Outline

- Why do we need to study combustion?
- Types of flames
  - Premixed
  - Nonpremixed
- Basics of chemical reaction rates
  - Law Of Mass Action (LOMA)
  - Arrhenius form of temperature dependence
- Premixed flames
  - Deflagrations
  - Turbulence effects
  - Homogeneous reaction
- Nonpremixed flames
  - General characteristics
  - Droplets
  - Gas-jet
  - Turbulence effects
Why do we need to study combustion?

- Chemical thermodynamics only tells us end states - what happens if we wait "forever and a day" for chemical reaction to occur
- We also need to know how fast reactions occur
  - How fast depends on both the inherent rates of reaction and the rates of heat and mass transport to the reaction zone(s)
  - Chemical reactions + heat & mass transport = combustion
  - Some reactions occur too slowly to matter, e.g.
    \[ 2 \text{NO} \rightarrow \text{N}_2 + \text{O}_2 \]
    has \( T_f = 2869 \text{K} \) (no dissociation) or 2650K (with dissociation, mostly NO & O) but no pure NO flames exist - reaction rates are too slow!
- What to do with this information?
  - Determine rates of flame propagation and heat generation
  - Determine conditions for "knock" in premixed-charge engines
  - Determine rates of pollutant formation and destruction

Types of flames

- Premixed - reactants are completely mixed down to the molecular scale before combustion is initiated; several flavors
  - Deflagration
  - Detonation
  - Homogeneous reaction
- Nonpremixed - reactants mix only at the time of combustion - have to mix first then burn; several flavors
  - Gas jet (Bic lighter)
  - Liquid fuel droplet
  - Liquid fuel jet (e.g. Diesel spray flame, candle)
  - Solid (e.g. coal particle, wood)
**Premixed flames - deflagration**

- Propagating, subsonic front sustained by conduction of heat from the hot (burned) gases to cold (unburned) gases which raises temperature enough for chemical reaction to occur
- Chemical reaction rates are very sensitive to temperature, thus most reaction concentrated in a thin zone near the high-T side
- May be laminar or turbulent

**Reaction zone**
- $T_{ad} = 2000\text{K}$
- Product concentration

**Direction of propagation**
- Speed relative to unburned gas $= S_L$
- Reactant concentration

**Temperature**
- $T_\infty = 300\text{K}$
- $\delta \approx \alpha / S_L = 0.3 - 6\text{ mm}$
- Distance from reaction zone

**Convection-diffusion zone**

**Premixed flames - detonation**

- Supersonic front sustained by heating of gas by shock wave
- After shock front, need time (thus distance = time x velocity) before reaction starts to occur ("induction zone")
- After induction zone, chemical reaction & heat release occur
- Ideally only $M_3 = 1$ "Chapman-Jouget detonation" is stable
- Not particularly relevant to automotive engines or gas turbines

**Heat release zone**

**Induction zone**

<table>
<thead>
<tr>
<th>Heat release zone</th>
<th>Induction zone</th>
</tr>
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<tbody>
<tr>
<td>Pressure</td>
<td>M = 1</td>
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<tr>
<td>Temperature</td>
<td>M &lt; 1</td>
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<td>Shock</td>
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<tbody>
<tr>
<td>M = 1</td>
<td>M &lt; 1</td>
<td>M &gt; 1</td>
</tr>
</tbody>
</table>
Premixed flames - homogeneous reaction

- Model for knock in premixed-charge engines
- Fixed mass with uniform (in space) T, P, composition
- No "propagation" in space but propagation in time
- In laboratory, could heat chamber to a certain T and measure time to react; in engine, compression of mixture (increases P & T, thus reaction rate) initiates reaction

*Non-premixed* or *diffusion* flames

- Only subsonic, generally assume "mixed is burned" - mixing slower than chemical reaction
Law of Mass Action (LoMA) (1/2)

- The Law of Mass Action (LoMA): rate of chemical reaction is proportional to number of collisions between the reactant molecules, which in turn is proportional to concentration of each reactant.
- For a chemical reaction of the form
  \[ \nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D \]
  e.g. \( 1 \text{H}_2 + 1 \text{I}_2 \rightarrow 2 \text{HI} \)
  \( A = \text{H}_2, \nu_A = 1, B = \text{I}_2, \nu_B = 1, C = \text{HI}, \nu_C = 2, D = \text{nothing}, \nu_D = 0 \)

LoMA states that the rate of reaction is given by

\[
\frac{1}{\nu_A} \frac{d[A]}{dt} = \frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_C} \frac{d[C]}{dt} = \frac{1}{\nu_D} \frac{d[D]}{dt} = -k_f \left[ A \right]^{\nu_A} \left[ B \right]^{\nu_B} 
\]

\([ i ] = \) concentration of molecule \( i \) (usually moles per liter)

\( k_f = \) "forward" reaction rate constant
Law of Mass Action (LoMA) (2/2)

- Minus sign on right-hand side since A & B depleted, C & D formed
- How to calculate $[i]$?
  - Ideal gas law: total moles of gas per unit volume (all molecules, not just type i) = $P/RT$
  - Then $[i] = (\text{Total moles} / \text{volume}) \times (\text{moles } i / \text{total moles})$, thus $[i] = (P/RT)X_i$ ($X_i$ = mole fraction of i (see lecture 2))
- The reaction rate constant $k_f$ is usually of the Arrhenius form
  $$k_f = ZT^ae^{-E/RT}$$
  - $Z$ = pre-exponential factor, $a$ = nameless constant,
  - $E$ = "activation energy" (cal/mole)
  - Working backwards, units of $Z$ are (moles per liter)$^{1-a}$$A^{-a}$$B^{-b}$/(K$^a$sec)
- The $e^{-E/RT}$ term causes extreme sensitivity to $T$ for $E/RT >> T$!

Activation energy

- Boltzmann (1800's): fraction of molecules in a gas with kinetic energy greater than a value $E \sim e^{-E/RT}$, thus $E$ is "energy barrier" to overcome for reaction
- $E$ is not the same as $\Delta h_f$ (or heating value $Q_R$) - $E$ affects reaction rates whereas $\Delta h_f$ & $Q_R$ only affect end states (e.g. $T_{ad}$), although $\Delta h_f$ & $Q_R$ affect reaction rates indirectly by affecting $T$
The full reaction rate expression is then

$$\frac{1}{v_A} \frac{d[A]}{dt} = \frac{1}{v_B} \frac{d[B]}{dt} = -Z [A]^{\nu_A} [B]^{\nu_B} T^\alpha \exp \left( -\frac{E}{RT} \right)$$

$H_2 + I_2 \rightarrow 2HI$ is one of few cases where reactants → products is a single step; most fuels go through many intermediates during oxidation - even for the simplest hydrocarbon ($CH_4$) the "standard" mechanism ([http://www.me.berkeley.edu/gri_mech/](http://www.me.berkeley.edu/gri_mech/)) includes 53 species and 325 individual reactions!

The only likely reactions in gases, where the molecules are far apart compared to their size, are 1-body, 2-body or 3-body reactions, i.e. $A \rightarrow$ products, $A + B \rightarrow$ products or $A + B + C \rightarrow$ products

In liquid or solid phases, the close proximity of molecules makes $n$-body reactions (with $n > 3$) plausible

**Comments on LoMA**

- Forward reaction rate
  $$\frac{1}{v_A} \frac{d[A]}{dt} = \frac{1}{v_B} \frac{d[B]}{dt} = -\frac{1}{v_C} \frac{d[C]}{dt} = \frac{1}{v_D} \frac{d[D]}{dt} = -k_f [A]^{\nu_A} [B]^{\nu_B}$$

- Reverse reaction rate
  $$\frac{1}{v_C} \frac{d[C]}{dt} = \frac{1}{v_D} \frac{d[D]}{dt} = -\frac{1}{v_A} \frac{d[A]}{dt} = \frac{1}{v_B} \frac{d[B]}{dt} = -k_b [C]^{\nu_C} [D]^{\nu_D}$$

$k_b$ = "backward" reaction rate constant

At equilibrium, forward rate = reverse rate

$$\frac{k_f}{k_b} = \left[ \frac{C}{A} \right]^{\nu_C \nu_D \nu_A \nu_B}$$

Conc. of $i$ = \[ X_i \frac{P}{RT} \]

This ties reaction rate constants ($k_f$, $k_b$) and equilibrium constants ($K_i$) together
Deflagrations - burning velocity

- Since the burning velocity \( S_L \) << sound speed, pressure across the front is almost constant
- How fast will flame propagate? Simplest estimate assumes
  
  Rate of heat conducted from hot gas to cold gas \( i \) =
  
  Rate at which enthalpy is convected through flame front \( ii \) =
  
  Rate at which enthalpy is produced by chemical reaction \( iii \) =

![Diagram showing reaction zone, direction of propagation, speed relative to unburned gas, reaction zone temperature, reactant and product concentration, convection-diffusion zone, and distance from reaction zone.]

\[ T_{ad} = 2000K \]

\[ T_\infty = 300K \]

\[ \delta \approx \alpha S_L = 0.3 - 6 \text{ mm} \]

**Estimate of \( i \)**

Conduction heat transfer rate = \(-kA(\Delta T/\delta)\)

\( k \) = gas thermal conductivity, \( A \) = cross-sectional area of flame

\( \Delta T \) = temperature rise across front = \( T_{ad} - T_\infty \)

\( \delta \) = thickness of front (unknown at this point)

**Estimate of \( ii \)**

Enthalpy flux through front = (mass flux) x \( C_p \) x \( \Delta T \)

Mass flux = \( \rho uA \) (\( \rho \) = density of reactants = \( \rho_\infty \), \( u \) = velocity = \( S_L \))

Enthalpy flux = \( \rho_\infty C_p S_L A \Delta T \)

**Estimate of \( iii \)**

Enthalpy generated by reaction = \( Q_R \) x (d\[F\]/dt) x \( M_{fuel} \) x Volume

\[ [F] = \text{fuel concentration (moles/volume); Volume} = A\delta \]

\[ Q_R = C_p \Delta T/\delta \]

\[ f = \frac{\text{Fuel mass}}{\text{Total mass}} = \frac{\text{(Mass fuel / volume)}}{\text{(Mass total / volume)}} \]

\[ = \frac{\text{(Moles fuel / volume)}(\text{mass fuel / moles fuel})}{\text{(Mass total / volume)}} \]

\[ [F]_\infty = \text{fuel concentration in the fresh reactants} \]

AME 436 - Lecture 4 - Spring 2016 - Basics of Combustion
Burning velocity, flame thickness

Combine (i) and (ii)

\[ \delta = \frac{k}{\rho C_p S_L} = \frac{\alpha}{S_L} \]  
(\( \delta \) = flame thickness)

where \( \alpha = \frac{k}{\rho C_p} \) = thermal diffusivity (units length\(^2\)/time)

- For air at 300K & 1 atm, \( \alpha \approx 0.2 \text{ cm}^2/\text{s} \)
- For gases \( \alpha \approx \nu = D \) (\( \nu \) = kinematic viscosity; \( D \) = mass diffusivity)
- For gases \( \alpha \approx P^{1.7} T^{-1} \) since \( k \approx P^{0.7} T^{1.7} \), \( \rho \approx P T^{-1} \), \( C_p \approx P^{0.7} T^{1.7} \)
- For typical stoichiometric hydrocarbon-air flame, \( S_L \approx 40 \text{ cm/s} \), thus
  \[ \delta \approx \frac{\alpha}{S_L} \approx 0.005 \text{ cm} \]
  (Actually when properties are temperature-averaged, \( \delta \approx 4\alpha/S_L \approx 0.02 \text{ cm} \) - still small!)

Combine (ii) and (iii)

\[ S_L = (\alpha \omega)^{1/2} \]

- \( \omega \) = overall reaction rate = \( (d[F]/dt)/[F]_\infty \) (units 1/s)
- For typical \( S_L \approx 40 \text{ cm/s} \), \( \alpha \approx 0.2 \text{ cm}^2/\text{s} \), \( \omega \approx 1600 \text{ s}^{-1} \)
- \( 1/\omega \) = characteristic reaction time = 625 microseconds

Enthalpy release rate per unit volume

\[ = (\text{enthalpy flux}) / (\text{volume}) = \left( \rho C_p S_L A\Delta T / (A\delta) \right) \]

\[ = (\rho C_p S_L / k)(k\Delta T)/\delta = (k\Delta T)/\delta^2 = (0.07 \text{ W/mK})(1900\text{K})/(0.0002 \text{ m})^2 \]

= \( 3 \times 10^9 \text{ W/m}^3 \) !!!

Moral: flames are thin, fast and generate a lot of thermal enthalpy (colloquially, heat) quickly!
More rigorous analysis (Zeldovich, 1940)

\[ S_L = \sqrt{2\alpha \left( \frac{E}{\mathcal{R} T_{ad}} \right)^{-(n+1)} \left( \frac{T_{ad}}{T_{ad} - T_*} \right)^{n+1}} Z[F]_*^{-1} \exp \left( -\frac{E}{\mathcal{R} T_{ad}} \right) \]

Same form as simple estimate \( S_L \sim (\alpha \omega)^{1/2} \) with additional constants

How does \( S_L \) vary with pressure?

Define order of reaction \( (n) = \nu_A + \nu_B \); since

Thus \( S_L \sim (\alpha \omega)^{1/2} \sim (P^{-1})^{n-1} \sim P^{-1} \sim P^{n-1} \)

For "real" hydrocarbons, working backwards from experimental results, we find typically \( S_L \sim P^{-0.4} \), thus \( n \approx 1.2 \)

Define Zeldovich number \( (\beta) >> 1 \)

\[ \beta = \frac{T_{ad}}{\omega(T_{ad})} \frac{\partial \omega}{\partial T} \bigg|_{T=T_{ad}} = \frac{T_{ad}}{e^{-E/\mathcal{R} T_{ad}}} \frac{\partial \left( \frac{-E}{\mathcal{R} T} \right)}{\partial T} \bigg|_{T=T_{ad}} = \frac{T_{ad}}{e^{-E/\mathcal{R} T_{ad}}} \frac{-E}{\mathcal{R} T^2} \bigg|_{T=T_{ad}} = \frac{E}{\mathcal{R} T_{ad}} \]

For typical hydrocarbon-air flames, \( \mathcal{E} \approx 40 \text{ kcal/mole} \)

\( \mathcal{R} = 1.987 \text{ cal/mole, } T_{ad} \approx 2200K \)

\( \Rightarrow \beta \approx 10, \text{ at } T \text{ close to } T_{ad}, \omega \sim T^{10} !!! \)

\( \Rightarrow \text{Thin reaction zone concentrated near highest temperature} \)

\( \Rightarrow \text{In Zeldovich (or any) estimate of } S_L, \text{ overall reaction rate } \omega \text{ must be evaluated at } T_{ad}, \text{ not } T_* \text{ or any other temperature} \)

How to estimate \( E \)? If reaction rate depends more on \( E \) than concentrations \([\_], S_L \sim (\alpha \omega)^{1/2} \sim [\exp(-E/\mathcal{R} T_{ad})]^{1/2} \sim \exp(-E/2\mathcal{R} T_{ad}) \)

thus plot of \( \ln(S_L) \) vs. \( 1/T_{ad} \) has slope \(-E/2\mathcal{R} \)

If \( \beta \) isn’t large, then \( \omega(T_*) = \omega(T_{ad}) \) and reaction occurs even in the cold gases, so no control over flame is possible!

Since \( S_L \sim \omega, S_L \sim (T_{ad})^{1/2} \sim T_{ad}^{-1} \) typically!
**Deflagrations - summary**

- These relations show the effect of \( T_{ad} \) (depends on fuel & stoichiometry), \( \alpha \) (depends on diluent gas (usually \( \text{N}_2 \)) & \( P \), \( w \) (depends on fuel, T, P) and pressure (engine condition) on laminar burning rates.
- Re-emphasize: these estimates are based on an overall reaction rate; real flames have 1000's of individual reactions between 100's of species - but we can work backwards from experiments or detailed calculations to get these estimates for the overall reaction rate parameters.

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**Schematic of flame temperatures and laminar burning velocities**

- \( S_L \) or \( T_{ad} \)
- \( \phi = 0.5 \) Lean limit
- \( \phi = 1 \) Stoichiometric
- \( \phi = 2 \) Rich limit
- \( T_{ad} \approx 5\,\text{cm/s} \)
- \( T_{ad} \approx 200\,\text{K} \)
- \( T_{ad} \approx 5\,\text{cm/s} \)
- \( T_{ad} \approx 1500\,\text{K} \)
- \( T_{ad} \approx 2200\,\text{K} \)

---

**Real data on \( S_L \) (Vagelopoulos & Egolfopoulos, 1998)**
Using the following experimental data, what are the apparent \( E \), \( n \) and \( Z \) for lean-to-stoichiometric methane-air flames?

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Equiv. ratio</th>
<th>( S_L ) (cm/s)</th>
</tr>
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<tr>
<td>0.25</td>
<td>0.70</td>
<td>61.6</td>
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<td>0.50</td>
<td>0.75</td>
<td>51.7</td>
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<tr>
<td>1.00</td>
<td>0.80</td>
<td>40.5</td>
</tr>
<tr>
<td>2.00</td>
<td>0.89</td>
<td>28.9</td>
</tr>
<tr>
<td>3.00</td>
<td>1.00</td>
<td>22.5</td>
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</table>

<table>
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<th>Pressure = 1 atm</th>
<th>Equiv. ratio</th>
<th>( S_L ) (cm/s)</th>
<th>( T_{ad} ) (K)</th>
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<tr>
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<td>15.8</td>
<td>1838</td>
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<tr>
<td>0.75</td>
<td>18.2</td>
<td>1919</td>
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<td>0.80</td>
<td>24.1</td>
<td>1997</td>
<td></td>
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<tr>
<td>0.89</td>
<td>31.3</td>
<td>2122</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>36.5</td>
<td>2226</td>
<td></td>
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</tbody>
</table>

Using \( S_L \) vs. pressure data, the best power-law fit is \( S_L \sim P^{-0.404} \), thus \( (n-2)/2 = -0.404 \) or \( n = 1.19 \)

From the Zeldovich equation

\[
S_L = 2\alpha \left( \frac{E}{3RT_{ad}} \right)^{(n+1)} \left( \frac{T_{ad}}{T_{ad} - T_{\infty}} \right)^{n+1} Z[F]^{n-1} \exp \left( \frac{-E}{3RT_{ad}} \right)^{1/2} 
\]

\[
\ln(S_L) = \frac{1}{2} \ln \left[ 2\alpha \left( \frac{E}{3RT_{ad}} \right)^{(n+1)} \left( \frac{T_{ad}}{T_{ad} - T_{\infty}} \right)^{n+1} Z[F]^{n-1} \right] - \frac{E}{2RT_{ad}} \left( \frac{1}{T_{ad}} \right)
\]

The \( \ln(\cdot) \) term hardly changes with \( T_{ad} \), so

\[
\ln(S_L) \approx \text{Const.} + \left( -\frac{E}{2R} \right) (1/T_{ad})
\]

thus the slope of \( \ln(S_L) \) vs. \( 1/T_{ad} \) \( \approx -E/2R \). From the linear fit the slope is -9273, hence

\[
E = -2(-9273)(1.987 \text{ cal/moleK}) = 36.85 \text{ kcal/mole}
\]
Deflagrations - example

- Finally estimate Z; for a stoichiometric mixture at 1 atm with n = 1.19, E = 36,850 cal/mole, S_L = 40.5 cm/s
  T_adi = 2226K, α = 0.22 cm^2/s = 2.2 x 10^-5 m^2/s
  [F]_∞ = X_r(P/\Re/\T) = 0.095(101325 N/m^2)/(8.314 J/moleK)(300K) = 3.86 moles/m^3

\[
S_L = \left(2\alpha \frac{E}{\Re T_{adi}} \right)^{1/(n+1)} \left(\frac{T_{adi}}{T_r} \right)^{1/n} Z [F]^n \exp\left(-\frac{E}{\Re T_{adi}}\right) \Rightarrow \\
Z = \left(\frac{S_L}{2\alpha \frac{E}{\Re T_{adi}}} \right)^{1/(n+1)} \left(\frac{T_{adi}}{T_r} \right)^{1/n} \left[F\right]^n \exp\left(-\frac{E}{\Re T_{adi}}\right) \\
Z = \left(\frac{0.405 m/s}{2(2.2 \times 10^{-5} m^2/s)} \right)^{1/(1.2+1)} \left(\frac{36850cal}{mole} \right) \left(\frac{1.987 cal}{moleK} \right)^{1.2+1} \left(\frac{2226K-300K}{2226K} \right) \left(\frac{3.86 mole}{m^3} \right)^{1.2} \exp\left(-\frac{36850cal}{1.987 cal/moleK} \right) \\
Z = 9.1 \times 10^2 \left(\frac{mole}{m^3} \right)^{1.2} \left(\frac{1}{s} \right) \left(\frac{mole}{m^3} \right)^{1.2} \left(\frac{1}{s} \right) \text{ (note strange units!)}
\]

Turbulent flames - motivation

- Almost all flames used in practical combustion devices are turbulent because turbulent mixing increases burning rates, allowing more power/volume

- Examples
  - Premixed turbulent flames
    - Gasoline-type (spark ignition, premixed-charge) internal combustion engines
    - Stationary gas turbines (used for power generation, not propulsion)
  - Nonpremixed flames
    - Diesel-type (compression ignition, nonpremixed-charge) internal combustion engines
    - Gas turbines
    - Most industrial boilers and furnaces
Basics of turbulence

- Need a measure of the strength of turbulence - define turbulence intensity \( u' \) as rms fluctuation of velocity \( u(t) \) about mean \( \overline{u} \)

\[
u' = \sqrt{\frac{1}{\tau} \int_0^\tau (u(t) - \overline{u})^2 dt} \quad \overline{u} = \frac{1}{\tau} \int_0^\tau u(t) dt \quad \tau = \text{averaging time}
\]

- Also need measure of size of turbulent motions: \( L_I = \text{"integral length scale" - scale of largest eddies - proportional to size of system (e.g. cylinder diameter)} \)

Characteristics of turbulent flames

- Most important property: turbulent flame speed \( (S_T) \)
- Behavior depends on Karlovitz number \( (Ka) \) - ratio of turbulent strain rate to chemical rate

\[
Ka = \frac{\text{Mean strain rate}}{\text{Mean chemical rate}} = \frac{\sqrt{u'^3/15\nu L_I}}{S_L^2/\alpha} = 0.157 \text{Re}_{L_I}^{-1/2} \left( \frac{u'}{S_L} \right)^2
\]

\[
\text{Re}_{L_I} = \frac{u'L_I}{\nu} \quad (\text{Reynolds number of turbulence})
\]

- Low Ka: "Huygens propagation," thin fronts wrinkled by turbulence but internal structure is unchanged
- High Ka: "Distributed reaction zones," broad "fuzzy" fronts
- Experiments
  - Low \( u'/S_L \), thus high \( Ka \sim (u'/S_L)^2 \): \( S_T/S_L \) increases rapidly with \( u'/S_L \)
  - Higher \( u'/S_L \): almost no increase in \( S_T/S_L \)
  - Flame quenching at sufficiently high \( u'/S_L \)
Characteristics of turbulent flames

"Thin" flame
(Re ≫ 1, Ka ≪ 1)

"Distributed" flame
(Re ≫ 1, Ka ≫ 1)

Burned gas
Unburned gas
Integral scale eddy
Kolmogorov scale eddy

"Thin" flame
Estimated integral scale
= S_T/S_L

"Distributed" flame
Integral scale
Temperature
Distance or time

Bradley et al. (1992)
"Thin-flame" behavior observed in most practical combustors

- Damköhler (1940): in Huygens propagation regime, flame front is wrinkled by turbulence but internal structure and $S_L$ are unchanged
- Propagation rate $S_T$ due only to area increase via wrinkling: $S_T/S_L = A_T/A_L$
- Many models, still much controversy about how to predict $A_T/A_L$
- For this class we'll assume $S_T/S_L \sim u'/S_L$ with possibility of "bending" or quenching at high $Ka \sim (u'/S_L)^2$

How to get high turbulence in engines?
- Geometry of intake valves, ports, etc. - cause gas to swirl as it enters combustion chamber
- Cup-shaped piston head ("squish")
- Obstacles in flow
Homogeneous reaction

- Given a homogeneous system (T, P, [ ] same everywhere at any instant in time, but may change over time), how long will it take for the mixture to react (explode?)
- Model for "knocking" in premixed-charge piston engines
- As reaction starts, heat is released, temperature increases, overall reaction rate $\Omega$ increases, heat is released faster, $T$ rises faster, $\omega$ increases faster, … <BOOM>
- Simple analysis - assumptions
  - Single-step reaction $\nu_A + \nu_B \rightarrow \nu_C + \nu_D$
  - Excess of B (example: "lean" mixture with A = fuel, B = oxygen)
  - $\nu_A = \nu_B = 1$
  - Adiabatic, constant-volume, ideal gas, constant $C_v$
  - Constant mass

Homogeneous reaction

- Energy equation - if all fuel consumed
  
  $C_v(T\text{ad} - T_\infty) = fQ_R = [Y_f(t = 0) - Y_f(t = \infty)]Q_R$

So at any instant in time

$C_v(T(t) - T_\infty) = [Y_f(0) - Y_f(t)]Q_R$

where $Y_f(t)$ is the instantaneous fuel mass fraction (at $t = 0$, no fuel consumed, $T = T_\infty$; at $t = \infty$, $Y_f = 0$, all fuel consumed, $T = T_{ad}$); then from page 16

$Y_f(t = 0) = f = \frac{[F]_wM_{fuel}}{\rho_w} \Rightarrow Y_f(t) = \frac{[F](t)M_{fuel}}{\rho_w}; [F] = \text{Fuel conc. (moles/m$^3$)}$

$\Rightarrow C_v(T(t) - T_\infty) = \frac{Q_RM_{fuel}[F]_w - [F](t)}{\rho_w}$ (Eq. 1)

(this simply says that there is a linear relationship between the amount of fuel consumed and the temperature rise)

- Since we assumed $\nu_A = \nu_B = 1$, where A = fuel, B = oxygen

$\frac{d[A]}{dt} = \frac{d[F]}{dt} = \frac{d[B]}{dt} = \frac{d[Ox]}{dt} \Rightarrow [Ox]_w - [Ox](t) = [F]_w - [F](t)$ (Eq. 2)
Homogeneous reaction

- Reaction rate equation (assume $n = 0$)
  \[ \frac{d[A]}{dt} = -ZT^n [A]^\gamma [B]^\nu \exp \left( \frac{-E}{RT} \right) \]
  \[ \Rightarrow \frac{d[F]}{dt} = -Z[F](t)[Ox](t)\exp \left( \frac{-E}{RT(t)} \right) \]  (Eq. 3)

- Combine Eqs. 1, 2, 3, non-dimensionalize:
  \[ \frac{d\varepsilon}{d\tau} = -\varepsilon \left( \frac{1}{\phi} - 1 + \varepsilon \right) \exp \left( \frac{-\beta}{1 + H(1 - \varepsilon)} \right) \]

\[ \varepsilon \equiv \frac{[F](t)}{[F](t = 0)}; \beta \equiv \frac{E}{RT}; \tau \equiv tZ[F]; \phi \equiv \frac{[F]}{[Ox]} < 1 \]

\[ H \equiv \frac{Q R M_{\text{fuel}}[F]}{\rho C_v T_{\infty}} = \frac{f Q R}{C_v T_{\infty}} \]

- Notes on this result
  - $\phi$ is the equivalence ratio for our special case $\nu_A = \nu_B = 1$; only valid for lean mixtures since we assumed surplus of $A = \text{fuel}$
  - Get pressure from $P(t) = \rho_{\infty}RT(t)$

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Homogeneous reaction

- Equation looks scary but just a 1st order nonlinear ordinary differential equation - integrate to find $\varepsilon(\tau)$ (amount of product formed as a function of time) for various $\phi$ (stoichiometry), $\beta$ (activation energy), initial temp. ($T_{\infty}$), $H$ (heat release)

- Initial condition is $\varepsilon = 1$ at $\tau = 0$ (no fuel burned at time = 0)

- What do we expect?
  - Since reaction rate is slowest at low $T$, reaction starts slowly then accelerates
  - “Induction time” (e.g. time to reach 90% completion of reaction, $\varepsilon = 0.1$) should depend mostly on initial temperature $T_{\infty}$, not final temperature $T_{\text{ad}}$ since most of the time needed to react is before self-acceleration occurs
  - Very different from propagating flames where $S_L$ depends mostly on $T_{\text{ad}}$ not $T_{\infty}$ because in for flames there is a source of high $T$ (burned gases) to raise gas $T$ to near $T_{\text{ad}}$ before reaction started; in the homogeneous case no such source exists
  - This means that the factors that affect flame propagation and knock are very different
Homogeneous reaction

- Double-click chart to edit or change parameters
- Case shown: $\phi = 0.7, \beta = 10, H = 6$
- Time to "ignite" depend strongly on $\beta$, much less on $\phi$ and $H$
  (homework problem...)

Homogeneous Chemical Kinetics

- This spreadsheet will compute the time evolution of a homogeneous reacting fuel gas mixture in a closed system. The model accounts for finite-size elementary chemical reactions, and also surface kinetics, although with minor for the reaction rate. The program considers four problem types: (1) constant pressure, (2) constant volume, (3) constant temperature and pressure, and (4) constant temperature and volume.

Homogeneous reaction

- Do “real” fuels behave this way? Check using CSU website
  (http://navier.engr.colostate.edu/~dandy/code/code-5/index.html)
- Input initial T, P, constraint (what is kept constant), “Integration time” (total simulation time), “Time interval” for displayed output, reaction mechanism (CH$_4$-N$_2$-O$_2$ includes some larger fuel molecules, e.g. C$_3$H$_8$)

Mechanisms

- All the present time, only pre-defined chemical mechanisms can be implemented by the code. Choose one of these from the pull-down data base.

Reactor Mixture Composition

- In the table below enter the names of the species initially present and their amounts. The composition may be entered in mole or mass fractions.

<table>
<thead>
<tr>
<th>Species Name</th>
<th>Mole or Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td></td>
</tr>
<tr>
<td>N$_2$O</td>
<td>1.27</td>
</tr>
</tbody>
</table>
Homogeneous reaction

- Output format not readily imported into Excel!
- Case shown: \( \text{C}_3\text{H}_8\)-air, \( \phi = 1 \), constant volume, \( T(0) = 1000 \, ^\circ\text{C} \), \( P(0) = 1 \text{ atm} \) – qualitatively similar to simple 1-reaction model

![Graph showing mole fractions and temperature over time for a homogeneous reaction]
Homogeneous reaction

- Example of ignition time for "real" fuels at engine-like T & P
  - Low T (1000/T > 1): VERY different times for different fuels, dominated by slow breakdown rate of fuel molecule
  - High T: Similar times because $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ branching rather than fuel molecule breakdown is slowest step (except for toluene - hard to "crack")
  - Note for some fuels ignition time increases with increasing T for 750 < T < 900K (negative effective activation energy!)

"Non-premixed" or "diffusion" flames

- Simplest approach to determining properties: "mixed is burned" - chemical reaction rates faster than mixing rates
- No inherent propagation rate (unlike premixed flames where $S_L \sim (\alpha \omega)^{1/2}$)
- No inherent thickness $\delta$ (unlike premixed flames where thickness $\sim \alpha/S_L$) - in nonpremixed flames, determined by equating convection time scale $\delta/u = \tau$ to diffusion time scale $\delta^2/\alpha \Rightarrow \delta \sim (\alpha \tau)^{1/2}$ where $\tau$ is a characteristic flow time scale (e.g. $d/u$ for a jet, where $d = $ diameter $u = $ velocity, or $L/u'$ for turbulent flow, etc.)
- Burning must occur near stoichiometric contour where reactant fluxes are in stoichiometric proportions (otherwise surplus of one reactant)
- Burning must occur near highest T since $\omega \sim \exp(-E/RT)$ is very sensitive to temperature (like premixed flames)
"Non-premixed" or "diffusion" flames

- We'll look at two examples of non-premixed flames representing opposite extremes of what might happen in a Diesel engine
- Droplet combustion – vaporization slow, so droplets burn as individuals
- Gas-jet flame - vaporization of droplets is so fast, there is effectively a jet of fuel vapor rather than individual droplets
- Reality in between, but in Diesels usually closer to gas jet "with extras"

![Diagram of non-premixed flames]


Droplet combustion

- Heat from flame is conducted to fuel surface, vaporizes fuel, fuel convects/diffuses to flame front, $O_2$ diffuses to flame front from outside, burning occurs at stoichiometric location
- Droplet diameter $d(t)$ decreases until $d = 0$ or extinguishment
- Experiments typically show $d(0)^2 - d(t)^2 \approx Kt$
Droplet combustion

- How fast does droplet burn? Spherically-symmetric model (Godsave, Spalding 1953), assuming "mixed is burned," called the "dee-squared law"

\[
[d(0)]^2 - [d(t)]^2 = Kt; K = \frac{8k}{\rho_lC_p} \ln(1 + B); \quad B = \frac{Q_R f + C_p(T_d - T_\infty)}{L_v}
\]

- Diameter of flame surrounding droplet (\(d_{\text{flame}}\))

\[
\frac{d_{\text{flame}}(t)}{d(t)} = \frac{\ln(1 + B)}{\ln(1 + f)}
\]

Droplet combustion

- \(d^2\)-law assumes no buoyant or forced convection, but in engines there is significant flow; one relation for the effect of flow on \(K\) is

\[
[d(0)]^2 - [d(t)]^2 = Kt; K = \frac{4 Nu k}{\rho_lC_p} \ln(1 + B); \quad Nu = 2 + \frac{0.555Re_d^{1/2}Pr^{1/3}}{[1 + 1.232/(Re_d Pr^{1/3})]^{3/2}}
\]

\(Re_d\) = Droplet Reynolds number = ud(t)/\(\nu\)

\(Nu\) = Nusselt number based on droplet diameter

\(u\) = droplet velocity relative to gas

\(Pr\) = Prandtl number = \(v/\alpha\) ≈ 0.7 for gases

\(v\) = gas kinematic viscosity

\(\alpha\) = gas thermal diffusivity = \(k_g/\rho_gC_{p,g}\)

- Note this result reduces to the previous one for \(u = 0\) (thus \(Re = 0\)
**Droplet combustion**

- Note all the heat release ($Q_R$), heat of vaporization ($L_v$), etc. is tied up in $B$ which appears only inside a $\ln()$, thus changing these properties hardly affects burning rate at all.
- Why? The faster fuel vaporizes, the more rapidly fuel vapor blows out, thus the harder it is for heat to be conducted to the fuel surface.

Marchese et al. (1999), space experiments, heptane in $O_2$–He

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**Nonpremixed-gas flames - laminar gas-jet flames**

- Flame height ($L_f$) determined by equating diffusion time ($d_j^2/D$, $d_j$ = jet diameter, $D$ = oxygen diffusivity) to convection time ($L_f/u$) ($u$ = jet exit velocity)
  
  $d_j^2/D \sim L_f/u \Rightarrow L_f \sim ud_j^2/D$ or $L_f/d_j \sim ud/D$

  Gases: $D = \nu \Rightarrow L_f/d_j \sim ud/\nu = Re_{d_j}$

- Consistent with more rigorous models

![Graph showing $L_f/d_j$ vs. Reynolds number (Re)]

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Nonpremixed turbulent jet flames

- Turbulent (Hottel and Hawthorne, 1949)
  - For turbulent flows D is not constant but rather \( D \sim u'L_i \)
  - \( U' \sim u; L_i \sim d_j \Rightarrow L_i \sim d_j \) (independent of Re)
  - High \( u \Rightarrow high u' \Rightarrow Ka \) large - flame "lifts off" near base
  - Still higher - more of flame lifted
  - When lift-off height = flame height, flame "blows off" (completely extinguished)

Example

Ronney Oil and Gas Company claims to have developed a chemical called PDR\textsuperscript{TM}, that, when an infinitesimal amount is added to air, increases the thermal conductivity (\( k \)) of air by 10\%. No other properties of air or fuels are affected. With this additive, how would each of the following be affected? In particular, state whether each of the above will increase or decrease or remain constant, and by less than 10\%, more than, or exactly 10\%?

(a) Heating value of \( \text{CH}_4 \). Unaffected, heating values and all thermodynamic properties are unrelated to thermal conductivity.

(b) \( S_l \) of a stoichiometric \( \text{CH}_4 \)-air flame. \( S_l \sim [\text{sto}]^{1/2} \) and \( \alpha = k/\rho C_p \sim k \), so a 10\% increase in \( k \) will lead to a \([1.1^{1/2} : 1.0^{1/2}]/1.0^{1/2} \approx 0.05\% \) increase in \( S_l \)

(c) \( S_f \) of a stoichiometric \( \text{CH}_4 \)-air flame in the "thin-flame" (low Ka) regime (same \( u' \)). To a first approximation, \( S_f/S_l \sim u'/u \), thus \( S_f \sim u' \), which is independent of \( S_l \) and thus \( k \)

(d) \( S_f \) of a stoichiometric \( \text{CH}_4 \)-air flame at high Ka (same \( u' \)). Under these conditions \( S_f/S_l \) increases more slowly than linearly with \( u'/S_l \), for example we might say \( S_f/S_l \sim (u'/S_l)^{0.5} \). Thus if \( S_l \) increased 5\%, \( (u'/S_l)^{0.5} \) would decrease by about 2.5\%, thus \( S_f/S_l \) would decrease 2.5\%, thus \( S_f \) \( (S_l/S_f) \) would increase about 2.5\%.

(e) Time for homogeneous explosion in a stoichiometric \( \text{CH}_4 \)-air mixture. Unaffected since homogeneous reactions are unaffected by transport processes.

(f) Time for a liquid fuel droplet to burn out completely. Since the burning rate constant \( K \sim k \) and no terms in the expression for \( B \) are affected by \( k \), the burning time decreases by exactly 10\%

(g) Length of a laminar gas-jet flame. Simple answer: no effect. Better answer: \( \alpha = k/\rho C_p \sim k \) and since \( \alpha \), \( v \), and \( D \) are similar for gases, if \( \alpha \) increases, \( D \) will probably increase by about the same amount, thus \( L \) would decrease by exactly 10\%

(h) Length of a turbulent gas-jet flame. No effect since \( L \sim d \), independent of transport properties like \( D \)
Summary – combustion (1/3)

- Combustion is the combination of chemical reaction with convective and diffusive transport of thermal energy and chemical species
- Most important distinction between flames is premixed vs. non-preamixed, i.e. whether the reactants are mixed before combustion
- Chemical reactions relevant to combustion are generally VERY complicated but can often be approximated by one reaction
- Chemical reactions relevant to combustion generally have high activation energy (more precisely, high Zeldovich number $\beta$) and thus are more sensitive to temperature than any other property

Summary – combustion (2/3)

- Premixed flames
  - Deflagrations - subsonic - burning velocity $S_L \sim (\alpha \omega)^{1/2}$ ($\omega = \text{reaction rate at } T_{\text{ad}}$)
  - Detonations - supersonic wave
  - Homogeneous reaction - time of reaction depends on $T_\infty$ not $T_{\text{ad}}$
- Nonpremixed flames
  - "Mixed is burned" - burning rates/times NOT affected by chemical reaction rates
  - Turbulence increases the rates of combustion by increasing surface area (premixed) or mixing rates (nonpremixed)
4 types of properties used to describe combustion

- Thermodynamic properties & combinations of them
  - Temperature (T), pressure (P), volume (V), internal energy (U), enthalpy (H), entropy (S), specific heat (C<sub>P</sub>, C<sub>v</sub>, γ = C<sub>P</sub>/C<sub>v</sub>), Gibbs free energy (G), equilibrium constants (K), density (ρ), mole fraction (X), fuel mass fraction (f), transfer number (B), molecular weight (M), gas constant (R), latent heat of vaporization (L<sub>V</sub>)

- Transport properties
  - Thermal conductivity (k), thermal diffusivity (α = k/ρC<sub>P</sub>), mass diffusivity (D), momentum diffusivity aka kinematic viscosity (ν)

- Chemical rate properties
  - Activation energy (E), pre-exponential factor (Z), order of reaction (n), exponent of temperature dependence outside Arrhenius term (a)

- Fluid mechanical properties
  - Velocity (u), turbulence intensity (u'), integral length scale (L<sub>I</sub>), Re

From these we determine other properties, e.g.

- Thermodynamic - T<sub>ad</sub>, X<sub>i</sub> at equilibrium, P for const-V combustion, work in/out due to compression/expansion
- Combustion - S<sub>L</sub>, S<sub>T</sub>, ignition time, droplet burning rate constant (K), jet flame length (L<sub>f</sub>)