In fire engineering, we analyze fuels based on their state (solid, liquid, gas), moisture content, and surface-area-to-mass ratio.
- **Oxidant:** Typically the ambient air, which contains about 21% oxygen. Fires generally need at least 16% oxygen to sustain flaming combustion.
- **Heat:** The energy required to raise the fuel to its ignition temperature and sustain pyrolysis (the thermal decomposition of solids into flammable gases).
- **Chemical Chain Reaction:** The rapid, self-sustaining transfer of energy at the molecular level via free radicals. If you disrupt this chain reaction (e.g., using clean agents or dry chemical powders), the fire dies even if fuel and oxygen are still present.

**Modes of Combustion**

Fire engineers classify combustion into two primary modes based on where the reaction occurs:

**1. Flaming Combustion (Gas-Phase)**

This occurs when volatile gases mix with oxygen and ignite.**Solid and Liquid Fuels:** Do not actually burn directly. Instead, heat causes liquids to evaporate and solids to undergo **pyrolysis**. The resulting vapors leave the surface and burn in the gas phase above the fuel.

**Premixed vs. Diffusion Flames:** * Premixed: Fuel and oxygen are mixed before ignition (like a Bunsen burner or a gas explosion).

Diffusion: Fuel vapor and oxygen meet at a flame front where diffusion takes place (like a standard house fire or a candle). Most structural fires are diffusion flames.

**2. Smoldering / Glowing Combustion (Solid-Phase)**

This is a slow, low-temperature, flameless form of combustion that occurs directly on the surface of porous solid fuels (e.g., charcoal, mattresses, insulation).It is uniquely dangerous because it can proceed at very low oxygen levels and produce massive amounts of toxic, incomplete combustion products (like Carbon Monoxide) before transitioning into an open flame.

**Chemistry of Combustion: Complete vs. Incomplete**

Fire engineers look closely at the chemical efficiency of a fire, represented by the general hydrocarbon combustion equation:

$$\text{Fuel} + O_2 \rightarrow CO_2 + H_2O + \text{Heat}$$

**Complete Combustion:** Occurs in ideal, well-ventilated laboratory conditions where the fuel is entirely converted to carbon dioxide and water vapor .

**Incomplete Combustion:** Occurs in almost all real-world structural fires. Because oxygen is limited or mixing is poor, the fuel doesn't burn completely. This yields highly toxic gases like Carbon Monoxide , Hydrogen Cyanide , and **soot** (unburnt carbon particles).

**Engineering Impact:** The production of soot reduces visibility, making evacuation difficult, while toxic gases are the leading cause of fatalities in fires, rather than burns.

**Key Metrics in Fire Engineering**

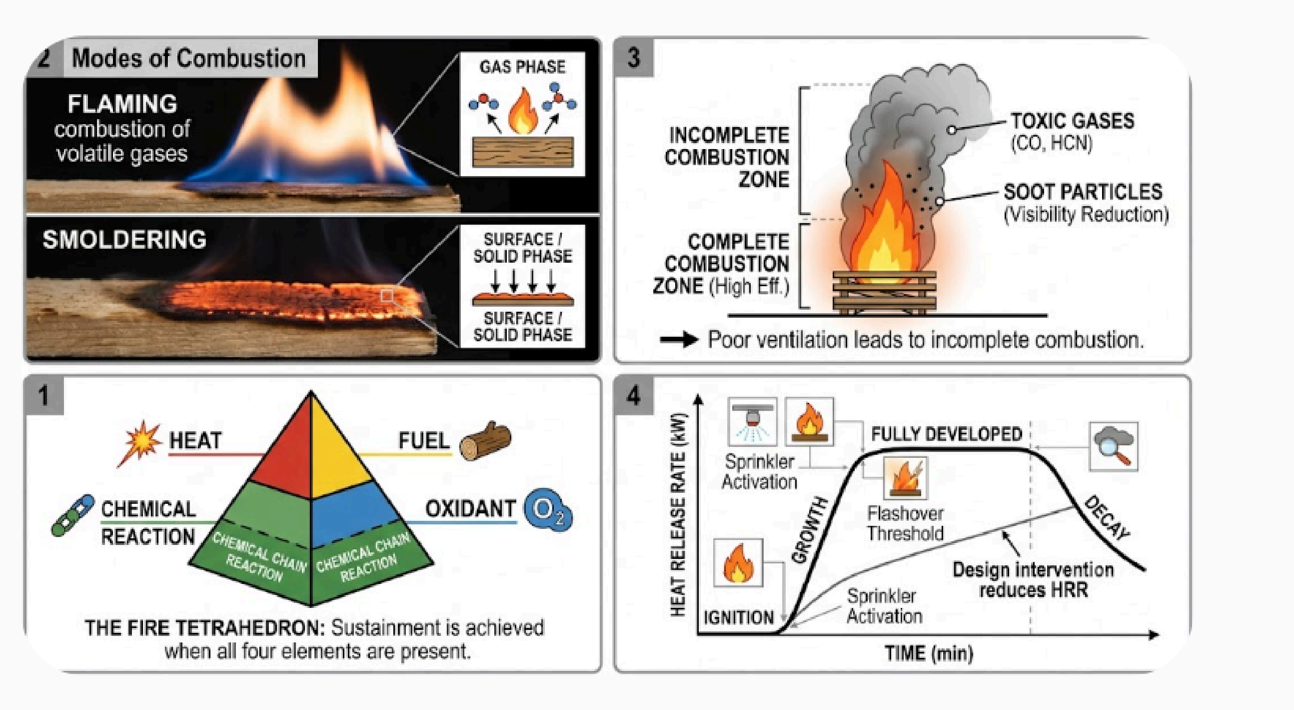
To design fire protection systems (like sprinklers or smoke control), engineers quantify combustion using several critical metrics:

**Heat Release Rate (HRR):** Measured in kilowatts (kW) or megawatts (MW), HRR is the single most important variable in fire protection engineering. It defines how much energy a fire outputs per second. A high HRR means rapid fire growth and faster structural failure.

**Flashpoint:** The lowest temperature at which a liquid produces enough vapor to form an ignitable mixture with air near its surface (but won't sustain burning).

**Fire Point:** The temperature at which the liquid produces enough vapor to sustain a continuous flame for at least 5 seconds.

**Flammability Limits:** The range of fuel vapor concentration in the air that can ignite. It is bounded by the Lower Flammable Limit (LFL)—too lean to burn—and the Upper Flammable Limit (UFL)—too rich to burn.




**Temperature :**

In fire engineering, **temperature** is not just a weather metric or a measure of hotness—it is the driving thermodynamic variable that governs fire growth, smoke movement, structural failure, and human tenability.

Engineers analyze temperature across different domains: the gas layer, the fuel surface, and the building's structural elements.

### 1. Key Temperature Thresholds in Fire Dynamics

Fire engineers use specific temperature milestones to predict how a fire will behave and when critical transitions will occur.

- **Ignition Temperature:** The minimum temperature to which a fuel must be heated in air to initiate self-sustained combustion without an external spark or flame.
- **Pyrolysis Temperature:** For solid fuels (like wood or plastics), this is the temperature range (typically **200°C to 400°C**) where the solid chemically decomposes into flammable gases.
- **Flashover Threshold (~500°C - 600°C):** This is the most critical temperature milestone in compartment fire dynamics. When the upper smoke layer in a room reaches roughly **500°C to 600°C** radiation causes all exposed combustible surfaces in the room to ignite simultaneously, transitioning the fire from a localized event to a fully developed room fire.

### 2. Compartment Fire Temperature Profiles

When a fire burns inside a building, temperature is never uniform. It splits the space into a distinct two-layer zone system:

- **The Upper Layer (Hot Gas Layer):** Buoyant hot smoke rises to the ceiling, forming a distinct upper layer. Temperatures here can rapidly rise from ambient to over **1000°C** during a fully developed fire.
- **The Lower Layer:** Air is drawn into the fire from below. This layer remains relatively cool and clear until the fire approaches flashover.
- **The Thermal Plume:** The column of hot gases rising above the fire. Fire engineers calculate the center-line plume temperature to determine exactly when ceiling-mounted **smoke detectors** or **fire sprinklers** will activate.

### 3. Temperature vs. Heat: The Critical Distinction

A common misconception corrected early in fire engineering is confusing temperature with heat.

- **Temperature (T, measured in °C or K):** A measure of the average kinetic energy of the molecules. It dictates the direction of heat transfer (heat always flows from higher to lower temperature).
- **Heat Energy (Q, measured in Joules):** The total thermal energy possessed by a material.
- **Heat Release Rate (HRR, measured in kW or MW):** The rate at which a fire releases energy.

### Tenability (Human Life Safety)

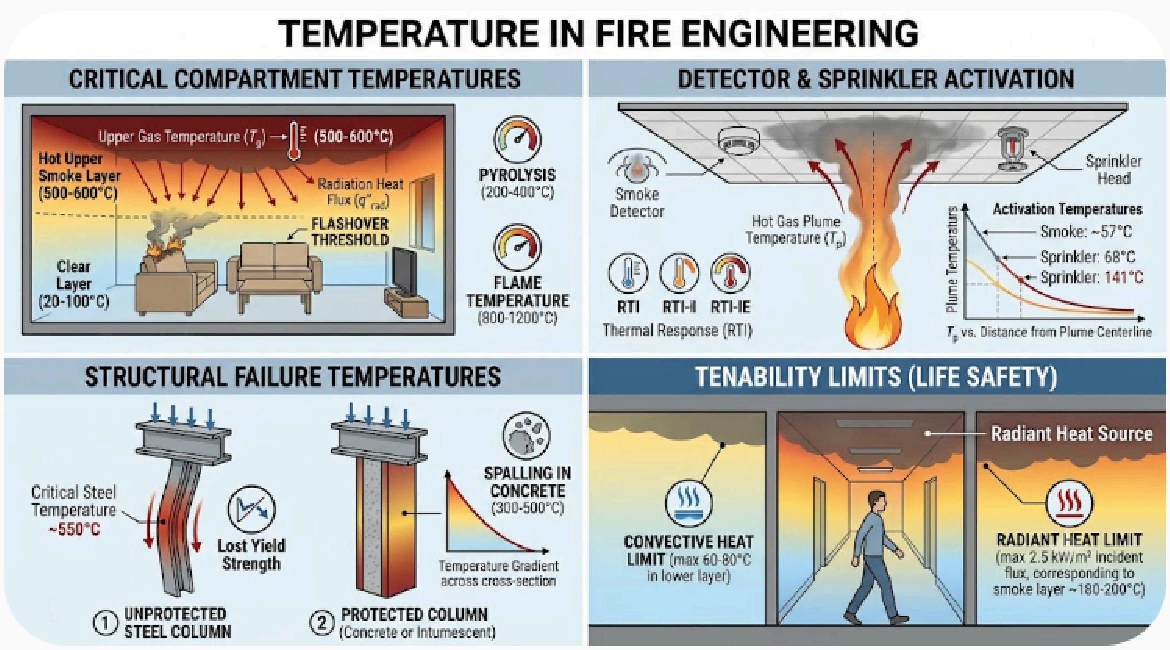
When designing evacuation timelines (Available Safe Egress Time, or ASET), engineers look at the maximum temperature a human can tolerate before incapacitation:

- **Convective Heat Limit:** The maximum air temperature a person can briefly withstand is roughly **60°C to 80°C** if the air is saturated with moisture. Above this, respiratory tract damage and hyperthermia occur rapidly.
- **Radiant Heat Limit:** A hot smoke layer radiating heat down at a level exceeding 2.5{ kW/m}^2 (which corresponds to a smoke layer temperature of roughly **180°C - 200°C**) will cause severe skin burns within seconds, blocking evacuation routes.

**Structural Integrity and Materials**

Fire protection engineers must understand how building materials degrade when exposed to elevated fire temperatures:

| Material | Temperature | Engineering Consequence |
|---|---|---|
| Structural Steel | ~550°C | Loses roughly 50% of its yield strength, risking catastrophic structural collapse if unprotected. |
| Concrete | 300°C - 500°C | Dehydration and chemical changes cause loss of strength; "spalling" (explosive breaking of concrete chunks) can occur. |
| Tempered Glass | ~250°C - 300°C | Thermal stress across the pane causes standard glazing to crack and fail, introducing new oxygen to the fire. |



## Specific heat capacity

In fire engineering, **specific heat capacity** measures how much thermal energy a substance must absorb per unit mass to raise its temperature by 1deg C

Its SI unit is

$$\mathrm{J/(kg \cdot K)}$$

It dictates two critical factors in fire dynamics:

1. **Fire Suppression:** How effectively a suppressant (like water) absorbs heat away from burning fuel.
2. **Structural Fire Resistance:** How quickly building materials (steel, concrete, timber) heat up, lose strength, or slow down fire propagation.

### Core Equation

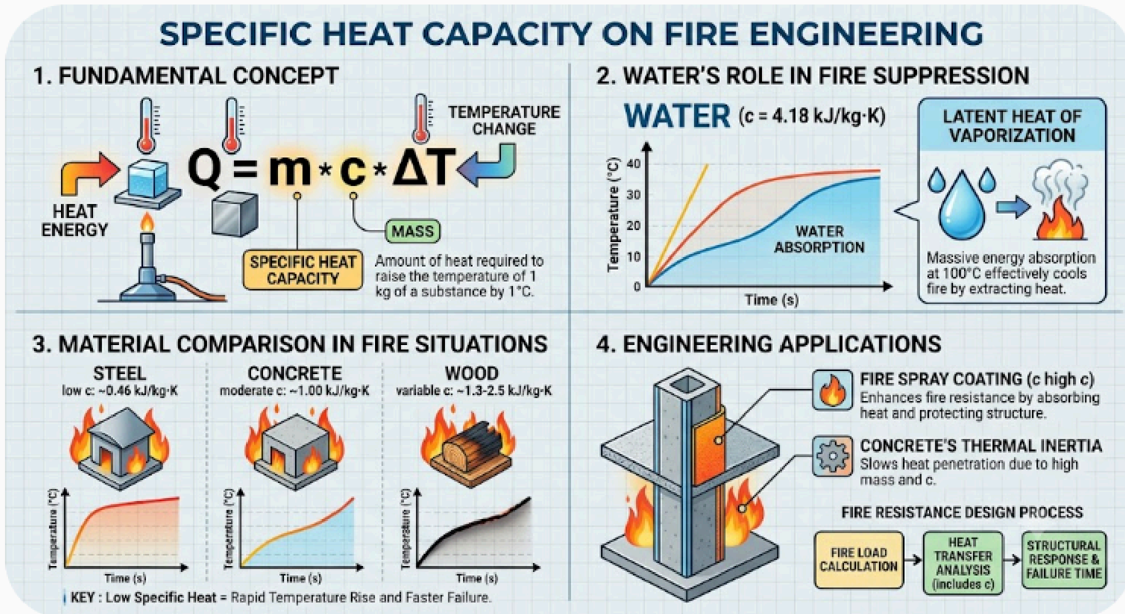
The sensible heat required to change a material's temperature is given by:

$$Q = m \cdot c_p \cdot \Delta T$$

- $Q$: Heat energy absorbed or released ($\mathrm{J}$ or $\mathrm{kJ}$)
- $m$: Mass of the material ($\mathrm{kg}$)
- $c_p$: Specific heat capacity at constant pressure ($\mathrm{kJ/kg \cdot K}$)
- $\Delta T$: Temperature change ($T_{\text{final}} - T_{\text{initial}}$ in $\mathrm{K}$ or $^\circ\mathrm{C}$)

## Key Values in Fire Engineering

| Material / Agent | Specific Heat $c_p$ $(\mathrm{kJ}/\mathrm{kg} \cdot \mathrm{K})$ | Relevance in Fire Engineering |
|---|---|---|
| **Water (Liquid)** | **4.184** | Exceptionally high capacity; absorbs massive energy before boiling. |
| **Air** | **1.005** | Governs heat rise in hot smoke layers and compartment gases. |
| **Concrete** | **0.88 - 1.00** | Provides high thermal inertia, slowing temperature rise across structural elements. |
| **Structural Steel** | **0.45 - 0.60** | Low specific heat; heats up rapidly in fires, causing quick loss of yield strength ($> 500^\circ\mathrm{C}$). |
| **Gypsum Board** | **0.95 - 1.10** | High effective heat capacity due to bound water chemically desorbing during fire (calcination). |
| **Wood / Timber** | **1.20 - 2.00** | Varies with moisture content and temperature; forms an insulating char layer. |




## Catalyst

In fire engineering, a **catalyst** is any chemical agent or material surface that alters the activation energy of combustion or thermal decomposition reactions—either speeding them up (positive catalysis) or slowing/inhibiting them down (negative catalysis or inhibition).

While catalysts can promote combustion in controlled industrial processes, fire safety engineering mainly focuses on **catalytic mechanisms that inhibit flames** or **materials that accidentally catalyze unwanted fires**.

### 1. Flame Retardancy & Intumescent Systems (Inhibition / Negative Catalysis)

The most widespread application of catalysts in fire protection is in **fire retardants and intumescent coatings**, where a chemical catalyst is added to force a material to protect itself rather than burn.

#### A. Catalytic Char Formation (Condensed Phase)

- **How it works:** Intumescent fireproofing systems rely on a catalyst—typically an acid source such as **Ammonium Polyphosphate (APP)** or **phosphorus/manganese derivatives**.
- **Mechanism:** When heated by a fire, the acid catalyst degrades and promotes the dehydration of polymers. Instead of decomposing into volatile, flammable gases, the polymer is catalyzed into forming a thick, carbonaceous **char layer**.
- **Effect:** The char layer acts as a physical shield, insulating underlying structural steel or timber and cutting off oxygen supply.

### B. Free Radical Scavenging (Gas Phase)

- **How it works:** Flame suppression agents (such as halogenated compounds, organophosphorus species, or metallic salts like Antimony Trioxide) release active radical species in the gas phase.
- **Mechanism:** Combustion relies on high-energy chain reactions driven by radicals . Active agents react with these radicals and neutralize them.
- **Effect:** By acting as "negative catalysts," they disrupt the chain reaction kinetics, rapidly extinguishing or cooling the flame without needing to cool the substrate completely.

## 2. Unintended Fire Hazards (Accelerated Ignition & Spontaneous Combustion)

In fire investigation and risk analysis, trace catalysts can accidentally promote fires by significantly lowering the ignition temperature or accelerating reaction rates.

### A. Surface Catalysis on Hot Metals

- Bare, heated metal surfaces (such as iron, nickel, or platinum in ductwork or structural assemblies) act as solid-state catalysts for gas-phase reactions.
- Hot metal surfaces can catalyze the oxidation of volatile organic compounds (VOCs), hydrogen, or carbon monoxide, igniting gaseous fuel-air mixtures at temperatures **far below** their standard auto-ignition temperatures.

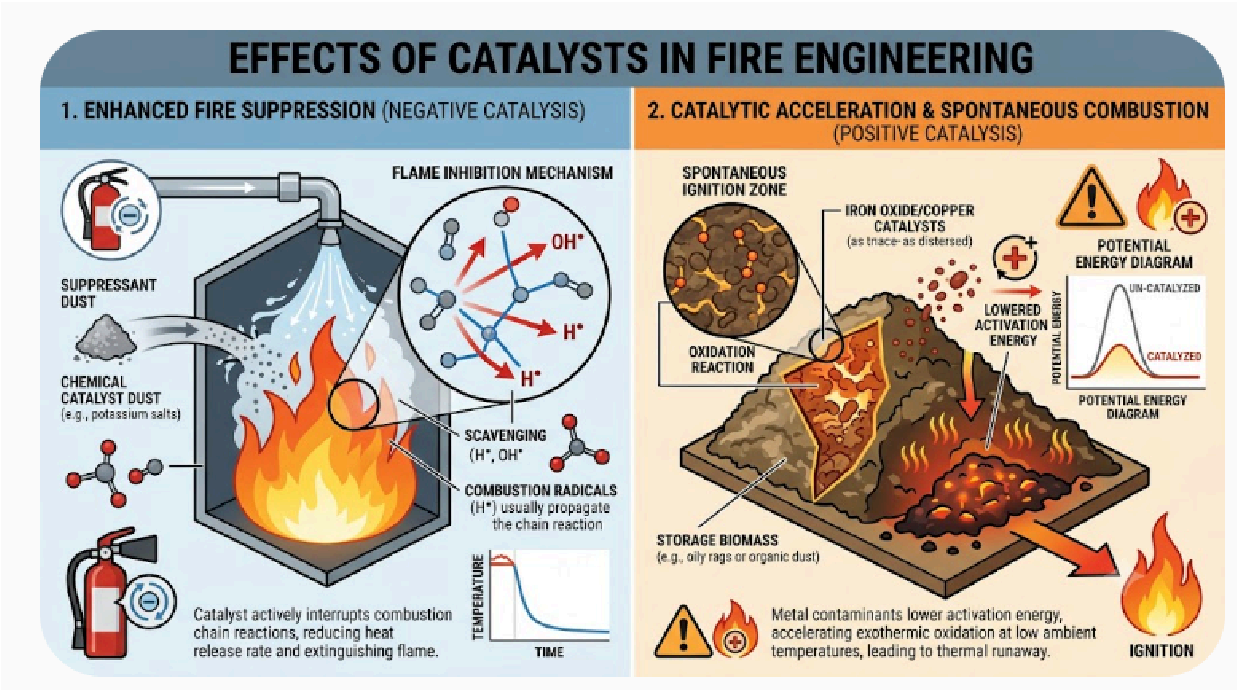
### B. Catalysts in Spontaneous Combustion

- Oils, organic dusts, or stored bio-mass can self-heat through slow ambient oxidation.
- Metal contaminants (like iron, copper, or manganese trace oxides) act as oxidation catalysts. They accelerate exothermic oxidation at room temperature, leading to runaway heating and spontaneous ignition.

## 3. Industrial Safety & Environmental Emission Controls

Fire safety engineers working in industrial plants, HVAC design, or automotive safety often deal with catalytic devices intended to eliminate flammable or toxic hazards safely:

- **Catalytic Afterburners / Gas Cleaners:** Industrial exhaust systems use platinum or palladium catalysts to oxidize residual flammable vapors (hydrocarbons, into harmless CO2 and H20 at low temperatures, preventing flammable vapor build-up inside ductwork.
- **Hydrogen Recombiners in Nuclear / Energy Storage Safety:** In battery storage rooms (e.g., lithium-ion off-gassing) or nuclear containment buildings, passive catalytic recombiners (PARs) use platinum/palladium to convert escaping hydrogen gas into water vapor at ambient temperatures, preventing explosive hydrogen accumulation.




## Neutralization

In fire safety and protection engineering, **neutralization** generally refers to one of three main processes depending on the context:

### 1. Acid-Base / Chemical Neutralization

When hazardous chemical fires involve corrosive liquids (such as concentrated acids or alkalis), or when burning plastics (like PVC) emit acidic gases (e.g., hydrogen chloride / $\text{HCl}$), direct water suppression can react violently or spread toxic, corrosive runoff.

- **Smoke & Gas Scrubbing:** Fixed or portable scrubbers use alkaline mists (such as dilute sodium hydroxide or sodium carbonate) to neutralize acid gases in smoke streams before they corrode structural elements, electronics, or escape into the environment.
- **Corrosive Spills & Runoff:** Neutralizing agents (e.g., sodium bicarbonate for acids, citric acid or dilute acetic acid for bases) are applied to neutralize fire runoff water, preventing environmental contamination and protecting emergency response gear.

### 2. Flame Neutralization & Chemical Inhibition

In gaseous fire suppression systems (clean agents like Novec 1230, FM-200, or Halon replacements), the extinguishing mechanism works partly by **thermally absorbing heat** and partly by **chemically neutralizing active flame radicals**.

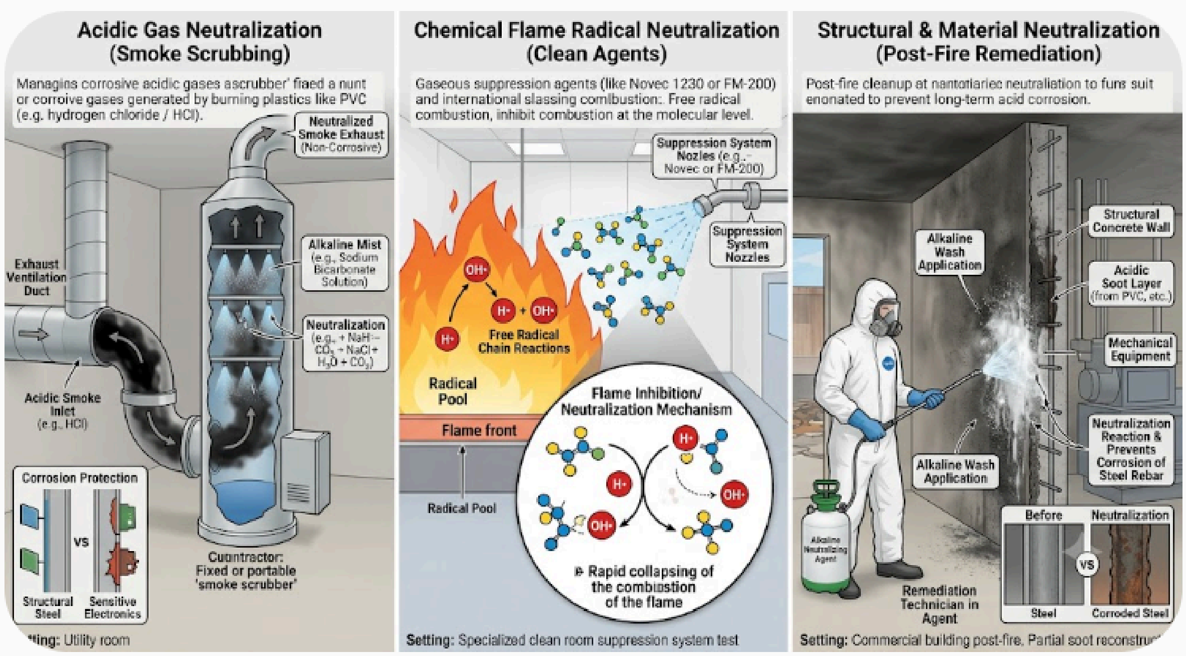
$$OH^{\bullet} + H^{\bullet} \longrightarrow H_2O$$

These chemical agents break the chain reaction of the fire triangle by scavenging free radicals in the combustion zone, halting the self-sustaining flame reaction.

**Structural & Material Neutralization (Post-Fire Remediation)**

After a fire has been extinguished, structural materials (concrete, steel, brickwork) and sensitive equipment often remain coated in acidic soot, ash, and combustion byproducts.
**Soot Acid Neutralization:** Plastic combustion products leave behind acidic residues that slowly eat away at steel reinforcement, circuit boards, and HVAC ducts.

**Remediation Process:** Restoration teams apply alkaline wash solutions to neutralize surface acids, preventing long-term structural decay and secondary equipment failure weeks or months after the fire event.
**Key Takeaway:** Chemical neutralization in fire engineering primarily protects both people and infrastructure—either by killing the radical chain reaction during combustion, or by managing corrosive combustion products and toxic fire runoff.



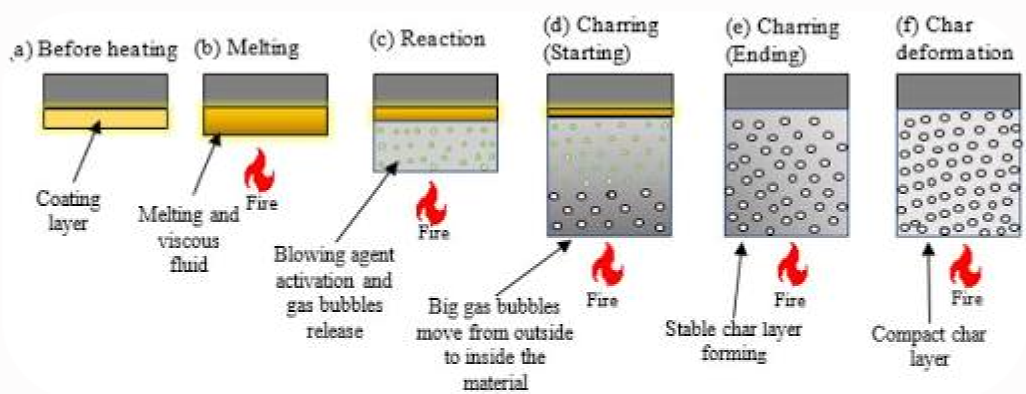
**Sublimation**

In fire engineering, **sublimation** — the direct phase transition of a substance from a solid into a gas without melting into a liquid first — is used as a powerful heat-absorption mechanism.
It plays three critical roles across passive fire protection, pyrotechnics, and fire dynamics:

### 1. Subliming Ablative Coatings (Passive Fire Protection)

Subliming materials are widely used in high-risk passive fireproofing for structural steel, offshore oil platforms, and aerospace components (such as rocket engine nozzles and heat shields).

**How it works:** Under extreme thermal stress, specialized subliming compounds absorb immense amounts of heat energy as **latent heat of sublimation**. They transition directly into gas, carrying thermal energy away from the underlying structural steel.
**Why not melt?** Liquid phases melt and run off vertical surfaces, leaving the structure exposed. Subliming coatings stay intact while slowly off-gassing, creating an insulating gas boundary layer that repels oncoming flame radiation.




### 2. Intumescent Blowing Agents & Flame Retardants

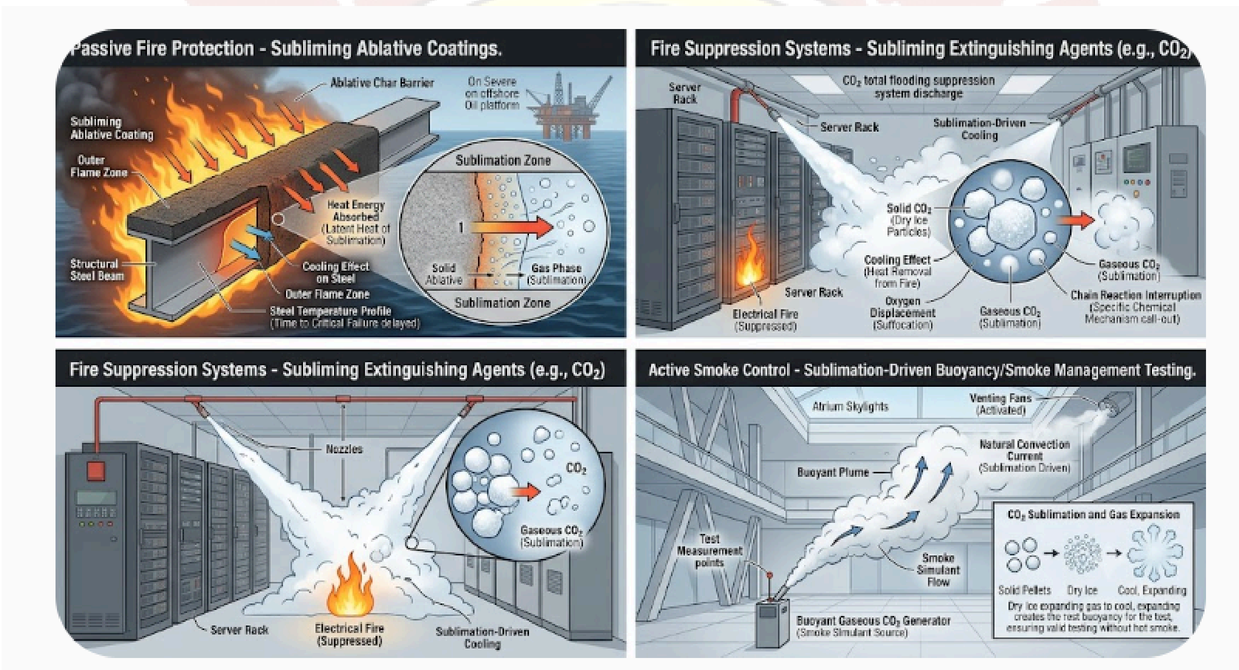
Intumescent paints expand when exposed to high temperatures, forming a thick, insulating carbonaceous char around structural beams.

- **Melamine & Blowing Agents:** Chemical additives like **melamine** act as blowing agents. At high temperatures (around 300°C–350°C), melamine sublimes and degrades into non-flammable gases (such as ammonia and nitrogen gas).
- **Expanding the Char:** The escaping gases trap within the melting resin binder, expanding the coating up to 50 times its original thickness into a protective foam barrier.

### 3. Solid Fuel Combustion Dynamics

In fire dynamics and wildland fire behavior, certain solid fuels transition straight from solid phase to gaseous pyrolysis products when exposed to intense radiative heat flux.

- **Direct Pyrolysis & Vaporization:** While most woods char and decompose through pyrolysis, certain volatile solid polymers and organic compounds vaporize directly into the flame front.
- **Dry Ice Fire Extinguishment:** Carbon dioxide snow generated by high-expansion discharge undergoes rapid sublimation. As solid absorbs heat from surrounding air to sublime into gas, it simultaneously chills the fuel below its ignition threshold and suffocates the fire by displacing oxygen.




**Passive Fire Protection (Subliming Ablative Coatings):** This image demonstrates how structural steel is protected during a severe fire (like an oil platform blaze). A thick ablative coating absorbs extreme heat through sublimation, converting directly to gas and creating a cooling, protective layer that keeps the steel from failing.

**Fire Suppression Systems (Subliming Extinguishing Agents):** This diagram shows how solid dry ice particles are discharged to extinguish an electrical equipment fire. The solid $\text{CO}_2$ quickly sublimes into a heavy gas, displacing oxygen and providing intense localized cooling to quench the flames without leaving water residue.

**Active Smoke Control (Sublimation-Driven Buoyancy):** This illustration explains how dry ice pellets are used to simulate hot smoke in building safety tests. The pellets sublime into cool, non-toxic gas, allowing engineers to visualize and optimize ventilation systems and ensure safe evacuation paths are clear of smoke.

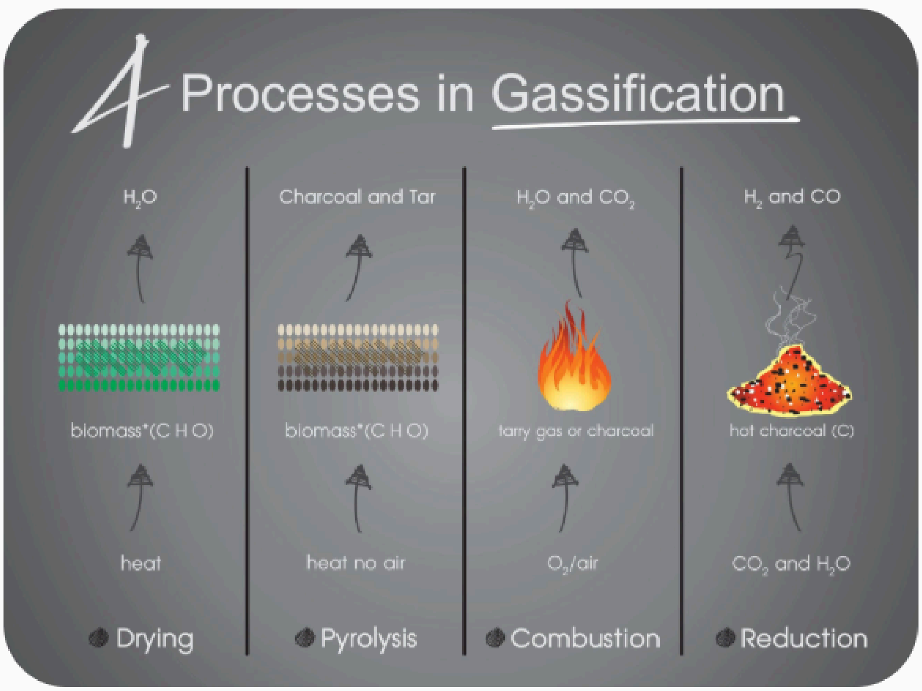
**Heat of Decomposing**

In fire engineering and fire dynamics, the heat of decomposition (more specifically known as the heat of pyrolysis is the amount of energy required to thermally break down a unit mass of a solid or liquid fuel into flammable gaseous species.

Because solid fuels (like wood, plastics, and polymers) cannot burn directly, they must first absorb heat to cleave their chemical bonds.

1. Pyrolysis and Energy Dynamics

Solids burn in a feedback loop. Radiative heat from the flame flux hits the solid surface, raising its temperature to the decomposition point.




*Thermal breakdown phases in solid fuel decomposition. Source: Graphic_BKK1979 / Getty Images*

$$\text{Solid Fuel} + \Delta H_p \longrightarrow \text{Pyrolysis Gases (Vapors)} + \text{Solid Char / Residue}$$

**Practical Applications in Fire Engineering**

Understanding decomposition enthalpy allows fire protection engineers to model and mitigate fire hazards:

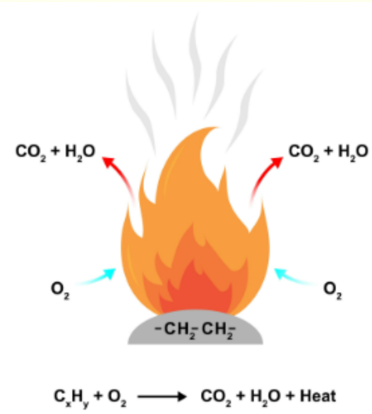
- **Flame Retardant Mechanisms:** Many chemical flame retardants increase the material's effective heat of decomposition or force endothermic reactions (e.g., alumina trihydrate releasing water vapor), soaking up heat energy before the material can release flammable gas.
- **Fire Modeling (FDS & Pyrolysis Models):** Computer models like NIST's Fire Dynamics Simulator (FDS) require precise inputs to predict flame spread, heat release rate (HRR), and time to flashover in a room fire.
- **Structural Timber (Mass Timber Fire Resistance):** Heavy timber structural elements decompose slowly because charring acts as a thick insulating layer, requiring continuous, high thermal energy inputs to sustain pyrolysis deeper within the wood beam.

While the heat of combustion measures how much energy a fire releases, the heat of decomposition measures the thermal energy required to feed the fire with gaseous fuel. A higher heat of decomposition makes a material harder to ignite and slower to burn.

## <u>Chemical Reaction</u>

In fire safety engineering, the primary chemical reaction is **combustion**—a high-temperature, exothermic redox reaction between a fuel and an oxidant .

While simple chemistry models combustion as a single-step equation, real-world fires involve a multi-stage chemical process driven by free-radical chain reactions, thermal degradation, and incomplete oxidation.



**1. Stoichiometric vs. Incomplete Combustion**

**Ideal (Stoichiometric) Combustion**

In an ideal environment with abundant oxygen, hydrocarbons react completely to produce only carbon dioxide, water vapor, and energy:

**(Incomplete) Combustion**

Real compartment fires rarely have perfect oxygen mixing. As fires consume available room air, they shift to incomplete combustion, producing hazardous, toxic byproducts:

$$\text{Fuel} + \text{Deficient } O_2 \longrightarrow CO_2 + H_2O + CO + \text{C solution (Soot)} + \text{Toxic Gases}$$

**Carbon Monoxide (CO):** Formed when oxygen is insufficient to oxidize carbon completely into CO2. It is responsible for the majority of fire fatalities due to toxic asphyxiation.
**Soot (Solid Carbon):** Unburned carbon particles that aggregate in the plume. Soot blocks visibility and absorbs thermal energy, radiating intense heat to surrounding surfaces.

**2. Radical Chain Mechanism (How Flame Propagates)**

The visible flame is maintained by high-energy free radicals {H},OH},{O} reacting at microsecond speeds in the gas phase:

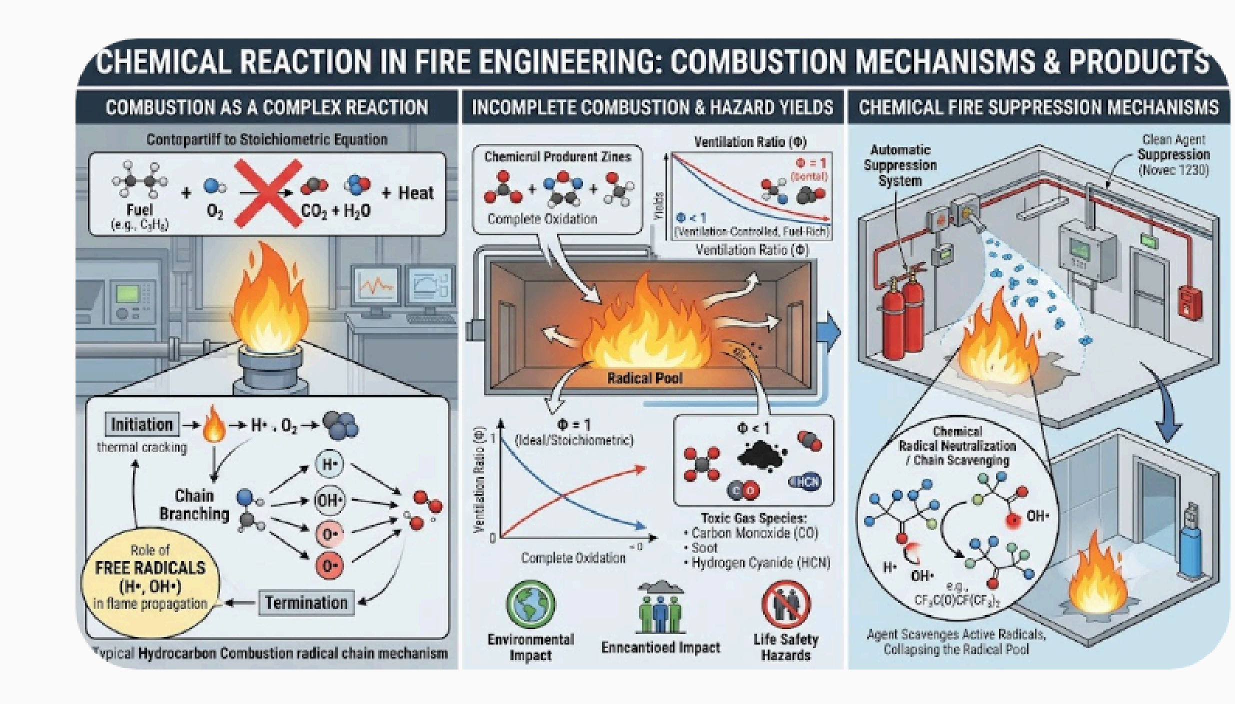
1. **Initiation:** Heat breaks hydrocarbon fuel bonds into reactive radical fragments.
2. **Chain Branching & Propagation:** High-energy radicals react with oxygen to multiply the radical pool:

$$H^\bullet + O_2 \longrightarrow OH^\bullet + O^\bullet$$

3. **Termination:** Radicals collide with surfaces, extinguishing agents, or recombine into stable molecules, halting the flame.

**3. Secondary Chemical Reactions in Fires**

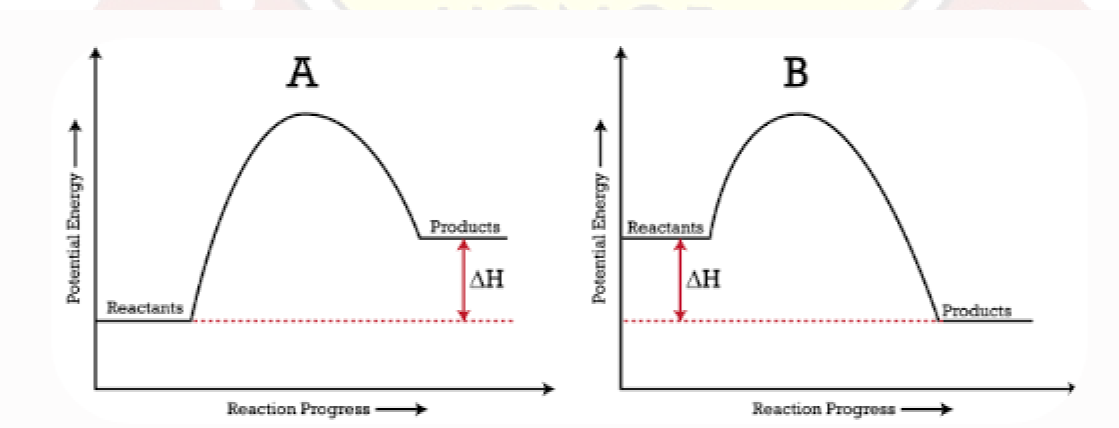
Beyond basic fuel burning, fire engineers analyze several distinct chemical processes occurring simultaneously within a blaze:




**Exothermic Reaction and Endothermic Reaction**

Every chemical reaction involves an energy exchange with its surroundings. The direction of this energy flow determines whether a reaction is **exothermic** or **endothermic**.

In fire engineering and chemistry, understanding this balance dictates how fires spread, how fuels decompose, and how suppression systems put flames out.



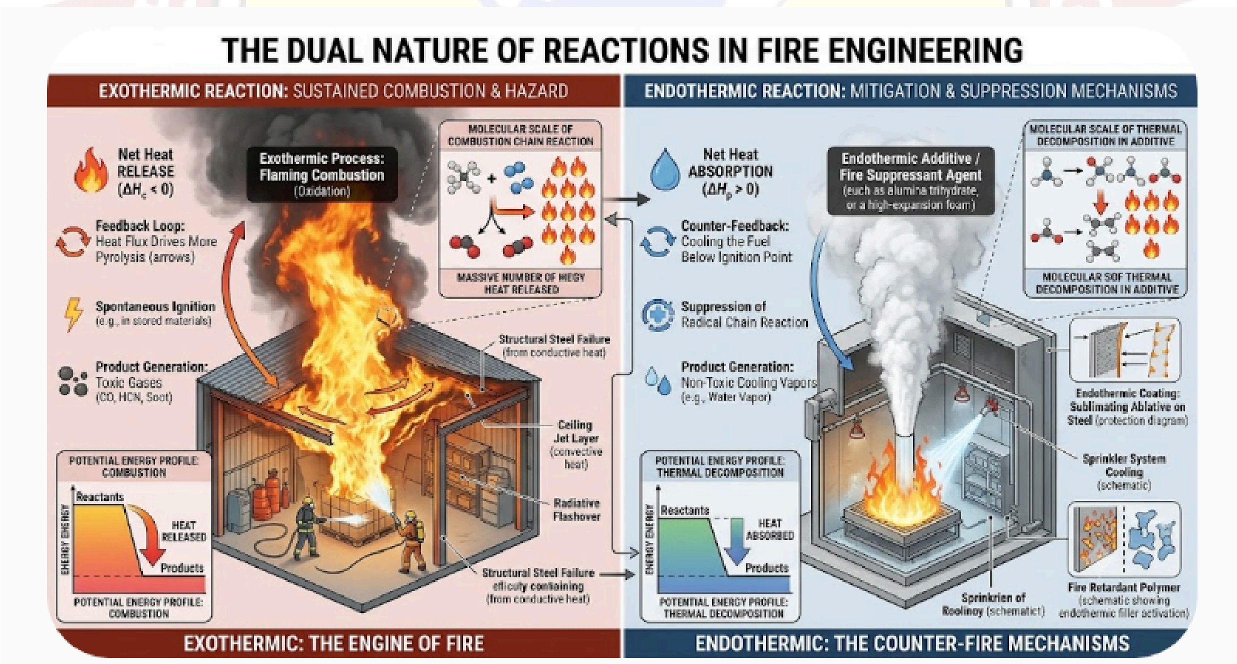

*Energy profiles: Endothermic (A) vs Exothermic (B). Source: Chemistry*

In the potential energy diagrams above, notice how the energy level shifts from **Reactants** to **Products**:

**Diagram A (Endothermic):** Products sit at a higher energy level than reactants because heat is absorbed from the environment
**Diagram B (Exothermic):** Products sit at a lower energy level because net heat is released into the environment

In fire dynamics, exothermic and endothermic processes occur simultaneously in a continuous feedback loop:

1. **Endothermic Phase (Pyrolysis & Vaporization):** Solid fuel (wood, plastic) absorbs radiative heat from surroundings to break its chemical bonds. This endothermic thermal decomposition releases gaseous fuel vapors.
2. **Exothermic Phase (Combustion):** Gas-phase fuel reacts with oxygen in the flame front, releasing massive amounts of heat
3. **The Feedback Loop:** If the **exothermic heat released** by the flame is greater than the **endothermic heat required** to pyrolyze more fuel (plus heat lost to the room), the fire accelerates and spreads.

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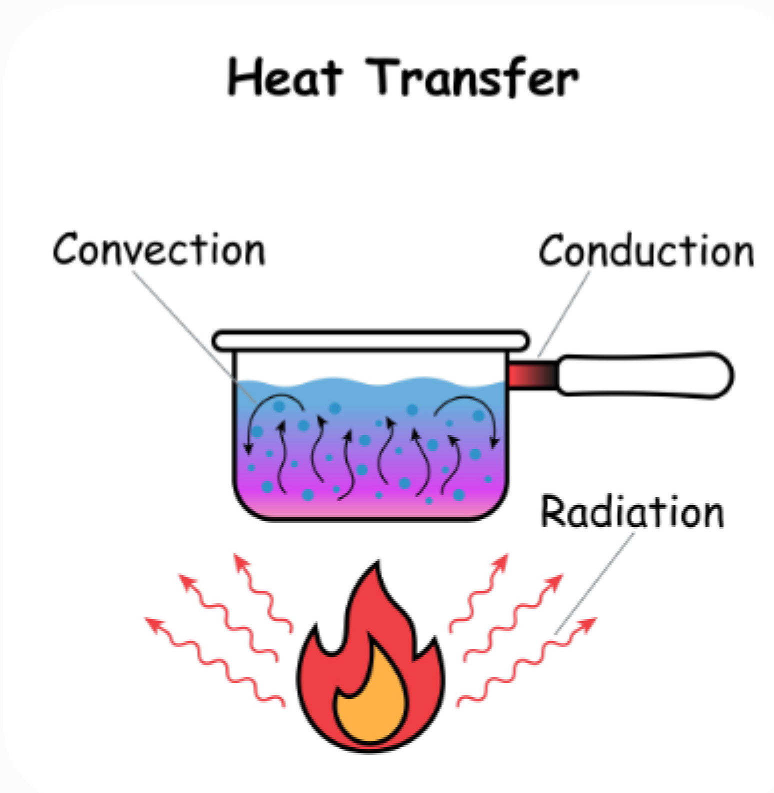
**Transmission of heat**

**Transmission of heat** (or heat transfer) is the movement of thermal energy from a hotter region to a cooler region. Thermal energy always flows naturally down a temperature gradient until thermal equilibrium is reached.

There are three primary mechanisms by which heat is transmitted: **Conduction**, **Convection**, and **Radiation**.




*The three fundamental modes of heat transfer. Source:*

**1. Conduction**

Conduction is the transfer of thermal energy through direct contact between neighboring atoms or molecules without any overall movement of the material itself.

- **Medium:** Primarily solids (especially metals due to free electrons), though it occurs weakly in liquids and gases.
- **Mechanism:** Fast-moving, energetic particles in the hotter section collide with slower, neighboring particles, passing along kinetic energy.

- **Key Equation (Fourier's Law):**

$$q = -kA\frac{dT}{dx}$$

*Where $q$ is heat transfer rate, $k$ is thermal conductivity, $A$ is surface area, and $\frac{dT}{dx}$ is temperature gradient.*

- **Everyday Example:** Heating a metal spoon left in a hot pot of soup.

**2. Convection**

Convection is heat transfer driven by the actual fluid motion (movement of molecules) within liquids or gases.

- **Medium:** Fluids only (liquids and gases).
- **Mechanism:** When a fluid is heated, it expands, becomes less dense, and rises. Cooler, denser fluid sinks to take its place, creating a continuous **convection current**.
- **Types:**
    - **Natural/Free Convection:** Driven purely by buoyancy forces due to density differences (e.g., hot air rising off a radiator).
    - **Forced Convection:** Driven by external mechanical means such as a fan, pump, or wind.
- **Key Equation (Newton's Law of Cooling):**

$$q = hA(T_s - T_\infty)$$

*Where $h$ is the convective heat transfer coefficient, $T_s$ is surface temperature, and $T_\infty$ is fluid temperature.*

- **Everyday Example:** Water circulating and boiling in a kettle, or sea breezes on a coast.

**3. Radiation**

Radiation is the emission and absorption of thermal energy as electromagnetic waves (primarily infrared light).

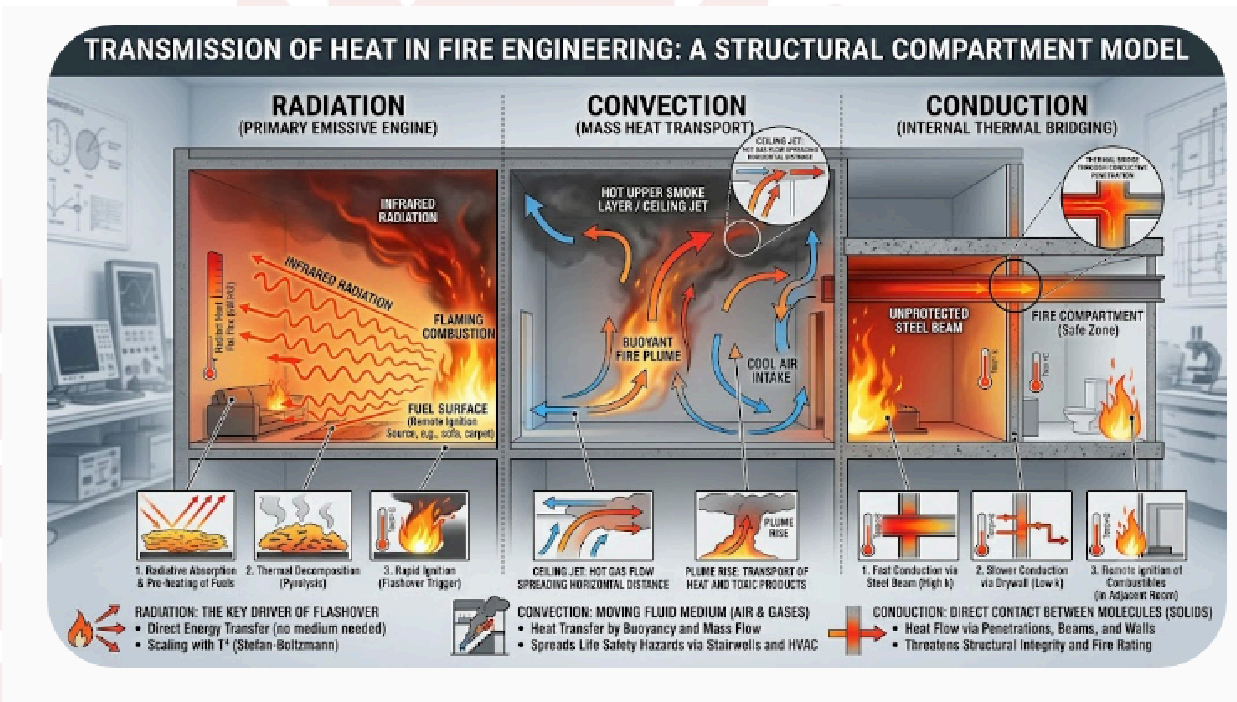
- **Medium:** Requires **no material medium**—it travels through air, gases, and empty vacuum at the speed of light.
- **Mechanism:** All matter above absolute zero ($0 \text{ K}$) emits thermal radiation due to the random movement of charged particles within its atoms.

- **Key Equation (Stefan-Boltzmann Law):**

$$q = \varepsilon \sigma A T^4$$

*Where $\varepsilon$ is emissivity, $\sigma$ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8}\ \mathrm{W/m^2 \cdot K^4}$), and $T$ is absolute temperature in Kelvin.*

- **Everyday Example:** Feeling the warmth of sunlight on your skin across the vacuum of space, or standing near a glowing campfire.




**Flash and Fire point:**

**Flash point** and **fire point** are two critical thermal properties used to measure the flammability, volatility, and safe operational limits of liquid fuels, lubricants, and solvents.

Because liquids themselves do not burn—their **vapors** do—both metrics measure the temperature at which a liquid produces enough vapor to ignite when exposed to an ignition source (like a spark or flame).

**What is Flash Point?**

The **flash point** is the lowest temperature at which a liquid produces enough vapor to form an ignitable mixture with air, producing a momentary, instantaneous "flash" of flame across its surface when exposed to an open flame.

- **Flame Duration:** The flame flashes and goes out almost immediately (less than 5 seconds).
- **Why it goes out:** At this temperature, the fuel isn't vaporizing fast enough to replace the vapor consumed by the initial flash.
- **Engineering Purpose:** It establishes safety thresholds for storing, handling, and transporting flammable liquids (e.g., NFPA classification of flammable vs. combustible liquids).

**What is Fire Point?**

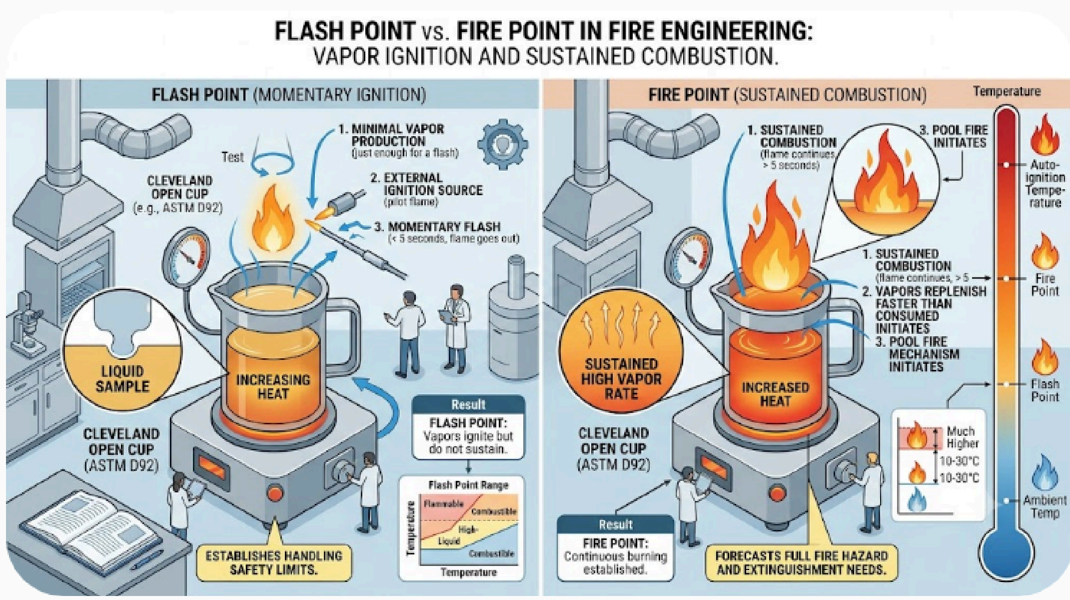
The **fire point** is the lowest temperature at which a liquid produces vapor fast enough to sustain continuous combustion for **at least 5 seconds** after being ignited by an external flame.

- **Flame Duration:** Sustained burning (continuous flame).
- **Temperature Difference:** The fire point is always **higher** than the flash point—typically by about 10°C to 30°C (18°F to 54°F) for most petroleum products.
- **Engineering Purpose:** It indicates the point at which a small local ignition will progress into a fully developed pool fire.

| **Feature** | **Flash Point** | **Fire Point** |
|---|---|---|
| Combustion Duration | Temporary flash < 5 seconds | Sustained flame >5seconds |
| Vapor Production Rate | Minimal (just enough to ignite once) | High (fast enough to continually replenish vapor) |
| Relative Temperature | Lower | Higher (10°C–30°C above flash point) |
| Primary Safety Focus | Storage, transport, and hazardous classification | Fire risk assessment and extinguishment requirements |

## Common Examples

| Substance | Flash Point | Fire Point |
|---|---|---|
| **Gasoline** | $-43^{\circ}C\ (-45^{\circ}F)$ | ~ $-38^{\circ}C\ (-36^{\circ}F)$ |
| **Ethanol (Pure)** | $13^{\circ}C\ (55^{\circ}F)$ | ~ $18^{\circ}C\ (64^{\circ}F)$ |
| **Diesel Fuel** | $> 52^{\circ}C\ (125^{\circ}F)$ | ~ $62^{\circ}C\ (144^{\circ}F)$ |
| **Transformer Oil** | $140^{\circ}C\ (284^{\circ}F)$ | ~ $160^{\circ}C\ (320^{\circ}F)$ |




### Ignition temperature

Ignition temperature (also known as the auto-ignition temperature or kindling point) is the minimum temperature at which a substance will spontaneously ignite in a normal atmosphere without any external spark, flame, or pilot light source.

At this temperature, the material absorbs enough ambient heat to overcome its chemical activation energy, initiating a self-sustaining exothermic combustion reaction.

1. How Ignition Temperature Differs from Flash Point & Fire Point

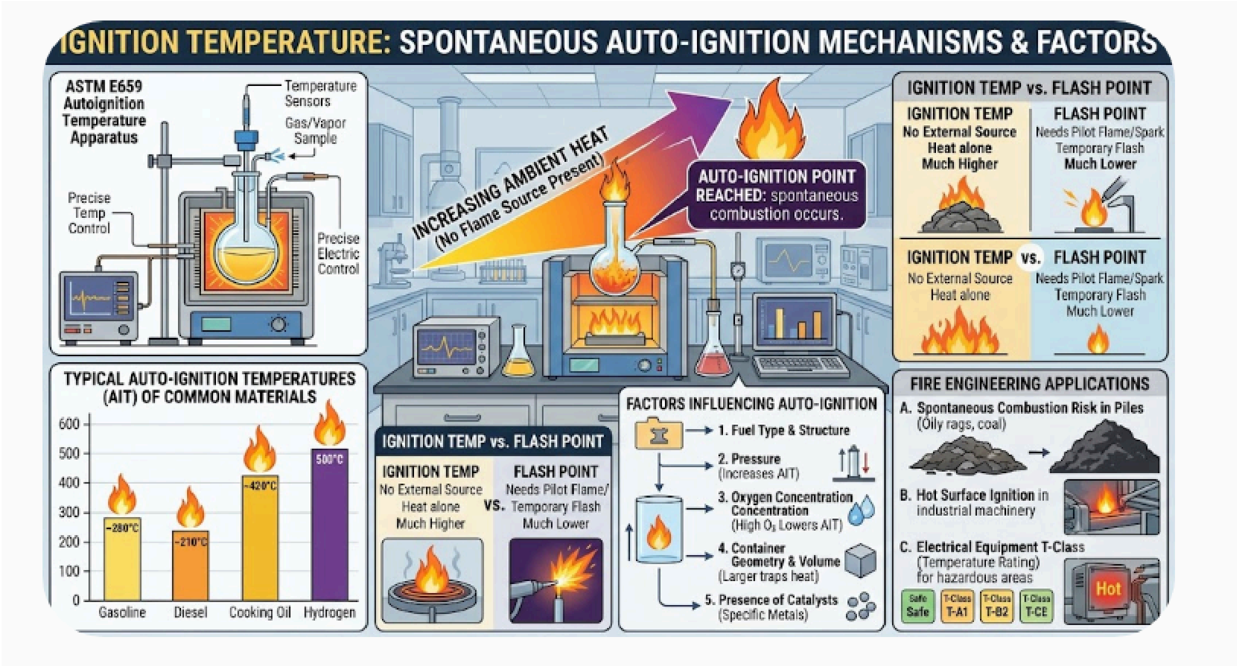
It is common to confuse these terms, but they describe very different thermal behaviors:

- Flash Point: Lowest temperature where vapors ignite only when exposed to an open flame/spark, producing a momentary flash
- Fire Point: Lowest temperature where vapors sustain continuous burning when ignited by an external pilot flame
- Ignition (Auto-Ignition) Temperature: Lowest temperature where no flame or spark is needed at all—heat alone causes the fuel to burst into flames spontaneously.

Key Rule: A fuel's auto-ignition temperature is much higher than its flash point. For example, gasoline has a flash point of -43^C, but its auto-ignition temperature is around 280^C.

**Practical Importance in Fire Engineering**

1. **Hot Surface Ignition:** In industrial facilities, hot steam pipes, exhaust manifolds, or overheated machinery bearings can ignite leaking hydraulic fluid or oil spray without any electrical spark.
2. **Spontaneous Combustion:** Materials like oily rags or linseed oil decompose exothermically. If stored in pile configurations where heat cannot escape, the internal core temperature gradually rises until it hits the auto-ignition point.
3. **Electrical Equipment Ratings (T-Class):** Explosion-proof equipment used in hazardous environments receives a Temperature Class (T1–T6) rating to ensure maximum surface temperatures stay well below the auto-ignition point of surrounding vapors.


IGNITION TEMPERATURE: SPONTANEOUS AUTO-IGNITION MECHANISMS & FACTORS
ASTM E659 Autoignition Temperature Apparatus
Temperature Sensors
Gas/Vapor Sample
Precise Temp Control
Precise Electric Control
INCREASING AMBIENT HEAT (No Flame Source Present)
AUTO-IGNITION POINT REACHED: spontaneous combustion occurs.
IGNITION TEMP vs. FLASH POINT
IGNITION TEMP No External Source Heat alone Much Higher
FLASH POINT Needs Pilot Flame/Spark Temporary Flash Much Lower
TYPICAL AUTO-IGNITION TEMPERATURES (AIT) OF COMMON MATERIALS
~280°C
~210°C
~420°C
500°C
Gasoline
Diesel
Cooking Oil
Hydrogen
FACTORS INFLUENCING AUTO-IGNITION
1. Fuel Type & Structure
2. Pressure (Increases AIT)
3. Oxygen Concentration (High O₂ Lowers AIT)
4. Container Geometry & Volume (Larger traps heat)
5. Presence of Catalysts (Specific Metals)
FIRE ENGINEERING APPLICATIONS
A. Spontaneous Combustion Risk in Piles (Oily rags, coal)
B. Hot Surface Ignition in industrial machinery
C. Electrical Equipment T-Class (Temperature Rating) for hazardous areas
Safe
T-A1
T-B2
T-CE
Hot

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