Fundamentals of Explosions
Definitions of Basic Combustion Parameters

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• Consequences of an explosion:
  ▫ Blast
  ▫ Fire
  ▫ Toxicity
• Given an accidental scenario, what is the volume of explosive mixture?
  ▫ A fluid mechanics problem of dispersion and turbulent mixing
• Given a volume of explosive gas mixture (within the flammability limits), what is the blast pressure?
  ▫ Depends on the burning rate (flame speed)
• What is the turbulent flame speed for initial and boundary conditions?
  ▫ Central problem in explosion risk assessment
Explosion Dynamics

- Chemical thermodynamics (stoichiometry, energetics)
- Chemical kinetics (reaction mechanisms, rates of reactions)
- Combustion (ignition, flame propagation and flammability limits, quenching, MESG)
- Gas dynamics (detonation waves, initiation, limits, DDT)
Chemical Thermodynamics

- Equilibrium species and concentrations in products

- Energetics of a reaction (for a given path, i.e., constant volume, pressure across a combustion wave)
Stoichiometry

• Relationship between the composition of the reactants and products.
  ▫ Atoms are conserved in a chemical reaction
  ▫ Stoichiometric mixture – just the right amount of oxidizer for the given fuel
  ▫ Assume complete combustion
    • C→CO₂, H→H₂O, S→SO₂, N₂→N₂
• e.g. \[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \]
\[ H_2 + \frac{1}{2} (O_2 + 3.76N_2) \rightarrow H_2O + 1.88N_2 \]
\[ H_2 + 2.38 \text{ air} \rightarrow H_2O + 1.88 \text{ N}_2 \]

• Percentage by mole  66.6% H₂, 33.4% O₂

• Percentage by weight  11.1 % H₂, 88.9% O₂

• Percentage by mole  29.6% H₂, 70.4% air
Fuel-air ratio

\[ FA = \frac{\text{moles of fuel}}{\text{moles of air}} \]

e.g. \( H_2 + \frac{1}{2} (O_2 + 3.76N_2) \rightarrow H_2O + 1.88N_2 \)

\[ FA = \frac{1}{2.38} = 0.42 \]

• by mass \( 2 \ H_2 + 68.64 \text{ air} \)

\[ FA_{\text{mass}} = \frac{2}{68.64} = 0.029 \]
Equivalence Ratio

$$\phi = \frac{(FA)_{\text{mixture}}}{(FA)_{\text{stoichiometric}}}$$

\(\phi = 1\) stoichiometric composition

\(H_2 + 2.38\ \text{air} \rightarrow H_2O + 1.88\ \text{N}_2\)

\(\phi < 1\) fuel lean

\(\phi > 1\) fuel rich
Enthalpy of a Compound

\[ \tilde{h}(T) = \tilde{h}_f^o + \int_{298}^{T} c_p \, dT \]

\[ = \tilde{h}_f^o + \Delta \tilde{h}(T) \]

- \( \tilde{h}_f^o \) enthalpy of formation
  - enthalpy change when a compound is formed from its stable elements at standard reference state, i.e. 298K, 1 atm.

- \( \tilde{h}_f^o = 0 \) for stable elements at reference state
Enthalpy (heat) of Reaction

- heat exchange when reactants go to products at constant pressure and temperature

\[
\Delta h_R = \frac{\sum_{\text{products}} n_i h_i(T) - \sum_{\text{reactants}} n_i h_i(T)}{\text{moles of fuel}}
\]

Adiabatic Flame Temperature \( T_a \)

- temperature of products in an adiabatic constant pressure process

\[
\Delta H = \sum_{\text{products}} n_i \tilde{h}_i(T_a) - \sum_{\text{reactants}} n_i \tilde{h}_i(298) = 0
\]
Constant Volume Explosion Pressure

- pressure rise in a constant volume adiabatic process

\[ \Delta U = \sum_{\text{products}} n_i \tilde{U}_i - \sum_{\text{reactants}} n_i \tilde{U}_i = 0 \]

\[ \tilde{U}_i = \tilde{h}_i(T) - P_i \tilde{V} \]

\[ \frac{P_{\text{product}}}{P_{\text{reactant}}} = \frac{n_{\text{product}} T_a}{n_{\text{reactant}} T_0} \]
Combustion Wave

\[ \begin{align*}
\rho_o u_o & = \rho_1 u_1 \\
p_o + \rho_o u_o^2 & = p_1 + \rho_1 u_1^2 \\
h_o + \frac{u_o^2}{2} & = h_1 + \frac{u_1^2}{2} \\
h_o & = \sum_{\text{reactants}} x_i h_i \\
h_1 & = \sum_{\text{products}} x_i h_i \\
h_i & = h_i^0 + \int_{298K}^T c_{p_i} T \\
P_V & = \rho RT
\end{align*} \]
Chemical Kinetics

- Deals with reaction mechanisms (details steps) and the rates of chemical reactions
Reaction Mechanisms

• Global
  ▫ Fuel + Oxidizer $\rightarrow$ Products

• Elementary
  e.g. $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ (global)

  $\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$
  $\text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M}$
  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$
  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$
  $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$
  etc.
Reduced mechanisms

• A few important intermediate steps to represent the overall reaction

  □ e.g.  \( \text{H}_2 - \text{O}_2 \)

    • Chain initiation:  \( \text{H}_2 + \text{O}_2 \rightarrow \text{H} + \text{HO}_2 \)
    • Main branching:  \( \text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH} \)
    • Main heat release:  \( \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \)
    • Chain termination:  \( \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \)
    • Secondary chain termination:  \( \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \)
    • Secondary chain branching:  \( \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH} \)
Reaction Rate

- **Unimolecular**
  \[ A \xrightarrow{k} B \]
  \[- \frac{d[A]}{dt} = k[A] \]

- **Bimolecular**
  \[ A + B \xrightarrow{k} C \]
  \[- \frac{d[A]}{dt} = - \frac{d[B]}{dt} = k[A][B] \]

- **Termolecular**
  \[ A + B + C \xrightarrow{k} D \]
  \[- \frac{d[A]}{dt} = - \frac{d[B]}{dt} = - \frac{d[C]}{dt} = k[A][B][C] \]
• $k \rightarrow$ rate constant fit to a law of the form

$$k(T) = AT^b \exp \left( \frac{E_a}{RT} \right)$$

- Can also fit global reaction to a global rate constant.
  - e.g. Hydrocarbon fuel $\text{CnHm}$

$$C_nH_m + \left( n + \frac{m}{4} \right)O_2 \xrightarrow{k_g} nCO_2 + \frac{m}{2}H_2O$$

$$k_g = AT^n [C_nH_m]^a [O_2]^b \exp \left( - \frac{E_a}{RT} \right)$$
Since for high activation energy the temperature dependence is controlled by the exponential term, the power law dependence is dropped, i.e.

\[ k = A[fuel]^a [O_2]^b \exp \left( -\frac{E_a}{RT} \right) \]

The exponential form of the rate law is referred to as the Arrhenius rate law.
Explosion (Rapid Runaway Reactions)

- Can be a consequence of rapid chain branching reaction

- Thermal runaway is a result of strong temperature dependence of reaction rate.
Explosion Limit

- Reaction rates are temperature and pressure dependent. There exist a critical state that defines if runaway reactions will occur or not.

- Represented by a curve in the thermodynamic state $(p, T)$ plane bounding regions of “explosion” and “no explosions”.
• Classical example is the Z-shaped curve for the explosion limit of \( \text{H}_2 - \text{O}_2 \) reaction.

• For a fixed temperature, “explosion” or “no explosion” depends on pressure.
Explosion limits for hydrogen-oxygen mixture.
• Consider a fixed temperature of 500°C

  - For $p \leq 1.5$ torr, no explosion
    - diffusion losses to wall (1st limit)

  - For $1.5$ torr $\leq p \leq 50$ torr, explosion occurs
    - chain branching dominates

  - For $50$ torr $\leq p \leq 3000$ torr, no explosion
    - Three body recombination chain terminating reactions dominate over chain branching
- For $p \geq 3000$ torr, explosion occurs
  - Formation of $\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$ dominates over diffusion losses of $\text{HO}_2$

- For $T \geq 580$ °C, explosion occurs for all pressures
  - Dissociation of $\text{H}_2\text{O}_2$ is important
Homogeneous Adiabatic Constant Volume Thermal Explosion

- First law
  \[ \frac{dU}{dt} = \dot{q}_R Q \]

  \[ \dot{Q}_R = k_o c^n \exp\left(-\frac{E_a}{RT}\right)Q \]

  \[ \Delta T \sim -\Delta c \]

  \[ \frac{dT}{dt^*} = (T_{\text{max}} - T)^n \exp\left(-\frac{E_a}{RT}\right) \]

  \[ t^* = k_o t \quad , \quad \text{consider } n=1 \]
• Integrating numerically from $T_o$ to $T_{max}$
  - e.g.: $T_o = 800$ K, $T_{max} = 2000$ K, $E_a = 20$ kcal/mol, $R = 1.98$ cal/(mol K)

  ▫ Results:
    - Very slow initial temperature rise
    - Very rapid rise in $T$ where $T \approx 1100$ K
    - Very rapid decrease in fuel when $T \geq 1100$K
Temperature, concentration and reaction rate profile.
• Induction period $\tau_i \rightarrow$ negligible duration of temperature rise

• Reaction time $\tau_R \rightarrow$ period of rapid temperature rise to $T_{max}$

• Strong dependence of $\frac{\tau_R}{\tau_i}$ on $E_a$
  
  e.g. $\frac{\tau_R}{\tau_i} \approx 0.3$ for $E_a = 20$ kcal
  
  $\frac{\tau_R}{\tau_i} \approx 0.00035$ for $E_a \approx 40$ kcal
Thermal Runaway (Ignition)

• Reaction rates are finite at finite temperatures, without losses all explosive mixtures will eventually undergo runaway reaction

• Runaway reaction occurs when rate of heat production due to reaction exceed rate of heat loss
• First law

\[ \frac{n \tilde{c}_v}{V} \frac{dT}{dt} = \dot{q}_R - \dot{q}_L \]

- L.H.S. Rate of change of internal energy per unit volume
- Rate of energy release per unit volume

\[ \dot{q}_R = A[F]^a [O]^b \exp \left( - \frac{E_a}{RT} \right) Q \]

- Rate of heat loss per volume

\[ \dot{q}_L = \frac{hS}{V} (T - T_o) \]
• At 1, stable if \( T < T_1 \) \( \dot{q}_R > \dot{q}_L \)
  \( T > T_1 \) \( \dot{q}_L > \dot{q}_R \)
• At 2, unstable \( T<T_2 \), \( \dot{q}_L > \dot{q}_R \)

system \( \rightarrow 1 \)

\( T>T_2 \), \( \dot{q}_R > \dot{q}_L \) runaway

\( T>T^* \), \( \dot{q}_R > \dot{q}_L \) ignition

\( T^* \) - ignition temperature
• At critical ignition point \( (T = T^*) \)

\[
\dot{q}_R = \dot{q}_L \quad \left( \frac{d\dot{q}_R}{dT} \right)^* = \left( \frac{d\dot{q}_L}{dT} \right)^*
\]

\[
AQ[F]^a [O]^b \exp \left( -\frac{E_a}{RT_i} \right) = \frac{hS}{V} (T - T_o)
\]

\[
AQ[F]^a [O]^b \frac{E_a}{RT_i^2} \exp \left( -\frac{E_a}{RT_i} \right) = \frac{hS}{V}
\]
• Dividing the two equations yield

\[
\frac{RT^*^2}{E_a} = T^* - T_o
\]

• Solving for \( T^* \)

\[
T^* = \frac{E_a}{2R} \left\{ 1 \pm \sqrt{1 - \frac{4RT_o}{E_a}} \right\}
\]

• Take the negative root

\[
0 \leq T_o \leq \frac{E_a}{4R} \quad 0 \leq T^* \leq \frac{E_a}{2R}
\]
• In general \( T_0 \ll \frac{E_a}{4R} \)

\[
T^* \approx \frac{E_a}{2R} \left\{ 1 - \left( 1 - 2 \frac{RT_0}{E_a} - 2 \frac{R^2T_0^2}{E_a^2} \ldots \right) \right\}
\]

• First approximation

\[ T^* \approx T_0 \]

• Second approximation

\[ T^* \approx T_0 + \frac{RT_0^2}{E_a} \]

\[
\frac{T^* - T_0}{T_0} = \frac{T^*}{T_0} - 1 \approx \frac{RT_0}{E_a}
\]
• Given a heat release curve and the size of the volume there exist a critical value of $T_o$ when runaway occurs.
• Given a $T_0$ and heat release curve $\dot{Q}_R$, there exist a critical volume above which runaway occurs

\[
\frac{d\dot{Q}_L}{dT} = \frac{A}{V}
\]
Minimum ignition energy

- Assume spherical volume
  \[ V = \frac{4\pi r^3}{3} \]
- From \( \dot{q}_R = \dot{q}_L \)
  \[
  AQ[F]^a[O]^b \exp\left(-\frac{E_a}{RT}\right) = \frac{hS}{V} (T - T_o)
  \]
  \[
  \frac{S}{V} = \frac{4\pi r^*^2}{4\pi r^*^3} = \frac{3}{r^*}
  \]
  \[
  r^* = \frac{3h(T_a - T_o)}{AQ[F]^a[O]^b \exp\left(-\frac{E_a}{RT}\right)}
  \]
- Adiabatic flame temperature \( T^* \approx T_a \)
Minimum ignition energy

- External energy to heat flame kernel to ignition temperature \( T^* \approx T_a \)

\[
E_{\text{min}} = \rho \frac{4 \pi r^*^3}{3} c_p (T_a - T_o)
\]

\[
r^* = \frac{3h(T_a - T_o)}{AQ[F]^a[O]^b \exp \left( -\frac{E_a}{RT} \right)}
\]

- Minimum ignition spark energy determinedexperimentally
  - Circuit parameter, electrode configuration, etc.
  - Standardized ASTM E582-07
Scheme of apparatus for determining minimum ignition energies for electric-spark ignition
Minimum ignition energies of combustible-air mixtures in relation to the stoichiometric percentage in air.
Quenching distance $d_q$

- Minimum tube diameter (or gap) in which self-sustained flame propagation is possible
- Balance between heat production by chemical reactions in flame zone and losses from boundaries of reaction zone, i.e. $\dot{q}_R = \dot{q}_L$
  \[
  d_q \approx r^* \approx \delta
  \]
- $\delta \rightarrow$ Laminar flame thickness
- Different methods used to determine quenching distance
• Flash back method

• Tapered tube

• Flanged electrode
Minimum ignition energies for free and glass-flanged electrode tips as function of electrode distance.
Minimum ignition energies for glass-flanged electrode tips as function of electrode distance and pressure
Minimum ignition energies and quenching distances for hydrogen-oxygen-inert gas mixtures at atmospheric pressure. $O_2/(O_2 + \text{inert gas}) = 0.21$
<table>
<thead>
<tr>
<th>Flame system</th>
<th>Quenching distance $D_q$(cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen-air</td>
<td>0.004, 0.050, 0.053, 0.006</td>
<td>19, 25, 26, 27</td>
</tr>
<tr>
<td>Hydrogen-oxygen</td>
<td>0.019, 0.023, 0.034</td>
<td>4, 8, 19</td>
</tr>
<tr>
<td>Methane-air</td>
<td>0.25, 0.24, 0.216</td>
<td>3, 5, 19</td>
</tr>
<tr>
<td>Methane-oxygen</td>
<td>0.02</td>
<td>19</td>
</tr>
<tr>
<td>Acetylene-air</td>
<td>0.052, 0.065</td>
<td>21, 27</td>
</tr>
<tr>
<td>Acetylene-oxygen</td>
<td>0.010, 0.008</td>
<td>8, 21</td>
</tr>
<tr>
<td>Ethylene-air</td>
<td>0.125</td>
<td>13</td>
</tr>
<tr>
<td>Ethylene-oxygen</td>
<td>0.019</td>
<td>8</td>
</tr>
<tr>
<td>Methyl acetylene-air</td>
<td>0.115</td>
<td>27</td>
</tr>
<tr>
<td>Propane-air</td>
<td>0.21, 0.203, 0.218, 0.228, 0.175</td>
<td>5, 6, 7, 19, 27</td>
</tr>
<tr>
<td>Propane-argon-air</td>
<td>0.104</td>
<td>41</td>
</tr>
<tr>
<td>Propane-helium-air</td>
<td>0.233</td>
<td>41</td>
</tr>
<tr>
<td>Propane-oxgen</td>
<td>0.027, 0.025, 0.0210</td>
<td>5, 8, 19</td>
</tr>
<tr>
<td>1,3-butadiene-air</td>
<td>0.125</td>
<td>27</td>
</tr>
<tr>
<td>iso-Butane-air</td>
<td>0.223</td>
<td>27</td>
</tr>
<tr>
<td>n-Butane-air</td>
<td>0.207</td>
<td>27</td>
</tr>
<tr>
<td>Benzene-air</td>
<td>0.194, 0.187, 0.195</td>
<td>25, 26, 27</td>
</tr>
<tr>
<td>Cyclohexene-air</td>
<td>0.213</td>
<td>27</td>
</tr>
<tr>
<td>Cyclohexane-air</td>
<td>0.301</td>
<td>27</td>
</tr>
<tr>
<td>n-Hexane-air</td>
<td>0.205</td>
<td>25</td>
</tr>
<tr>
<td>Hexene-1-air</td>
<td>0.187</td>
<td>25</td>
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<tr>
<td>n-Hexyne-air</td>
<td>0.185</td>
<td>27</td>
</tr>
<tr>
<td>n-Heptene-air</td>
<td>0.208, 0.220</td>
<td>26, 27</td>
</tr>
<tr>
<td>Diisobutylene-air</td>
<td>0.322</td>
<td>27</td>
</tr>
<tr>
<td>Isocotane-air</td>
<td>0.264, 0.241, 0.347</td>
<td>25, 26, 27</td>
</tr>
<tr>
<td>n-Decane-air</td>
<td>0.206</td>
<td>25</td>
</tr>
<tr>
<td>Decene-1-air</td>
<td>0.197</td>
<td>25</td>
</tr>
<tr>
<td>n-Butyl benzene-air</td>
<td>0.228</td>
<td>25</td>
</tr>
<tr>
<td>Ethylene oxide-air</td>
<td>0.118</td>
<td>27</td>
</tr>
<tr>
<td>Propylene oxide-air</td>
<td>0.131</td>
<td>27</td>
</tr>
<tr>
<td>Propionaldehyde-air</td>
<td>0.175</td>
<td>27</td>
</tr>
<tr>
<td>Methyl formate-air</td>
<td>0.165</td>
<td>27</td>
</tr>
<tr>
<td>Vinyl acetate-air</td>
<td>0.235</td>
<td>27</td>
</tr>
<tr>
<td>Diethyl ether-air</td>
<td>0.193, 0.185</td>
<td>26, 27</td>
</tr>
<tr>
<td>Diisopropyl ether-air</td>
<td>0.300</td>
<td>27</td>
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<tr>
<td>Acetylene-nitrous oxide</td>
<td>0.036</td>
<td>22</td>
</tr>
<tr>
<td>Ethylene-nitrous oxide</td>
<td>0.048</td>
<td>22</td>
</tr>
<tr>
<td>Ethane-nitrous oxide</td>
<td>0.059</td>
<td>22</td>
</tr>
<tr>
<td>Acetylene-nitric oxide</td>
<td>0.024</td>
<td>22</td>
</tr>
<tr>
<td>Ethylene-nitric oxide</td>
<td>0.044</td>
<td>22</td>
</tr>
<tr>
<td>Ethane-nitric oxide</td>
<td>0.061</td>
<td>22</td>
</tr>
<tr>
<td>Carbon disulfide-air</td>
<td>0.035</td>
<td>27</td>
</tr>
<tr>
<td>55% Hydrogen-45% bromine</td>
<td>0.45, 0.39, 0.25</td>
<td>14, 73, 73</td>
</tr>
</tbody>
</table>

Quenching distance for various flames at 1 atmosphere for stoichiometric mixtures at room temperature.
Comparison of quenching distances from different methods

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Flanged Electrode Quenching Distance (cm)</th>
<th>Burner Quenching Diameter (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.216, 0.201</td>
<td>0.24, 0.24</td>
</tr>
<tr>
<td>Propane</td>
<td>0.228, 0.175, 0.185</td>
<td>0.203, 0.20, 0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.208, 0.20, 0.189</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.190</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.195</td>
<td>0.194, 0.187</td>
</tr>
<tr>
<td>n-Haptane</td>
<td>0.22</td>
<td>0.208</td>
</tr>
<tr>
<td>iso-octane</td>
<td>0.347</td>
<td>0.264, 0.241</td>
</tr>
<tr>
<td>Diethyle Ether</td>
<td>0.185</td>
<td>0.193</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.06, 0.064</td>
<td>0.050, 0.053</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Burner</th>
<th>Tube</th>
<th>Stability Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-octane-air stoich. 0.2 atm 50°C</td>
<td>1.48</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>Propane-air, stoich. 100 mm Hg, room temp.</td>
<td>1.78</td>
<td>1.68</td>
<td>1.8</td>
</tr>
<tr>
<td>Acetylene-oxygen stoich. 100 mm Hg, room temp.</td>
<td>0.10</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Hydrogen-air stoich. 150 mm Hg, room temp.</td>
<td>0.50</td>
<td>-</td>
<td>0.90</td>
</tr>
<tr>
<td>Propane-50% O₂, 50% N₂ stoich., 150 mm Hg, room temp.</td>
<td>0.36</td>
<td>-</td>
<td>0.53</td>
</tr>
</tbody>
</table>
MESG (maximum experimental safe gap)

- Maximum gad in which explosion can be transmitted from one chamber to another standard apparatus used 20 ml vessel European standard 8 L sphere

- Westerburg apparatus
  - (Underwriter’s lab)
20 ml explosion vessel.
8 L explosion vessel. (SMRE 25.4 mm (1 inch) Flanges, Assembly: 4 or 6 G Clamps
Flammability Limits

- Conditions that define whether self-sustained flame propagation is possible or not

  - **Conditions**:
    - Thermodynamic state \((p, T)\)
    - Boundary condition (tube diameter)
    - Composition (equivalence ratio)
    - Percentage of inert diluent
• Physics involved in flammability limits – very diverse (heat losses, flame stretch, buoyancy, stability)

• In general, flammability limits are defined for fuel composition, lean and rich limit
• Effect of buoyancy give rise to upward, downward, horizontal limits

• Effect of tube diameter resolved by choosing a sufficiently large diameter where dependence is weak \( d \geq 5 \) cm

• Standard apparatus → Flammability tube used by Coward and Jones 1.5m long, 5cm diameter
• Closed explosion vessel also used criterion based on achieving some arbitrary pressure rise

• Flame stretch and thermo-diffusive instability play important role near limits
For mixture of different fuels Le Chatelier rule is used, i.e.

\[
\frac{c_A}{c_A^*} + \frac{c_B}{c_B^*} = 1
\]

- \(c_A, c_B\) - concentration of fuel A and B of mixture
- \(c_A^*, c_B^*\) - limiting concentration of fuel A and B respectively
• Le Chatelier rule is essentially based on energetics of fuels.
  ▫ Works for fuels having same physical properties, i.e.
    • molecular weights
    • diffusivity
    • reaction rates, etc.
Combustion in a closed vessel

- Can be used to determine flammability limits
- Constant volume explosion pressure → energetics of mixture
- Burning velocity
- $k_g$ factor for explosion venting design
Can derive relationship between $p$, $\Delta P_{\text{max}}$, $\frac{d\Delta p}{dt}$ and $S$

$$\frac{d\Delta p}{dt} = \frac{3\Delta P_{\text{max}}}{R} S \left( \frac{p}{p_o} \right)^{\frac{1}{\gamma}} \left[ 1 - \left( \frac{p_o}{p} \right)^{\frac{1}{\gamma}} \left( 1 - \frac{\Delta p}{\Delta P_{\text{max}}} \right) \right]^{\frac{2}{3}}$$

- $P(t)$, $\Delta P_{\text{max}}$ measured
- $S$ is the burning velocity and can be determined
• *k* sub*g* factor is defined as

\[
    k_g = V^{\frac{1}{3}} \left( \frac{d\Delta p}{dt} \right)_{\text{max}}
\]

\[
    = V^{\frac{1}{3}} (\Delta p_{\text{max}}, S)
\]

• A measure of the rate of pressure rise in the vessel

\[
    V^{\frac{1}{3}}
\]

• $V^{\frac{1}{3}} \sim$ Length scale of the vessel to normalize the rate of pressure rise for different size vessel
Explosion Venting

- Reactants (or products) are discharged from vessel to limit maximum overpressure developed.

- Rate of enthalpy vented equal rate of chemical energy release.

- NFPA Guideline 68 for vent area-volume ratio, $k_g$ factor.
• Given explosive mixture at given initial conditions \((p,T, \text{chemical composition, etc.})\), there are two mode of combustion:
  - deflagration
  - detonation

• Product temperature more or less the same but combustion rate differs by \(10^4\) times
Deflagration Wave (Propagating Flame)

- Subsonic relative to unburned mixture ahead of it

- Expansion wave, pressure drops across flame

- Unburned mixture ahead is set into motion due to increase in specific volume across flame
• Burning velocity $S$ relative to mixture ahead

• Flame speed $\dot{R}_f$ relative to fixed coordinate system

• If the deflagration is fast, there is a precursor shock ahead of flame front
• Deflagration propagates as a diffusion wave

  ▫ Heat and radical species diffuses from reaction zone ahead to effect ignition

  ▫ Burning velocity $S \sim \sqrt{\alpha \over t_c}$ $\alpha$-diffusivity $t_c \sim {1 \over \omega_c}$ reaction time, $S$~cm/s

  ▫ Laminar flame thickness $\delta$~1mm

  ▫ Effect of curvature and stretch on burning velocity

  ▫ Laminar flame unstable-cellular
• Propagating flame – deflagration
  ▫ Self accelerate due to positive feedback mechanism

• Max deflagration speed \( \sim \frac{1}{2} \) CJ detonation speed

• DDT transition to detonation
Detonation Wave

- Propagate at supersonic speed relative to reactants in front of it

- Compression shock wave that initiate chemical reaction via adiabatic compression to auto-ignition temperature

- Expansion in reaction zone and products (Taylor wave) produce forward thrust to derive leading shock front
• ZND structure (Zeldovich- von Neumann – Döring) model of detonation zone – leading shock followed by induction zone and reaction zone
• Chapman-Jouguet detonation $\rightarrow$ sonic velocity of product (relative to the detonation)
  ▫ Minimum velocity solution of steady conservation laws (tangent of Rayleigh line to Hugoniot)
• Typical stoichiometric mixtures at 1atm, 298K, $D_{CJ} \sim 1800$ms

• Detonation pressure $\Delta p_{CJ} \approx 15$

• A detonation is generally unstable

• Longitudinal instability → Pulsating detonation
• Transverse instability $\rightarrow$ cellular structure

• Detonation cell size measure by smoked foil technique

• Useful length scale to characterize detonation zone thickness

• Cell size $\sim$ ZND reaction zone length

• Spinning detonation – lowest transverse unstable mode in a circular tube. Stationary structure with respect to rotating frame fixed to spinning head
(a) Side wall and (b) end-on soot records of a multiheaded detonation

Courtesy of S.B. Murray
Detonability Limits

• Critical conditions that define if self-sustained detonation can propagate

• Critical conditions:
  ▫ initial state \((p,T)\), composition, amount of inert diluent, tube diameter, nature of tube wall

• Composition limit → given a tube diameter, lean and rich limits
• Given a mixture composition there is a limiting:
  ▫ tube diameter
  ▫ pressure limit (e.g. too low, too high)

• No theory for detonation limit prediction

• Experiment determination lacks an operational definition of a limit criterion

• Complex near limit phenomena:
  ▫ Single headed spin, pulsating, galloping detonation, etc.
• Failure mechanism
  ▫ Stable detonation $\rightarrow$ curvature
  ▫ Unstable detonation $\rightarrow$ suppressing instability

• Sensitivity of mixture measured by detonation cell size $\lambda$.

• $\lambda$ depends on mixture composition, inert diluent, initial pressure, etc.
• Boundary conditions characterized by tube diameter

• $\lambda = \pi d$ may serve as limit criterion for spinning detonation
Direct Initiation

- Formation of detonation from the conditions generated by the ignition source directly

- By pass the flame acceleration and pre-detonation deflagration stage

- Blast initiation → strong decaying blast wave generated by powerful ignition source
  - high energy spark, exploding wire, condensed explosive charge
Sequence of schlieren photographs of supercritical regime

• Direct initiation possible if decaying blast is of sufficient duration

• Zeldovich criterion:
  ▫ blast strength > Chapman-Jouguet detonation for a duration > induction time

• Propagation distance of black wave (above Chapman-Jouguet detonation strength) > detonation zone thickness
• Blast decay characterized by explosion length

\[ R_o = \left( \frac{E_c}{P_o} \right)^{\frac{1}{3}} \]

• Detonation sensitivity characterized by reaction zone thickness (or cell size \( \lambda \))

• Zeldovich criterion \( \rightarrow E_c \sim \lambda^3 \)
• Explosion length scaling for different geometry

\[
\left( \frac{E_c}{p_o} \right)_{\text{planar}} = \left( \frac{E_c}{p_o} \right)_{\text{cylindrical}}^{1/2} = \left( \frac{E_c}{p_o} \right)_{\text{spherical}}^{1/3}
\]

• Direct initiation also possible by flash photolysis, turbulent jet mixing

• SWACER mechanism → induction time gradient to permit energy release in phase with shock wave
Critical Tube Diameter

- Minimum diameter of tube that permits planar detonation to diffract to a spherical detonation
  - Failure mechanisms
  - Stable detonations → curvature
  - Unstable detonations → suppresses growth of instability

- S & M criterion for unstable detonation $d_c \sim \frac{13\lambda}{85}$
Sequence of schliere photographs of a planar detonation emerging from a tube into unconfined space in (A) the subcritical case and (B) supercritical case.

Courtesy of R.I. Soloukin
• Stable detonation \( d_c > 13 \lambda \quad d_c \approx 40\lambda \)

• Effect of wall
  
  ▫ Acoustic absorbing walls \( d_c \approx 6\lambda \)
  ▫ Readily deformable wall \( d_c \approx 5\lambda \)
  ▫ Rough wall \( \rightarrow \) quasi detonation

\[ 0.3V_{\text{CJ}} \leq V_D \leq V_{\text{CJ}} \]
Transition from Deflagration to Detonation DDT

- Flame acceleration phase subsequent to ignition

- Mechanisms of flame acceleration:
  - Flame folding
  - Turbulence
  - Instability
  - Acoustic-flame interaction
  - Metastable deflagration
Typical streak photograph of the abrupt transition to detonation via a jet of hot combustion products

Lee et al. 1996
Mechanisms of flame acceleration (continued):

- Explosion centers
- Growth of instability
- Transverse acoustic amplification
- Onset of detonation
- Effect of wall roughness
- Obstacles Schelkin spiral