Overview of Combustion

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• Fuel – Typically an organic compound or processed metal, basically anything that can burn.

• Oxidizer – is usually oxygen but can be any atom or group of atoms that have an electron deficiency.

• Combustion – a chemical reaction involving fuel and an oxidizer, which results in a release of energy and the formation of chemical products.

• Flame – the visible portion of the volume within which the oxidation process is occurring. A flame is a gas phase phenomenon.

• Flaming combustion of liquids and solids must first be converted to a gaseous state.
• Burning of liquids occurs through evaporation, but for solids the conversion process is pyrolysis.

• For almost all solids, a chemical decomposition or pyrolysis is necessary (pre-flame reactions) to yield products of sufficiently low molecular weight that can volatilize from the solid surface and enter the flame.

• However some solids sublime on heating. This is the process of going directly from a solid to a gas.
Combustion Process

- Liquids typically undergo evaporative boiling at the fuel surface.
- Released thermal energy is transferred to the fuel to maintain its conversion into gaseous fuel vapor.
- This maintains the fuel temperature and ensures the chemical reaction can continue.
- Gaseous fuels will burn if:
  - fuel is well mixed with oxygen prior to burning.
  - fuel and oxygen are initially separated, but will burn in the region where they mix.

Types of Combustion

- **Premixed flames** - when gaseous fuel and oxygen are mixed prior to ignition and propagation occur.
- **Diffusion flames** - fuel vapor & oxygen are transported into the reaction zone due to fluid convection and concentration differences.
- **Spontaneous** - initiation of a chemical reaction that leads to a smoldering or diffusion flame.
- **Smoldering** – when surface oxidation or char provides the heat necessary to cause further thermal degradation of the neighboring layer of combustible material.
- **Glowing** - surface oxidation of carbonaceous materials or char and the emission of heat & light.
Rate of Burning

- Strictly defined as the rate of fuel mass consumed by the chemical reaction.
- For a diffusion flame it’s equal to the rate of gaseous fuel supply, and independent of the actual combustion process.
- For combustible solids and liquids the rate of burning is equal to the rate of supply of volatiles (flammable products) from the fuel surface.
  - these flammable products are directly linked to the rate of heat transfer from the flame to the fuel.

\[
\text{Fuel mass loss rate} = \text{Fuel burning rate} + \text{rate of inert gas released from the Fuel} + \text{rate of Fuel gases (and soot) not burned in the flame}.
\]

\[
m'' = \frac{\dot{Q}_w'' - \dot{Q}_f''}{L} (g/sm^3) = \text{[Fuel burning rate]}
\]

\[
\dot{Q}_w'' - \text{heat flux supplied by flame } (kW/m^2)
\]

\[
\dot{Q}_f'' - \text{heat flux loss through the fuel surface } (kW/m^2)
\]

\[
L_r - \text{heat required to produce the volatiles } (kJ/g)
\]
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Rate of Burning

Schematic representation of a burning surface, showing the heat & mass transfer processes.

- \( m^n \): mass flux from the surface \( \left( \frac{g}{s \ m^2} \right) \)
- \( \dot{Q}^n_f \): heat flux supplied by the flame \( \left( \frac{kW}{m^2} \right) \)
- \( \dot{Q}^n_a \): heat flux loss from surface \( \left( \frac{kW}{m^2} \right) \)

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Rate of Energy Released

\( \dot{Q}^n_f \): heat flux supplied by the flame.

- The most important single factor which characterizes fire behavior is the rate at which energy is released.

\[
\dot{Q}_c = \chi \dot{m}^n A_r \Delta H_c \ (kW) = \text{rate of energy release}
\]

- \( \chi \): incomplete combustion factor \( (\leq 1.0) \)
- \( \dot{m}^n \): rate of fuel burning \( \left( \frac{g}{m^2 s} \right) \)
- \( A_r \): fuel surface area \( (m^2) \)
- \( \Delta H_c \): heat of combustion of the volatiles \( \left( \frac{kJ}{g} \right) \)
"Equal volumes of different gases at the same T & P contain the same number of molecules (or atoms)."
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Ideal Gas Law

\[ PV = nRT \]

\[ n = \text{is the number of moles} \]

\[ \mathcal{R} = \text{universal gas constant} = 8.31446 \text{ J/mole K} \]

Three different gases (with different mass) are at STP (i.e., same T & P), how does their volumes compare? P = 101.33 kPa and T = 25 °C

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Composition & Properties of Air

<table>
<thead>
<tr>
<th>CONSTITUENT</th>
<th>MOLECULAR WEIGHT</th>
<th>DENSITY (32°F) lb/cubic foot</th>
<th>SPECIFIC GRAVITY</th>
<th>SPECIFIC HEAT BTU/lb°F</th>
<th>CONTENT VOLUME %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NITROGEN</td>
<td>28.01</td>
<td>0.0781</td>
<td>0.968</td>
<td>0.249</td>
<td>78.09</td>
</tr>
<tr>
<td>OXYGEN</td>
<td>32</td>
<td>0.0892</td>
<td>1.105</td>
<td>0.219</td>
<td>20.95</td>
</tr>
<tr>
<td>ARGON</td>
<td>39.94</td>
<td>0.1114</td>
<td>1.38</td>
<td>0.124</td>
<td>0.93</td>
</tr>
<tr>
<td>CO2</td>
<td>44.01</td>
<td>0.1234</td>
<td>1.529</td>
<td>0.2</td>
<td>0.03</td>
</tr>
<tr>
<td>AIR</td>
<td>28.97</td>
<td>0.0807</td>
<td>1</td>
<td>0.24</td>
<td>100</td>
</tr>
</tbody>
</table>

- For convenience air is assumed to consist of 21% oxygen and 79% nitrogen.
- The molar ratio of \( \text{N}_2/\text{O}_2 = 79/21 = 3.76 \)
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Ideal Gas Law

The molecular weight \((M_w)\) of air = 28.97 gm.
Find the density of air at STP?

\[ M_w \]

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The Gas Constant

Find \(R\) for air, where \(M_w\) of air = 28.97 gm.

Find \(R\) for \(O_2\), where \(M_w\) of \(O_2\) = 32 gm.
Compressibility Factor

- Real gases at either high pressure or cryogenic temperatures deviate from the Ideal gas law and must be modified with a compressibility factor.

- The generalized compressibility chart shows that states where the pressure $P$ is small relative to the critical pressure $P_c$ (where $P_R$ is small), the compressibility factor $Z$ is approximately 1.

Critical Definitions

**Critical temperature ($T_c$)** - maximum temperature at which a gas can be converted into a liquid by an increase in pressure.

**Critical pressure ($P_c$)** - minimum pressure which would enable liquefaction of a substance at its $T_c$.

**Critical point** – the characteristic $T_c$ and $P_c$ above which a gas cannot be liquefied.
**Basic Definitions**

**Supercritical fluid** – the state of a compound, mixture, or element above its Tc and Pc.

**Reduced temperature (Tr)** – ratio of temperature (T) in the system to the Tc.

\[ Tr = \frac{T}{T_c} \]

**Reduced pressure (Pr)** – the ratio of pressure in the system (P) to the Pc.

\[ Pr = \frac{P}{P_c} \]

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**Generalized Compressibility Chart**

\[ R = \text{universal gas const.} \]

\[ R = \begin{cases} 8.314 \text{ kJ/kmol·K} \\ 1.986 \text{ Btu/lbmol·°R} \\ 1545 \text{ ft·lbf/lbmol·°R} \end{cases} \]

\[ Z = \frac{P \tilde{V}}{RT} \]
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Generalized Compressibility Chart

**Example:** Find Z for Air @ 200 K, 132 bar;
where for air
\[ T_c = 133 \text{ K} \]
and
\[ P_c = 37.7 \text{ bar} \]

So:
\[ T_R = \frac{200}{133} = 1.5 \]
and
\[ P_R = \frac{132}{37.7} = 3.5 \]

Then: \( Z = 0.8 \)

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**Combustion Chemistry**

**Mass and Mole Fraction**

- **Mass Fraction** \( w_i \): ratio of the separate species mass to the total mass of the mixture:
  \[ w_i = \frac{m_i}{m_{tot}} \]
  \[ \sum w_i = 1 \]
  \[ m = \sum m_i \]

- **Mole Fraction** \( y_i \): ratio of component's moles to the total moles of the mixture:
  \[ y_i = \frac{x_i}{N_{tot}} \]
  \[ N_i \]
  \[ \sum y_i = 1 \]
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Mass and Mole Fraction

Molecular Weight of Mixture:

\[ M_{\text{mix}} = \frac{m_{\text{tot}}}{N_{\text{tot}}} = \sum y_i (M_{w_i}) \]

Mass to Mole Fraction Conversion:

\[ y_i = \frac{w_i}{\sum w_{w_i}} \]

Mole to Mass Fraction Conversion:

\[ w_i = \frac{y_i (M_{w_i})}{\sum y_i (M_{w_i})} \]

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Mass and Mole Fraction

Find the molecular weight & gas constant for a gaseous mixture consisting of:

- CO₂ = 14%,
- O₂ = 5%,
- N₂ = 78% and
- CO = 3%

<table>
<thead>
<tr>
<th>Gas</th>
<th>% Volume</th>
<th>Mole Fraction</th>
<th>Molecular Weight</th>
<th>Mass (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>14</td>
<td>0.14</td>
<td>44</td>
<td>6.16</td>
</tr>
<tr>
<td>O₂</td>
<td>5</td>
<td>0.05</td>
<td>32</td>
<td>1.6</td>
</tr>
<tr>
<td>N₂</td>
<td>78</td>
<td>0.78</td>
<td>28</td>
<td>21.84</td>
</tr>
<tr>
<td>CO</td>
<td>3</td>
<td>0.03</td>
<td>28</td>
<td>0.84</td>
</tr>
</tbody>
</table>

\[ Y=1 \quad \text{Total Mass} = 30.44 \]

Note: \( Mass(i) = \text{Mole fraction} \times M_{w_i} \)

\[ M_{w_{\text{mix}}} = \sum y_i (M_{w_i}) \]
Partial Pressure

- A mixture of gases (at pressure $P$) can also be expressed in terms of partial pressures ($P_i$) of each of the $i^{th}$ components ($i$);

$$P = \sum_i P_i$$

and

$$P_i = \frac{m_i R T P}{V}$$

Recall

$$V_i = \frac{m_i R T}{P}$$

Mole Fraction:

$$y_i = \frac{P_i}{P} = \frac{V_i}{V}$$

Partial Volume

- Total volume = the sum of partial volumes

$$V = \sum_i V_i$$
Partial Pressure

- Since the volume fraction of $O_2$ in air = 0.2095, than its partial pressure will be 0.2095 atm.
- Find mass concentration (density) of $O_2$ @ 0 °C?

Mass Fraction

- Since the density of $O_2$ = 0.2993 kg $O_2/m^3$ in air find the mass fraction at STP?
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Fuel/Air Mass Ratio & Volume Percent

- Find a relationship for the F/A ratio of a mixture within the enclosed volume.

\[
F/A = \frac{m_f}{m_a} = \frac{\rho_f f}{\rho_a a} = \frac{(\varphi PMw RT)^f}{(\varphi PMw RT)_a}
\]

- Now consider 2 cases: a) components of the mixture are separated by a thin membrane, and b) components are mixed together.

Case a: components of the mixture are separated by a thin membrane, find F/A in terms of Vf%.

\[
F/A = \frac{(\varphi PMw)^f}{(\varphi PMw)^a}
\]

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Fuel/Air Mass Ratio & Volume Percent

- Case a: components of the mixture are separated by a thin membrane, find F/A in terms of Vf%.

\[
F/A = \frac{(\varphi Mw)^f}{(\varphi Mw)^a} \quad (1)
\]

\[
\forall f \% = \frac{\forall f \times 100}{\forall T}
\]

\[
\forall f \% = \frac{\forall f \times 100}{(\forall a + \forall f)}
\]

\[
\forall f = \frac{\forall a \times \forall f \%/ (100 - \forall f \%)}{\forall a}
\]

eqs 1 & 2 combined

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Fuel/Air Mass Ratio & Volume Percent

- **Case b:** Using Daltons Law: pressure of a mixture is equal to the pressure of the individual components. Find F/A in terms of partial pressures?

\[
F/A = \frac{\left(\frac{M_w}{M_a}\right)_f \times \%_{\text{Vol.}}^f}{\left(\frac{M_w}{M_a}\right)_a (100 - \%_{\text{Vol.}}^f)}
\]

but \(\%_{\text{Vol.}}^f = 100 \times \frac{P_f}{P_T}\)

so,

\[
F/A = \frac{\left(\frac{M_w}{M_a}\right)_f P_f}{\left(\frac{M_w}{M_a}\right)_a P_a}
\]

Note: \(M_w\) must be the molecular weight of the fuel vapor, not the liquid fuel used in the Fuel/Air Mass Ratio.

Fuel/Air Mass Ratio & Volume Percent

- We also know?

\(\%_{\text{Vol.}}^f = 100 \times \frac{n_f}{n_T}\) and \(F/A = \frac{\left(\frac{M_w}{M_a}\right)_f n_f}{\left(\frac{M_w}{M_a}\right)_a n_a}\)

- Therefore how much liquid Hexane is necessary to make a 1000 ft\(^3\) room flammable at 14.7 psia and 155°F?

- **Given:** \(LL = 1.2 \text{ Volume } % \text{ (Lower Limit)}\)

\(C_6H_{14} = M_w = 86.17 \text{ lbm/lbm-mole}\)

- So; \(\frac{\%_{\text{Vol.}}^f}{\%_{\text{Vol.}}^T} = 0.012\)

and therefore: \(\%_{\text{Vol.}}^f = 12 \text{ ft}^3\) (remember this is the vapor volume)
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Fuel/Air Mass Ratio & Volume Percent

• The mass \( M_f \) is then found:

\[
M_f = \text{P} \cdot \frac{\text{P \text{\textregistered}}}{\text{RT}}
\]

• Now use the \( M_f \) to determine the amount of liquid fuel:

\[
1 \text{ ft}^3 = 957.506 \text{ oz}
\]

Volume of liquid Hexane: 53.14 oz