

Outline

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- Why do we need to study combustion?
- Types of flames
 - Premixed
 - Nonpremixed
- 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?

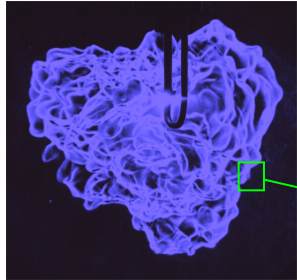
- Chemical thermodynamics only tells us **end states** - what happens if we wait "forever and a day" for chemical reaction to occur
- We also need to know **how fast** reactions occur
 - How fast depends on both the inherent rates of chemical reaction and the rates of heat and mass transport to the chemical reaction zone(s)
 - Chemical reactions + heat & mass transport = **combustion**
 - Some chemical reactions occur too slowly to matter, e.g.
 $2 \text{NO} \rightarrow \text{N}_2 + \text{O}_2$
has $T_{\text{ad}} = 2869\text{K}$ (no dissociation) or 2650K (with dissociation, mostly NO & O) but no pure NO flames exist – chemical 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

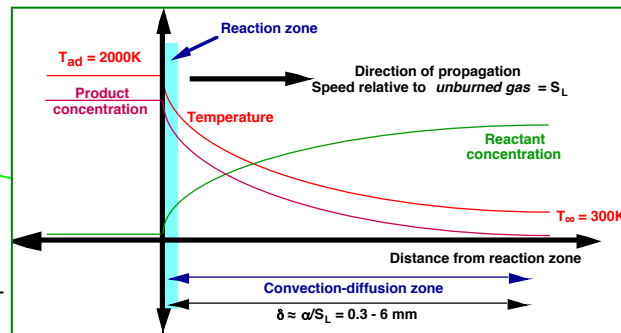
- **Premixed** - reactants are completely mixed down to the molecular scale before combustion is initiated; several flavors
 - Deflagration
 - Detonation
 - Homogeneous reaction
- **Nonpremixed** - reactants mix only at the time of combustion - have to **mix** first then **burn**; several flavors
 - 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
- Flow may be laminar or turbulent (real engines always turbulent)



Turbulent premixed flame in fan-stirred chamber (Leeds Univ.)

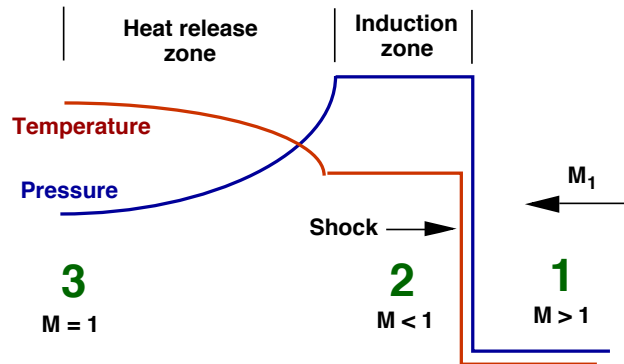


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Premixed flames - detonation

- 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

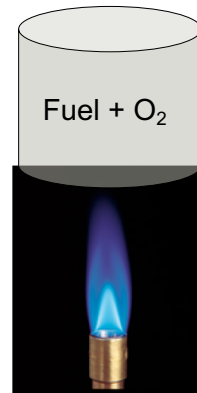
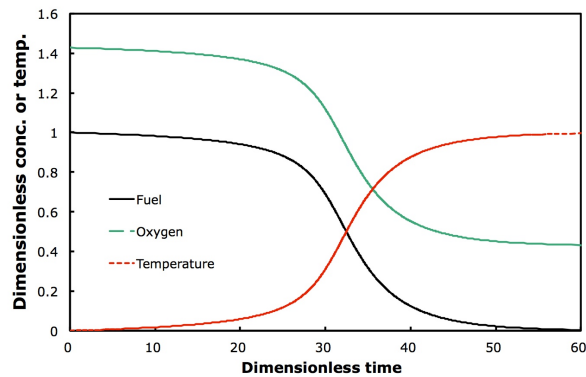


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Premixed flames - homogeneous reaction USC Viterbi School of Engineering

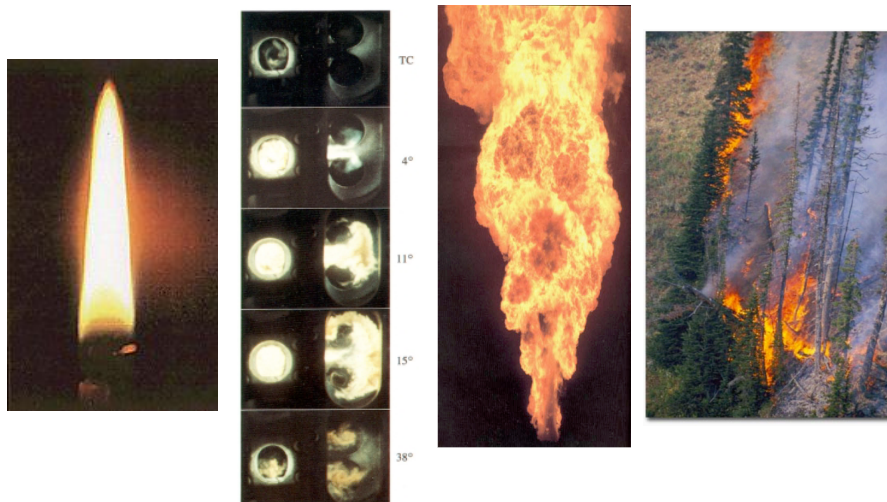
- Model for knock in premixed-charge engines
- Fixed mass with uniform (in space) T, P, composition
- No "propagation" in space but propagation in time
- In laboratory, could heat chamber to a certain T and measure time to react; in engine, compression of mixture (increases P & T, thus reaction rate)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



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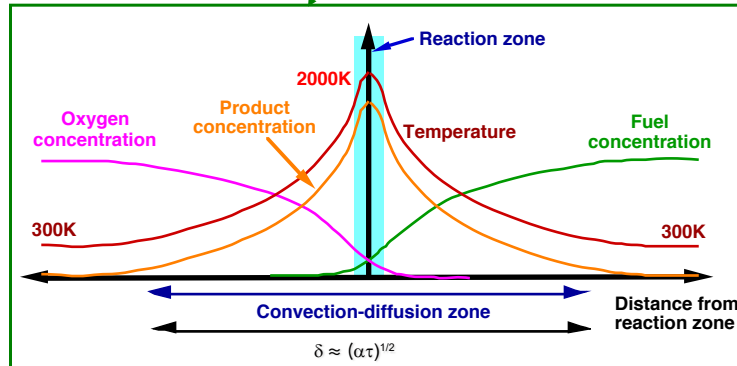
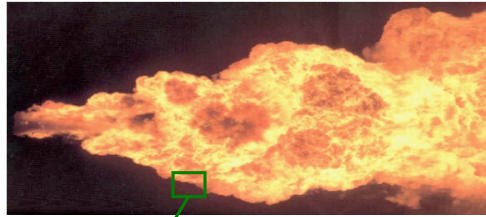
"Non-premixed" or "diffusion" flames USC Viterbi School of Engineering

- Only subsonic, generally assume "mixed is burned" - mixing slower than chemical reaction



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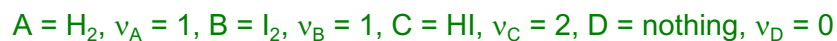
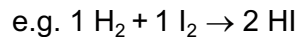
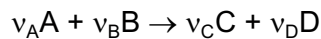


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Law of Mass Action (LoMA) (1/2)

- 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



LoMA states that the rate of reaction is given by

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

[i] = concentration of molecule i (moles per volume)

k_f = "forward" reaction rate constant

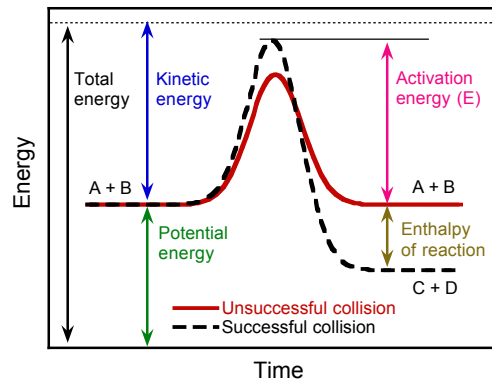
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Law of Mass Action (LoMA) (2/2)

- 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) = $P/\mathfrak{R}T$
 - Then [i] = (Total moles / volume)*(moles i / total moles), thus
 $[i] = (P/\mathfrak{R}T)X_i$ (X_i = mole fraction of i (see lecture 2))
- The reaction rate constant k_f is usually of the Arrhenius form
$$k_f = Z T^a \exp\left(-\frac{E}{\mathfrak{R}T}\right)$$
 - Z = pre-exponential factor, a = nameless constant,
 - E = "activation energy" (cal/mole)
 - Working backwards, units of Z are (moles per liter) $^{1-v_A-v_B}/(K^a s)$
- The $\exp(-E/\mathfrak{R}T)$ term causes extreme sensitivity of reaction rates to T when $E/\mathfrak{R} \gg T$! (which is typical for flames)

Activation energy

- Boltzman (1868): fraction of molecules in a gas with kinetic energy greater than a value $E \sim \exp(-E/\mathfrak{R}T)$, thus E is "energy barrier" to overcome for reaction
- E is not the same as Δh_f or heating value Q_R - E affects reaction rates whereas Δh_f & Q_R only affect end states (e.g. T_{ad}), although Δh_f & Q_R affect reaction rates indirectly by affecting T



- Full reaction rate expression for $\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$ is then

$$\frac{1}{\nu_A} \frac{d[A]}{dt} = \frac{1}{\nu_B} \frac{d[B]}{dt} = -Z [A]^{\nu_A} [B]^{\nu_B} T^a \exp\left(-\frac{E}{\mathcal{R}T}\right)$$

- The aforementioned $H_2 + I_2 \rightarrow 2HI$ example is one of few cases where reactants \rightarrow 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/) 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 ($N > 3$) plausible

- Forward reaction rate

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

- Reverse reaction rate

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

k_b = "backward" reaction rate constant

- At equilibrium, forward rate = reverse rate

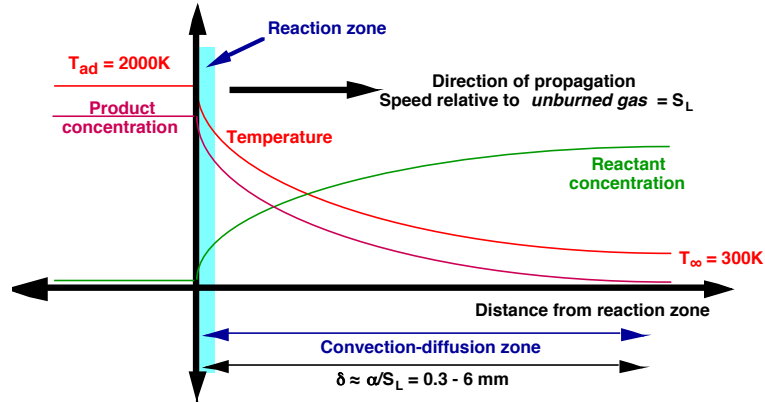
$$\frac{k_f}{k_b} = \frac{[C]^{\nu_C} [D]^{\nu_D}}{[A]^{\nu_A} [B]^{\nu_B}}; \text{ conc. of } i = []_i = \frac{X_i P}{\mathcal{R}T} \Rightarrow \frac{k_f}{k_b} = \frac{X_C^{\nu_C} X_D^{\nu_D}}{X_A^{\nu_A} X_B^{\nu_B}} \left(\frac{P}{\mathcal{R}T}\right)^{\nu_C + \nu_D - \nu_A - \nu_B}$$

$$= \frac{X_C^{\nu_C} X_D^{\nu_D}}{X_A^{\nu_A} X_B^{\nu_B}} \left(\frac{P}{P_{ref}} \frac{P_{ref}}{\mathcal{R}T}\right)^{\nu_C + \nu_D - \nu_A - \nu_B} \Rightarrow \frac{k_f}{k_b} = \left(\frac{P_{ref}}{\mathcal{R}T}\right)^{\nu_C + \nu_D - \nu_A - \nu_B} \frac{K_C^{\nu_C} K_D^{\nu_D}}{K_A^{\nu_A} K_B^{\nu_B}}$$

This ties reaction rate constants (k_f , k_b) and equilibrium constants (K_i) together

Deflagrations - burning velocity

- Since the burning velocity (S_L) \ll 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 chemical enthalpy is convected through flame front (ii) =
 - Rate at which thermal enthalpy is produced by chemical reaction (iii)



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Deflagrations - burning velocity

- Estimate of i
 - Conduction heat transfer rate = $-kA(\Delta T/\delta)$
 - k = gas thermal conductivity, A = cross-sectional area of flame
 - ΔT = temperature rise across front = $T_{ad} - T_\infty$
 - δ = thickness of front (unknown at this point)
- Estimate of ii
 - Chemical enthalpy flux through front = (mass flow) $fQ_R = \dot{m}C_p\Delta T$
 - $\dot{m} = \rho u A$ (ρ = density of reactants = ρ_∞ , u = velocity = S_L)
 - Chemical enthalpy flux = $\rho_\infty C_p S_L A (\Delta T)$
- Estimate of iii
 - Rate of thermal enthalpy generation by reaction = $Q_R \times (d[F]/dt) \times M_{fuel} \times \text{Volume}$
 - $[F]$ = fuel concentration (moles/volume); $\text{Volume} = A\delta$; $Q_R = C_p(\Delta T)/f$
 - $$f = \frac{\text{Fuel mass}}{\text{Total mass}} = \frac{(\text{Mass fuel / volume})}{(\text{Mass total / volume})} = \frac{(\text{Moles fuel / volume})(\text{mass fuel / moles fuel})}{(\text{Mass total / volume})} = \frac{[F]_\infty M_{fuel}}{\rho_\infty}$$
 - $[F]_\infty$ = fuel concentration in the fresh reactants
 - Combining: rate of thermal enthalpy generation = $\rho_\infty C_p (\Delta T) \omega A \delta$
 - ω = overall reaction rate = $(d[F]/dt)/[F]_\infty$ (units 1/s)

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Burning velocity, flame thickness

- Combine (i) and (ii)

$$\delta = k/\rho C_p S_L = \alpha/S_L \quad (\delta = \text{flame thickness})$$

where $\alpha = k/\rho C_p =$ thermal diffusivity (units length²/time)

- For air at 300K & 1 atm, $\alpha \approx 0.2 \text{ cm}^2/\text{s}$
- For gases $\alpha \approx \nu \approx D$ (ν = kinematic viscosity; D = mass diffusivity)
- For gases $\alpha \sim P^{-1}T^{1.7}$ since $k \sim P^0T^{-7}$, $\rho \sim P^1T^{-1}$, $C_p \sim P^0T^0$
- For typical stoichiometric hydrocarbon-air flame, $S_L \approx 40 \text{ cm/s}$, thus $\delta \approx \alpha/S_L \approx 0.005 \text{ cm}$ (!) (Actually when properties are temperature-averaged, $\delta \approx 4\alpha/S_L \approx 0.02 \text{ cm}$ - still small!)

Burning velocity, flame thickness

- Combine (ii) and (iii)

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

- 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
- Thermal enthalpy generation rate per unit volume
= (thermal enthalpy flux) / (volume) = $(\rho C_p S_L A \Delta T)/(A \delta)$
= $(\rho C_p S_L/k)(k \Delta T)/\delta = (k \Delta T)/\delta^2 = (0.07 \text{ W/mK})(1900\text{K})/(0.0002 \text{ m})^2$
= $3 \times 10^9 \text{ W/m}^3$!!!
- Moral: flames are thin, fast and generate a lot of thermal enthalpy (colloquially, heat) quickly!

Deflagrations - burning velocity

- More rigorous analysis (Zeldovich, 1940)

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

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

$$\frac{d[A]}{dt} = -k_f [A]^{\nu_A} [B]^{\nu_B} \sim P^{\nu_A} P^{\nu_B} \sim P^{\nu_A + \nu_B} \sim P^n \quad (A = \text{fuel}, B = \text{oxidant})$$

$$\omega \sim \frac{1}{[F]_\infty} \frac{d[F]}{dt} \sim P^{-1} P^n \sim P^{n-1}$$

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

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

Deflagrations - temperature effect

- Define **Zeldovich number (β)**

$$\beta \equiv \frac{T_{ad}}{\omega(T_{ad})} \frac{\partial \omega}{\partial T} \Big|_{T=T_{ad}} = \frac{T_{ad}}{e^{-E/\Re T_{ad}}} \frac{\partial (e^{-E/\Re T})}{\partial T} \Big|_{T=T_{ad}} = \frac{T_{ad}}{e^{-E/\Re T_{ad}}} \frac{-E}{\Re} \left(\frac{-e^{-E/\Re T}}{T^2} \right) \Big|_{T=T_{ad}} = \frac{E}{\Re T_{ad}}$$

For typical hydrocarbon-air flames, $E \approx 40$ kcal/mole

$\Re = 1.987$ cal/mole, $T_{ad} \approx 2200$ K

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

\Rightarrow Thin reaction zone concentrated near highest temperature

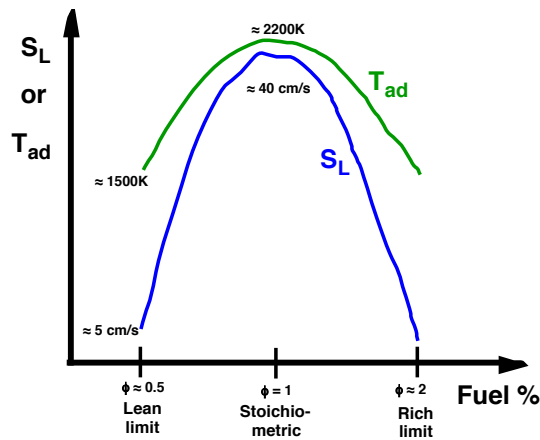
\Rightarrow **In Zeldovich (or any) estimate of S_L , overall reaction rate ω must be evaluated at T_{ad} , not T_∞ or any other temperature**

- How to estimate E ? If reaction rate depends more on E than concentrations [], $S_L \sim (\alpha\omega)^{1/2} \sim [\exp(-E/\Re T_{ad})]^{1/2} \sim \exp(-E/2\Re T_{ad})$, thus plot of $\ln(S_L)$ vs. $1/T_{ad}$ has slope $-E/2\Re$
- If β isn't large, then $\omega(T_\infty) \approx \omega(T_{ad})$ and reaction occurs even in the cold gases, so no control over flame is possible!
- Since $S_L \sim \omega^{1/2}$, $S_L \sim (T_{ad}^\beta)^{1/2} \sim T_{ad}^{5/2}$ typically!

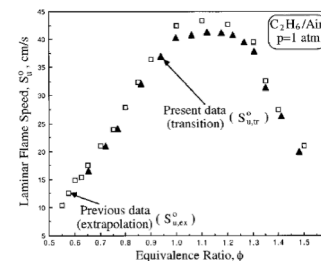
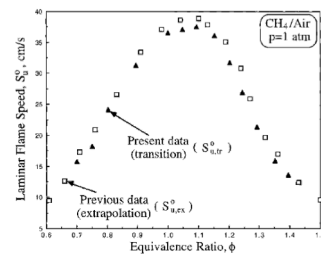
Deflagrations - summary

- These relations show the effect of adiabatic flame temperature T_{ad} (depends on fuel & stoichiometry), thermal diffusivity α (depends on diluent gas (usually N_2) & P), overall reaction rate ω (depends on fuel, T , P) and pressure P (depends on 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

Deflagrations



Schematic of flame temperatures and laminar burning velocities



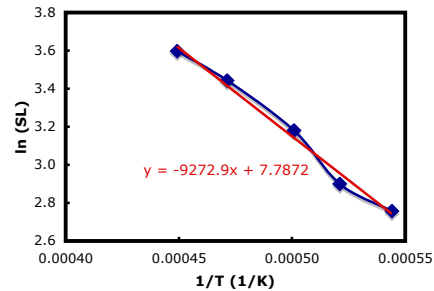
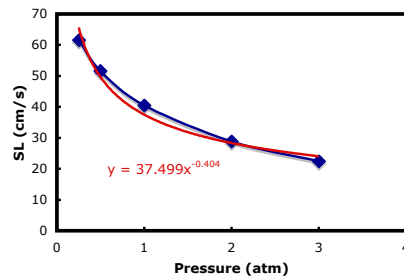
Real data on S_L (Vagelopoulos & Egolfopoulos, 1998)

Deflagrations - example

- Using the following experimental data, what are the apparent E, n and Z for lean-to-stoichiometric methane-air flames?

Equiv. ratio = 1	
Pressure (atm)	S _L (cm/s)
0.25	61.6
0.50	51.7
1.00	40.5
2.00	28.9
3.00	22.5

Pressure = 1 atm		
Equiv. ratio	S _L (cm/s)	T _{ad} (K)
0.70	15.8	1838
0.75	18.2	1919
0.80	24.1	1997
0.89	31.3	2122
1.00	36.5	2226



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Deflagrations - example

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

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

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

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

$$\ln(S_L) \approx \text{Const.} + (-E/2\Re)(1/T_{ad})$$

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

$$E = -2(-9273)(1.987 \text{ cal/moleK}) = 36.85 \text{ kcal/mole}$$

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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
 $T_{ad} = 2226$ K, $\alpha = 0.22$ cm²/s = 2.2×10^{-5} m²/s
 $[F]_{\infty} = X_F(P/\mathfrak{R}T) = 0.095(101325 \text{ N/m}^2)/(8.314 \text{ J/moleK})(300\text{K}) = 3.86$ moles/m³

$$S_L = \left\{ 2\alpha \left(\frac{E}{\mathfrak{R}T_{ad}} \right)^{-(n+1)} \left(\frac{T_{ad}}{T_{ad} - T_{\infty}} \right)^{n+1} Z [F]_{\infty}^{n-1} \exp \left(\frac{-E}{\mathfrak{R}T_{ad}} \right) \right\}^{1/2} \Rightarrow$$

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

$$Z = \frac{(0.405 \text{ m/s})^2}{2(2.2 \times 10^{-5} \text{ m}^2/\text{s})} \left(\frac{36850 \text{ cal}}{\frac{\text{mole}}{1.987 \text{ cal}} 2226 \text{ K}} \right)^{(1.2+1)} \left(\frac{2226 \text{ K} - 300 \text{ K}}{2226 \text{ K}} \right)^{1.2+1} \left[\frac{3.86 \text{ mole}}{\text{m}^3} \right]^{1-1.2} \exp \left(\frac{36850 \text{ cal}}{\frac{\text{mole}}{1.987 \text{ cal}} 2226 \text{ K}} \right)$$

$$Z = 9.1 \times 10^8 \left(\frac{\text{mole}}{\text{m}^3} \right)^{-0.2} \frac{1}{\text{s}} \quad (\text{note strange units!})$$

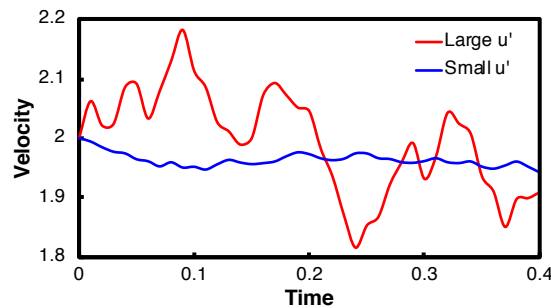
Turbulent flames - motivation

- 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 (\bar{u})

$$u' \equiv \sqrt{\frac{1}{\tau} \int_0^{\tau} (u(t) - \bar{u})^2 dt} ; \quad \bar{u} \equiv \frac{1}{\tau} \int_0^{\tau} u(t) dt ; \quad \tau = \text{averaging time}$$



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

Characteristics of turbulent flames

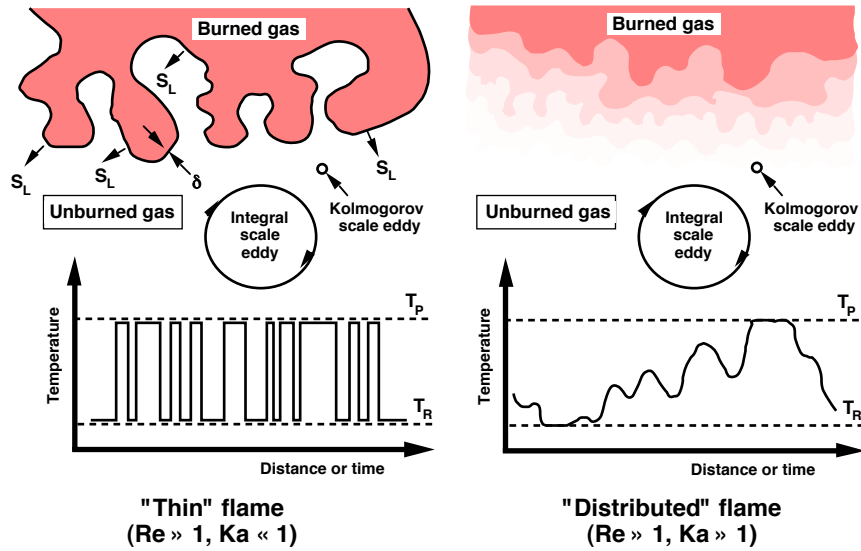
- Most important property: turbulent flame speed (S_T)
- Behavior depends on Karlovitz number (Ka) - ratio of turbulent strain rate to chemical rate

$$Ka \equiv \frac{\text{Mean strain rate}}{\text{Mean chemical rate } (\omega)} \approx \frac{\sqrt{u'^3 / 15\nu L_I}}{S_L^2 / \alpha} = 0.157 \text{Re}_L^{-1/2} \left(\frac{u'}{S_L} \right)^2$$

$$\text{Re}_L \equiv \frac{u' L_I}{\nu} \quad (\text{Reynolds number of turbulence})$$

- 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 low $Ka \sim (u'/S_L)^2$: 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 (thus high Ka)

Characteristics of turbulent flames

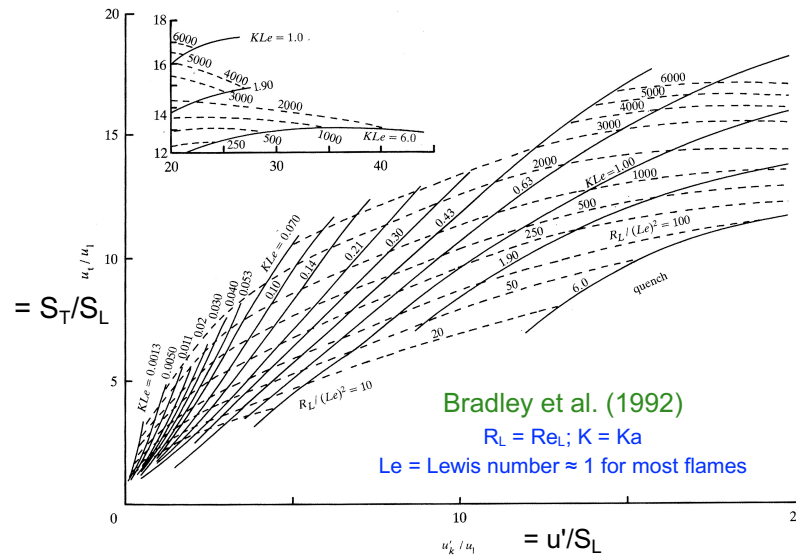


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Turbulent burning velocity data

➤ Compilation of data from many sources

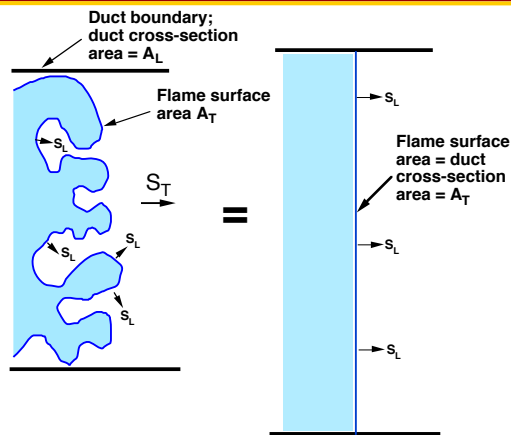


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Turbulent premixed flame modeling

- "Thin-flame" behavior observed in most practical combustors
- Damköhler (1940): flame front is wrinkled by turbulence S_L unchanged
- 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 , but most predict $A_T/A_L \sim u'/S_L$
- Distributed combustion:



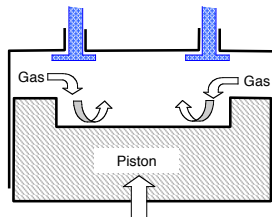
$$\frac{S_T}{S_L} \approx \sqrt{\frac{\omega_T \alpha_T}{\omega_L \alpha_L}} \approx \sqrt{\frac{\alpha_T}{\alpha_L}} \approx \sqrt{0.061 Re_L} \sim \sqrt{u'} \text{ if } L_f, \nu \text{ fixed}$$

S_T increases more slowly with u' in distributed than in thin-flame regime

- For this class we'll assume $S_T/S_L \sim u'/S_L$ with "bending" and possibly quenching at high $Ka \sim (u'/S_L)^2$

Turbulence in engines

- How to get high turbulence in engines?
 - Generally $u' \sim u_p$ (piston speed) Geometry of intake valves, ports, etc. - cause gas to swirl as it enters combustion chamber
 - Cup-shaped piston head ("squish")



- Obstacles in flow
- Side note
 - If $S_T/S_L \sim u'/S_L$ then $S_T \sim u' \sim u_p \sim N$ (N = engine rotation rate)
 - Time available for combustion $\sim 1/N$, time needed $\sim 1/S_T$
 - Burn duration is a constant number of crank angle degrees – performance nearly independent of N !
 - This is one reason premixed-charge engine is so ubiquitous!

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 ω increases, heat is released faster, T rises faster, ω increases faster, ... <BOOM>
- Simple analysis - assumptions
 - Single-step reaction $\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$
 - 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

$$C_v(T_{ad} - T_\infty) = f Q_R = [Y_f(t=0) - Y_f(t=\infty)] Q_R \quad (Y_f = \text{fuel mass fraction})$$

So at any instant in time (assuming no heat loss)

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

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

$$Y_f(t=0) = f = \frac{[F]_\infty M_{fuel}}{\rho_\infty} \Rightarrow Y_f(t) = \frac{[F](t) M_{fuel}}{\rho_\infty}; [F] \equiv \text{Fuel conc.} \left(\frac{\text{moles}}{m^3} \right)$$

$$\Rightarrow C_v(T(t) - T_\infty) = \frac{Q_R M_{fuel} \{ [F]_\infty - [F](t) \}}{\rho_\infty} \quad (\text{Eq. 1})$$

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

- Mass conservation – with $\nu_A = \nu_B = 1$, where A = fuel, B = oxygen

$$\frac{d[A]}{dt} = \frac{d[F]}{dt} = \frac{d[B]}{dt} = \frac{d[Ox]}{dt} \Rightarrow [Ox]_\infty - [Ox](t) = [F]_\infty - [F](t) \quad (\text{Eq. 2})$$

Homogeneous reaction

- Reaction rate equation (assume $n = 0$)

$$\frac{d[A]}{dt} = -ZT^n [A]^{v_A} [B]^{v_B} \exp\left(\frac{-E}{\mathfrak{R}T}\right) \Rightarrow \frac{d[F]}{dt} = -Z[F](t)[Ox](t) \exp\left(\frac{-E}{\mathfrak{R}T(t)}\right) \quad (\text{Eq. 3})$$

- Combine Eqs. 1, 2, 3, non-dimensionalize:

$$\frac{d\varepsilon}{d\tau} = -\varepsilon \left(\frac{1}{\phi} - 1 + \varepsilon \right) \exp\left(\frac{-\beta}{1 + H(1 - \varepsilon)}\right)$$

$$\varepsilon \equiv \frac{[F](t)}{[F](t=0)} = \frac{[F](t)}{[F]_{\infty}}; \beta \equiv \frac{E}{\mathfrak{R}T_{\infty}}; \tau \equiv tZ[F]_{\infty}; \phi \equiv \frac{[F]_{\infty}}{[Ox]_{\infty}} < 1$$

$$H \equiv \frac{Q_R M_{fuel} [F]_{\infty}}{\rho_{\infty} C_V T_{\infty}} = \frac{f Q_R}{C_V T_{\infty}} = \frac{C_V (T_{ad} - T_{\infty})}{C_V T_{\infty}} = \frac{T_{ad}}{T_{\infty}} - 1$$

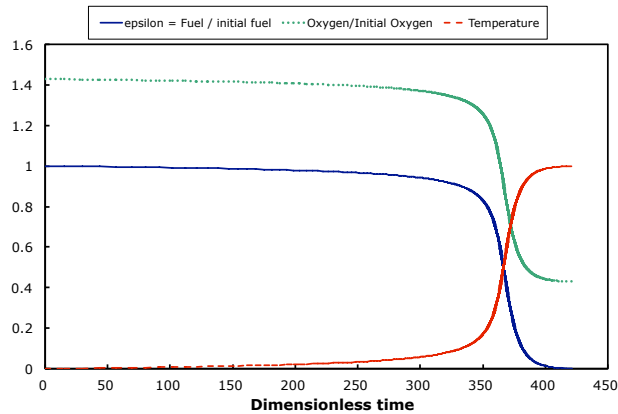
- Notes on this result
 - ϕ is the equivalence ratio for our special case $v_A = v_B = 1$; only valid for lean mixtures since we assumed surplus of A = fuel
 - Get pressure from $P(t) = \rho_{\infty} \mathfrak{R}T(t)$; since volume = constant, $\rho =$ constant, thus $P \sim T$

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 ϕ (stoichiometry), β (activation energy), initial temp. (T_{∞}), 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_{∞} , not final temperature T_{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_{ad} not T_{∞} because in for flames there is a source of high T (burned gases) to raise gas T to near T_{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: $\phi = 0.7$, $\beta = 10$, $H = 6$
- Dimensionless temperature shown = $\{T(t)-T_{\infty}\}/\{T_{ad}-T_{\infty}\} = 1 - \epsilon$
- Time to "ignite" depend strongly on β , much less on ϕ and H (homework problem...)



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Homogeneous reaction

- Do "real" fuels behave this way? Check using CSU website (<http://navier.engr.colostate.edu/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 (CH₄-N₂-O₂ includes some larger fuel molecules, e.g. C₃H₈)

Homogeneous Chemical Kinetics

This spreadsheet will compute the time evolution of a homogeneous reacting ideal gas mixture in a closed system. The model accounts for finite-rate elementary chemical reactions, and can perform kinetic sensitivity analysis with respect to the reaction rates. The program considers four problem types: (1) constant pressure; (2) constant volume; (3) constant temperature and pressure; and (4) constant temperature and volume.

Initial Temperature: 1273 Kelvin (Required)

Initial Pressure: 760 Torr (Required)

Integration Time: .002 seconds (Required)

Time Interval: .0001 seconds (Required)

Ignition Temperature: Kelvin (Optional)

Calculation Constraints

You must choose exactly one constraint for the calculation. Time dependent volume and temperature calculations are not currently supported.

Constant Pressure Constant Volume

Constant Temperature & Pressure Constant Temperature & Volume

Mechanisms

At the present time, only pre-defined chemical mechanisms can be implemented by the code. Choose one of these from the pull-down menu below.

MethaneNitrogenOxygen

Species List

N NH NH2 NH3
 NNH NO NO2
 N2O HNO CN
 HCN H2CN
 HCCN HCNO
 HOCN HNCO
 NCO N2 AR
 C3H7 C3H8
 CH2CHO
 CH3CHO

Reactant Mixture Composition

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

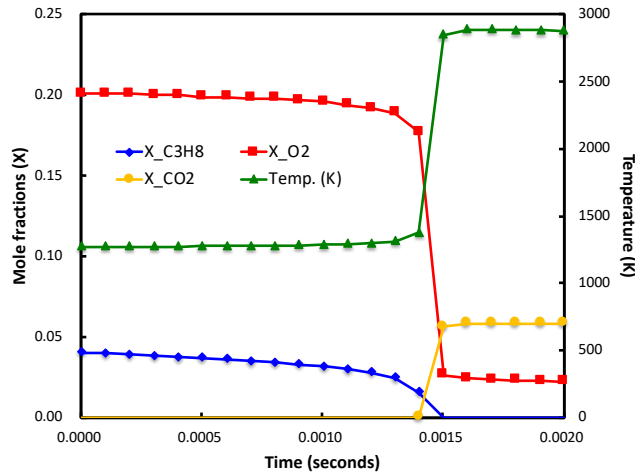
Species Name	Moles or Mole Fraction
C3H8	2
O2	1
N2	3.77

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Homogeneous reaction

- Output format of CSU website not readily imported into Excel!
- Case shown: C_3H_8 -air, $\phi = 1$, constant volume, $T(0) = 1000^\circ C$, $P(0) = 1$ atm – results similar to simple 1-reaction model

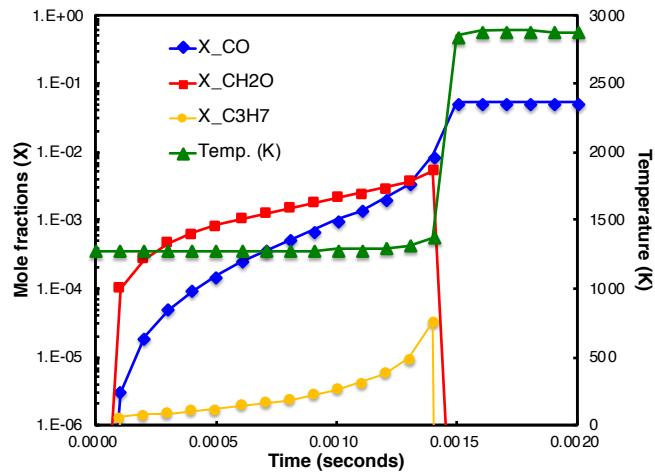


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Homogeneous reaction

- Not considered by simple 1-step model: **radicals** that may not be present in reactants or products, but are important intermediates that affect reaction rates (CH_2O and C_3H_7 shown)



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Homogeneous reaction

- In case of "real" chemistry, besides the thermal acceleration mechanism there is also a chemical or "chain branching" acceleration mechanism, e.g. for H_2-O_2

$$H + O_2 \rightarrow OH + O$$

$$H_2 + OH \rightarrow H + H_2O$$

$$O + H_2 \rightarrow OH + H \quad \text{etc.}$$

where 1 "radical" (H, OH, O) leads to 2, then 4, then 8, ... radicals
- In the case above, the "net" reaction would be
$$2 H_2 + O_2 \rightarrow H + OH + H_2O$$

which shows the increase in the radical "pool"
- This "chain branching" mechanism leads to even faster "runaway" than thermal runaway since $2^x > e^{-a/x}$ for sufficiently large x
- What if no H to start with?
$$H_2 + O_2 \rightarrow HO_2 + H \quad (\text{mostly this: } \Delta h = 55 \text{ kcal/mole})$$

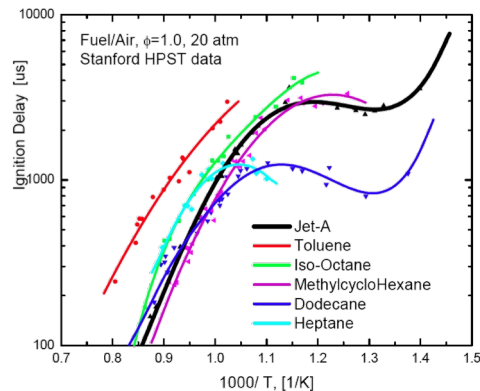
$$H_2 + M \rightarrow H + H + M \quad (\text{slower since } \Delta h = 104 \text{ kcal/mole - too big})$$

$$O_2 + M \rightarrow O + O + M \quad (\Delta h = 119 \text{ kcal/mole - even worse})$$

(M = any molecule)

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 $H + O_2 \rightarrow OH + O$ 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!) (simple 1-step model fails!)

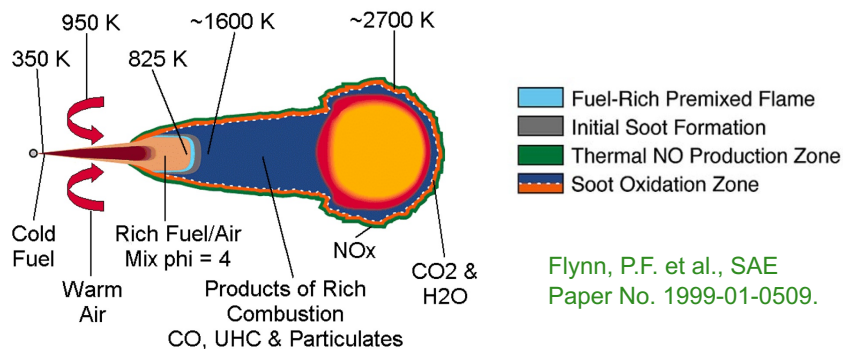


"Non-premixed" or "diffusion" flames

- 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 δ (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 τ is a characteristic flow time scale (e.g. d/u for a jet, where d = diameter u = velocity, or L_t/u' for turbulent flow, etc.)
- Burning must occur near stoichiometric surface 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)

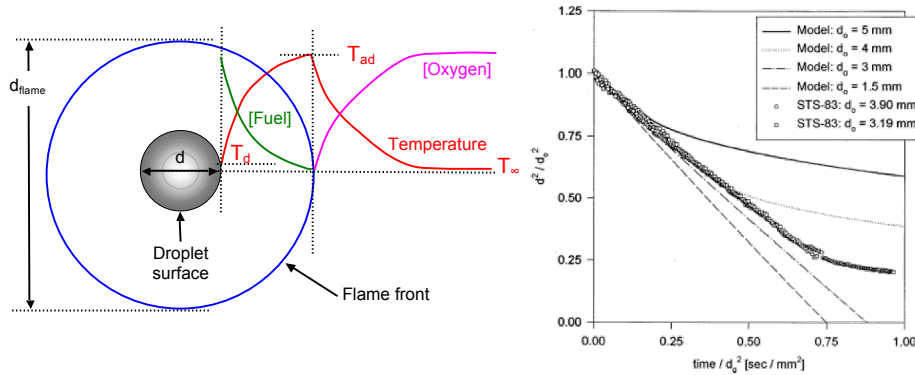
"Non-premixed" or "diffusion" flames

- We'll look at two examples of non-premixed flames representing opposite extremes of what might happen in a Diesel engine or gas turbine combustor
- 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"



Droplet combustion

- Heat from flame is conducted to fuel surface, vaporizes fuel, fuel convects/diffuses to flame front, O₂ diffuses to flame front from outside, burning occurs at stoichiometric location
- Droplet diameter d(t) decreases until d = 0 or extinguishment
- Experiments typically show $d(0)^2 - d(t)^2 \approx Kt$



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Droplet combustion

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

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

d(0) = droplet diameter at time = 0; d(t) = droplet diameter at later time t

K = droplet burning rate constant (m²/s)

k = gas thermal conductivity (W/mK); ρ_l = droplet density (kg/m³)

C_p = gas specific heat at constant pressure (J/kgK)

Q_R = fuel heating value (J/kg); L_v = latent heat of vaporization of fuel (J/kg)

f = stoichiometric fuel mass fraction

T_∞ = ambient air temp.; T_d = droplet vaporization (boiling) temperature (K)

- B ("Transfer number") ≈ ratio of heat generation by chemical reaction to heat needed to vaporize fuel; typical values: methanol 3, hydrocarbons 8 - 10
- Total time to burn droplet (when d(t) → 0) = [d(0)]²/K
- Diameter of flame surrounding droplet (d_{flame})

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

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Droplet combustion

- d²-law assumes no buoyant or forced convection, but in engines there is significant flow; one relation for the effect of flow on K is

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

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

Nu = Nusselt number based on droplet diameter

u = droplet velocity relative to gas

Pr = Prandtl number = $\nu/\alpha \approx 0.7$ for gases

ν = gas kinematic viscosity

α = gas thermal diffusivity = $k_g/\rho_g C_{p,g}$

- 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 O₂-He

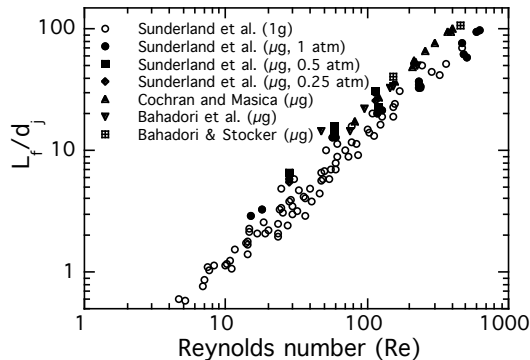
Nonpremixed-gas flames - laminar gas-jet flames

- 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)

$$d_j^2/D \sim L_f/u \Rightarrow L_f \sim u d_j^2/D \text{ or } L_f/d_j \sim u d_j/D$$

$$\text{Gases: } D \approx \nu \Rightarrow L_f/d_j \sim u d_j/\nu = Re_d$$

- Consistent with more rigorous models

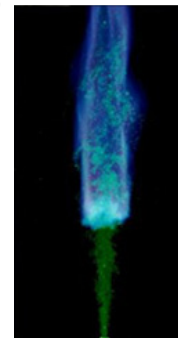
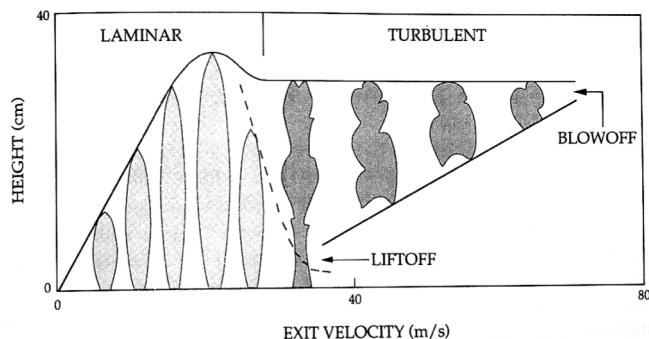


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Nonpremixed turbulent jet flames

- Turbulent (Hottel and Hawthorne, 1949)
 - For turbulent flows D is not constant but rather $D \sim u'L_1$
 - $u' \sim u$; $L_1 \sim d_j \Rightarrow L_f \sim d_j$ (independent of Re)
 - High $u \Rightarrow$ high $u' \Rightarrow Ka$ large - flame "lifts off" near base ("mixed is burned" assumption not valid any more)
 - Still higher - more of flame lifted
 - When lift-off height = flame height, flame "blows off" (completely extinguished)



Lifted flame (green = fuel; blue = flame)

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Example

Ronney Oil and Gas Company claims to have developed a chemical called PDRTM, 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 properties be affected? In particular, state whether each of these properties will increase, decrease or remain constant, and by less than 10%, more than, or exactly 10%.

- Heating value of CH₄.** Unaffected because heating values (and all thermodynamic properties) are unrelated to thermal conductivity and other transport properties.
- S_L of a stoichiometric CH₄-air flame.** $S_L \sim [\alpha\omega]^{1/2}$ and $\alpha = k/\rho C_p \sim k$, so a 10% increase in k will lead to a $[1.1^{1/2} - 1.0^{1/2}]/1.0^{1/2} \approx 0.05 = 5\%$ increase in S_L .
- S_T of a stoichiometric CH₄-air flame in the "thin-flame" (low Ka) regime (same u').** To a first approximation, $S_T/S_L \sim u'/S_L$, thus $S_T \sim u'$, which is independent of S_L and thus k .
- S_T of a stoichiometric CH₄-air flame at high Ka (same u').** In the "distributed combustion" regime, $S_T/S_L \sim Re_L^{0.5}$. Since $Re_L = u'L_1/\nu$, none of which are affected by k , Re_L doesn't change. In part (b) it was shown that S_L increased 5%, thus $S_T \sim Re_L^{0.5}S_L$ would also increase by 5%.
- Time for homogeneous explosion in a stoichiometric CH₄-air mixture.** Unaffected since homogeneous reactions are unaffected by transport processes.
- 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%.
- Length of a laminar gas-jet flame.** Simple answer: no effect. Better answer: $\alpha = k/\rho C_p \sim k$ and since α , ν , and D are similar for gases, if α increases, D will probably increase by about the same amount, thus L would decrease by exactly 10%.
- 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-premixed, *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 overall reaction
- **Chemical reactions relevant to combustion generally have high activation energy (more precisely, high Zeldovich number β) and thus are more sensitive to temperature than any other property**

Summary – combustion (2/3)

- Premixed flames
 - Deflagrations - subsonic - burning velocity $S_L \sim (\alpha\omega)^{1/2}$ (ω = reaction rate at T_{ad})
 - Detonations - supersonic wave
 - Homogeneous reaction - time of reaction depends on T_∞ not T_{ad}
- Nonpremixed flames
 - In simplest approximation, "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)

Summary – combustion (3/3)

- 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_P , C_V , $\gamma = C_P/C_V$), Gibbs free energy (G), equilibrium constants (K), density (ρ), mole fraction (X), fuel mass fraction (f), transfer number (B), molecular weight (M), gas constant (\mathfrak{R} or R), sound speed (c), heating value (Q_R), latent heat of vaporization (L_V)
 - Transport properties
 - » Thermal conductivity (k), thermal diffusivity ($\alpha = k/\rho C_P$), 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_I), Re_L
- From these we determine other properties, e.g.
 - Thermodynamic - T_{ad} , X_i at equilibrium, P for const-V combustion, work in/out due to compression/expansion
 - Combustion - S_L , S_T , ignition time, droplet burning rate constant (K), jet flame length (L_f)