# AME 513b

## Fundamentals and Applications of Combustion II

## Lecture 2
## Extension of AME 513a: Chemical Kinetics

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### *Outline*

- ➢ Chemical thermodynamics
- ➢ Kinetic theory of gases as applied to chemical reactions
- ➢ Types of reactions in combustion processes
- ➢ Experimental methods
- ➢ Analytical solutions for 1-step reactions
  - ➢ Irreversible
  - ➢ Reversible
- ➢ Approximations for multi-step reactions
  - ➢ Steady-state approximation
  - ➢ Pressure effects – Lindemann mechanism
  - ➢ Partial equilibrium approximation
  - ➢ Chain branching
- ➢ Combining 1-step reaction with thermodynamics (but not transport)
  - ➢ Homogeneous reaction
  - ➢ Well-stirred reactor
- ➢ "Real" chemistry
  - ➢ Online chemical kinetics calculator
  - ➢ $H_2 - O_2$ reaction
  - ➢ CO-$O_2$
  - ➢ Hydrocarbons

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## Chemical thermo - adiabatic flame temp

➢ More info:
   ➢ http://ronney.usc.edu/AME436/Lecture2 (1st Law)
   ➢ http://ronney.usc.edu/AME436/Lecture3 (2nd Law)
➢ Assumptions
   ➢ Conservation of energy (1st Law)
   ➢ Conservation of each type of atom
   ➢ No heat transfer (adiabatic)
   ➢ No work transfer other than PdV expansion work
   ➢ No kinetic or potential energy change
   ➢ Minumum of Gibbs free energy = h – Ts (2nd Law)
   ➢ Constant pressure or constant volume

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## Adiabatic flame temp. - hydrocarbons



Initial temperature $T_\infty$ = 300K
Initial pressure = 1 atm

- CH4-air (const. P)
- C3H8-air (const. P)
- C8H18-air (const. P)
- H2-air (const. P)
- CH4-O2 (const. P)
- CH4-air (const. V)

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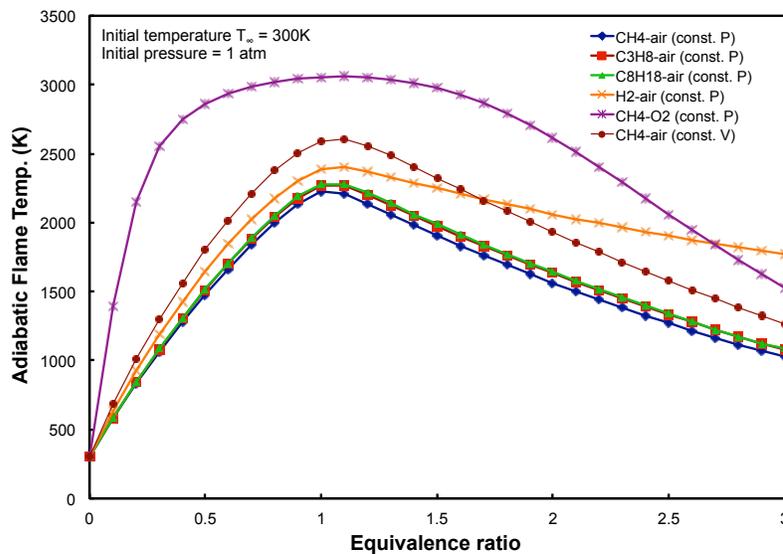
## *Adiabatic flame temp - hydrocarbons*

- Adiabatic flame temperature ($T_{ad}$) peaks slightly rich of stoichiometric - since $O_2$ is highly diluted with $N_2$, burning slightly rich ensures all of $O_2$ is consumed without adding a lot of extra unburnable molecules
- $T_{ad}$ peaks at ≈ 2200K for $CH_4$, slightly higher for $C_3H_8$, iso-octane ($C_8H_{18}$) practically indistinguishable from $C_3H_8$
- $H_2$ has far heating value per unit fuel mass, but only slightly higher per unit total mass (due to "heavy" air), so $T_{ad}$ not that much higher
    - Also - massive dissociation as T increases above ≈ 2400K, keeps peak temperature down near stoichiometric
    - Also - since stoichiometric is already 29.6% $H_2$ in air (vs. 9.52% for $CH_4$, 4.03% for $C_3H_8$), so going rich does not add as many excess fuel molecules
- $CH_4$ - $O_2$ MUCH higher - no $N_2$ to soak up thermal energy without contributing enthalpy release
- Constant volume - same trends but higher $T_{ad}$ – no PdV work

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## *Chemical kinetics - Law of Mass Action*

- Thermodynamics tells us end state but not **RATE** of reactions
- For a chemical reaction of the form

$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$

e.g. $1\ H_2 + 1\ I_2 \rightarrow 2\ HI$

A = $H_2$, $\nu_A$ = 1, B = $I_2$, $\nu_B$ = 1, C = HI, $\nu_C$ = 2, D = nothing, $\nu_D$ = 0

the Law of Mass Action (LoMA) states that the rate of reaction

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

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

$k_f$ = "forward" reaction rate constant

- Define "order of reaction" = $\Sigma\nu_i$ for reactants - # of molecules that must collide for reaction to occur
- How to calculate [A]?
    - Ideal gas law, the total moles of gas per unit volume = $P/\Re T$
    - Then [A] = (Total moles / volume)*(moles i / total moles), thus
      [A] = $(P/\Re T)X_A$  ($X_A$ = mole fraction of A)
- Minus sign on d[A]/dt and d[B]/dt since A & B are being depleted
- LoMA states that the rate of reaction is proportional to rate of collisions between reactant molecules, which is proportional to concentration of each reactant

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## Chemical kinetics - collision rate

- Maximum possible reaction rate = collision rate ($Z_{coll}$)
- Kinetic theory of gases provides number of collisions per unit volume (V) per unit time for A & B ([A], [B] in units of molecules/$m^3$, not moles/$m^3$)

$$\frac{Z_{coll}}{V} = [A][B]\pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8kT}{\pi\mu}}; \mu \equiv \frac{m_A m_B}{m_A + m_B}$$

$k$ = Boltzmann's constant = $1.38 \times 10^{-23} J/K$; $m_i$ = mass of molecule i

- Example: how often do $N_2$ molecules collide at 298K & 1 atm?
  $\sigma$ = 3.61 x $10^{-10}$ m, mass = 4.65 x $10^{-26}$ kg ($\mu_{N2-N2}$ = 2.32 x $10^{-26}$ kg)

$$[N_2] = N_{Avogadro}(P/\Re T) = \frac{(6.02 \times 10^{23}/mole)(101325 N/m^2)}{(8.314 J/moleK)(298K)} = \frac{2.46 \times 10^{25}}{m^3}$$

$$\frac{Z_{coll}}{V} = \left[\frac{2.46 \times 10^{25}}{m^3}\right]\left[\frac{2.46 \times 10^{25}}{m^3}\right]\pi\left(\frac{2(3.61 \times 10^{-10} m)}{2}\right)^2 \sqrt{\frac{8(1.38 \times 10^{-23} J/K)(298K)}{\pi(2.32 \times 10^{-26} kg)}} = \frac{1.66 \times 10^{35} coll}{m^3 s}$$

$$\text{Collisions per molecule} = \frac{Z_{AB}}{V}\frac{1}{[N_2]} = \frac{1.66 \times 10^{35} coll}{m^3 s}\frac{m^3}{2.46 \times 10^{25} molecules}\frac{2\ molecules}{coll} = \frac{1.35 \times 10^{10}}{s}$$

- At 2200K, 1 atm: $Z_{coll}$ = 4.98 x $10^9$/s; typical time for stoich. hydrocarbon oxidation ≈ $10^{-3}$ s, thus each molecule collides ≈ 5 x $10^6$ times before reaction is completed!

## Chemical kinetics – activation energy

- Boltzman (1868): fraction of gas molecules with kinetic energy (KE) greater than $E_a$ ~ exp($-E_a/\Re T$), thus $E_a$ = "activation energy" represents "energy barrier" that must be overcome for reaction to occur
- Not all collisions with sufficient KE result in reaction - orientation matters!
- $E_a$ is <u>not</u> enthalpy of reaction $\Delta h_f$; in general there is no relation between $E_a$ & $\Delta h_f$ - $E_a$ affects reaction rates whereas $\Delta h_f$ affect end states (e.g. $T_{ad}$), though $\Delta h_f$ affect reaction rates indirectly by affecting T



"Diary of a collision"

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- Based on collision rate & activiation energy concepts with orientation (and "luck"), $k_f$ is usually expressed in Arrhenius form:

$$k_f = Z\,T^n \exp\left(-E_a \middle/ \Re T\right)$$

  Z = pre-exponential factor, n = another (nameless) constant, $E_a$ = activation energy (cal/mole); $\Re$ = gas constant
- Working backwards, units of Z must be $(moles/m^3)^{1-vA-vB}/(K^{-n}\ s)$
- With 3 parameters (Z, n, $E_a$) any curve can be fit!
- The exponential term causes extreme sensitivity to T for $E_a/\Re \gg$ T!

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- The full reaction rate expression is then

$$\frac{1}{v_A}\frac{d[A]}{dt} = \frac{1}{v_B}\frac{d[B]}{dt} = -Z\left[A\right]^{v_A}\left[B\right]^{v_B} T^a \exp\left(-E_a \middle/ \Re T\right)$$

- The $H_2 + I_2 \rightarrow$ 2HI example is one of few where reactants → products occurs in a single step; most fuels go through <u>many</u> intermediates during oxidation - even for the simplest hydrocarbon ($CH_4$) the "standard" mechanism http://combustion.berkeley.edu/gri-mech/version30/text30.html 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 → products, A + B → products or A + B + C → products
- In liquid or solid phases, the close proximity of molecules makes n-body reactions plausible

## Chemical kinetics – reaction rate const. USC Viterbi School of Engineering

- Recall that the forward reaction rate is

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

- Similarly, the rate of the reverse reaction can be written as

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

  $k_b$ = "backward" reaction rate constant

- At equilibrium, the forward and reverse rates must be equal, thus

$$\frac{k_f}{k_b} = \frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}}; [\ ]_i = \frac{X_i P}{\Re T} \Rightarrow \frac{k_f}{k_b} = \frac{X_C^{\nu_C} X_D^{\nu_D}}{X_A^{\nu_A} X_B^{\nu_B}}\left(\frac{P}{\Re T}\right)^{\nu_C+\nu_D-\nu_A-\nu_B} = \frac{X_C^{\nu_C} X_D^{\nu_D}}{X_A^{\nu_A} X_B^{\nu_B}}\left(\frac{P}{P_{ref}}\frac{P_{ref}}{\Re T}\right)^{\nu_C+\nu_D-\nu_A-\nu_B}$$

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

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

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## Types of reactions (1/2) USC Viterbi School of Engineering

- Global reaction
  - Example: $CH_4 + 2O_2 \rightarrow CO_2 + 2\,H_2O$
  - NOT an actual reaction that occurs
  - No relation between order of reaction (3 in this example) and actual pressure effect on reaction rate
- Chain initiation
  - Example: $H_2 + M \rightarrow H + H + M$
  - Break stable molecule into radical(s)
  - High $E_a$ – endothermic, must break strong bond
  - High Z (i.e. not very orientation sensitive)
  - Not needed in flames, where radical source (products) exists
- Chain branching
  - Example: $H + O_2 \rightarrow OH + O$
  - Use a radical to create more radicals
  - High $E_a$ - endothermic, must break strong bond, but also make a bond, so not as high as chain initiation
  - Moderate Z (somewhat orientation sensitive)

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## Types of reactions (2/2)

- Chain propagation or "shuffle" reaction
  - Example: $OH + H_2 \rightarrow H_2O + H$
  - Use radical + stable molecule to create another pair
  - Moderate $E_a$ – may be nearly thermo-neutral
  - Moderate Z (somewhat orientation sensitive)
- Chain termination
  - Example: $H + OH + M \rightarrow H_2O + M$
  - Recombine radicals into stable molecules (usually products)
  - Low or zero $E_a$ – exothermic, no activation barrier
  - Need 3$^{rd}$ body to absorb enthalpy and conserve momentum
  - Moderate Z (may be orientation sensitive)
- Schematic multi-step mechanism (e.g. Hautman *et al.*, 1981)

  $C_3H_8 \rightarrow 1.5\ C_2H_4 + H_2$ (Initial breakdown of fuel)
  $C_2H_4 + O_2 \rightarrow 2\ CO + 2\ H_2$ ($C_2H_4$ = surrogate for radicals)
  $2H_2 + O_2 \rightarrow 2\ H_2O$ (oxidation of $H_2$)
  $2CO + O_2 \rightarrow 2\ CO_2$ (oxidation of CO)

  Reaction rates crazy (see Hautman) – sometimes order of reaction is negative – causes problems as concentration $\rightarrow 0$

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## Experimental methods – 1/6

- Constant volume "explosion vessel"
  - "Classic" "legacy" experiment, with issues in interpretation
  - Heat evacuated vessel, inject reactants quickly (shorter than reaction time scale), see if reaction occurs explosively or just slowly
  - Ideally constant T & P
  - Not well-defined limit, depends on injection / mixing time ~ d$^2$/D (d = vessel dimension, D = diffusivity) being much faster that reaction, only useful for conditions with "slow" reaction
  - For gases, both mass D & thermal D ~ 1/P, so reaction time required for explosion varies with P!
  - Wall effects! (radical sink)
  - Only yields qualitiative trends, not detailed quantitative properties
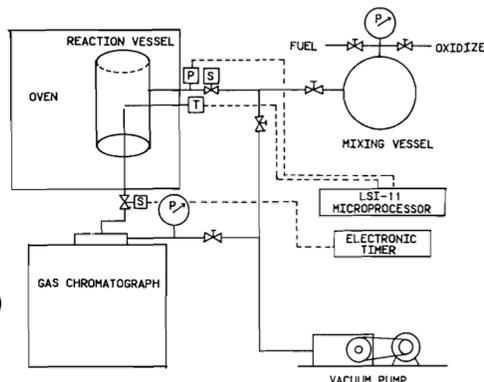


Wilk *et al.*, 1986

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## Experimental methods – 2/6

- ➢ Well-stirred reactor
  - ➢ Another "legacy" apparatus; requires time for mixing of fresh reactants with products already in reactor to be much shorter than residence time in reactor – not always true as "brilliant" work shows
  - ➢ If mixing is "fast" then zero-dimensional in space & time (i.e., steady)
  - ➢ Generally limited to "slow" reactions (time scale > 0.1 s, thus overall reaction rate $\omega$ < 10/s
  - ➢ Yields global properties ($\omega$) and can obtain data on evolution of individual species, thus infer some elementary reaction rates



Dagaut *et al.*, 1986

Battin-Leclerc, 2014

LeCong and Dagaut, 2009

Davani & Ronney, 2020

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## Experimental methods – 3/6

- ➢ Plug-flow reactors
  - ➢ Flow reactants down a preheated tube (usually constant T), measure species at varying distances along tube (~ time)
  - ➢ Ideally 0D in time (steady), 1D in space
  - ➢ Can obtain data on evolution of individual species, not just global properties, thus infer elementary reaction rates
  - ➢ Laminar or turbulent flow
  - ➢ Only useful for "slow" reactions (low temperature, not flame-like conditions) (tens of milliseconds)
  - ➢ Need to address issue of axial dispersion of reactants



Sen et al., 2016

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➢ Shock tube
  ➢ Pass shock wave through mixture, watch evolution of species behind reflected shock
  ➢ Step-like change in T and P, well defined, nearly homogeneous
  ➢ Ideally 0D in space, 1D in time
  ➢ Can obtain data on individual reactions
  ➢ Amenable to quantitative laser diagnostics
  ➢ Only useful for "fast" reactions (few ms)
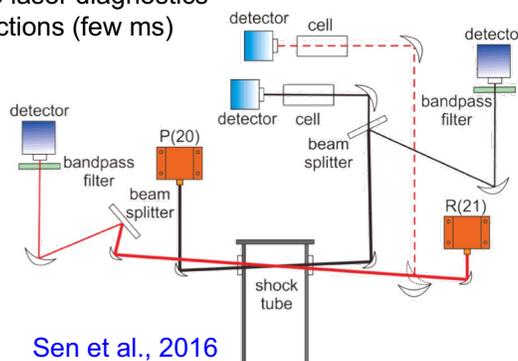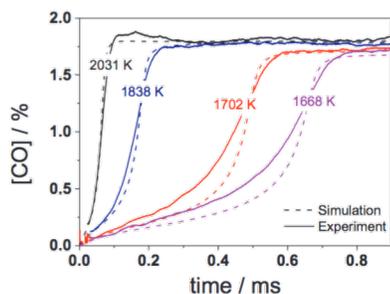


Sen et al., 2016

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➢ Rapid compression machine (piston/cylinder)
  ➢ "Rapidly" compress mixture to reactive state at high T & P
  ➢ Ideally 0D in space, 1D in time
  ➢ Can obtain data on individual reactions
  ➢ Amenable to quantitative laser diagnostics
  ➢ Mostly useful for "moderately fast" reactions (10s of ms)
  ➢ Heat losses & boundary layer rollup may cause nonuniform T & P
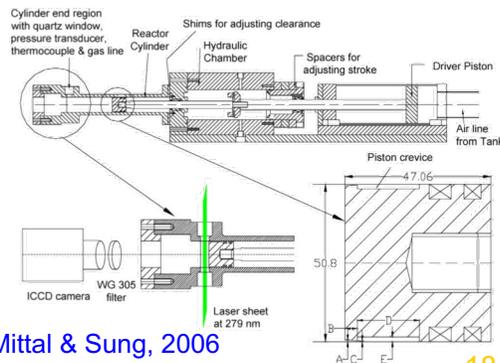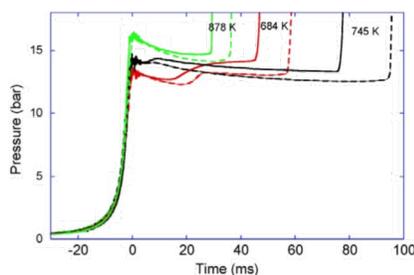


Mittal & Sung, 2006

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- Laminar flame
  - "Simple" setup – measure burning velocity $S_L$
  - Obviously applicable to "real" flame chemistry but flames are very thin (< 1mm); hard to probe inside to measure species evolution
  - Interaction with transport via convection and diffusion – need to compare results with computations using detailed flame models
  - Not a sensitive test: $\omega \sim S_L^{1/2}$ although extinction strain rate a more sensitive test ($\omega \sim \Sigma_{ext}$)



Park et al., 2015

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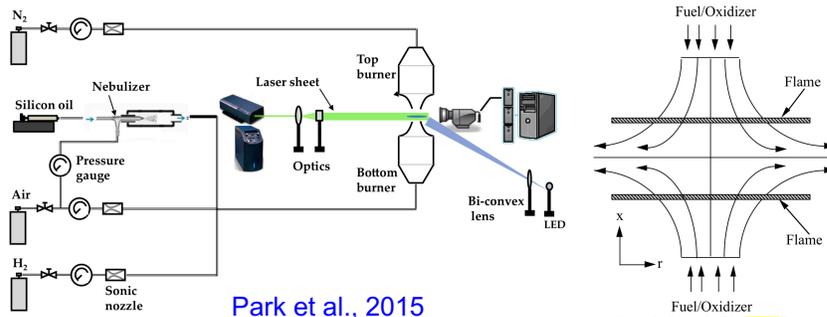
- First consider 1 single (irreversible) reaction at constant T, P:

  A + B → C + D   (forward reaction, rate constant $k_f$)

$$\frac{d[A]}{dt} = -k_f[A][B]; \; k_f = \text{constant}$$

But [A] and [B] are not independent, any decrease in [A] results in an identical decrease in [B] and increase in [C] & [D]; for a stoichiometric excess of [B], i.e. $[B]_o > [A]_o$

$$[A]_o - [A] = [B]_o - [B] \Rightarrow [B] = ([B]_o - [A]_o) + [A]$$

$$\Rightarrow \frac{d[A]}{dt} = -k_f[A]\{([B]_o - [A]_o) + [A]\} \Rightarrow -k_f dt = \frac{d[A]}{[A]^2 + ([B]_o - [A]_o)[A]}$$

$$\Rightarrow -k_f([B]_o - [A]_o)t = \ln\left(\frac{[A]}{[A] + ([B]_o - [A]_o)}\right) + \text{Constant}$$

$$t = 0 : [A] = [A]_o \Rightarrow \text{Constant} = -\ln\left(\frac{[A]_o}{[B]_o}\right) \Rightarrow -k_f([B]_o - [A]_o)t = \ln\left(\frac{[A]}{[A] + ([B]_o - [A]_o)}\right) - \ln\left(\frac{[A]_o}{[B]_o}\right)$$

$$\Rightarrow \frac{[A]}{[A]_o} = \frac{e^{-k_f([B]_o - [A]_o)t}\left(1 - [A]_o/[B]_o\right)}{1 - ([A]_o/[B]_o)e^{-k_f([B]_o - [A]_o)t}}$$

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## 1-step reversible reaction (1/4)

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➢ Now consider 1 single (but reversible) reaction:

A + B → C + D  (forward reaction, rate constant $k_f$)

C + D → A + B  (reverse reaction, rate constant $k_b$)

$$\frac{d[A]}{dt} = -k_f[A][B] + k_b[C][D]$$

$$[A]_o - [A] = [B]_o - [B] = [C] - [C]_o = [D] - [D]_o$$

$$\Rightarrow [B] = [B]_o - [A]_o + [A]; [C] = [C]_o + [A]_o - [A]; [D] = [D]_o + [A]_o - [A]$$

$$\Rightarrow \frac{d[A]}{dt} = -k_f[A]\{[B]_o - [A]_o + [A]\} + k_b\{[C]_o + [A]_o - [A]\}\{[D]_o + [A]_o - [A]\}$$

$$\Rightarrow \frac{1}{(k_b - k_f)}\frac{d[A]}{dt} = [A]^2 + a[A] + b \Rightarrow (k_b - k_f)dt = \frac{d[A]}{[A]^2 - a[A] + b} \text{ where}$$

$$a \equiv \frac{k_f([B]_o - [A]_o) + k_b(2[A]_o + [C]_o + [D]_o)}{(k_b - k_f)}; b \equiv \frac{k_b([A]_o + [C]_o)([A]_o + [D]_o)}{(k_b - k_f)}$$

$$\Rightarrow (k_b - k_f)t = -\frac{1}{\sqrt{a^2 + 4b}}\ln\left(\frac{\sqrt{a^2 + 4b} + a + 2[A]}{\sqrt{a^2 + 4b} - a - 2[A]}\right) + \text{Constant}$$

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## 1-step reversible reaction (2/4)

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➢ Initial condition:  t = 0, [A]= $[A]_o$

$$t = 0, [A] = [A]_o \Rightarrow (k_b - k_f)(0) = -\frac{1}{\sqrt{a^2 + 4b}}\ln\left(\frac{\sqrt{a^2 + 4b} + a + 2[A]_o}{\sqrt{a^2 + 4b} - a - 2[A]_o}\right) + \text{Constant}$$

$$\Rightarrow \text{Constant} = \frac{1}{\sqrt{a^2 + 4b}}\ln\left(\frac{\sqrt{a^2 + 4b} + a + 2[A]_o}{\sqrt{a^2 + 4b} - a - 2[A]_o}\right)$$

$$\Rightarrow (k_b - k_f)t = \frac{1}{\sqrt{a^2 + 4b}}\ln\left(\frac{\sqrt{a^2 + 4b} + a + 2[A]_o}{\sqrt{a^2 + 4b} - a - 2[A]_o}\frac{\sqrt{a^2 + 4b} - a - 2[A]}{\sqrt{a^2 + 4b} + a + 2[A]}\right)$$

➢ In general the algebra to "simplify" is horrendous but consider special case $[A]_o = [B]_o$, $[C]_o = [D]_o = 0$

$$[A]_o = [B]_o, [C]_o = [D]_o = 0 \Rightarrow a = -\frac{2k_b[A]_o}{k_b - k_f}; b = -\frac{k_b[A]_o^2}{k_b - k_f}; \sqrt{a^2 + 4b} = \frac{2\sqrt{k_b k_f}[A]_o}{k_b - k_f}$$

$$\Rightarrow \frac{\sqrt{a^2 + 4b} + a + 2[A]_o}{\sqrt{a^2 + 4b} - a - 2[A]_o} = \frac{1 - \sqrt{k_f/k_b}}{1 + \sqrt{k_f/k_b}}$$

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## 1-step reversible reaction (3/4)

$$\Rightarrow (k_b - k_f)t = \frac{(k_b - k_f)}{2\sqrt{k_b k_f}[A]_o} \ln\left(\frac{\sqrt{a^2+4b}+a+2[A]}{\sqrt{a^2+4b}-a-2[A]} \frac{1-\sqrt{k_f/k_b}}{1+\sqrt{k_f/k_b}}\right)$$

$$\Rightarrow t = \frac{1}{2\sqrt{k_b k_f}[A]_o} \ln\left[\frac{[A]\left(\sqrt{k_f/k_b}-1\right)+[A]_o}{[A]\left(\sqrt{k_f/k_b}+1\right)-[A]_o}\right]$$

Check #1: $[A]=[A]_o \Rightarrow t = \frac{1}{2\sqrt{k_b k_f}[A]_o}\ln\left[\frac{[A]_o\left(\sqrt{k_f/k_b}-1\right)+[A]_o}{[A]_o\left(\sqrt{k_f/k_b}+1\right)-[A]_o}\right] = \frac{1}{2\sqrt{k_b k_f}[A]_o}\ln[1]=0$ OK

Check #2: As $t \to \infty$, need to approach equilbrium concentration $[A]_{eq}$

$$t \to \infty \Rightarrow [A]\left(\sqrt{k_f/k_b}+1\right)-[A]_o \to 0 \Rightarrow [A]_{eq} = \frac{[A]_o}{\sqrt{k_f/k_b}+1}$$

Check #2: At equilbrium forward & reverse rates are equal, *i.e.*,

$$-k_f[A][B] = -k_b[C][D] \Rightarrow -k_f[A][A] = -k_b([A]_o-[A])([A]_o-[A])$$

$$\Rightarrow -k_f[A]^2 = -k_b([A]_o-[A])^2 \Rightarrow \sqrt{k_f/k_b}[A] = [A]_o-[A] \Rightarrow [A] = \frac{[A]_o}{\sqrt{k_f/k_b}+1} = [A]_{eq}$$ OK

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## 1-step reversible reaction (4/4)

$k_f = 10$, $k_b = 1$ or $0$
$[A]_o = 1$, $[A]_{eq} = 0.240$

$k_f = 1$, $k_b = 10$
$[A]_o = 10$, $[A]_{eq} = 7.60$

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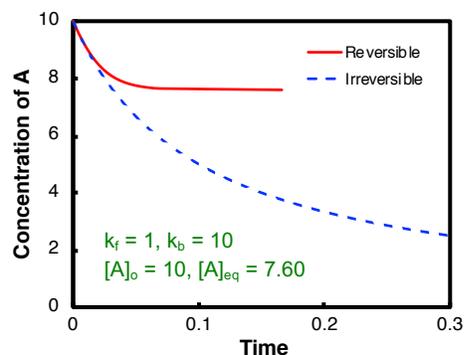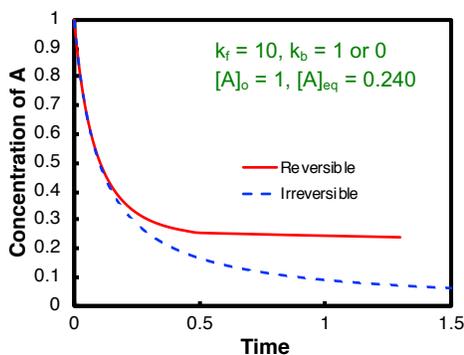
## Steady-state approximation - concept

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- These calculations are tedious, need some simplifications to handle more complex reaction mechanisms!
- Consider a two-step reaction with very reactive radical N

  $O + N_2 \rightarrow NO + N$     (rate constant $k_1$)

  $N + O_2 \rightarrow NO + O$     (rate constant $k_2$)

- Net production of N:    $d[N]/dt = k_1[O][N_2] - k_2[N][O_2]$
- The steady-state approximation assumes $d[N]/dt \approx 0$, i.e.

$$k_1[O][N_2] >> \left|\frac{d[N]}{dt}\right| ; k_2[N][O_2] >> \left|\frac{d[N]}{dt}\right| \Rightarrow [N] \approx \frac{k_1[O][N_2]}{k_2[O_2]}$$

  in which case

$$\frac{d[NO]}{dt} = k_1[O][N_2] + k_2[N][O_2] = k_1[O][N_2] + k_2\frac{k_1[O][N_2]}{k_2[O_2]}[O_2] = 2k_1[O][N_2]$$

- Does NOT imply [N] = constant, only that [N] varies slowly compared to its production & consumption rates individually
- When valid? Typically when a rapidly-reacting intermediate (N in this case) is produced by a slow reaction ($O + N_2 \rightarrow NO + N$)

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## Lindemann (1922) - P effects on decomposition

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- Unimolecular decomposition of A (e.g. $H_2O_2 + M \rightarrow 2\ OH$)

  $A + M \rightarrow A^* + M$     (rate constant $k_{1f}$; $A^*$ = activated state of A)

  $A^* + M \rightarrow A + M$     (rate constant $k_{1b}$; $k_{1f}/k_{1b} = K_{equilibrium} = K_A/K_{A^*}$)

  $A^* \rightarrow B$     (rate constant $k_2$, assumed irreversible)

- Steady state assumption for $A^*$ yields

$$\frac{d[A^*]}{dt} = k_{1f}[A][M] - k_{1b}[A^*][M] - k_2[A^*] \approx 0 \Rightarrow [A^*] \approx \frac{k_{1f}[A][M]}{k_{1b}[M] + k_2} \Rightarrow \frac{d[B]}{dt} = k_2[A^*] = \frac{k_2 k_{1f}[A][M]}{k_{1b}[M] + k_2}$$

- "Apparent" overall reaction rate: find $k_{eff}$ such that $d[A]/dt = -d[B]/dt$ (i.e. rate of consumption of reactant A = rate of production of product B):

$$\frac{d[A^*]}{dt} = k_{1f}[A][M] - k_{1b}[A^*][M] - k_2[A^*] \approx 0 \Rightarrow [A^*] \approx \frac{k_{1f}[A][M]}{k_{1b}[M] + k_2}$$

$$\Rightarrow \frac{d[A]}{dt} = -k_{eff}[A] = -\frac{d[B]}{dt} \Rightarrow k_{eff} = \frac{k_{1f}[M]}{1 + (k_{1b}/k_2)[M]}$$

- Note at low P ([M] small): $k_{eff} \rightarrow k_{1f}[M] \sim P^1$;

  high P: $k_{eff} \rightarrow k_{1f}k_2/k_{1b} \sim P^0$ (falloff in rate at high P)

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## Slide 27

➢ Overall reaction $A_2 + B_2 \rightarrow 2AB$

$\quad A_2 + M \rightarrow A + A + M$ (rate constant $k_1$, chain initiation)

$\quad A + B_2 \rightarrow AB + B$ (rate constant $k_2$, chain branching)

$\quad A_2 + B \rightarrow AB + A$ (rate constant $k_3$, chain branching)

$\quad A + B + M \rightarrow AB + M$ (rate constant $k_4$, chain termination)
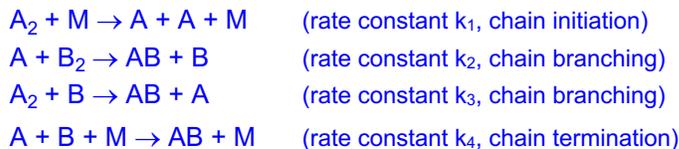
➢ Steady state assumption for A and B:

$$\frac{d[A]}{dt} = 2k_1[A_2][M] - k_2[A][B_2] + k_3[A_2][B] - k_4[A][B][M] \approx 0 \Rightarrow [A] \approx \frac{2k_1[A_2][M] + k_3[A_2][B]}{k_2[B_2] + k_4[B][M]}$$

$$\frac{d[B]}{dt} = k_2[A][B_2] - k_3[A_2][B] - k_4[A][B][M] \approx 0 \Rightarrow [B] \approx \frac{k_2[A][B_2]}{k_3[A_2] + k_4[A][M]}$$

$$\Rightarrow 2k_1[A_2][M] - k_2[A][B_2] + k_3[A_2]\frac{k_2[A][B_2]}{k_3[A_2] + k_4[A][M]} - k_4[A]\frac{k_2[A][B_2]}{k_3[A_2] + k_4[A][M]}[M] \approx 0$$

$$[A]^2 - \left\{\frac{k_1[A_2][M]}{k_2[B_2]}\right\}[A] - \left\{\frac{k_1 k_3[A_2]^2}{k_2 k_4[B_2]}\right\} = 0 \Rightarrow [A] = \frac{k_1[A_2][M]}{2k_2[B_2]}\left\{1 + \sqrt{1 + \frac{4k_2 k_3[B_2]}{k_1 k_4[M]^2}}\right\}$$

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## Slide 28

➢ Turns textbook states that $k_1$ & $k_4$ should be much smaller than $k_2$ & $k_3$ since $k_2$ & $k_3$ are radical-molecule reactions – what is **seriously** wrong with that statement?

➢ Anyway if the 2nd term inside the square root is >> 1 then

$$[A] \approx [A_2]\sqrt{\frac{k_1 k_3}{k_2 k_4[B_2]}} \Rightarrow \frac{d[B_2]}{dt} \approx -[A_2]\sqrt{\frac{k_1 k_2 k_3[B_2]}{k_4}}$$

➢ Rate of $[B_2]$ consumption increases with $k_1$, $k_2$, $k_3$ but decreases with $k_4$ due to loss of A and B radicals

➢ Note that the requirement $4k_2 k_3[B_2]\big/k_1 k_4[M]^2$ >> 1 always breaks down at sufficiently high P since $[B_2] \sim P$ but $[M]^2 \sim P^2$, thus steady-state assumption for this reaction mechanism fails at high enough P

## Steady-state approx. – chain branching

➢ OK is this for real?  Create Excel spreadsheet model and compare "exact" solutions using Euler's method to advance solution from time step t to t+Δt: f(t+Δt) ≈ f(t) + {df(t)/dt}Δt, e.g.

$$f(t+\Delta t) \approx f(t) + \frac{df(t)}{dt}\Delta t \Rightarrow [A]_{t+\Delta t} \approx [A]_t + \frac{d[A]}{dt}\bigg|_t \Delta t$$

$$\frac{d[A]}{dt} = 2k_1[A_2][M] - k_2[A][B_2] + k_3[A_2][B] - k_4[A][B][M]$$

$$\Rightarrow [A]_{t+\Delta t} \approx [A]_t + \Delta[A]_t = [A]_t + \{2k_1[A_2][M] - k_2[A][B_2] + k_3[A_2][B] - k_4[A][B][M]\}\Delta t$$

Euler's method is simple but not very stable or accurate – use e.g. 4th order Runge-Kutta when Euler fails (actually Euler's method gives first term in the 4th order Runge-Kutta)

➢ Spreadsheet inputs: $k_1 - k_4$; initial concentrations of $A_2$, $B_2$, A, B, AB, M; Δt

➢ Outputs: concentrations vs. time; time to reach 90% completion of reaction to AB; time to peak [A]; time to peak [B]; validity of steady-state approximation (rates of formation & destruction of A > 10x net rate of change of [A])

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## Steady-state approx. – chain branching

$k_1 = 0.01$, $k_2 = 2$, $k_3 = 1$, $k_4 = 1$
Time = 0: $[A_2] = 1$, $[B_2] = 1$, $[M] = 10$, $[A] = [B] = [AB] = 0$

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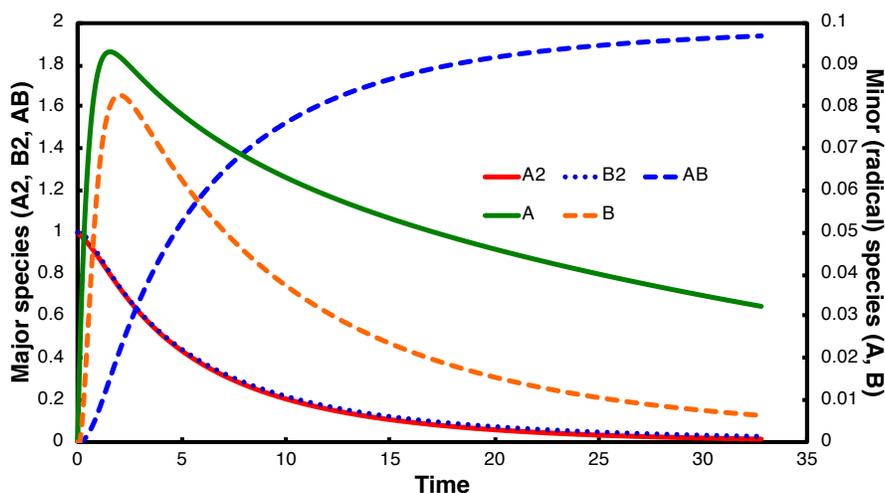
## Validity of steady-state approximation

- Criteria: total $d[A]/dt$ & $d[B]/dt$ < 10% of individual source/sink terms
- Approximation invalid initially when no radical pool exists
- Also invalid when reactants $A_2$ & $B_2$ have been depleted significantly, thus chain branching rates $k_2[A][B_2]$ & $k_3[B][A_2]$ are not large compared to chain termination rate $k_4[A][B][M]$



Steady state OK? (1 = yes, 0 = no)
Steady state [A] / Actual [A]

Time
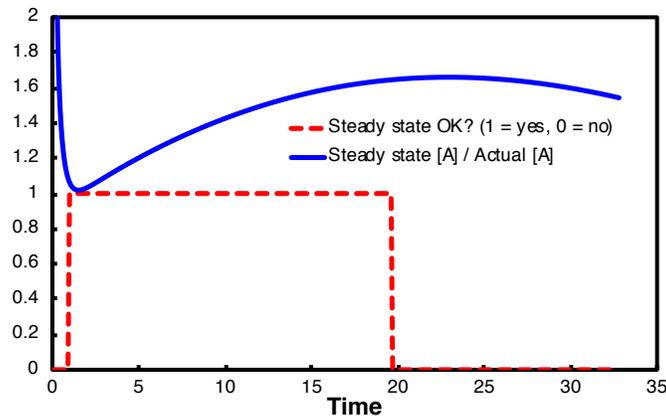
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## Validity of steady-state approximation

- Radical (A, B) concentrations are much lower than major (stable) species ($A_2$, $B_2$, AB)
- Radical pool builds quickly to peak, reaches steady-state, then decreases slowly as reactants are consumed
- Product AB follows mirror-image of reactants $A_2$ & $B_2$, showing that steady-state exists, radical concentrations shift quickly as reactant concentrations shift
- How do changes in input parameters affect reaction time (90% of AB formed)?  For 10% increase in parameter (in case of [A], [B], [AB], added 0.1 to initial mixture), % change in reaction time:

| Property | $k_1$ | $k_2$ | $k_3$ | $k_4$ | [M] | $[A_2]$ | $[B_2]$ | [A] | [B] |
|----------|-------|-------|-------|-------|-----|---------|---------|-----|-----|
| % change | -6 | -4 | -2 | 2 | -4 | 36 | -11 | -17 | -8 |

$k_1$, $k_2$, $k_3$ increases overall reaction rate, $k_4$ decreases rate due to loss of radicals; adding [A] decreases rate more than adding [B] due to bottleneck of initiation $A_2 + M \rightarrow 2A + M$

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## Partial equilibrium approximation

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- Analogous to steady-state approximation, but applies to a single (reversible) reaction rather than a single species
- Requires both forward and reverse rates to be fast compared to net rate, e.g. for A + B$_2$ ⇔ AB + B

$$k_{1f}[A][B_2] >> |k_{1f}[A][B_2] - k_{1b}[AB][B]|; k_{1b}[AB][B] >> |k_{1f}[A][B_2] - k_{1b}[AB][B]|$$

- Example:  for reactants A$_2$, B$_2$, product A$_2$B, radicals A, B, AB

<div style="color:blue">

A + B$_2$ → AB + B      Rate constant $k_{1f}$

AB + B → A + B$_2$      Rate constant $k_{1b}$

B + A$_2$ → AB + A      Rate constant $k_{2f}$

AB + A → B + A$_2$      Rate constant $k_{2b}$

AB + A$_2$ → A$_2$B + A      Rate constant $k_{3f}$

A$_2$B + A → AB + A$_2$      Rate constant $k_{3b}$

A + AB + M → A$_2$B + M   Rate constant $k_4$   (NOT in partial equil.)

</div>
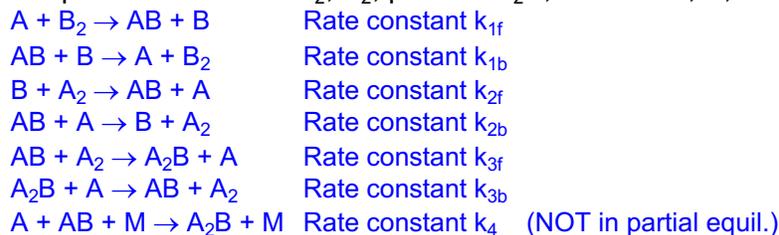
$$\frac{[AB][B]}{[A][B_2]} \approx \frac{K_{AB}K_B}{K_A K_{B_2}} \equiv K_{eq,1}; \frac{[AB][A]}{[B][A_2]} \approx \frac{K_{AB}K_A}{K_B K_{A_2}} \equiv K_{eq,2}; \frac{[A_2B][A]}{[AB][A_2]} \approx \frac{K_{A_2B}K_A}{K_{AB}K_{A_2}} \equiv K_{eq,3}$$

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## Partial equilibrium approximation

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- Combining these results to solve for radical species A, B, AB

$$[A] = \frac{\sqrt{K_{eq,1}K_{eq,2}[A_2]^3[B_2]}K_{eq,3}}{[A_2B]}; [B] = \frac{K_{eq,1}K_{eq,3}[A_2][B_2]}{[A_2B]}; [AB] = \sqrt{K_{eq,1}K_{eq,2}[A_2][B_2]};$$

- Then the product formation rate is

$$\frac{d[A_2B]}{dt} = k_4[A][AB][M] = k_4 \frac{\sqrt{K_{eq,1}K_{eq,2}[A_2]^3[B_2]}K_{eq,3}}{[A_2B]}\sqrt{K_{eq,1}K_{eq,2}[A_2][B_2]}[M]$$

$$= k_4 \frac{K_{eq,1}K_{eq,2}K_{eq,3}[A_2]^2[B_2][M]}{[A_2B]}$$

- Obviously cannot apply at t = 0 since [A$_2$B] = 0, but early on, before [A$_2$] and [B$_2$] depletion is significant,

$$[A_2B] \approx \sqrt{2k_4 K_{eq,1}K_{eq,2}K_{eq,3}[A_2]^2[B_2][M]t}$$

t$^{1/2}$ behavior

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## Online chemical kinetics calculator

- ➤ What if the mechanism is more complex or less stable?
  http://navier.engr.colostate.edu/code/code-5/index.html
- ➤ Chemical mechanisms for $H_2$-$O_2$, $CH_4$-$O_2$ and a few others
- ➤ Input page simple except for need to choose by trial & error:
  - ➤ Total integration time (long enough to see fuel consumption & product formation)
  - ➤ Time interval for printout ($\Delta t$) (small enough to resolve transients)
- ➤ Output format hard to feed into to Excel!

```
t(sec)= 0.0000E+00   P(atm)= 1.0000E+00   T(K)= 8.5000E+02
O2        = 3.33E-01  H         = 0.00E+00  O         = 0.00E+00
OH        = 0.00E+00  HO2       = 0.00E+00  H2O2      = 0.00E+00
H2O       = 0.00E+00  H2        = 6.67E-01

t(sec)= 1.0019E-01   P(atm)= 1.0000E+00   T(K)= 8.5000E+02
O2        = 3.33E-01  H         = 3.52E-10  O         = 2.54E-11
OH        = 1.68E-11  HO2       = 1.55E-06  H2O2      = 5.81E-06
H2O       = 1.06E-05  H2        = 6.67E-01

t(sec)= 2.0085E-01   P(atm)= 1.0000E+00   T(K)= 8.5000E+02
O2        = 3.33E-01  H         = 5.44E-10  O         = 3.93E-11
OH        = 2.69E-11  HO2       = 1.97E-06  H2O2      = 1.42E-05
H2O       = 2.89E-05  H2        = 6.67E-01

t(sec)= 3.0801E-01   P(atm)= 1.0000E+00   T(K)= 8.5000E+02
O2        = 3.33E-01  H         = 7.92E-10  O         = 5.72E-11
OH        = 4.03E-11  HO2       = 2.41E-06  H2O2      = 2.52E-05
H2O       = 5.90E-05  H2        = 6.67E-01
```

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## Online chemical kinetics calculator

- ➤ Typical example - stoich. $H_2$-$O_2$, T = 850K, P = 1 atm, near 3rd explosion limit, above 2nd limit so mole fractions of H, O, OH very small, $\approx 10^{-9}$
- ➤ Similar to schematic $A_2 + B_2$ results



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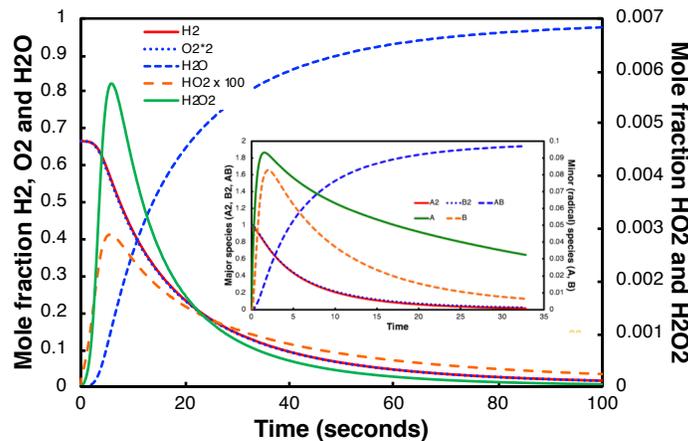
➢ "Chain branching" acceleration mechanism for H$_2$-O$_2$

H + O$_2$ → OH + O    (only way to break O=O bond directly)

H$_2$ + OH → H + H$_2$O

O + H$_2$ → OH + H    etc.

where 1 radical (H, OH, O) leads to 2, then 4, then 8, … radicals

➢ "Chain branching" mechanism leads to faster "runaway" than thermal runaway (discussed later) since $2^x > e^{-a/x}$ for large x

➢ In the case above, the "net" reaction would be

2 H$_2$ + O$_2$ → H + OH + H$_2$O

which shows the increase in the radical "pool"

➢ H can also be removed from the system via

H + O$_2$ + M → HO$_2$ + M    (M = any molecule)

➢ H can also be removed from the system via

H + wall → H(wall); H(wall) + H(wall) → H$_2$(wall) → H$_2$(gas)

… and similarly with other radicals

---

➢ But at the beginning there is no H – how to get it?

H$_2$ + O$_2$ → HO$_2$ + H    (mostly this: Δh = 55 kcal/mole )

H$_2$ + M → H + H + M    (slower since Δh = 104 kcal/mole - too big)

O$_2$ + M → O + O + M    (Δh = 119 kcal/mole - even worse)

(M = any molecule)

➢ What happens to HO$_2$?

HO$_2$ + H$_2$ → HOOH + H    (HOOH = H$_2$O$_2$ = hydrogen peroxide)

HO$_2$ + HO$_2$ → HOOH + O$_2$ (radical-radical – is it more important?)

HOOH + M → 2OH    (chain branching if H + O$_2$ → OH + O ineffective)

➢ Which chain-branching route is more important, H or HO$_2$?

H + O$_2$ → OH + O; d[O$_2$]/dt = -10$^{16.7}$[H][O$_2$]T$^{-0.8}$$e^{-16500/RT}$

[ ]: mole/cm$^3$; T: K; R: cal/moleK; t: sec

Depends on P$^2$ since [ ] ~ P, strongly dependent on T

H + O$_2$ + M → HO$_2$ + M; {M = any molecule}

d[O$_2$]/dt = -10$^{15.2}$[H][O$_2$][M]T$^0$$e^{+1000/RT}$ for M = N$_2$

(higher rate for M = CO$_2$ and especially for M = H$_2$O)

Depends on P$^3$, nearly independent of T

## "Real" chemistry: $H_2$-$O_2$ system (3/6)

- Rates equal ("crossover") when
  $[M] = 10^{1.5}T^{-0.8}e^{-17500/RT}$
- Ideal gas law: $P = [M]RT$ thus
  $P = 10^{3.4}T^{0.2}e^{-17500/RT}$ (P in atm)
  - $\Rightarrow$ crossover at 950K for 1 atm, higher T for higher P, thus at low T / high P, $H + O_2 \rightarrow OH + O$ branching does not occur; relatively inactive $HO_2$ forms:
- Causes "2nd explosion limit" of $H_2 - O_2$ system in "explosion vessel" with constant-T walls
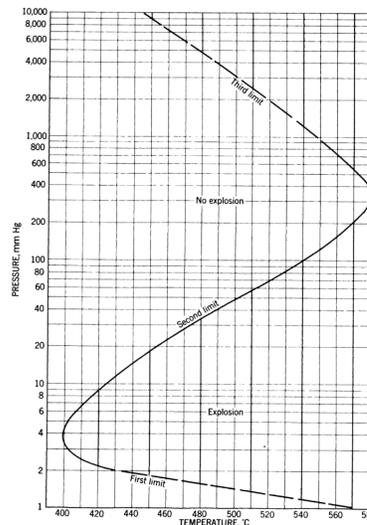


Lewis & von Elbe, 1987
(7.4 cm diameter vessel)

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## "Real" chemistry: $H_2$-$O_2$ system (4/6)

- What causes 2 other limits??? Rules:
  - H, OH, O more reactive than $HO_2$
  - When radicals hit wall, they may adsorb and be converted to stable species
  - Radical concentrations small, thus radical-radical reactions unlikely (but maybe $HO_2 + HO_2$ … homework problem!)
  - Reaction rates vary with pressure (P)
    » Collisions (of any molecule) with wall ~ $P^1$ (P = pressure)
    » Bimolecular reactions (e.g. $H + O_2 \rightarrow OH + O$) ~ $P^2$
    » Trimolecular reactions (e.g. $H + O_2 + M \rightarrow HO_2 + M$ ) ~ $P^3$
- First limit
  - $H + O_2 \rightarrow OH + O$ dominates $H + O_2 + M \rightarrow HO_2 + M$
  - As P↑, molecule-wall collisions increase more slowly than molecule-molecule collisions, thus probability of radicals reaching wall and being converted to stable species decreases – chain branching can occur - explosion
  - As T↑, branching rates (e.g. $H + O_2 \rightarrow OH + O$) increase (high $E_a$) thus impact of loss at walls decreases – explosion

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## "Real" chemistry: H₂-O₂ system (5/6)

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- Third limit
  - $HO_2$ not a stable species, just much less active radical than H, OH, O
  - As P increases, molecule-wall collisions increase more slowly than molecule-molecule collisions, thus probability of $HO_2$ reacting in gas phase to produce HOOH before reaching wall and being converted to stable species decreases – chain branching can occur: explosion

    $HO_2 + H_2 \rightarrow HOOH + H$ or $HO_2 + HO_2 \rightarrow HOOH + O_2$
    $HOOH + M \rightarrow 2\ OH$
    $OH + H_2 \rightarrow HOH + H$
    $H + O_2 + M \rightarrow HO_2 + M$ … and the cycle continues

- Key point – the 3-limit behavior shows unequivocally that
  - There are two sets of intermediates, one set ($HO_2$) much less active than the other set (OH, H, O)
  - There is an inhibiting step ($H + O_2 + M \rightarrow HO_2 + M$) which has a stronger pressure dependence than the main rate accelerating process ($H + O_2 \rightarrow OH + O$)

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## "Real" chemistry: H₂-O₂ system (6/6)

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- Simulate "explosion vessel" limits using online chemistry calculator
  - Use time (t) to 50% $H_2$ consumption as measure of explosion limit
  - Diffusion time ~ P so scale accordingly, e.g. at 10 atm, allow 10x more time than at 1 atm
  - Results using t at 1 atm = 25 s close to experiments by L&vE
  - Second limit independent of time (vessel size & wall material)
  - Second limit where branching vs. recombination rates ≈ same



$H + O_2 \rightarrow OH + O =$
$H + O_2 + M \rightarrow HO_2 + M$
when $P = 10^{3.4}T^{0.2}e^{-17500/RT}$
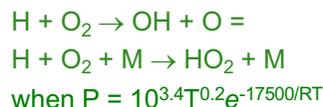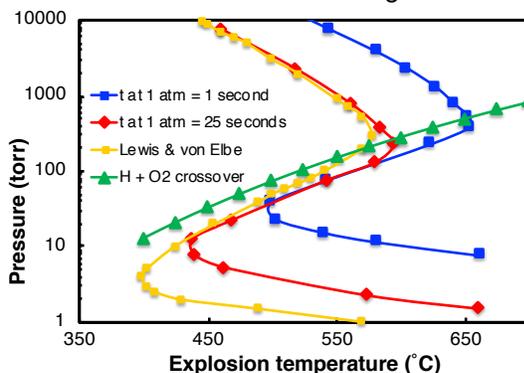
$t \approx d^2/\alpha$, d = 7.4 cm
1 atm, 550°C: $\alpha \approx 4.7$ cm²/s
$t \approx 12$ s, not 25 s, but close!

Legend:
- t at 1 atm = 1 second
- t at 1 atm = 25 seconds
- Lewis & von Elbe
- H + O2 crossover

Pressure (torr) vs Explosion temperature (°C)

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## *"Real" chemistry: CO-O$_2$ system (1/4)*

- CO MUCH different because no chain branching and no "shuffle" reaction to create product

  $CO + O_2 \rightarrow CO_2 + O$      Very slow, but needed as source of O
  $O_2 + M \rightarrow O + O$      Very high activation energy, even slower
  $CO + M \rightarrow C + O + M$      No way! C=O is strongest chemical bond!
  $CO + O + M \rightarrow CO_2 + M$    Creates product but removes radicals
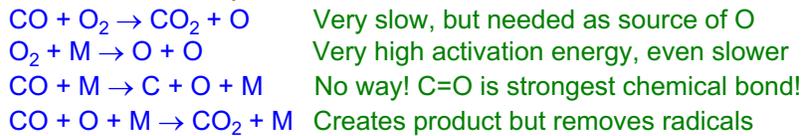
- As a result, pure $CO - O_2$ oxidation is extremely slow!
- Early experiments showed widely varying results because of contamination with water; with any hydrogen source

  $CO + OH \rightarrow CO_2 + H$      Shuffle reaction to create $CO_2$
  $H + O_2 \rightarrow OH + O$      Regenerate OH plus another O

  Neither are fast, but better than alternatives!

- Stoich. $CO + O_2$, 1 atm, 1500K, time to consume 50% of CO:
  - No $H_2O$: 1.03 s; 1 ppm $H_2O$: 0.27 s; 10 ppm: 0.038 s;
  - 100 ppm 0.0043 s; 1,000 ppm 0.00080 s; 10,000 ppm 0.00023 s

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## *"Real" chemistry: CO-O$_2$ system (2/4)*

- Case shown: const. T = 1000K, P = 1 atm, CO:H$_2$:O$_2$ = 1:1:10
- H$_2$-O$_2$ acts as almost infinitely fast (*i.e.*, steady-state) radical source for CO
- CO does not affect H$_2$-O$_2$ process, CO reaction just too slow
- 50% H$_2$ consumption in ≈ 400 μs, ≈ same with or without CO

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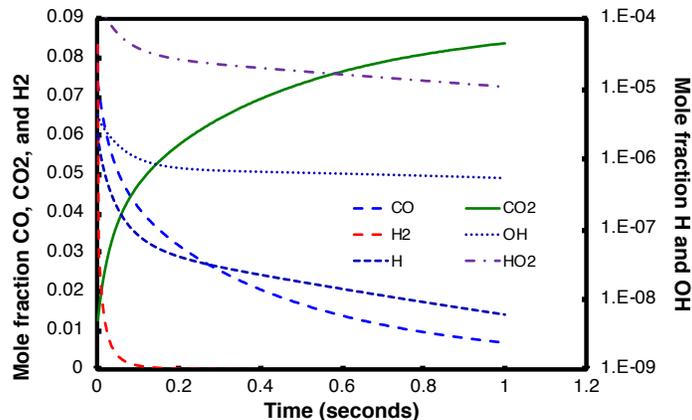
## *"Real" chemistry: CO-$O_2$ system (4/4)*

➤ CSU homogenous kinetics calculator predicts that dry CO has only a single limit
➤ With $H_2O$ addition, behavior is very similar to $H_2$-$O_2$ with offset to higher T - CO is a "parasite" on the OH source



Legend:
- CO (Dry)
- CO (1% H2O)
- H2-O2

Axis labels:
- Pressure (torr)
- Explosion temperature (°C)
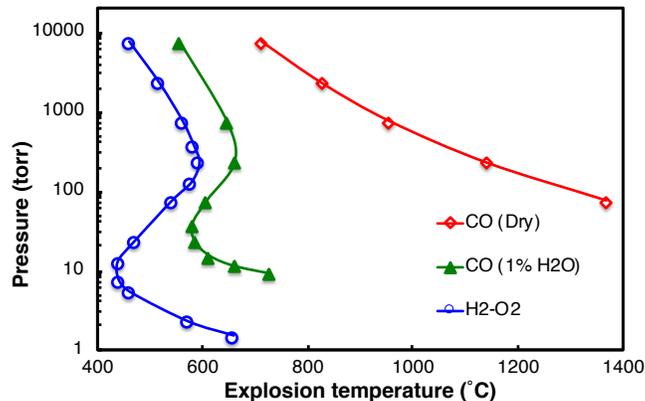
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## *"Real" chemistry: HC-$O_2$ system (1/9)*

➤ Hydrocarbons inhibit their own oxidation because they react with radicals more readily than $O_2$ reacts with radicals, thus inhibiting $O_2$ breakdown
➤ Nearly all of fuel must be consumed before radical pool needed to consume CO can build up
➤ CO oxidation is the last step
➤ β-scission – fuel molecule breaks apart 1 C-C bond away from C missing an H atom (avoids having to move an H atom to an adjacent C atom)
➤ This only matters at "low" temperatures (<1500K) where H + $O_2$ branching is inhibited by the hydrocarbons; at higher temperatures, H + $O_2$ branching is sufficiently rapid

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## "Real" chemistry: HC-O₂ system (2/9)

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➤ Hydrocarbons have no 1st or 2nd explosion limit; instead of $H + O_2 + M \rightarrow HO_2 + M$ being the dominant recombination reaction at low T, it's $RH + H \rightarrow R + H_2$, which has same pressure dependence as the branching reaction $H + O_2 \rightarrow OH + O$

➤ C-H bonds stronger in $CH_4$ than $C_3H_8$, thus higher explosion T
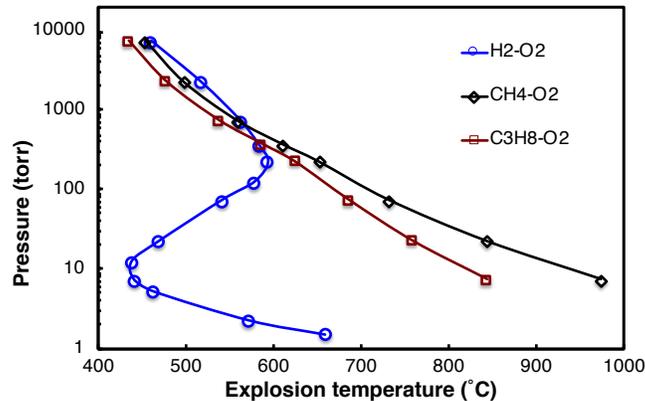


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## "Real" chemistry: HC-O₂ system (3/9)

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➤ Start with fuel molecule RH, where R is an "organic radical", e.g. propane without an H



propyl radical            propane
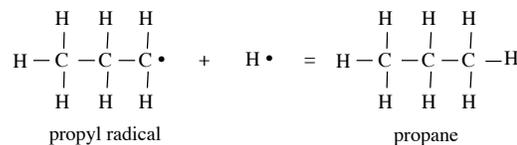
➤ Abstract an H atom from RH
    $RH + O_2 \rightarrow R\bullet + HOO\bullet$

➤ Add an $O_2$ to $R\bullet$
    $R\bullet + O_2 \rightarrow ROO\bullet$

➤ Produce peroxides with O-O single bond (half as strong as O=O double bond (120 kcal/mole vs. 60 kcal/mole), much easier to break)
    $ROO\bullet + RH \rightarrow R\bullet + ROOH$ or $HOO\bullet + RH \rightarrow R\bullet + HOOH$

➤ Break O-O single bond, create "chain branching" process
    $ROOH + M \rightarrow RO\bullet + \bullet OH$ or $HOOH + M \rightarrow HO\bullet + \bullet OH$

➤ Newly created radicals generate more organic radicals
    $RH + \bullet OH \rightarrow R\bullet + HOH$ or $RH + RO\bullet \rightarrow R\bullet + ROH$

➤ Note that rate of reaction will be sensitive to rates of H atom removal from fuel molecule RH

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➤ Rate of H atom removal depends on strength of C-H bond, which in turn depends on how many other carbons are bonded to that C - stronger bond, slower reaction, less knock



| methane | primary C-H bond | secondary C-H bond | tertiary C-H bond |
| 105 kcal/mole | 98 kcal/mole | 95 kcal/mole | 93 kcal/mole |
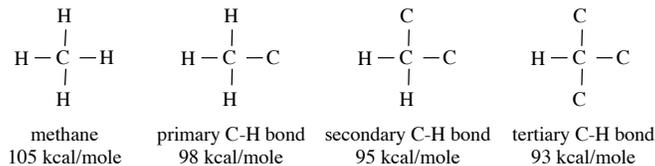
➤ Examples:  n-heptane:  6 primary, 12 secondary C-H bonds
2, 2, 4 trimethy pentane:  15 primary, 2 secondary, 1 tertiary



n-heptane

❙ primary ❙ secondary ❙ tertiary

2, 2, 4 trimethylpentane
(iso-octane)

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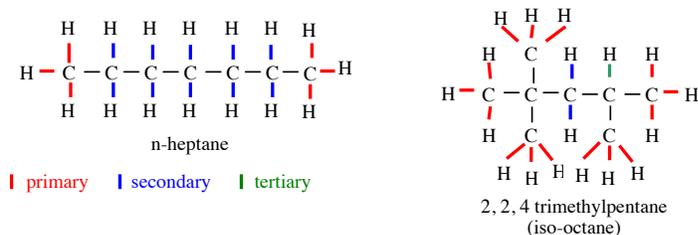
➤ Does this small difference in bond strength matter?  YES because activation energy is high

➤ If we use bond strength as a measure of activation energy (dangerous in general, but ok here…) then at a typical 900K

$\omega_{methane} : \omega_{primary} : \omega_{secondary} : \omega_{tertiary}$

$\exp(-E_{methane}/\Re T) : \exp(-E_{primary}/\Re T) : \exp(-E_{secondary}/\Re T) : \exp(-E_{tertiary}/\Re T)$

$\approx \exp(-105{,}000 \text{ cal/mole}/(1.987 \text{ cal/mole-K})(900K))$ :

$\exp(-98000/1.987*900) : \exp(-95000/1.987*900) : \exp(-93000/1.987*900)$

$\approx 1 : 50 : 268 : 820$

➤ As a result, fuels with mostly primary C-H bonds will decompose much more slowly than isomers with more secondary & tertiary C-H bonds – higher octane number in gasoline-type fuels

➤ How to make CO?  RO• formed by cleavage of O-O bond in peroxide then enter aldehyde route

RO• + M → R'HCO + H + M, e.g. C$_2$H$_5$O• + M → CH$_3$HCO + H + M

➤ Aldehydes have weakest C-H bond (≈87 kcal/mole) thus

R'HCO + M → R'CO• + H• + M, e.g. CH$_3$HCO + M → CH$_3$CO + H• + M
R'HCO + O$_2$ → R'CO• + HO$_2$•, e.g. CH$_3$HCO + O$_2$ → CH$_3$CO• + HO$_2$•

➤ Aldehydes also have weak C-C bond thus

R'CO• + M → R' + CO + M, e.g. CH$_3$CO• + M → CH$_3$• + CO + M

➤ Somewhat roundabout but easiest way to make CO, still takes a "long" time, see flow reactor result – first aldehydes CH$_2$O and C$_2$H$_4$O form, then CO rises as aldehydes decompose

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➤ Constant T (1000˚C) & P (1 atm); 0.1% C$_3$H$_8$ / 1% O$_2$ / 98.9% N$_2$ (equivalence ratio 0.5 but not fuel/air – highly diluted with N$_2$)

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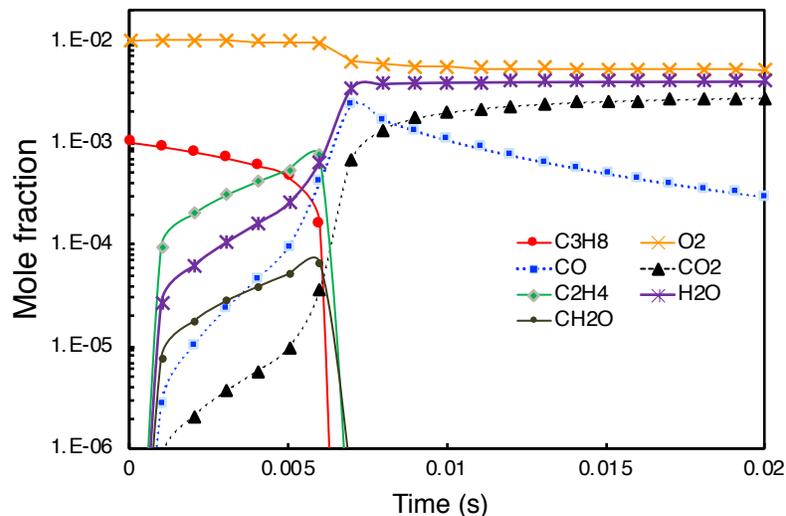
➢ Larger hydrocarbons also have negative temperature coefficient (NTC) behavior at low T (below H + O$_2$ branching)
➢ NTC especially prevalent in rich mixtures – reaction rate decreases with increasing T
➢ R• + O$_2$ → ROO• is very reversible due to weak R-O bond
➢ Equilibrium favors dissociation (ROO• → R• + O$_2$) at higher T, so ROO• won't stick around long enough to make ROOH
➢ At higher temperatures HOO• + RH → R• + HOOH forms peroxides, lessening the need for ROO•
➢ (HOOH reaction has higher E$_a$ than ROO• + RH → R• + ROOH because the former is more exothermic; C-O bond strength 86 vs 111 kcal/mole for H-O, thus HOOH reaction more dominant at higher temperature)
➢ Also forms "cool flames" – exothermic propagating waves that don't consume all reactants because of NTC shut-down – no longer "homogeneous" reaction

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➢ Example of ignition time for "real" fuels at engine-like T & P
  ➢ Low T (1000/T > 1): VERY different ignition delay times (in shock tube experiment) for different fuels, dominated by slow breakdown rate of fuel
    High T: Similar times because H + O$_2$ → OH + O branching rather than fuel molecule breakdown (except for toluene which is hard to "crack")
  ➢ Note ignition time <u>increases</u> with increasing T for 750 < T < 900K (negative effective activation energy!)



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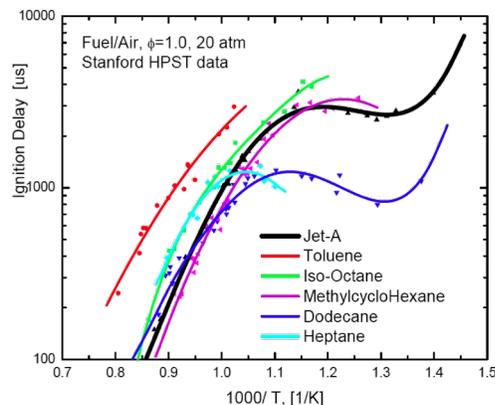
## Chemical fire suppressants (1/2)

➤ Key to suppression is removal of H atoms; most effective element is Br:

$$H + HBr \rightarrow H_2 + Br$$
$$H + Br_2 \rightarrow HBr + Br$$
$$Br + Br + M \rightarrow Br_2 + M$$
--------------------------------
$$H + H \rightarrow H_2$$
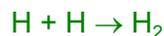
➤ Why Br and not Cl or F?  HCl and HF too stable, 1st reaction too slow

➤ HBr is a corrosive liquid, not convenient - use $CF_3Br$ (Halon 1301) - Br easily removed, remaining $CF_3$ very stable, high $C_P$ to soak up thermal enthalpy

➤ Problem - $CF_3Br$ very powerful ozone depleter - banned!

➤ Alternatives not very good; best ozone-friendly chemical alternative is probably $CF_3CH_2CF_3$ or $CF_3H$

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## Chemical fire suppressants (2/2)

| Agent | Name | Boiling point (K) | % volume required for total fire suppression in air[*] | Relative effectiveness on mass basis | ODF[*,**] | Mass inert / mass propane required for total fire suppression |
|---|---|---|---|---|---|---|
| $CF_3B_r$ | Halon-1301 | 215 | 2.9 | 432.10 | 13 | 2.44 |
| $CF_3CH_2CF_3$ | HFC-236fa | 272 | 5.6 | 851.20 | 0 | 4.89 |
| $CF_3H$ | HFC-23 | 188 | 12.6 | 882.00 | 0 | 5.48 |
| $CF_3CHClF$ | HCFC-124 | 262 | 6.7 | 994.95 | 0.03 | 5.79 |
| $CF_2HCl$ | HCFC-22 | 230 | 11.6 | 1003.40 | 0.055 | 6.16 |
| $CF_3CFH_2$ | HFC-134a | 247 | 10.5 | 1071.00 | 0 | 6.49 |
| $CF_3CFHCF_3$ | HFC-227ea | 293 | 6.3 | 1071.00 | 0 | 6.20 |
| $C_2F_6$ | FC-116 | 195 | 7.8 | 1076.40 | 0 | 6.33 |
| $CF_3CHF_2$ | HFC-125 | 225 | 9.4 | 1128.00 | 0 | 6.76 |
| $C_3F_8$ | FC-218 | 235 | 6.1 | 1146.80 | 0 | 6.63 |
| $C_4F_{10}$ | FC-31-10 | 275 | 5 | 1190.00 | 0 | 6.80 |
| $CF_4$ | FC-14 | 145 | 13.8 | 1214.40 | 0 | 7.64 |
| $CF_3CHCl_2$ | HCFC-123 | 300 | 7.5 | 1237.50 | 0.02 | 7.26 |

[*]Source:  National Research Council, *Fire suppression substitutes and alternatives to Halon for U. S. Navy applications*, National Academy Press, Washington, D. C., 1997.
[**]ODF = Ozone depletion factor relative to $CFCl_2 = 1$

- Given a homogeneous system (T, P, [conc] 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 and Homogeneous Charge Compression Ignition (HCCI) piston engines
- As reaction starts, heat is released, temperature increases, reaction rate $\omega$ increases, heat is released faster, T rises faster, $\omega$ 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-pressure or constant-volume, ideal gas, constant $C_P$ and $C_V$
  - Constant mass

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- Energy equation (constant volume) - if all fuel consumed

$$C_V(T_{ad} - T_\infty) = fQ_R = \left[Y_f(t=0) - Y_f(t=\infty)\right]Q_R \quad (Y_f = \text{fuel mass fraction})$$

So at any instant in time

$$C_V(T(t) - T_\infty) = \left[Y_f(0) - Y_f(t)\right]Q_R$$

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

$$Y_f(t=0) = f = \frac{[fuel]_\infty M_{fuel}}{\rho_\infty} \Rightarrow Y_f(t) = \frac{[fuel](t) M_{fuel}}{\rho_\infty}$$

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

(this simply says that there is a linear relationship between the amount of fuel consumed and the temperature rise) (If constant pressure $C_V \rightarrow C_P$)

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

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

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## Homogeneous reaction (3/5)

- Reaction rate equation (assume n = 0)

$$\frac{d[A]}{dt} = -ZT^n[A]^{\nu_A}[B]^{\nu_B}\exp\left(\frac{-E}{\Re T}\right) \Rightarrow \frac{d[fuel]}{dt} = -Z[fuel](t)[Ox](t)\exp\left(\frac{-E}{\Re T(t)}\right) \text{ (Eq. 3)}$$

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

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

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

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

- Notes on this result
  - $\phi$ is the equivalence ratio for our special case $\nu_A = \nu_B = 1$; only valid for lean mixtures since we assumed surplus of A = fuel
  - Get pressure from P(t) = $\rho_\infty$RT(t); if constant pressure, equation are exactly the same except $T_{ad}$ is the constant-P value

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## Homogeneous reaction (4/5)

- 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 $\varphi$ (stoichiometry), $\beta$ (activation energy), initial temp. ($T_\infty$), H (heat release)
- Initial condition is $\varepsilon$ = 1 at $\tau$ = 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 $T_{ad}$ 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 $T_\infty$ 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 homogeneous reaction are very different

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## *Homogeneous reaction (5/5)*

- Double-click chart to edit or change parameters
- Case shown: $\varphi$ = 0.7, $\beta$ = 10, H = 6
- Note profile and time to "ignite" depend strongly on $\beta$, much less on $\varphi$ and H

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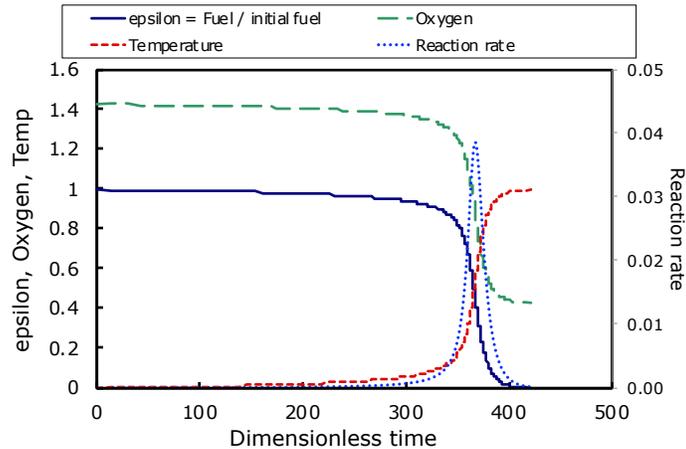
## *Well-stirred reactor (1/5)*

- The homogeneous-reaction example was for time-dependent behavior of a fixed mass with no flow; what about the opposite (steady, fixed volume, with flow in/out)?
- Assume reactants and products are perfectly stirred, *i.e.*, as soon as reactants flow into the reactor, they are completely mixed with products (constant T, P and composition throughout reactor)
- Again will have low fuel + high T or high fuel + low T in reactor
- Energy balance assuming 1 A + 1 B $\rightarrow$ products; ( )$_R$ = in reactor:

$$\left(\text{Mass of A burned per unit time}\right)Q_R = \text{thermal enthalpy rise in reactor} = \dot{m}C_P\left(T_R - T_\infty\right)$$

$$Y_{A,\infty}Q_R = C_P\left(T_{ad} - T_\infty\right) \Rightarrow \left(\text{Mass of A burned per unit time}\right) = \dot{m}Y_{A,\infty}\frac{T_R - T_\infty}{T_{ad} - T_\infty}$$

$$\text{Also, } \frac{\text{mass of A burned}}{\text{time}} = \frac{\text{mass of fuel burned}}{\text{moles of fuel burned}}\frac{\text{moles of fuel burned}}{\text{time} \times \text{volume}}\text{volume}$$

$$= M_A\left.\frac{d[A]}{dt}\right|_R V_R = M_A V_R Z[A]_R[B]_R \exp\left(\frac{-E}{\Re T_R}\right) = \dot{m}Y_{A,\infty}\frac{T_R - T_\infty}{T_{ad} - T_\infty} \quad \text{(Eq. 1)}$$

$$\text{Note } [A]_R = \frac{\text{moles A}}{\text{volume A}} = \frac{\text{moles A}}{\text{mass A}}\frac{\text{mass A}}{\text{total mass}}\frac{\text{total mass}}{\text{volume A}} = \frac{1}{M_A}Y_{A,R}\rho_R; [B]_R = \frac{1}{M_B}Y_{B,R}\rho_R$$

➢ But how to find $Y_{A,R}$ and $Y_{B,R}$? Mass balance on A:

Mass A burned per unit time = (total mass flow)(change in mass fraction A) $= \dot{m}\left(Y_{A,\infty} - Y_{A,R}\right)$

$$Y_{A,\infty} - Y_{A,R} = \frac{C_P\left(T_R - T_\infty\right)}{Q_R} = C_P\left(T_R - T_\infty\right)\frac{Y_{A,\infty}}{C_P\left(T_{ad} - T_\infty\right)} = Y_{A,\infty}\frac{T_R - T_\infty}{T_{ad} - T_\infty} \Rightarrow Y_{A,R} = Y_{A,\infty}\frac{T_{ad} - T_R}{T_{ad} - T_\infty}$$

Then since $\left[A\right]_R = \dfrac{1}{M_A}Y_{A,R}\rho_R$, $\left[A\right]_R = \dfrac{\rho_R Y_{A,\infty}}{M_A}\dfrac{T_{ad} - T_R}{T_{ad} - T_\infty}$ (Eq. 2)

➢ Mass balance on B: since one B molecule is consumed for every A

$$Y_{B,\infty} - Y_{B,R} = \nu\left(Y_{A,\infty} - Y_{A,R}\right); \ \nu = \text{stoichiometric oxygen to fuel mass ratio}; \ Y_{B,\infty} = Y_{A,\infty}\nu / \phi$$

$$\Rightarrow Y_{B,R} = \frac{Y_{A,\infty}\nu}{\phi} - \nu\left(Y_{A,\infty} - Y_{A,R}\right) \Rightarrow Y_{B,R} = \nu\left[\frac{1}{\phi}\frac{C_P\left(T_{ad} - T_\infty\right)}{Q_R} - \frac{C_P\left(T_R - T_\infty\right)}{Q_R}\right]$$

$$\Rightarrow Y_{B,R} = \frac{\nu C_P}{Q_R}\left[\frac{1}{\phi}\left(T_{ad} - T_\infty\right) - \left(T_R - T_\infty\right)\right] = \nu Y_{A,\infty}\left[\frac{1}{\phi} - \frac{T_R - T_\infty}{T_{ad} - T_\infty}\right]$$

Then since $\left[B\right]_R = \dfrac{1}{M_B}Y_{B,R}\rho_R$, $\left[B\right]_R = \dfrac{\rho_R \nu Y_{A,\infty}}{M_B}\left[\dfrac{1}{\phi} - \dfrac{T_R - T_\infty}{T_{ad} - T_\infty}\right]$ (Eq. 3)

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➢ Finally combining Eqs. 1, 2, 3:

$$\dot{m} = \frac{M_A V_R Z}{Y_{A,\infty}}\frac{T_{ad} - T_\infty}{T_R - T_\infty}\left[A\right]_R\left[B\right]_R\exp\left(\frac{-E}{\Re T_R}\right)$$

$$\dot{m} = \frac{M_A V_R Z}{Y_{A,\infty}}\frac{T_{ad} - T_\infty}{T_R - T_\infty}\frac{\rho_R Y_{A,\infty}}{M_A}\frac{T_{ad} - T_R}{T_{ad} - T_\infty}\frac{\rho_R \nu Y_{A,\infty}}{M_B}\left[\frac{1}{\phi} - \frac{T_R - T_\infty}{T_{ad} - T_\infty}\right]\exp\left(\frac{-E}{\Re T_R}\right)$$

$$\dot{m} = \frac{\rho_R^2 V_R \nu Y_{A,\infty} Z}{M_B}\frac{T_{ad} - T_R}{T_R - T_\infty}\left[\frac{1}{\phi} - \frac{T_R - T_\infty}{T_{ad} - T_\infty}\right]\exp\left(\frac{-E}{\Re T_R}\right)$$

$$\dot{m} = \frac{P_R^2 V_R \nu Y_{A,\infty} Z}{R^2 M_B T_{ad}^2}\frac{T_{ad}^2}{T_R^2}\frac{T_{ad} - T_R}{T_R - T_\infty}\left[\frac{1}{\phi} - \frac{T_R - T_\infty}{T_{ad} - T_\infty}\right]\exp\left(\frac{-E}{\Re T_R}\right)$$

$$\boxed{\frac{\dot{m}}{\dot{m}_{ref}} = \frac{1}{\overline{T}_R^2}\frac{1 - \overline{T}_R}{\overline{T}_R - \varepsilon}\left[\frac{1}{\phi} - \frac{\overline{T}_R - \varepsilon}{1 - \varepsilon}\right]\exp\left(\frac{-\beta}{\overline{T}_R}\right);} \quad \dot{m}_{ref} \equiv \frac{P_R^2 V_R \nu Y_{A,\infty} Z}{R^2 M_B T_{ad}^2}; \overline{T}_R \equiv \frac{T_R}{T_{ad}}; \varepsilon \equiv \frac{T_\infty}{T_{ad}}; \beta \equiv \frac{E}{\Re T_{ad}}$$

➢ Equation for reactor temperature $T_R$ as a function mass flow rate for varying values of the properties: reference mass flow, enthalpy release parameter ($\varepsilon$) and dimensionless activation energy ($\beta$)

## Well-stirred reactor (4/5)

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- Very low flow – plenty of time, nearly complete reaction, $T_R \approx T_{ad}$
- Very high flow – not enough time, very little reaction, $T_R \approx T_\infty$
- Results show classical Z-shaped response with hysteresis for small $\varepsilon$
  - Upper – "extinction" branch – when mass flow increased too much, reactor "extinguishes" due to insufficient residence time – $T_R$ drops to lowest branch
  - Lower – "ignition" branch – when mass flow decreased enough, reactor "ignites" due to adequate residence time, $T_R$ rises to highest branch
  - $\varepsilon$ close to 1: exothermicity not significant, monotonic behavior (better approach for chemical kinetic studies - less effect of temperature fluctuations due to imperfect mixing on apparent overall reaction rates)



$\beta = 5, \; \phi = 1$

e = 0.2
e = 0.43
e = 0.8

Reactor Temperature TR

mdot/mdot_ref

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## Well-stirred reactor (5/5)

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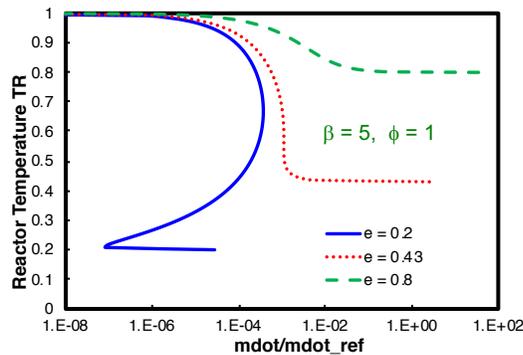
- Middle branch generally unstable
  - Small increase in mass flow for momentarily fixed $T_R$ (thus reaction rate) will increase reactant leakage, thus decrease T, moving reaction rate still lower, eventually dropping to lower branch
  - Opposite for small decrease in mass flow (jump to upper branch)
  - Upper and lower branches stable – e.g. increase in mass flow decreases $T_R$ and takes you back to same branch
- Results very sensitive to $\beta$
  - As $\beta$ increases, extinction point rises to higher T, i.e. closer to $T_{ad}$
  - At realistic values of $\beta$, curve spans many decades of mass flow – never looks like textbook plots
  - $\beta = 5$ plotted – not realistic, 10 or more for hydrocarbon oxidation
- Weaker effects of $\varepsilon$ and $\phi$
- Who cares about this? Can use this apparatus to study kinetics and obtain estimates of reaction rate parameters Z and E by measuring mass flow at extinction and/or intermediate & product concentration vs mass flow

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## Summary (1/2)

➢ Chemical reactions require collisions; collision rates determined by kinetic theory of gases

➢ Chemical kinetic systems for realistic fuels are comprised of many individual reactions, resulting in coupled Ordinary Differential Equations in terms of the concentrations of reactants [A], [B], [C], [D], … of the form (for A + B → C + D)

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

➢ Reaction rate $k_f$ requires adequate kinetic energy (exp(-$E_a$/$\mathcal{R}$T) term) and steric (luck) factor, resulting in $k_f = ZT^n\exp(-E_a/\mathcal{R}T)$ expression with 3 adjustable parameters Z, n, $E_a$

➢ Analytical solution of these equations is possible only for simplest cases

➢ Techniques exist for simplifying these large sets of equations
  ➢ Steady-state (for one species)
  ➢ Partial equilibrium (for one reversible reaction)
  ➢ Many others…

➢ Simplifying methods exploit the fact that some reactions (e.g. radical + stable species) are typically faster than others (e.g. chain initiation, 3-body recombination, radical + radical) and so adjust to changing concentrations on a shorter time scale

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## Summary (2/2)

➢ Real fuels have very complex chemistry, not just 1 or 2 steps
➢ Need chain branching for fast reaction
➢ Hydrogen oxidation
  ➢ Initiation – $H_2 + M \rightarrow H + H + M$, $RH + M \rightarrow R + H + M$
  ➢ Branching
    » Typically $H + O_2 \rightarrow OH + O$ at high T / low P
    » Peroxide path (with HOOH or ROOH) at low T / high P where H atoms are lost due to recombination
  ➢ Recombination - $H + O_2 + M \rightarrow HO_2 + M$
  ➢ Radical termination at walls in explosion vessel
➢ CO oxidation
  ➢ Requires $CO + OH \rightarrow CO_2 + H$
  ➢ Parasitic on $H_2 – O_2$ mechanism since CO + OH relatively slow
➢ Hydrocarbons
  ➢ Inhibit their own oxidation due to $RH + H \rightarrow R + H_2$
  ➢ Decomposition rate depends on C-H bond strength
  ➢ First fuel decomposes, generates radical pool, generates CO then oxidizes it
➢ Much information can be deduced from well-characterized experiments (e.g. constant P, T vessel)
➢ Reaction rates + thermodynamics can be used to describe model systems, e.g. (time-dependent) homogeneous reaction or (steady-state) Well-Stirred Reactor

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