Combustion Chemistry

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2014 Princeton-CEFRC Summer School on Combustion

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- Hai Wang, Stanford University
- Tim Wallington, Ford Motor Company
- Charlie Westbrook (formerly of LLNL)
- Stephen J. Klippenstein (Argonne)

…and many of my hard-working students and postdocs from MIT

Overview

Part 1:	Big picture & Motivation

Part 2:	Intro to Kinetics, Combustion Chem

Part 3:	Thermochemistry

Part 4:	Kinetics & Mechanism

Part 5:	Computational Kinetics

Be Prepared: There will be some Quizzes and Homework

# Part 1: The Big Picture on Fuels and Combustion Chemistry

What is a Fuel?

- Fuel is a material that carries energy in chemical form.
- When the fuel is reacted (e.g. through combustion), most of the energy is released as heat
  - Though sometimes e.g. in fuel cells or flow batteries it can be released as electric power
- Fuels have much higher energy densities than other ways of carrying energy. Very convenient for transportation.
- The energy is released via chemical reactions. Each fuel undergoes different reactions, with different rates. Chemical details matter.

Transportation Fuel: Big Issues

- ## People want, economy depends on transportation
  - Cars (growing rapidly in Asia)
  - Trucks (critical for economy everywhere)
  - Airplanes (growing rapidly everywhere)
  - Demand for Fuel is "Inelastic": once they have invested in a vehicle, people will pay to fuel it even if price is high

- ## Liquid Fuels are Best
  - Liquids Flow (solids are hard to handle!)
  - High volumetric and mass energy density
  - Easy to store, distribute.
  - **Huge volume of liquid fuel is being used now: ~80 Mbpd**
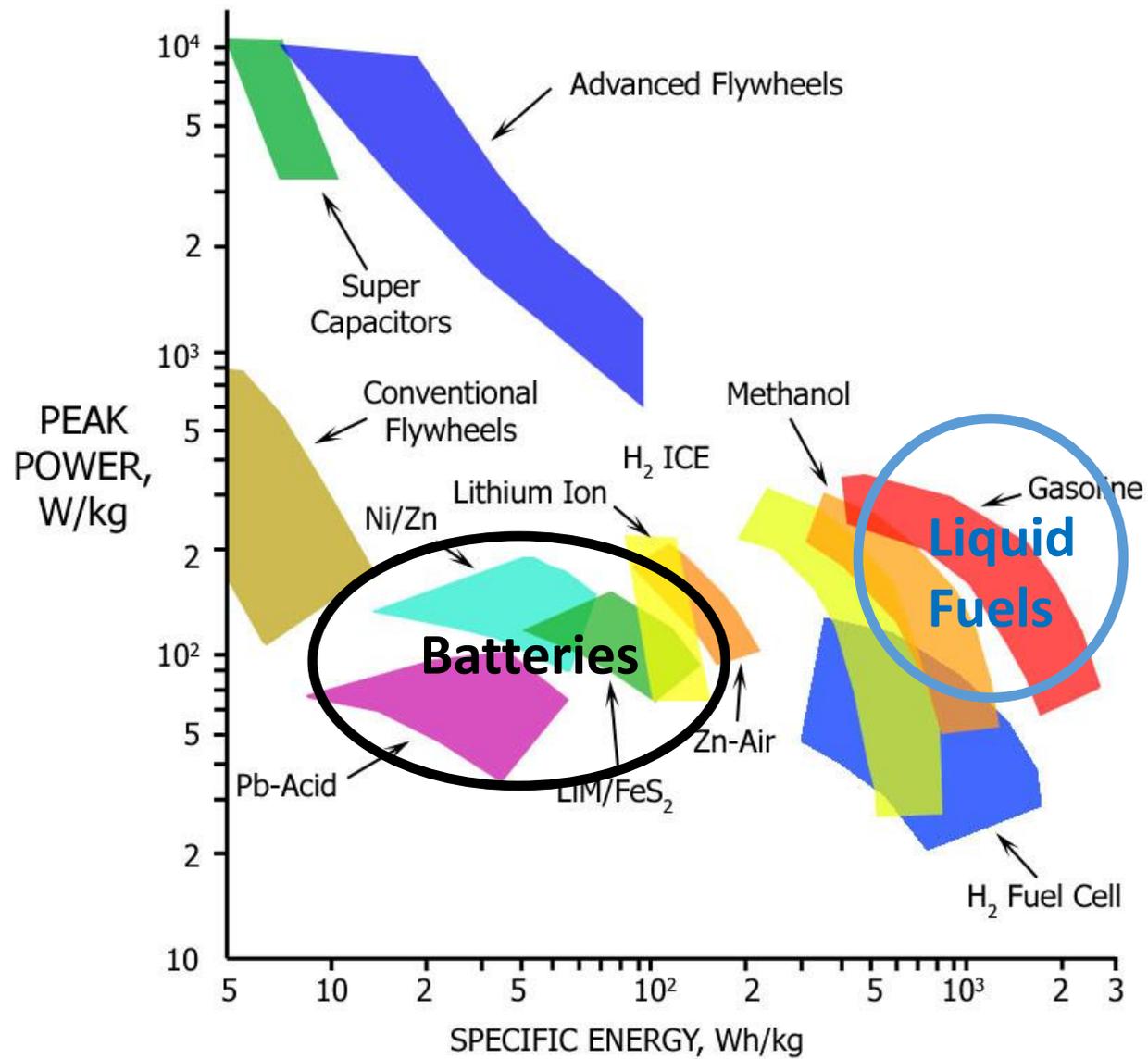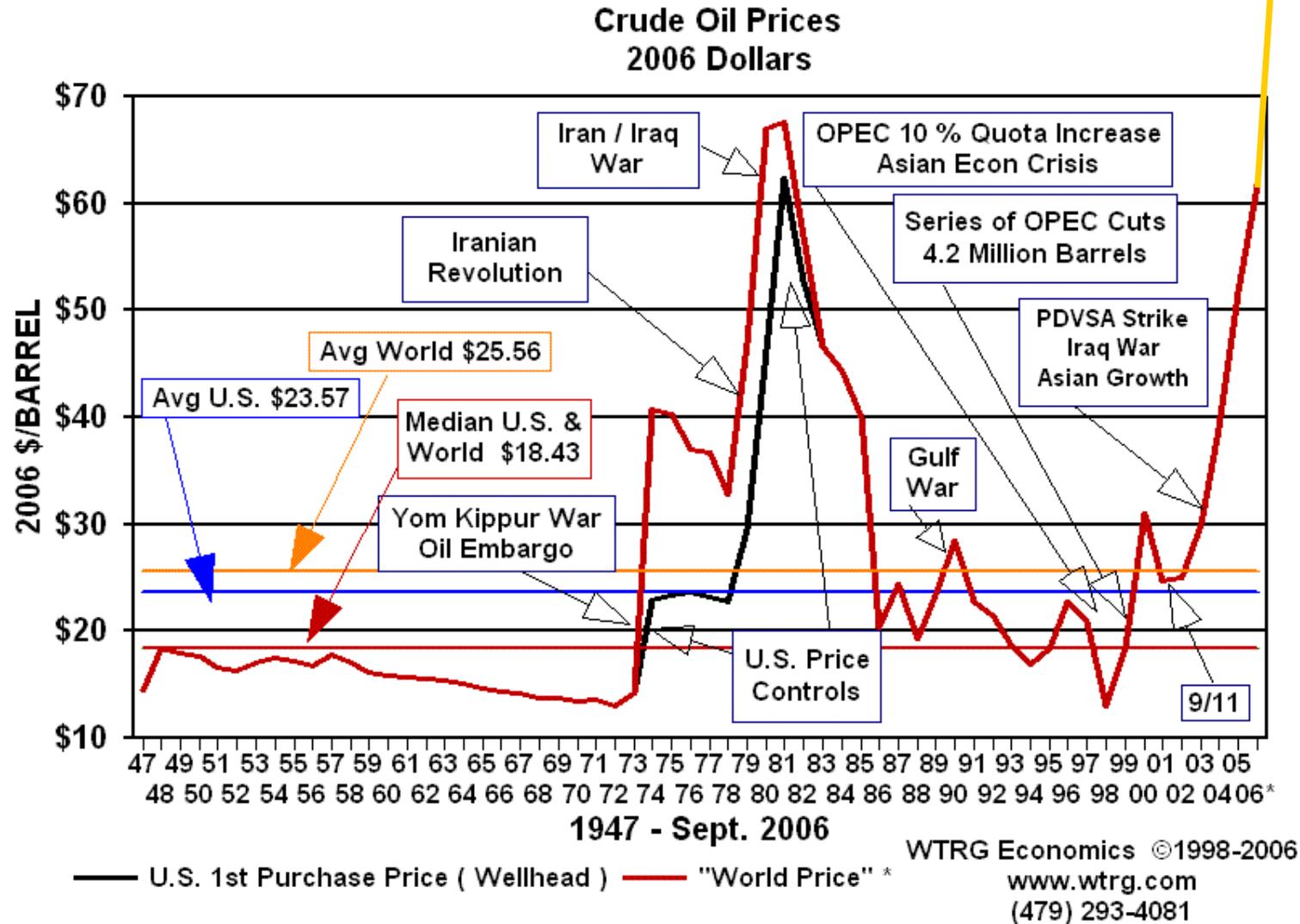
Energy Density Matters!

Downsides of Liquid Fuels

- Liquid Fuels are Expensive
  - 3-10x more $/Joule than coal and natural gas
  - The Big Money in Energy is in liquid fuels & vehicles
  - Trillion $/yr balance-of-payments flows
    - ~ $2000/yr/person in USA (~5% of total income)
    - Prices are very high compared to incomes in poor countries
- Energy Security: oil located far from populations
  - Several Blockades, Embargoes in last 100 years
- Big part of greenhouse gas problem (~30%)
  - Also major contributor to Urban air pollution
- Important...so Government is heavily involved
  - Must consider political and behavioral as well as technological and economic issues

Quiz Question #1

Diesel engines are significantly more efficient than Otto cycle (SI) engines, but also more expensive to manufacture. Why does it make sense for Europeans to use diesel cars, but the case for diesels is not so compelling to Americans?

Price Matters! Almost *impossible* to predict.
Fuel taxes, subsidies & regulations even worse.

**Crude Oil Prices
2006 Dollars**

1947 - Sept. 2006

WTRG Economics ©1998-2006
www.wtrg.com
(479) 293-4081

Quiz Question #2

- Fuel Price started rising dramatically ~2000, and has remained very high ever since (except for a brief drop during the economic crash of 2008). In part because of the high price, gasoline consumption has been dropping in USA and Western Europe. The oil price has been much higher than the cost of producing oil through this whole period.

Why do you think the price rose and is staying high during this time period even though world oil production is increasing?

Fuel Price Fluctuations are a Big Problem

- Very high fuel prices help drive the world economy into recession (1974, 1980, 2008)

- Adds Large Risk to Alternative Fuel projects
  - Many dramatic business failures in late 1980's
  - Price fluctuation often larger than technological & political uncertainties, biggest investment risk
  - Possibility that OPEC will intentionally drop oil price to drive competitors into bankruptcy.
  - Investors demand high rate of return because of risk; less lucrative processes are never built.

Why & Why Not use Fossil Fuels?

- **Finite but Very Large Amount of Fossil Fuel**
  - We are definitely going to run out of fossil fuel energy… in a century or two: *Long Term issue*
  - Fossil fuels are available now in huge scale

    (unlike most other energy sources)

  - Although oil price is high at the moment, cost of production is low. (Coal price is low everywhere. Natural Gas prices varies.)

- **Greenhouse Effect on Climate Change is the *Medium-Term issue***

  - **We'll "run out of atmosphere" to hold the CO_2 before we run out of fossil fuel.**

  - Might run out of capacity to store CO_2 underground or in ocean…

Conventional Oil is
      Expensive (at the moment)
      (Maybe) Running Out
      Not Secure
      A Greenhouse Gas Problem

So we might want to use alternative
  fuels...with different combustion
  chemistry

Quiz Question #2

- Shell has invested in Gas-to-Liquids to make liquid diesel fuel in Qatar. US truck companies are investing to develop trucks that burn Compressed Natural Gas. Can they both be right?

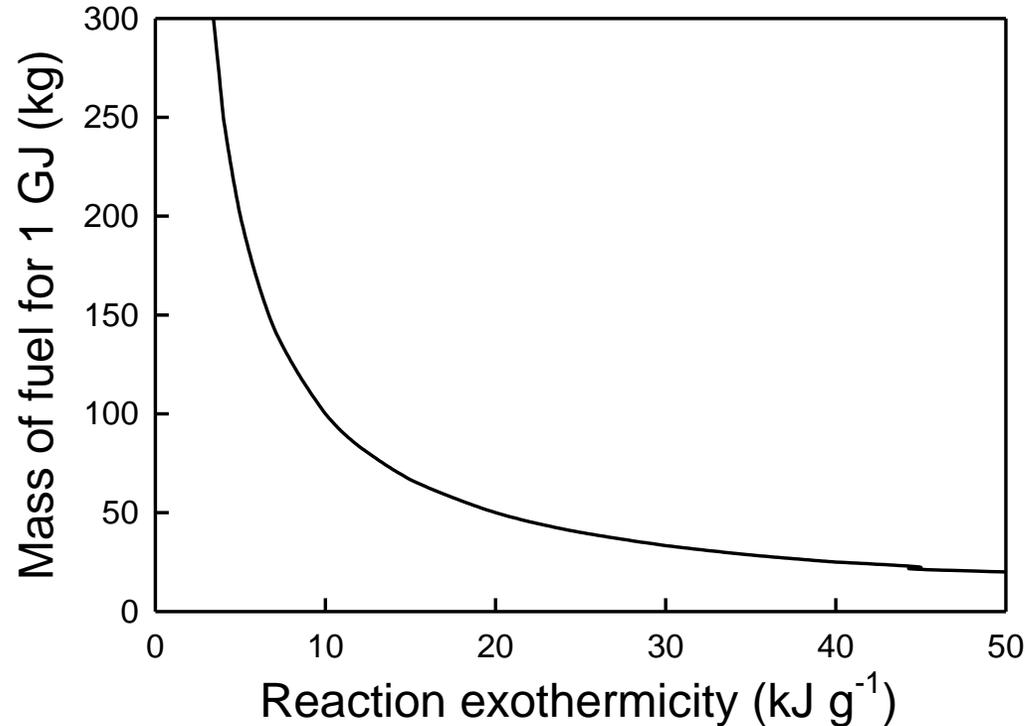# What do you want in a fuel?

And what constraints does any new fuel need to satisfy?

What properties do we desire in a fuel?

- **Prefer not to carry more than one reactant on vehicle; take second reactant from the atmosphere.**
  - Air is 78% N_2, 21% O_2, 1% Ar. N_2 is poor reactant (N≡N bond too strong), Ar is unreactive, leaves O_2.
- **Fuel should have highly exothermic reaction with O_2**
- **Fuel should be abundant in nature or easy to make. And cheap.**
  - We need need millions of tons every day.
- **Fuel itself should be environmentally benign and renewable**
- **Prefer to dump exhaust so we don't have to carry its weight. Exhaust should be environmentally benign (even if we carry it: we are making Mtons/day!)**
- **Both fuel & exhaust must be liquids or gases: no solids handling!**

Thanks to Tim Wallington.

Periodic Table

What Gravimetric Energy Density do we need?

* 10-20 gallons of gasoline weighs approximately 30-60 kg, and releases approximately 45 kJ/g.

Need to carry about 1-2 GJ (equivalent to approx.10-20 gallons of gasoline*) to match functionality of current vehicles. Impractical to carry > 100 kg fuel. Hence, fuel needs to release > 10 kJ/g

Highly endothermic compounds tend to be unstable, so below we equate maximum exothermicity of oxidation of compounds with exothermicity of oxidation of their constituent elements.
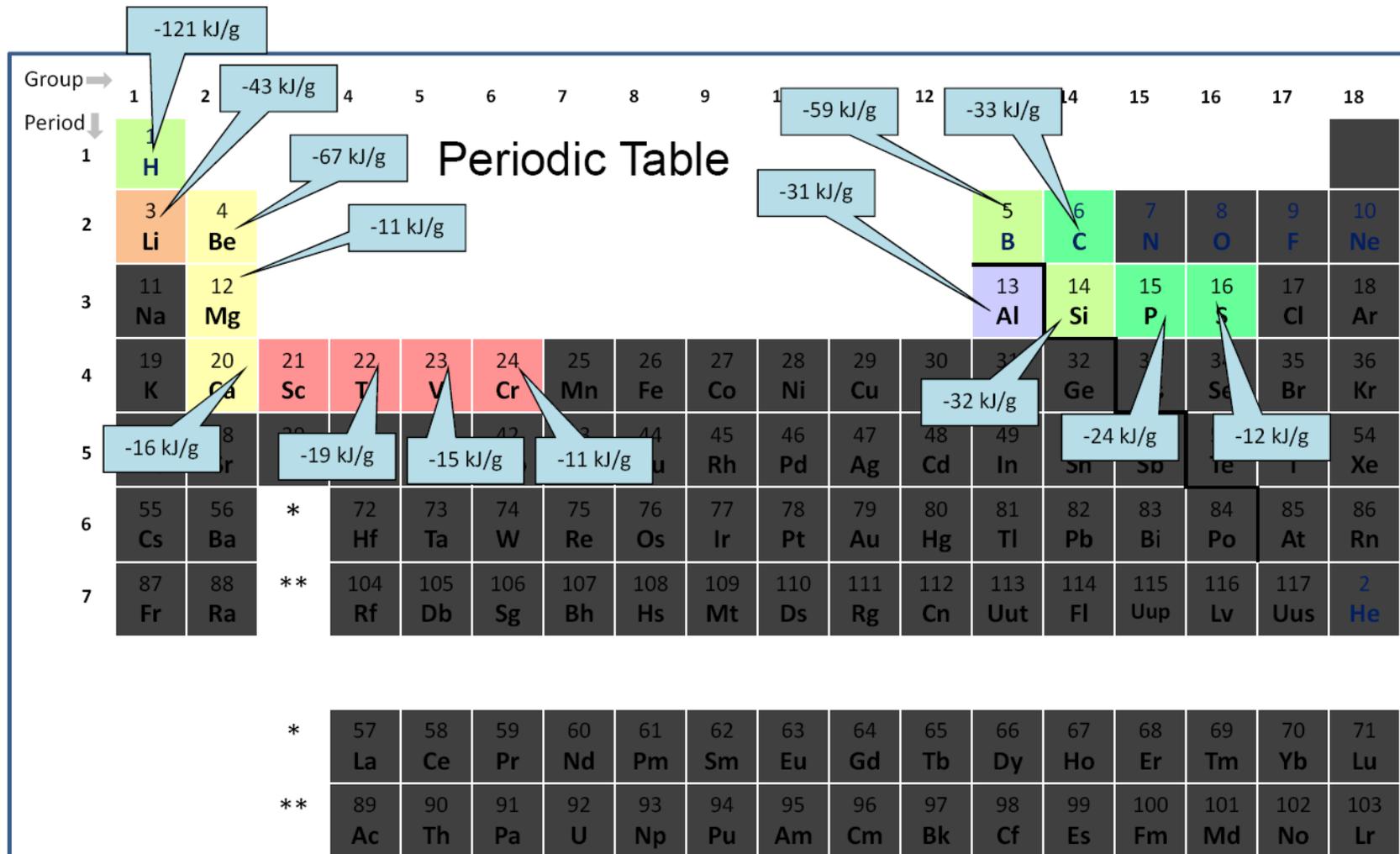
Periodic Table

Elements with enthalpy of oxidation > 10 kJ g^{-1}

Periodic Table

Elements whose oxides are not solids.

Hydrogen and Carbon are Unique

Elements with enthalpy of oxidation > 10 kJ g^{-1} and non- solid (or non-toxic) oxides.

Nitrogen may also be viable since NOx can be converted to harmless N2. O can be included in fuel, but it reduces energy density.

Oxygen and Nitrogen

Not desirable from a gravimetric and volumetric energy density standpoint, but…

Oxygenated fuels tend to have lower emissions of carbon monoxide, soot, and unburned hydrocarbons.

N containing fuels have higher NOx emissions, but can reduce to N_2 with catalyst and CO or urea. A little bit of N is good for cleaning fuel injectors.

Hydrogen bonding in liquid fuels containing O and N results in enhanced evaporative cooling
> \+ decreases the likelihood of autoignition; increases fuel octane
> \+ increases amount of air in cylinder, and so power density

Biomass feedstocks (and some fossil fuels) contain a lot of O (glucose = $C_6H_{12}O_6$, cellulose = glucose polymer = $(C_6H_{10}O_5)_n$). Also some N. Perhaps it is not necessary to remove all the O and N from biofuels?

Hydrogen, Carbon, and Oxygen

Successful alternative fuels will be compounds containing H, C, and possibly O. (Maybe also some N.)

Elaborating on requirements

- Liquid with reasonably high energy density
  - Must remain liquid to -20 C, maybe lower
    - Serious safety issue in aircraft, cold countries
  - Want energy density > 8 MJ/liter
    - Comparable to or better than CNG
- Only contains C,H,O, maybe N
  - So it burns to CO_2 + H_2O. Other elements burn to harmful products.
  - Some N will burn to NO_x, but maybe catalyst can convert NO_x to N_2.

Requirements, Continued

- Not Corrosive
  - "Corrosive" depends on materials used in engine
  - "Backwards Compatible": want new fuel to work in old vehicles
  - Known issues with acids (in biofuels), high concentrations of alcohols
- Suitable Volatility
  - Must match fuel injection system
  - Want liquid to quickly evaporate to flammable gas.
  - Some molecules (e.g. sugars) pyrolyze to solids before they evaporate – <u>not</u> good transportation fuels.

Ignition Delay Suitable for Engine Cycle

- Ignition Delay Fundamentals:
  - Hot fuel+air mixtures spontaneously ignite after a delay.
  - Ignition Delay is *very sensitive* to fuel structure
  - Ignition delay also sensitive to T, P, stoichiometry
  - Measured as "octane" or "cetane"
- Different Engines require different delays
  - Diesels require spontaneous ignition (short delay)
    - Short delay also beneficial for turbines.
  - Spark Ignited engines do not want spontaneous ignition called "knock": (want long ignition delays)
  - Not yet clear what is best for HCCI / Low-T combustion engines
    - Rely on spontaneous ignition, but don't want all fuel to ignite simultaneously.
    - Rolf Reitz's engine wants 2 fuels with very different ignition delays.

In Engine-Relevant Range, Ignition Delay Sensitive to T, P, [O_2], Molecular structure

3.38% n-butanol, P = 15 bar
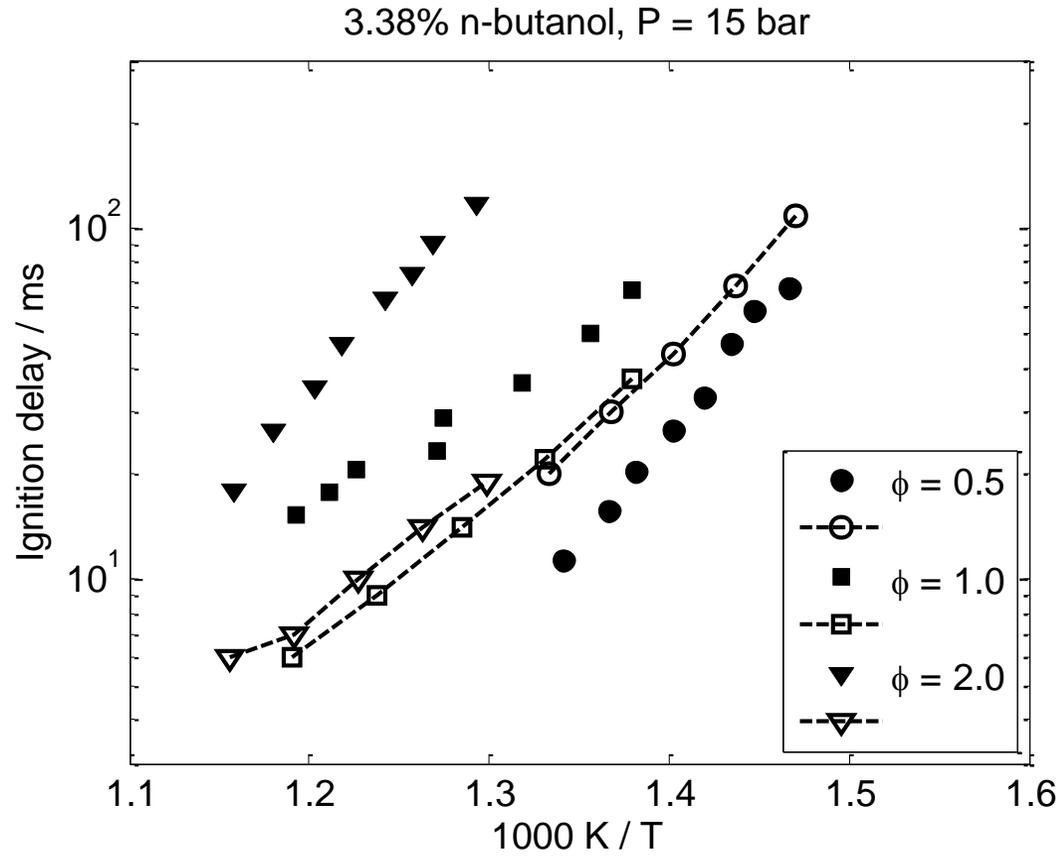
10% change in T:
Order of magnitude in τ

Factor of 3 change in [O2]:
Order of magnitude in τ

n-butanol to iso-butanol:
86 to 98 octane

Sufficient Flame Speed

- Sensitive to T, P, stoichiometry, dilution
- Many fuels have very similar flame speeds
  - H_2, acetylene have unusually high flame speeds
- Flame speed very important in turbines running near lean limit, or in high speed flows
  - Flame can "blow out"
- Helpful in Spark-Ignited Engines

New Fuel Must be Cheap, Plentiful!

- New Fuel will be competing with petroleum.
  - Subsidies or regulations favoring new fuel will not last forever!
- It takes work to verify new fuel will not cause problems.
- It takes capital to build fuel production facilities.
- **This work will not be done, and investors will not provide the capital, unless fuel looks economically viable and likely to be available in huge volumes (~ million barrels per day).**

Summary: What do you want in a fuel?

- **Reasonably high energy density**
- **Only contains C,H,O, maybe N.**
  - **So will burn to non-polluting products.**
- **Not Corrosive to Tanks. Not too horrible if it spills.**
- **Suitable Volatility for fuel injection system.**
- **Ignition delay correct for engine cycle.**
- **Flame speed fast enough for engine.**
- **Cheap! Plentiful! Will be competing with fossil fuels.**

Usually less important but still significant:

- **Solubility/Phase behavior**
- **Consistency from batch-to-batch of fuel.**
- **Environmental impacts**
- **Safety issues in handling/storing**
- **Stable in Storage**
- **Right Viscosity**

Combustion Chemistry Basics

- Combustion involves the oxidation of a fuel, ideally leading, for an organic fuel such as octane or ethanol, to the formation of carbon dioxide and water, with the release of heat.

- The overall chemical equation, e.g.

$$C_2H_5OH + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$$

does not describe the way in which the reaction occurs.

- Instead the reaction involves a sequence of <u>elementary</u>, or single step reactions, many of which involve <u>atoms</u> or <u>radicals,</u> which are short-lived species with high reaction rates.

An example – $H_2 + O_2$

The overall reaction is: $2H_2 + O_2 \rightarrow 2H_2O$

Some important component elementary reactions:

1. $H_2 + O_2 \rightarrow \quad H + HO_2$
2. $H + O_2 \rightarrow \quad OH + O$
3. $O + H_2 \rightarrow \quad OH + H$
4. $OH + H_2 \rightarrow \quad H + H_2O$
5. $H + O_2 + M \rightarrow \quad HO_2 + M$
6. $H, O, OH \qquad \rightarrow \qquad$ wall
7. $HO_2 + HO_2 \rightarrow \quad H_2O_2 + O_2$
8. $H_2O_2 + M \qquad \rightarrow \qquad OH + OH + M$
9. $OH + H_2O_2 \rightarrow \quad HO_2 + H_2O$
10. $O + H_2O_2 \rightarrow \quad OH + HO_2$

Best current models for H_2/O_2 include about 20 elementary reactions.

Overall kinetics are definitely NOT single-step Arrhenius!

Rates of elementary reactions

- The rate of each elementary reaction is determined by the reactant concentrations and the underline rate coefficient, k. k depends on T and, in some cases p.

  We also need to know the products of the reaction, which in some cases isn't clear.

- Example: reaction 2: H + O_2 →   OH + O; k_2

$$\text{Rate of this forward reaction} = r_{2,\text{forward}} = k_2[H][O_2]$$

- k_2 depends on temperature and this is usually expressed in Arrhenius form:

$$k_2 = A\exp(-E_a/RT)$$

or modified Arrhenius form:

$$k_2 = AT^n\exp(-E_a/RT)$$

A is the A factor, E_a the activation energy, n the temperature exponent and R the gas constant. k can also depend on P.

- One aim of experimental and theoretical studies of elementary reactions is to determine A, E_a, n

- Definitions: order of reaction; units of rate coefficients

Some Definitions and Cautions

- The net rate of change of the local concentration of a species "i" depends on chemical reactions and on transport of the species (e.g. diffusion). We usually write this as a differential equation

$$dc_i/dt = \text{reactions} + \text{diffusion} + \ldots$$

- The net rate of change of a species due to chemical reactions is usually called ω_i by people simulating combustion. Usually each species is involved in several reactions, each with its own net rate r_n with a stoichiometric coefficient ν_{in} .

$$\omega_i = \Sigma \; \nu_{in} \; r_n$$

- Note the equation above is algebraic not a differential equation. Please do not write $dc_i/dt = \Sigma \; \nu_{in} \; r_n$, that is only true for a very special case (perfectly homogeneous, closed system, constant volume). Most combustion systems are inhomogeneous and either open or have time-varying volumes.

- All reactions are reversible, so

$$r_n = (\text{forward rate})_n - (\text{reverse rate})_n$$

The quantity k(T) is called a "rate coefficient", not a "rate" or a "rate constant" (since obviously it is not constant, it depends on T). k(T) is however a "physical constant" in the sense that anyone anywhere measuring the rate coefficient for a certain reaction will always get the same number. Also one can compute k(T) from first principles.

Most combustion systems are extremely inhomogeneous. Often chemistry and transport/mixing are comparably important.
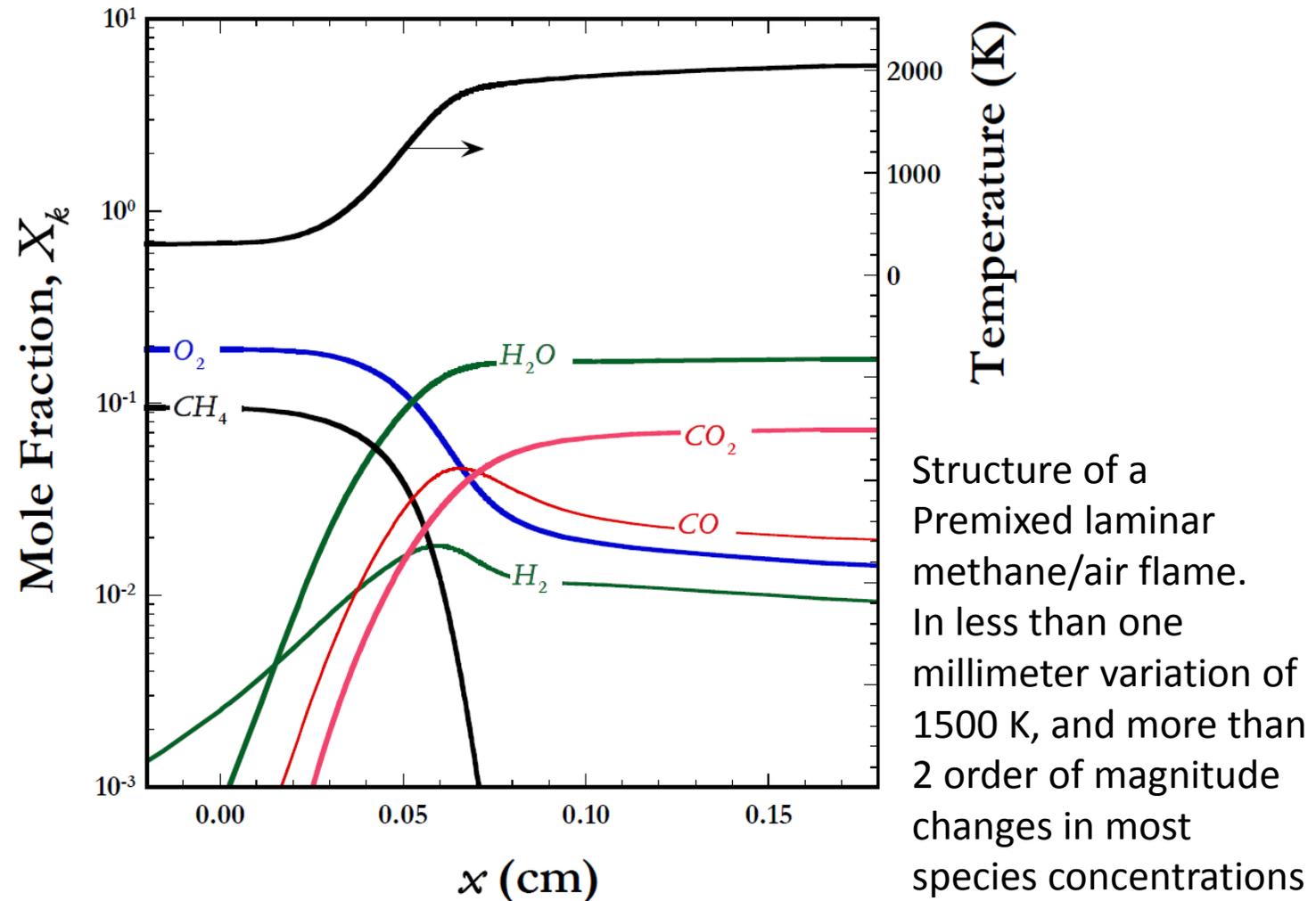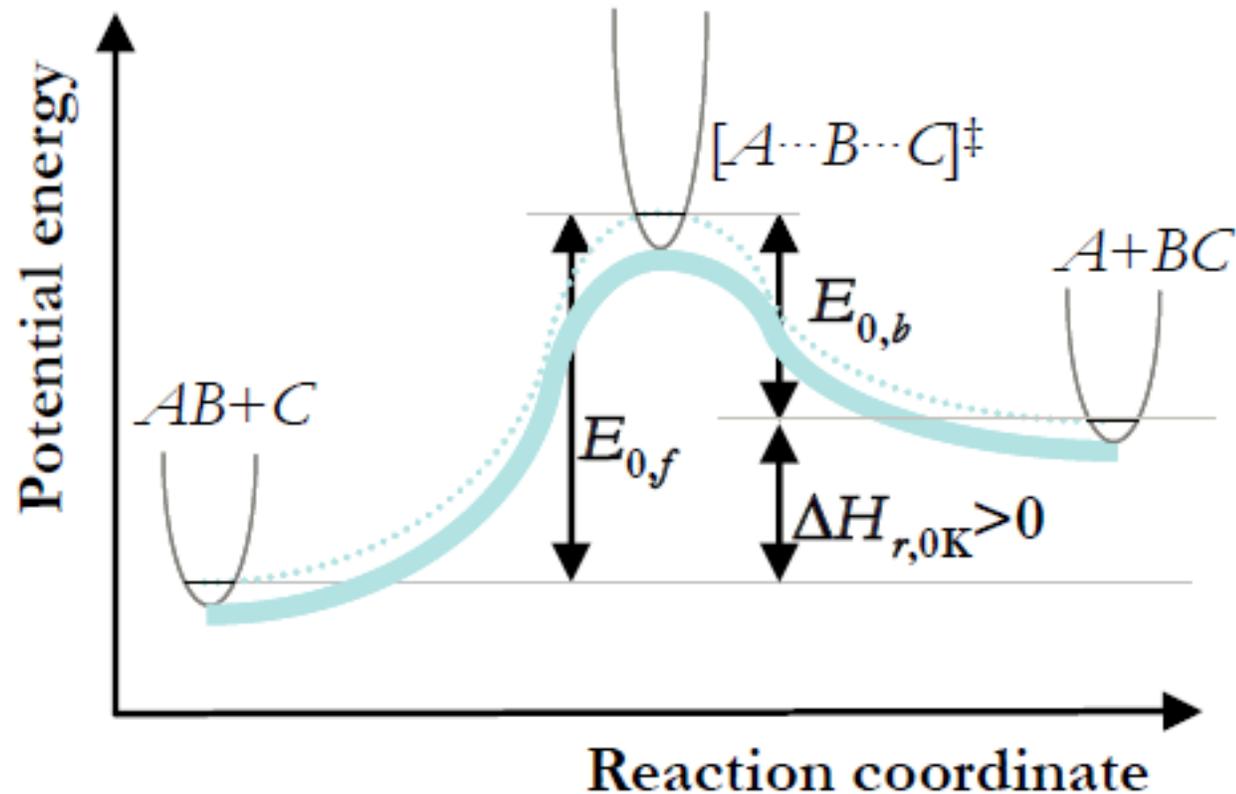

Structure of a Premixed laminar methane/air flame. In less than one millimeter variation of 1500 K, and more than 2 order of magnitude changes in most species concentrations

Figure 7.13. Flame structure of a stoichiometric methane-air flame at the ambient pressure, computed using the GRI-Mech.

Typical Reaction over a Barrier

Parabolas represent potential energy in modes orthogonal to the reaction coordinate. The width of the mountain pass at the top of the barrier affects the rate. The zero-point-energy in the vibrations changes the effective barrier

Arrhenius Dependence on T comes from Boltzmann population. Only molecules / collisions with energy above the reaction barrier can react.
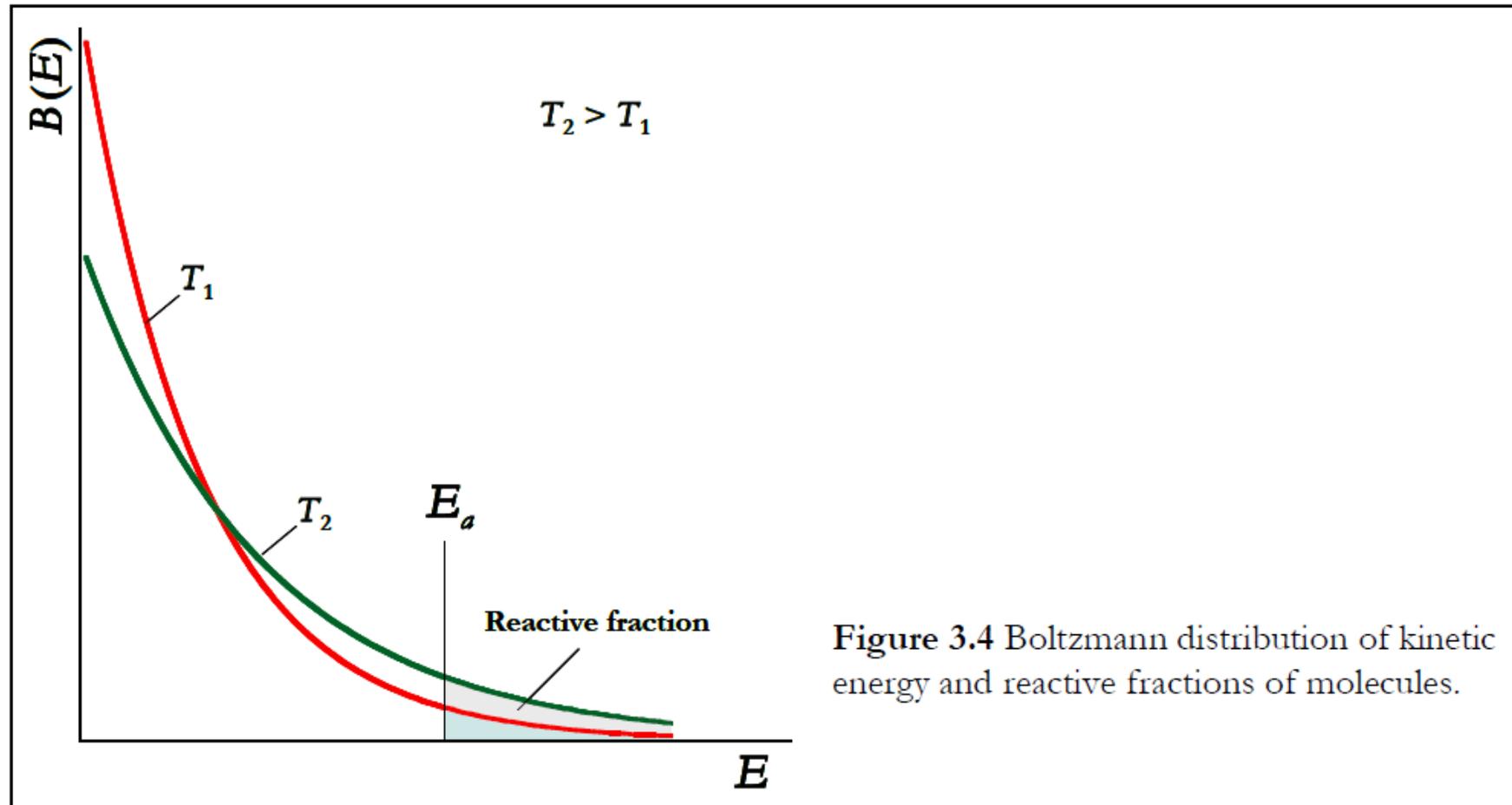Their population grows as $\exp(-Ea/k_B T)$

Figure 3.4 Boltzmann distribution of kinetic energy and reactive fractions of molecules.

Constructing coupled differential (rate) equations from chemical mechanisms

1. $H_2 + O_2 \rightarrow H + HO_2$

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

3. $O + H_2 \rightarrow OH + H$

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

5. $H + O_2 + M \rightarrow HO_2 + M$

6. $H, O, OH \rightarrow$ wall

7. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

The chemical mechanism is set up together with the associated rate coefficients

The coupled rate equations are then written down for each species

d[X]/dt = Total rate of forming X -Total rate of removing X:

$$\frac{d[H]}{dt} = k_1[H_2][O_2] - k_2[H][O_2] + k_3[O][H_2] + k_4[OH][H_2]$$
$$- k_5[H][O_2][M] - k_6[H]$$

$$\frac{d[O]}{dt} = k_2[H][O_2] - k_3[O][H_2] - k_6[O]$$

etc ......
Solve the set of coupled differential equations numerically, subject to initial conditions.

Stiff Differential Equations

- Huge range of timescales in combustion kinetics.
  - Major species' concentrations might change on a timescale of seconds
  - Reactive intermediates like OH typically have lifetimes measured in nanoseconds. Sometimes picoseconds.
  - Nine orders of magnitude between smallest Δt and overall reaction time!
- The system of differential equations describing chemical kinetics is usually "stiff".
- Normal explicit ODE solvers like Runge-Kutta usually fail. Need to use specialized implicit solvers e.g. DASPK, SunDials, VODE.

The high-rate bimolecular reactions in combustion: one reactive radical + one stable molecule

Reaction type	Concentrations		Rate	Rate
	Reactant 1	Reactant 2	Coefficient	
Molecule + molecule	*large*	*large*	*very small*	*small*
Molecule + radical	*large*	*small*	*intermediate*	*large*
Radical + radical	*small*	*small*	*large*	*small*

The radical and the stable are consumed at the same rate in these reactions,
but the effects are very different. Only a small fraction of the stable molecule
is consumed, because its concentration is so large.

$$\tau = [\text{Concentration}]/(\text{Consumption Rate})$$

So lifetime of the stable can be very long, while a radical's average lifetime is tiny

The quasi steady state approximation, QSSA

- The QSSA is sometimes used to simplify kinetic problems and to reduce stiffness of the ODE system

- Consider the scheme:

  A → B → C, with rate coefficients k_1 and k_2

  Set up the rate equations, with a = [A], etc.

  $$\frac{da}{dt} = -k_1 a; \frac{db}{dt} = k_1 a - k_2 b$$

  $$a = a_0 \exp(-k_1 t)$$

  $$b = \frac{a_0 k_1}{(k_2 - k_1)} \{\exp(-k_1 t) - \exp(-k_2 t)\}$$

  $$c = a_0 - a - b$$

QSSA continued

Figure (a): $k_1 > k_2$ $\quad b = \dfrac{a_0 k_1}{(k_1 - k_2)} \{\exp(-k_2 t) - \exp(-k_1 t)\}$

(a)

(b)

For $\quad \underset{\text{reactant}}{A} \xrightarrow{k_1} \underset{\text{intermediate}}{B} \xrightarrow{k_2} \underset{\text{product}}{C}$
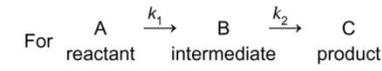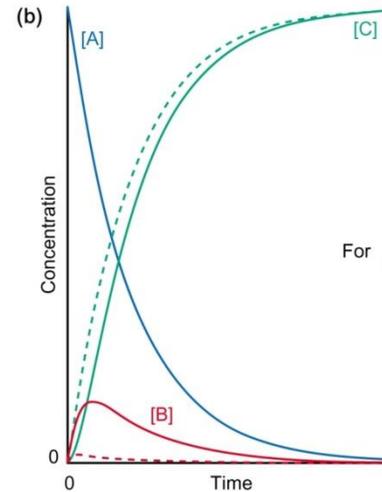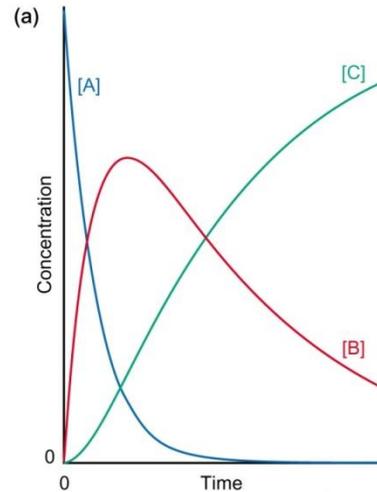
Figure (b): full, $k_2 = 5k_1$
dashed, $k_2 = 50k_1$

Figure (b): $k_1 < k_2$ $\quad b = \dfrac{a_0 k_1}{(k_2 - k_1)} \{\exp(-k_1 t) - \exp(-k_2 t)\}$

For $k_1 \ll k_2$ and for times long compared with $(k_2)^{-1}$

$$b = \frac{a_0 k_1}{(k_2 - k_1)} \{\exp(-k_1 t)\} \approx \frac{a_0 k_1}{k_2} \{\exp(-k_1 t)\} = \frac{a k_1}{k_2}$$

$$\therefore b \ll a \text{ and } \frac{db}{dt} \ll \frac{da}{dt}$$

- QSSA: $db/dt \approx 0$: rate of forming of B $\approx$ rate of removing B

Use of QSSA

- Before ~1980 it was impossible to solve stiff systems of ODEs, so everyone used QSSA

- With the very good modern stiff ODE solvers, one can solve almost all systems of ODE numerically without the need of making approximations like QSSA

- Sometimes QSSA is helpful for understanding
  - provides analytical expressions.

- Note that QSSA replaces the ODE db/dt = f(a,b,c) with the algebraic equation 0 = f(a,b,c). For numerical solution, the db/dt form is often more convenient as well as being more accurate
  - otherwise one may need to use a DAE solver.

Thermodynamic relations (more detail later)

At constant *T, t*he Gibbs energy, *G* is given by:

$$\Delta G = \Delta H - T\Delta S$$

and the equilibrium constant is related to ΔG at standard state by:

$$RT \ln K = - \Delta G^o$$

The equilibrium constant, *K*, can be calculated from tabulated values of the enthalpy *H* and entropy *S*, and hence the reverse rate coefficient (say) determined from the forward rate coefficient and *K*.

Relationship between forward and reverse rate coefficients

$$K = \frac{\prod_{products}(a_i^{\nu_i})}{\prod_{reactants}(a_i^{\nu_i})}$$

a is the *activity*. For ideal systems, $a = p/p^{\ominus} = c/c^{\ominus}$

so that K is dimensionless. Other definitions of equilibrium constants are:

$$K_c = \frac{\prod_{products}(c_i^{\nu_i})}{\prod_{reactants}(c_i^{\nu_i})} \qquad K_p = \frac{\prod_{products}(p_i^{\nu_i})}{\prod_{reactants}(p_i^{\nu_i})}$$

Kc and Kp have dimensions if $(\Sigma\nu_i)_{reactants} \neq (\Sigma\nu_{i)products}$

At equilibrium, forward rate = reverse rate:

$$k_f \prod_{products}(c_i^{\nu_i}) = k_r \prod_{reactants}(c_i^{\nu_i}) \qquad \frac{k_f}{k_r} = K_c \qquad \text{"Detailed balance"}$$
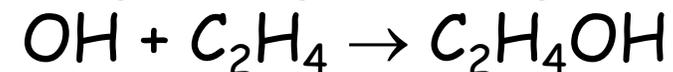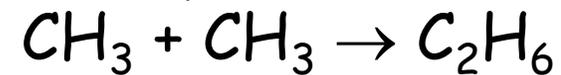
Pressure dependent association reaction

An association reaction involves collisional stabilisation of the adduct:

$$A + B \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} AB^* \overset{k_s[M]}{\rightarrow} AB.$$

Examples include
$$CH_3 + CH_3 \rightarrow C_2H_6$$
$$OH + C_2H_4 \rightarrow C_2H_4OH$$
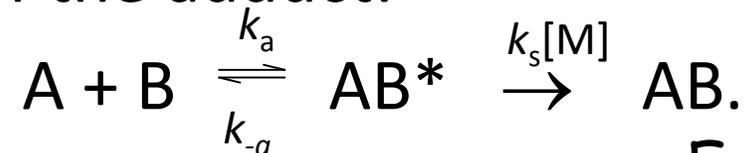
Apply QSSA:

$$k = \frac{k_a \, k_s [M]}{k_{-a} + k_s [M]}$$

As $[M] \rightarrow \infty, k \rightarrow k_a = k^\infty$

As $[M] \rightarrow 0, k \rightarrow \dfrac{k_a k_s [M]}{k_{-a}} = k_0 [M]$
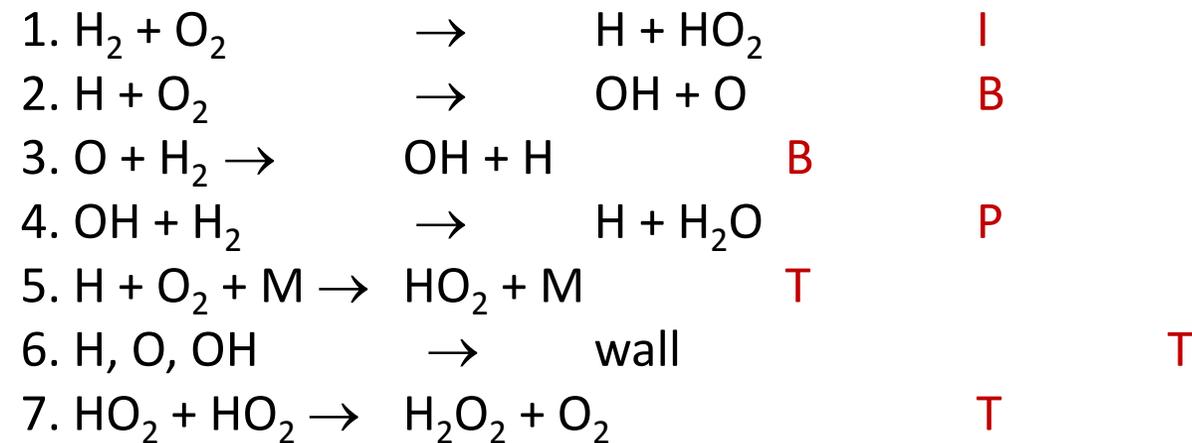
Substituting in first equation

$$k = \frac{k_0 [M] k^\infty}{k^\infty + k_0 [M]}$$

Similar treatment for dissociation reactions

48

Types of elementary reaction in combustion

A minimal set of the component elementary reactions is:

1. $H_2 + O_2 \rightarrow H + HO_2$ I
2. $H + O_2 \rightarrow OH + O$ B
3. $O + H_2 \rightarrow OH + H$ B
4. $OH + H_2 \rightarrow H + H_2O$ P
5. $H + O_2 + M \rightarrow HO_2 + M$ T
6. $H, O, OH \rightarrow$ wall   T
7. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ T

- Types of reaction: I = initiation; B = branching; P = propagation, T = termination

The explosion limits of H2:O2 mixtures. Combining a few reactions gives wild combustion behavior!

$$2k_{41}[H\bullet][O_2] - k_{45}[H\bullet][O_2][M] = 0$$

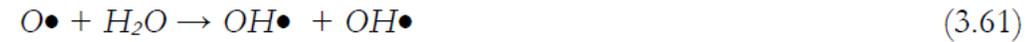$$[M] = \frac{p}{R_u T} = 2\frac{k_{41}}{k_{45}}$$
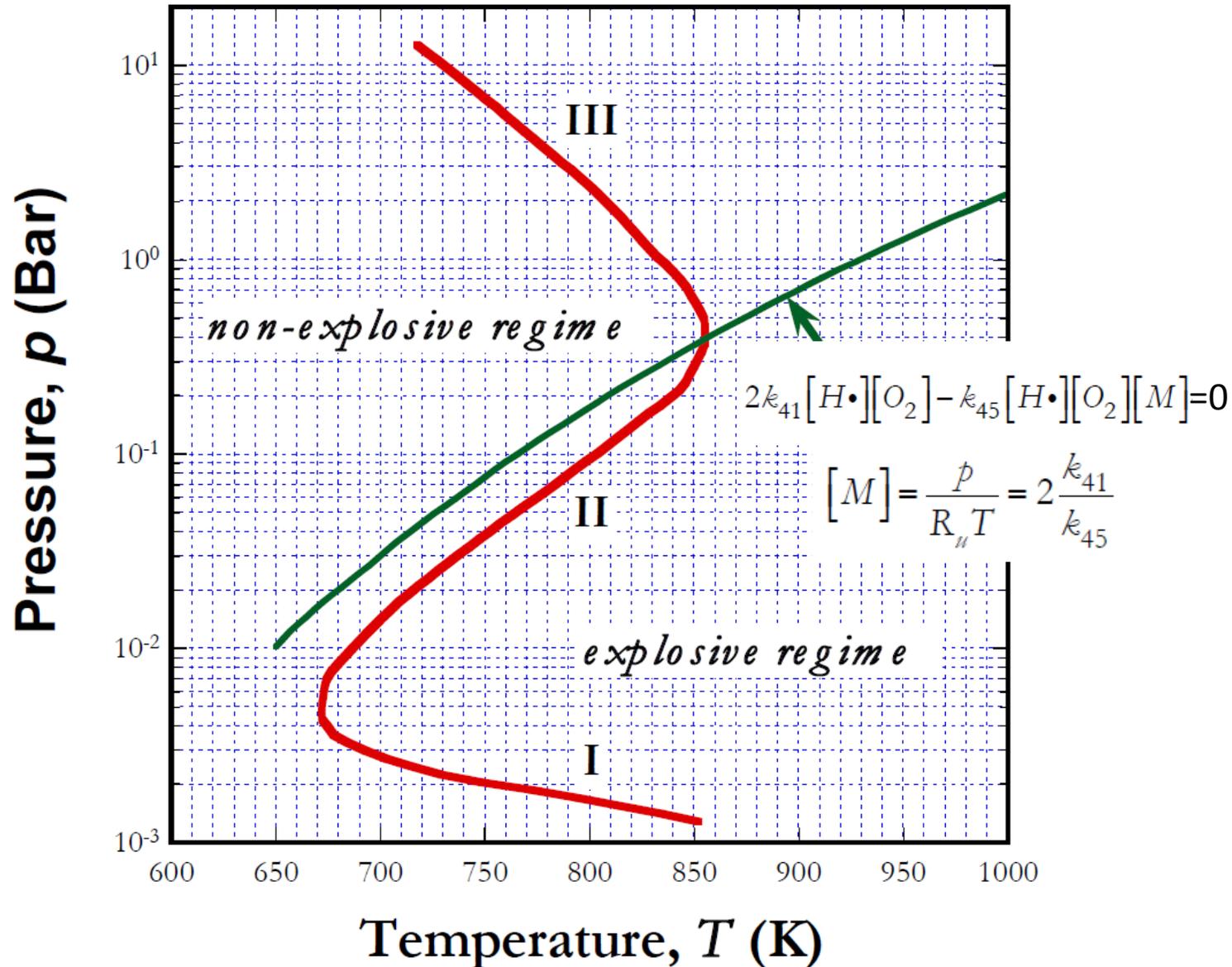
3.2.2 The Oxidation of Carbon Monoxide

Pure and dry carbon monoxide is difficult to burn. The principal cause is that there lacks a free radical chain branching and propagation mechanism to facilitate continuous and accelerated CO conversion to CO_2. Here the reaction steps may be postulated as

$$CO + O_2 \rightarrow CO_2 + O\bullet \qquad \text{(chain initiation)} \qquad (3.60)$$
$$CO + O\bullet + M \rightarrow CO_2 + M \, . \qquad \text{(chain termination)} \qquad (3.61)$$

In early studies, a vast number of CO oxidation data appeared to be difficult to reconcile amongst themselves. It was realized later that a trace amount of water, resulting from the impurity in CO or moisture brought by air can notably affect the oxidation rates of carbon monoxide. The explanation lies in the hydrogen brought by water. Specifically, in the presence of water we have the following sequence of reactions:

$$CO + O_2 \rightarrow CO_2 + O\bullet \qquad \text{(chain initiation)} \qquad (3.60)$$
$$O\bullet + H_2O \rightarrow OH\bullet + OH\bullet \qquad\qquad\qquad\quad (3.61)$$
$$CO + OH\bullet \rightarrow CO_2 + H\bullet \qquad \text{(chain propagation)} \qquad (3.62)$$
$$H\bullet + O_2 \rightarrow O\bullet + OH\bullet \, , \qquad \text{(chain branching)} \qquad (3.41)$$

Notice that the trace amount of water essentially supplies the $H\bullet$ otherwise not available in dry CO oxidation. In this way, the conversion of CO to CO_2 is now catalyzed by the $OH\bullet$ radical (3.62) and by the chain branching reaction (3.41). If H_2 is present, the reactions

$$O\bullet + H_2 \rightarrow OH\bullet + H\bullet \qquad \text{(chain branching)} \qquad (3.42)$$
$$OH\bullet + H_2 \rightarrow H_2O + H\bullet \, . \qquad \text{(chain propagation)} \qquad (3.43)$$

will participate in the chain reaction process, again with $H\bullet$ production to be crucial to the overall oxidation rates.

Many fuels have peculiar ignition/explosion kinetics
Great Practical Importance,
Basis of Fuel Rating System (e.g. Octane Number)

Figure 3.8. Explosion limits of methane, ethane and propane.
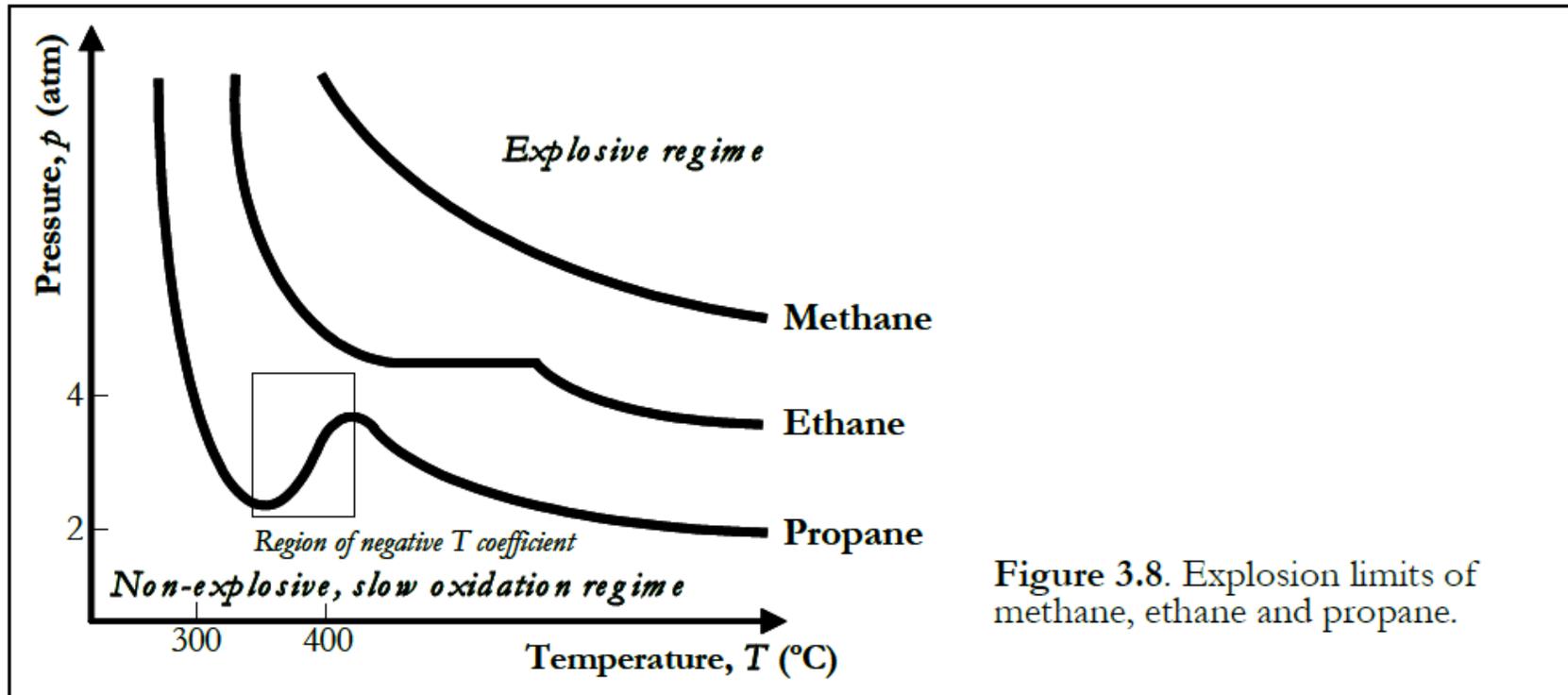
Many fuels even show "Negative Temperature Coefficient" (NTC), where increasing T slows down the reaction (!?).
We'll discuss this more later in the course....

Reaction kinetics contributions to combustion models
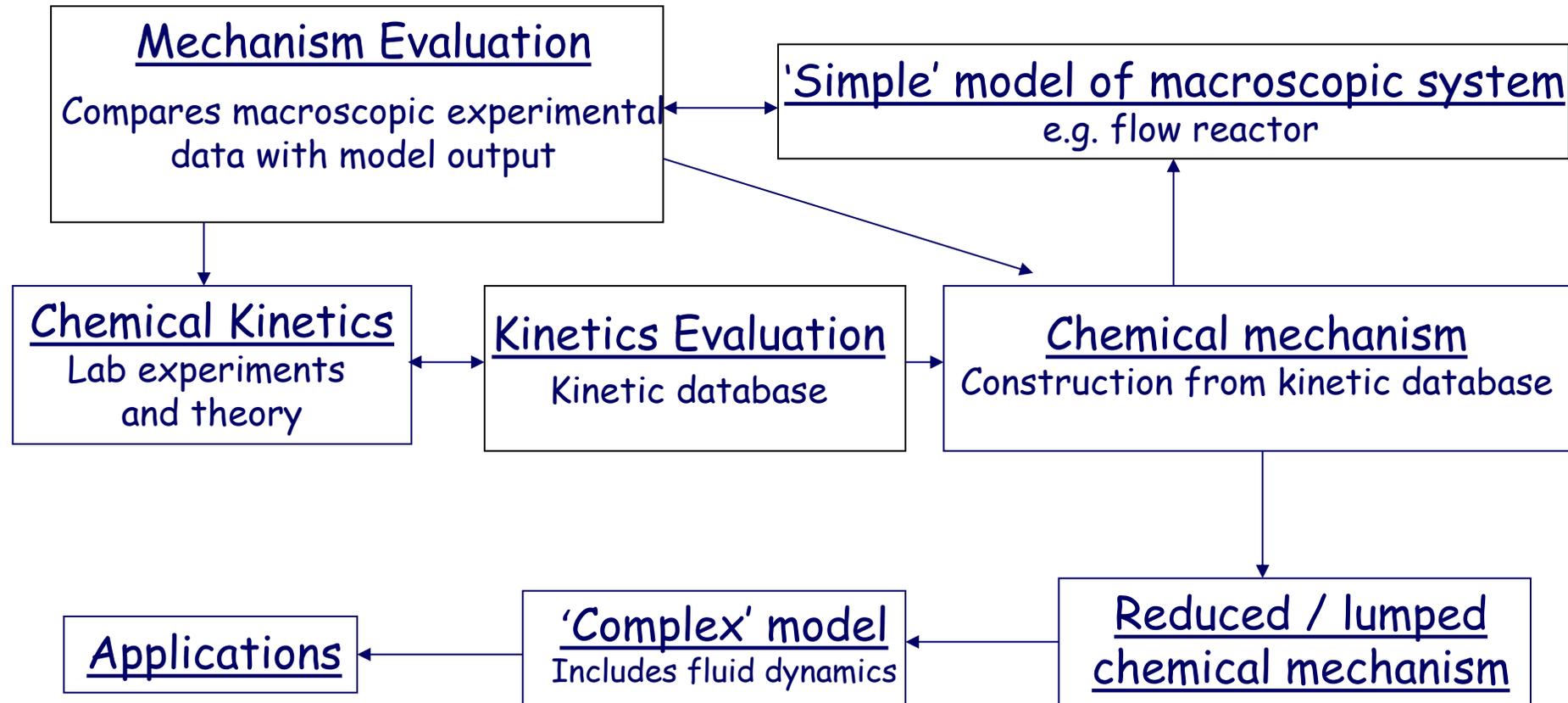
Understanding
Similar approaches in atmospheric chemistry, interstellar chemistry.

Measurement of rates of elementary reactions

- Ideally, isolate the individual reaction and study it at the appropriate combustion conditions.
- Not always possible:
  - May have to model the system to extract k of interest. Problems in other parts of the model can contaminate inferred value of k
  - May need to extrapolate to appropriate T, p. At high T reactant may disappear faster than you can make it.
  - Ideally extrapolate with the help of theory, but extrapolation always introduces uncertainties.

Measurement Techniques

- Pulsed laser photolysis (laser flash photolysis)
- Shock tubes
- Flow tubes for elementary reactions and whole systems
- Static studies of whole systems

- Usually an experiment measures either rate coefficient (time-dependence) or product distribution. Hard to do both at same time.
- Product yields require (absolute) calibrations. Often need to consider side-reactions affecting measured yields.
- Pseudo-first-order measurement of bimolecular rate coefficients does not require absolute calibration of a reactive intermediate...making this approach much easier and more popular than other types of kinetics measurements!
- X + Y $\rightarrow$ products. If [X]<<[Y] can approximate

$$[X]/[Xo] = \exp(-k[Y]t)$$

Only need relative measurement of X. But need absolute calibration of [Y]. That is not too hard if Y is stable.

Pulsed laser photolysis

Laser flash photolysis (LFP) / laser induced fluorescence (LIF) for the study of OH + reactant

Signal $\propto$ exp($-kt$)

Set delay between Photolysis laser and Probe laser; repeat with different delay times

57
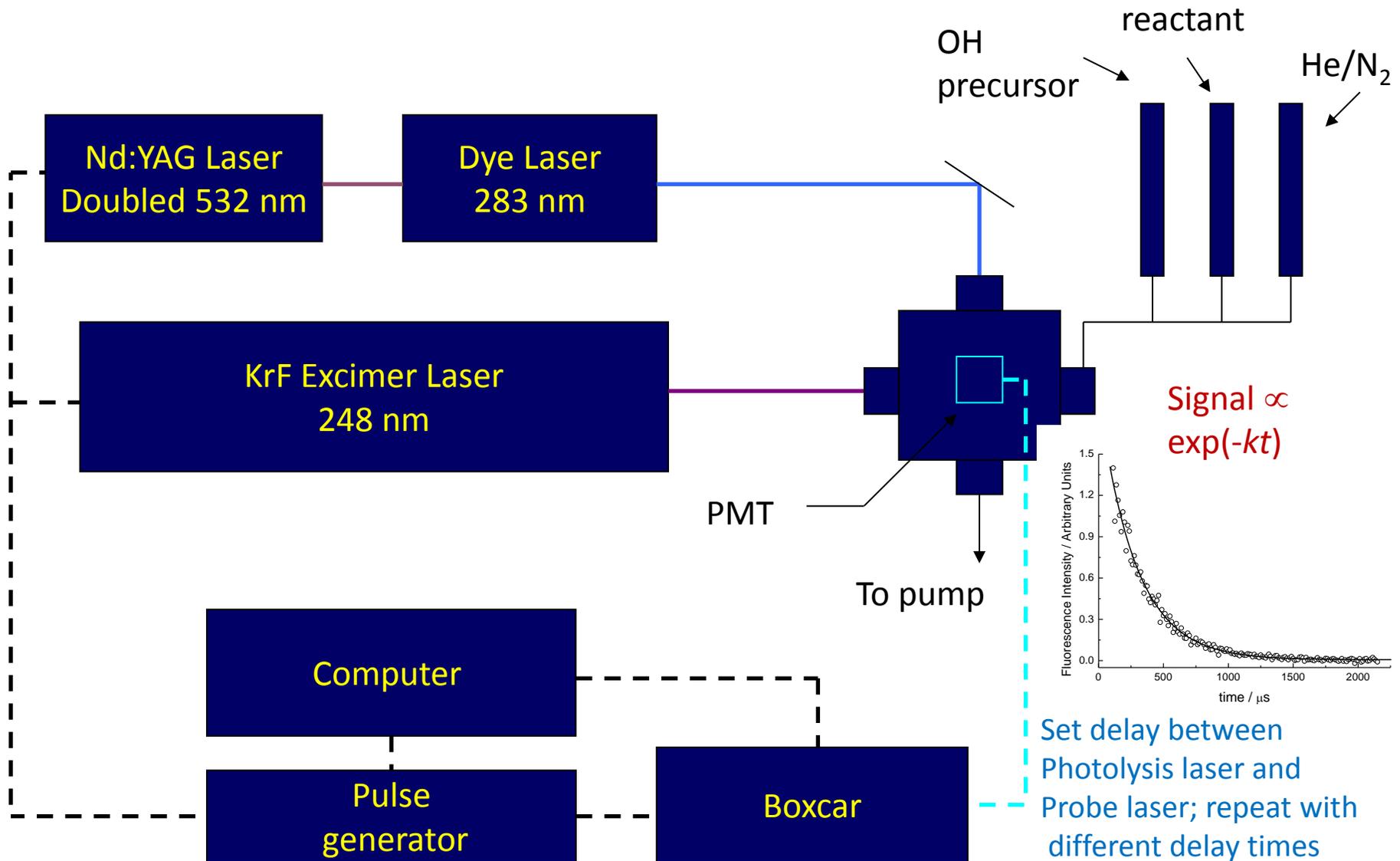
Procedure for determining rate coefficients for pseudo first order reactions using LFP for OH + SO$_2$
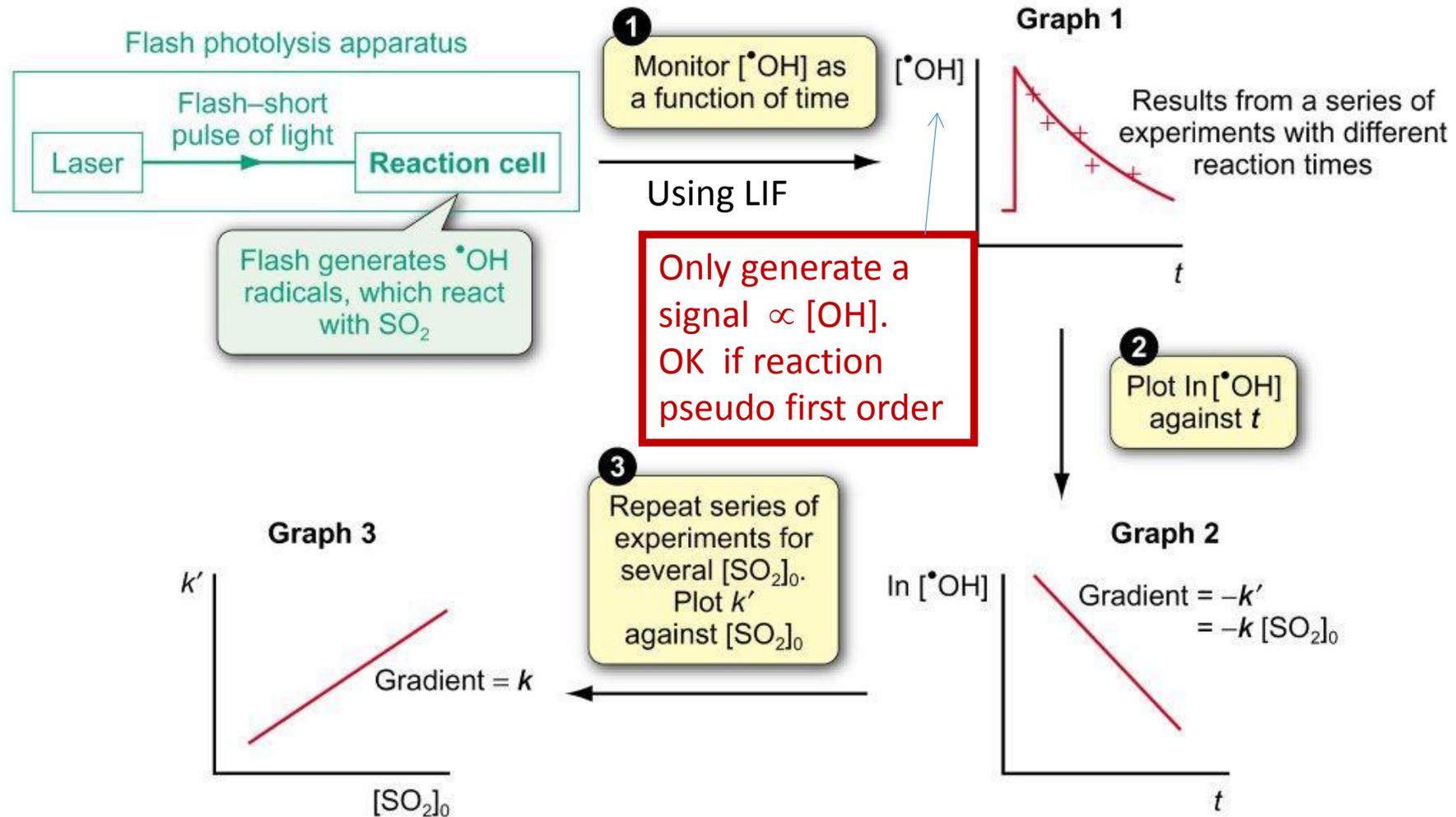
OH + acetone, J N Crowley, JPCA, 2000, **104**,2695

laser flash photolysis, resonance fluorescence/laser induced fluorescence to measure [OH] (relative). Optical measurement of [acetone] before and after reactor.
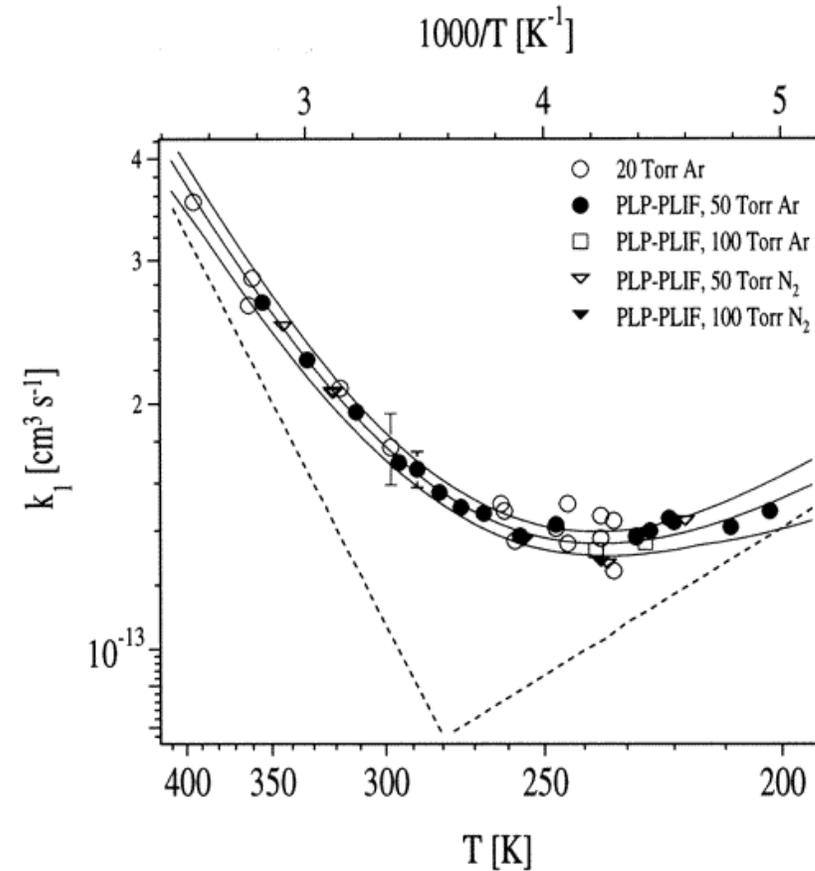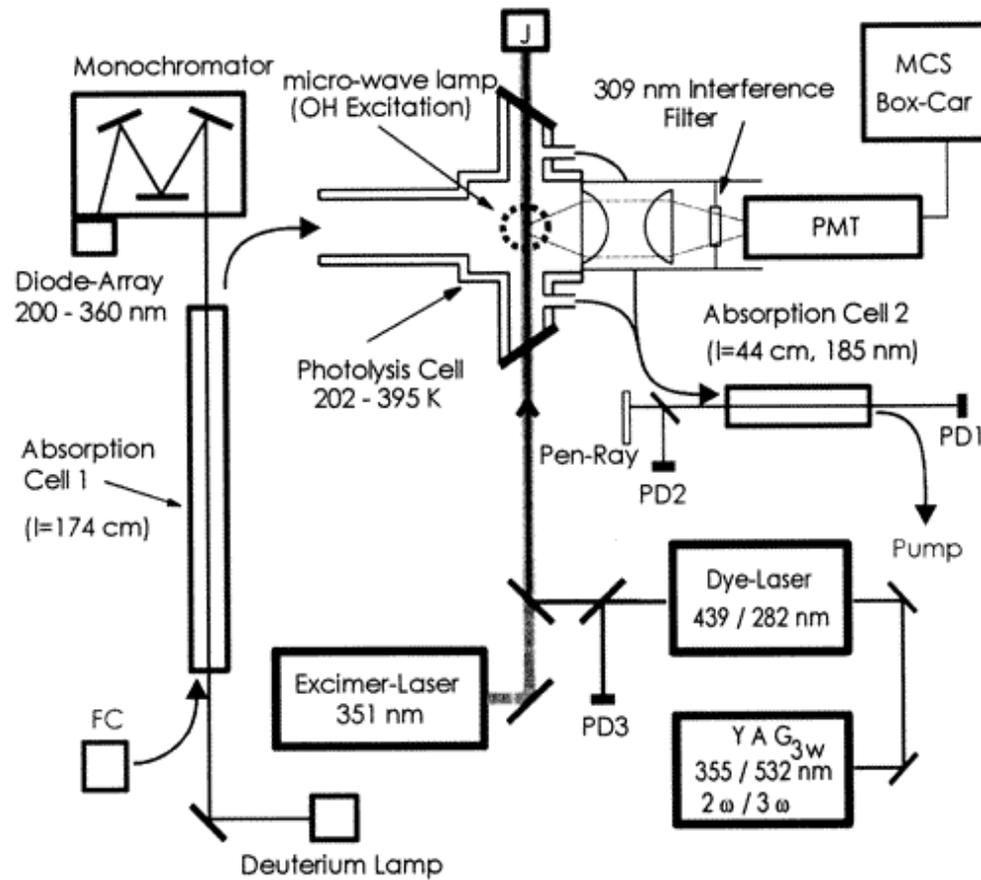
Often the biggest source of error in k is knowing concentration of the stable species (for pseudo-first-order kinetics measurements).

Detection using time of flight mass spectrometry

Blitz et al. Rev. Sci. Inst. 2007, 78, 034103

ToFMS

Turbo Pump 300 l/s

VUV-Photoionisation

Flight Tube ~$5*10^{-6}$ Torr

248 nm Excimer Laser Beam

1 mm

d= 1.27 cm, l = 70 cm

Metal/ Quartz Flow Reactor

Quartz window

Pump 28 l/h

Diffusion Pump 3000 l/h

Main Vacuum Chamber 10^{-3}-10^{-4} Torr
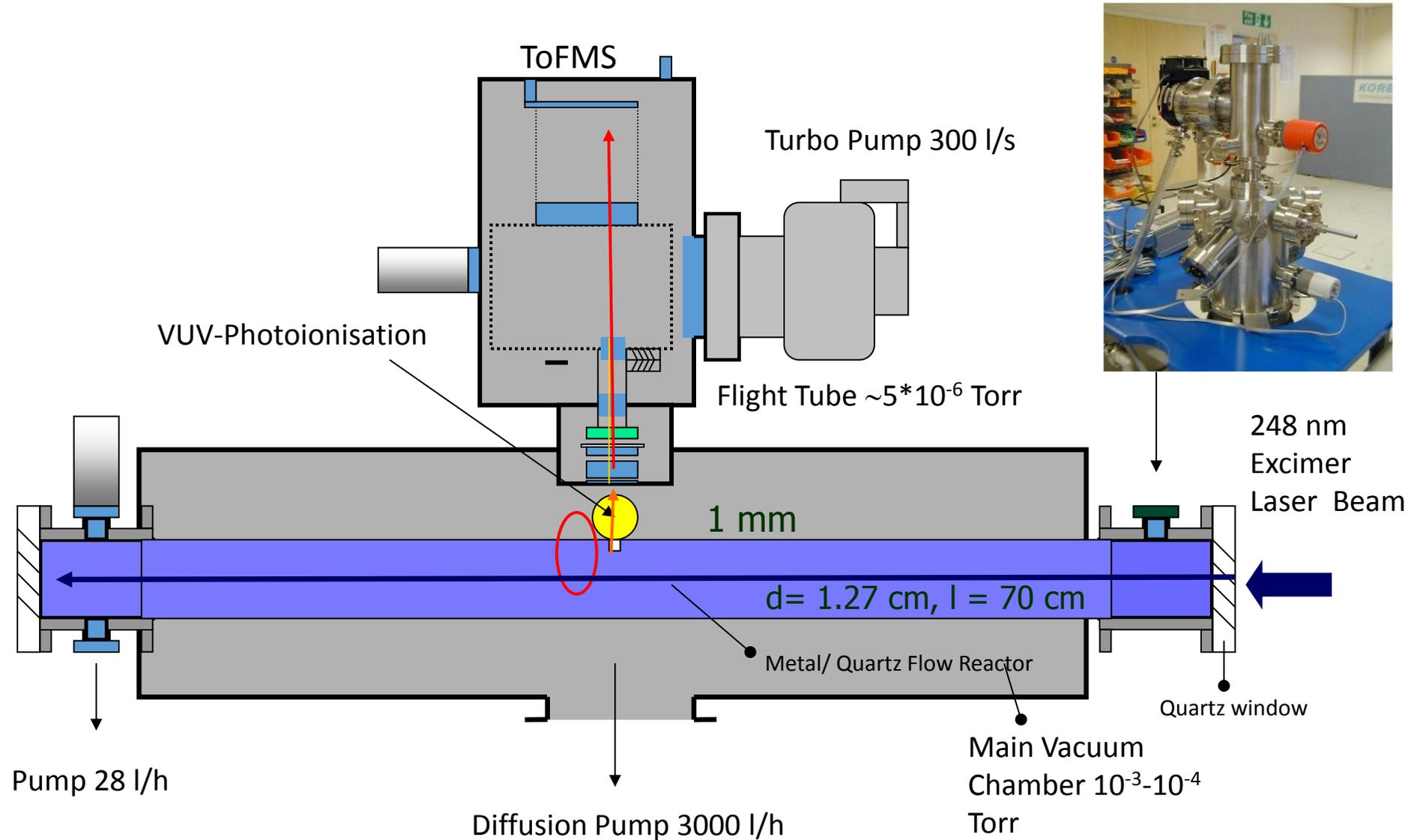
Application of synchrotron radiation for photoionization (SVUV-PIMS) to distinguish isomers in flames (Advanced Light Source, Berkeley, CA)

- ALS is tuneable and so it is feasible to distinguish isomers, which have the same mass, through their differing photoionization efficiency curves.

- Traces show m/z=44 for different flames:

  acetaldehyde: CH_3CHO

  ethenol: $CH_2=CHOH$
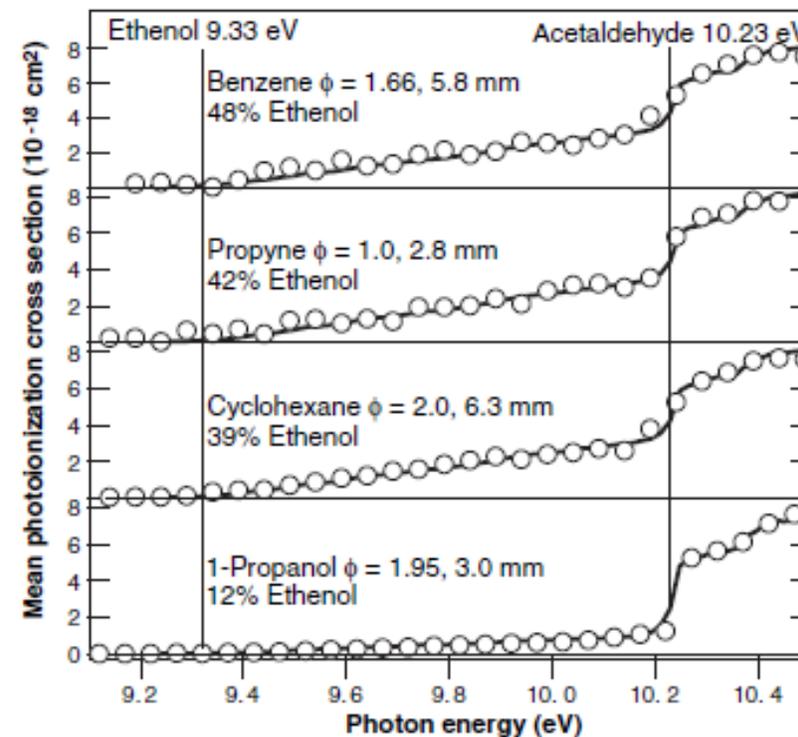
Taatjes et al. *Science* 2005, **308**, 1887

SVUV-PIMS for kinetics

Taatjes et al., PCCP, 2008, 10, 20 – 34
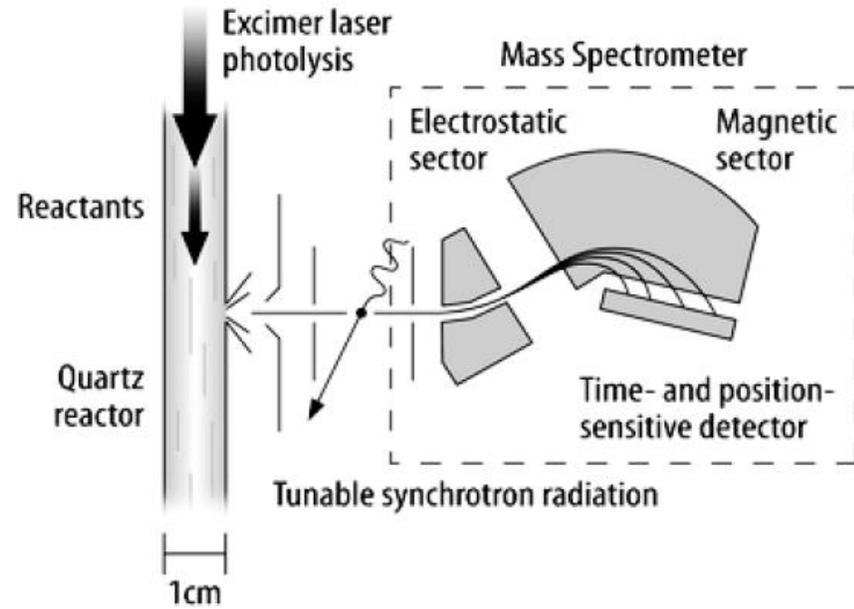
The calculated photoionization spectra of the Criegee intermediate CH_2OO and dioxirane, the experimental photoionization spectrum for formic acid, as well as schematic chemical structures, are shown [127].

- (b) Time-dependent CH_2OO signals for various concentrations of SO_2. Solid lines represent fits to the data traces, including convolution with a measured instrument response function, from which pseudo–first order decay constants are derived Welz et al. Science 335, 204-207

OH + C$_2$H$_2$ + M → C$_2$H$_2$OH + M
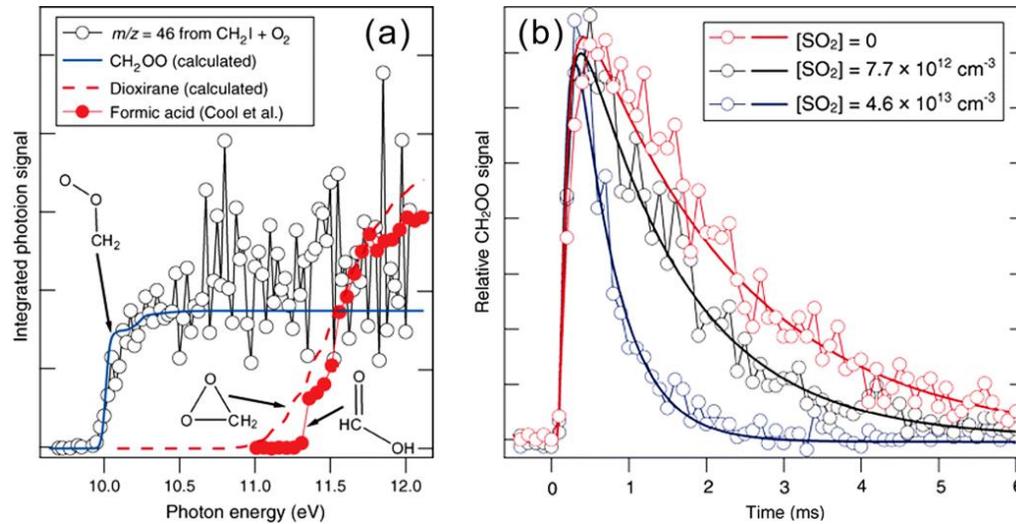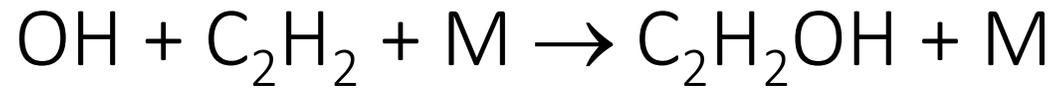
Cleary et al. J. Phys. Chem., 2007,
111, 4043-4055

- Pressure dependent (association) reaction.

- Measure as a function of temperature and pressure
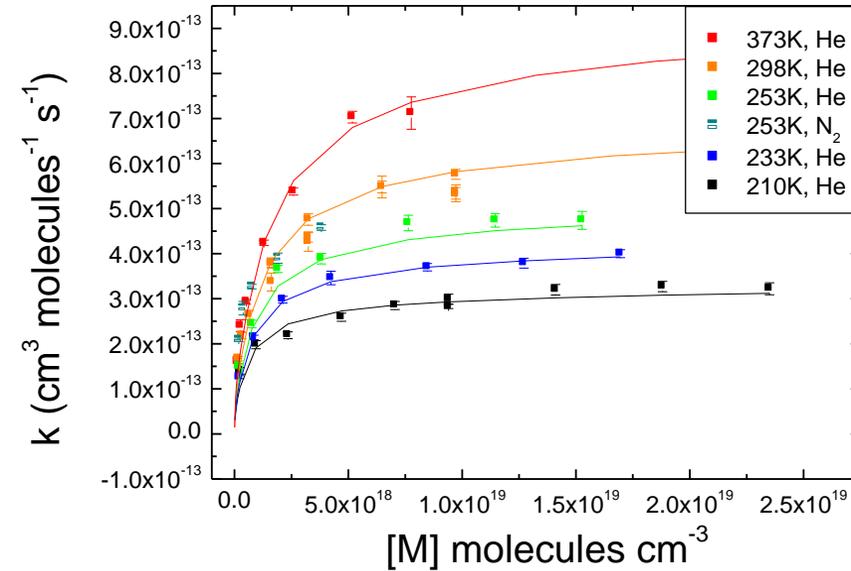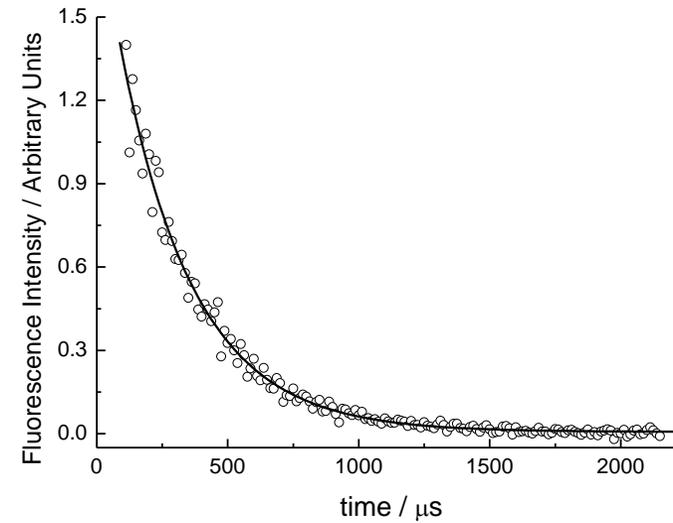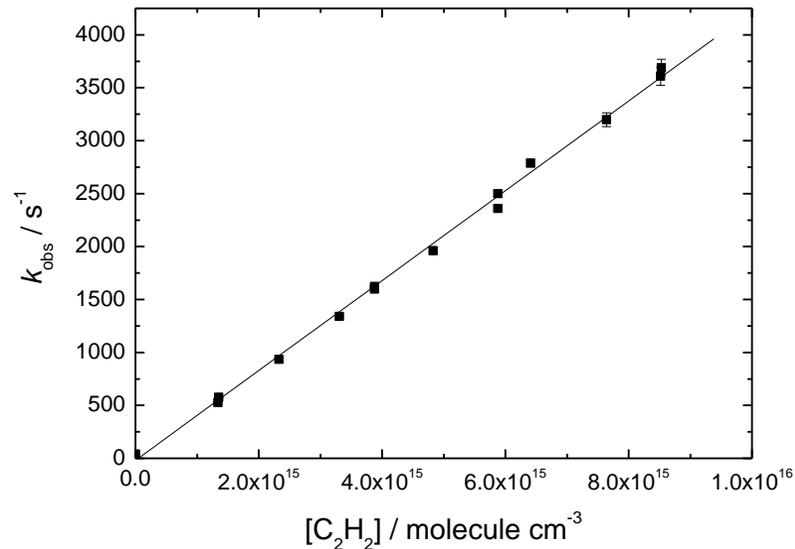
Radical detection using absorption spectroscopy: $C_3H_5 + C_3H_5$
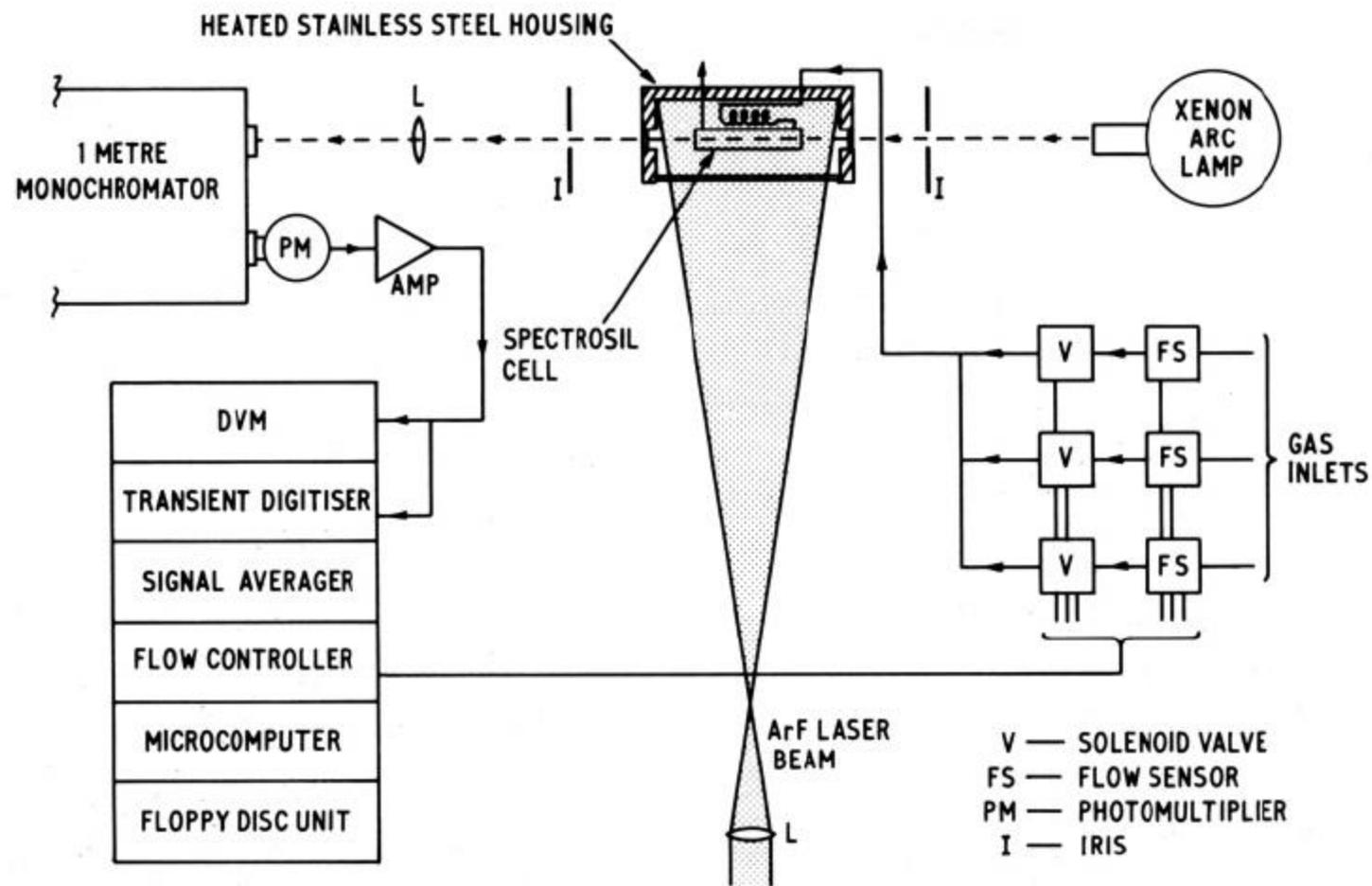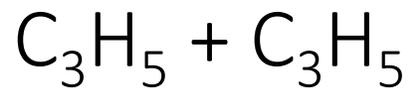
Reaction is <u>second order </u> in the radical – need the <u>absolute</u> concentration to determine *k*.

Tulloch et al. *J. Phys. Chem. l982, 86, 3812-3819*

$C_3H_5 + C_3H_5$:Absorption spectroscopy 2

- Reaction is second order in C_3H_5

- Need to know absolute concentration of radical – absorption spectroscopy provides a good route to this. (see J. Phys. Chem. 1985, 89, 2268-2274 for discussion for CH_3)

- But to determine absorption coefficient σ, someone needed a way to know absolute concentration!
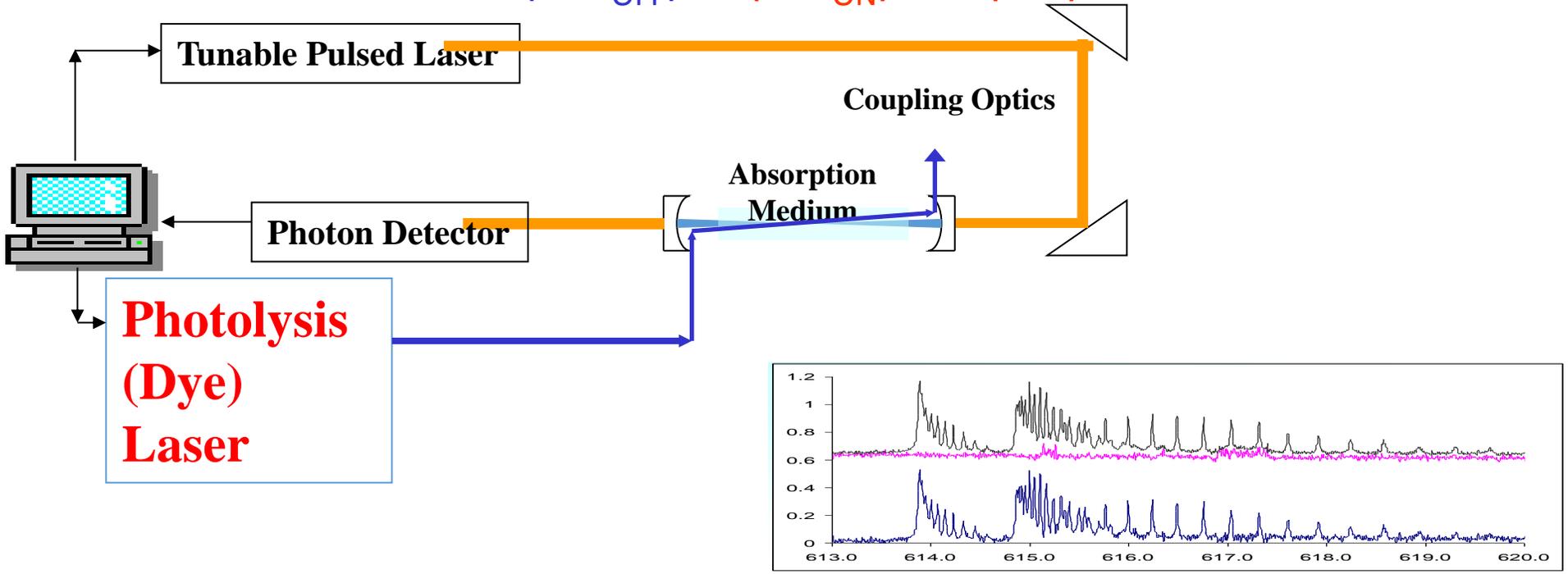
- $I/I_0 = \exp(-\sigma[C_3H_5]l)$
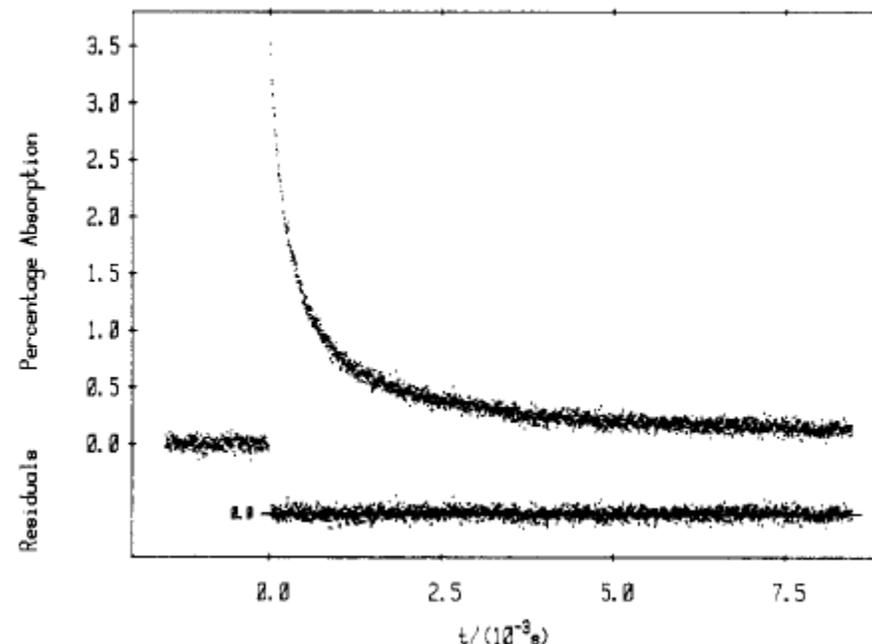
If you start with C3H5I and photolyze, and assume one C3H5 formed for each I atom, you can measure [I] and so infer [C3H5].

Often time-decay is combined first-order and second-order (since C3H5 can vanish by other processes)

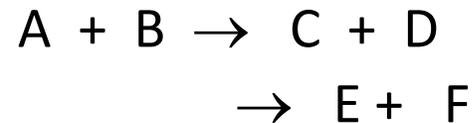# Detection of HCO using cavity ring down spectroscopy (CRDS)
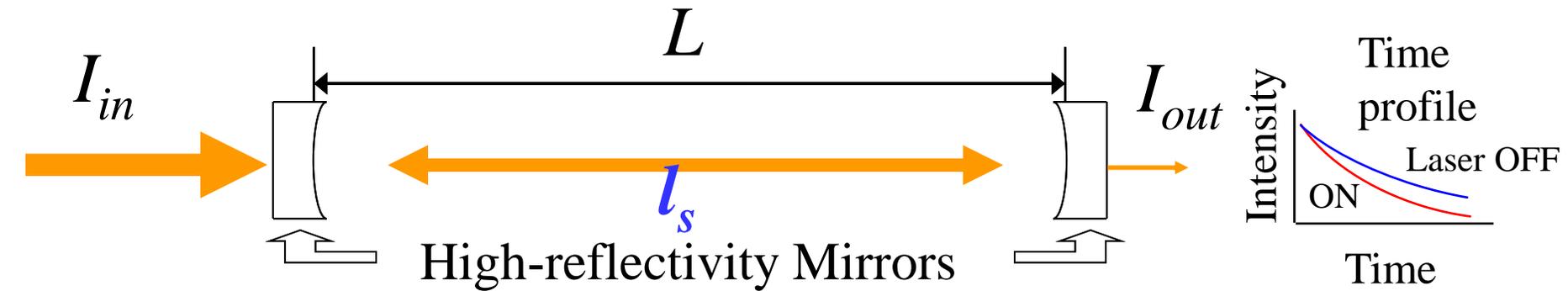
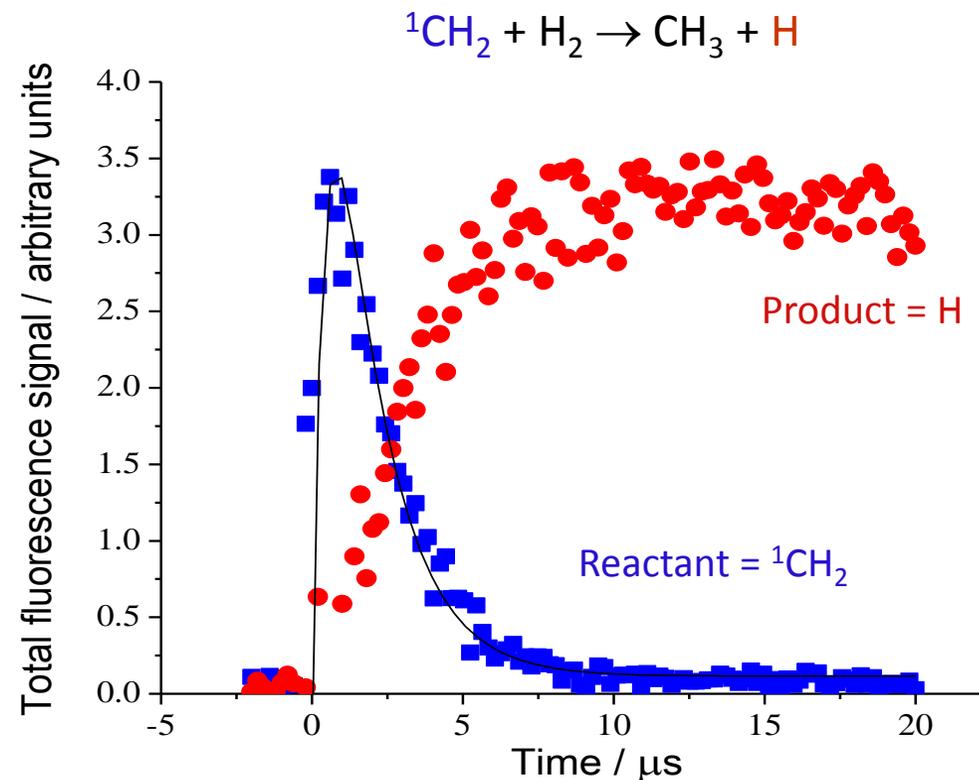$$(1/k_{OFF}) - (1/k_{ON}) = A\ (\sigma cl)$$

- Use laser pulse to generate radical on short timescale (~10 ns)

- Observe radical concentration vs time. Obtain kinetics from decay time constant

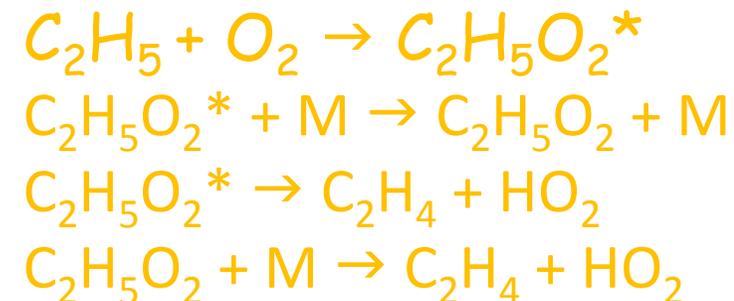- Also observe product – calibration gives channel yield for a multi channel reaction:
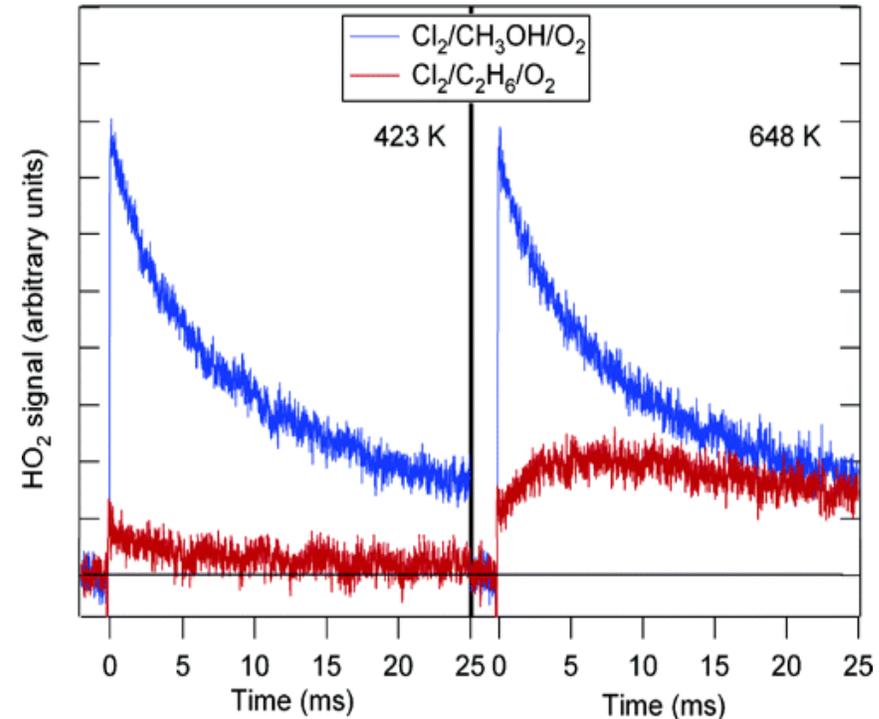
$$A + B \rightarrow C + D$$
$$\rightarrow E + F$$

Detection technique :
 laser induced
fluorescence
for CH_2 and H

Need absolute
calibrations for both
reactive intermediates!

$^1CH_2 + H_2 \rightarrow CH_3 + H$
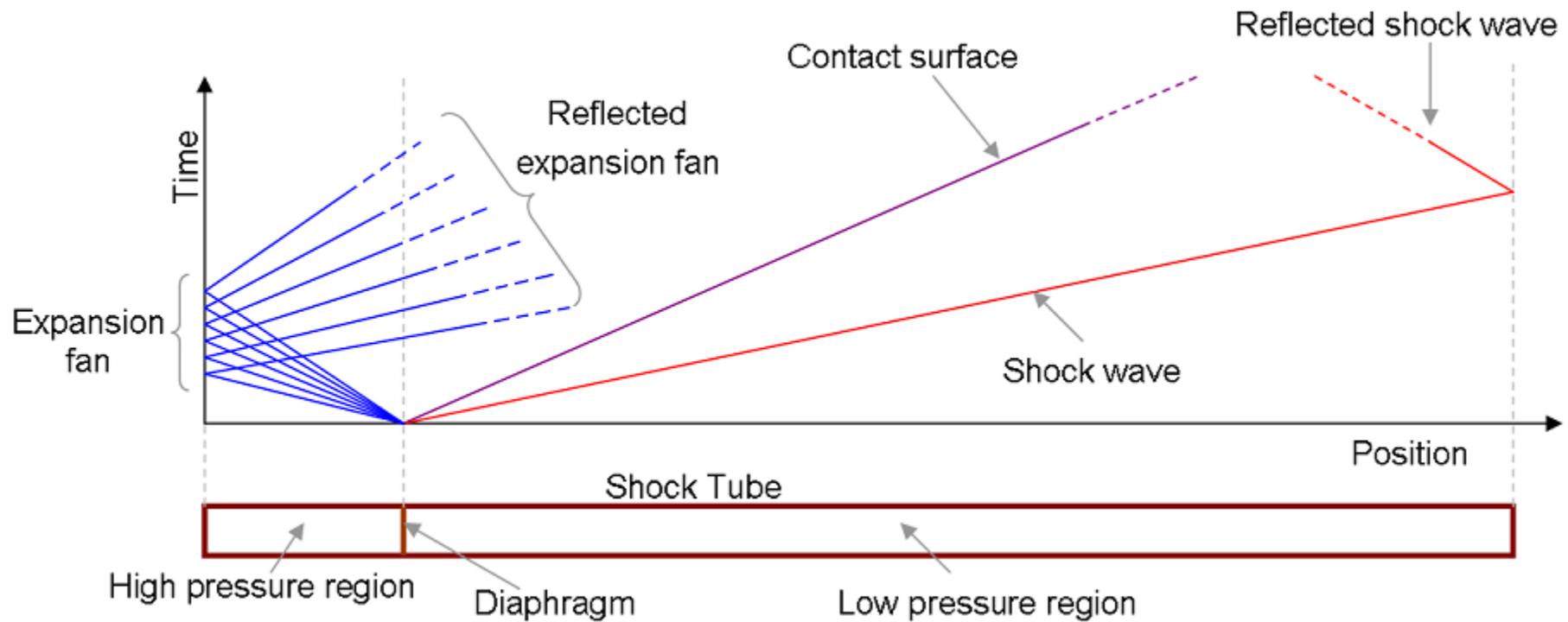
Product = H

Reactant = $^1CH_2$

Total fluorescence signal / arbitrary units

Time / µs

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- Taatjes et al. (J. Phys. Chem. A 104 (2000) 11549 – 11560) observed the formation of OH and HO_2, determining the fractional yields. Used 100% yield of HO_2 from CH_2OH + O_2 to calibrate the system.

- HO_2 yield↑ as T↑ and p↓

- Two timescales at higher T

- OH yield is small.

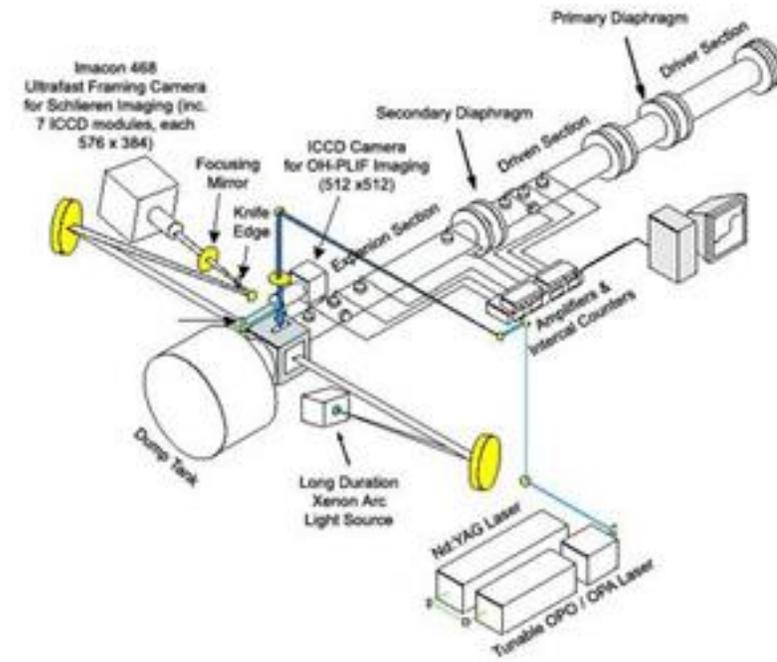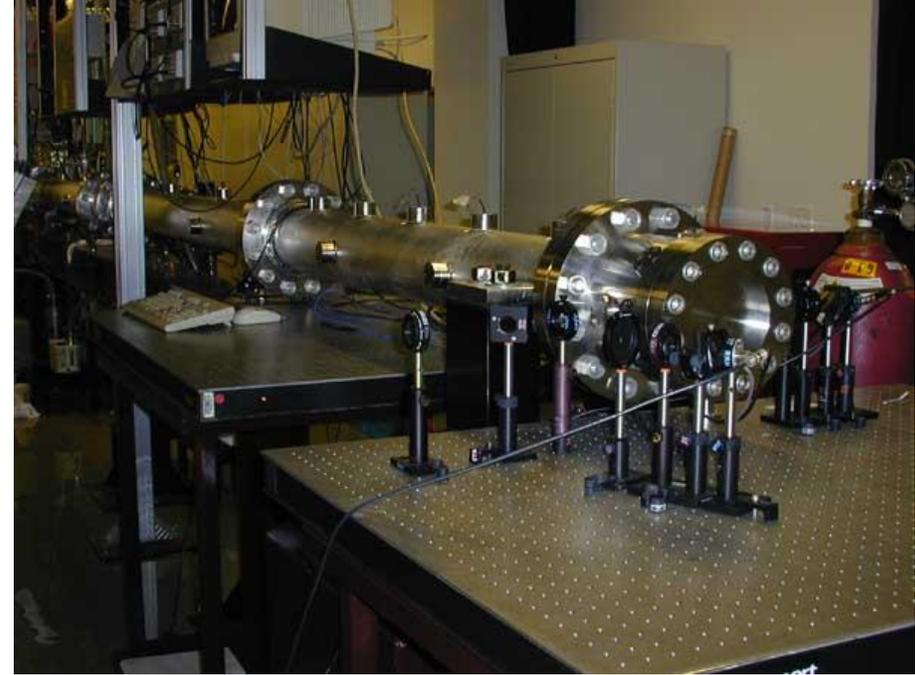- Theoretical interpretation and relevance to autoignition chemistry will be discussed later

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2*$$
$$C_2H_5O_2* + M \rightarrow C_2H_5O_2 + M$$
$$C_2H_5O_2* \rightarrow C_2H_4 + HO_2$$
$$C_2H_5O_2 + M \rightarrow C_2H_4 + HO_2$$

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# Shock tubes

Shock tube - basics

Shock tube:
Hanson lab at Stanford

Shock tubes

- Compressive heating of reaction mixture
- Radicals generally formed from thermal dissociation of precursor
- Single shot, so no signal averaging, but impressive optimisation of signal
- Generally need to assess secondary reactions and use numerical chemical model with sensitivity analysis to show viability of measurements.
- Example: Measurement of CH_3 + OH by the Hanson group
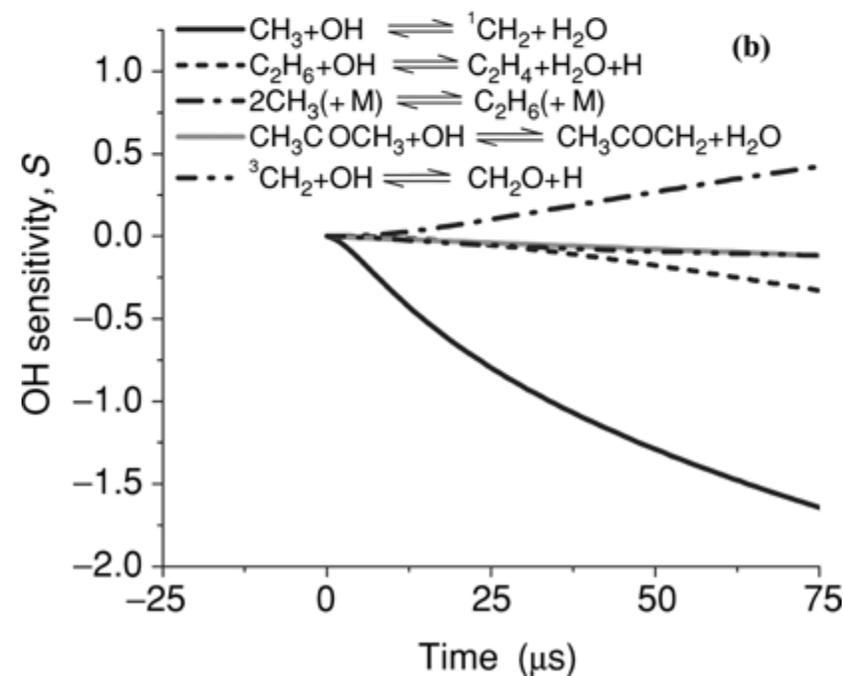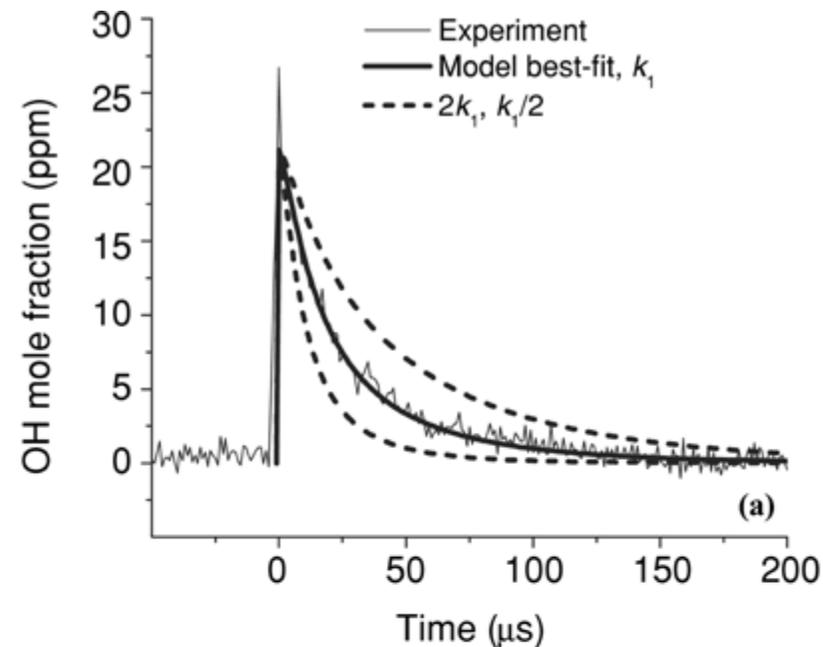
Vasudevan et al, International Journal of Chemical Kinetics (2008), 40(8), 488-495.

- Behind reflected shock waves. OH radicals formed by shock-heating tert-butyl hydroperoxide

- OH concentration time-histories were inferred from laser absorption using the R1(5) line of the OH A-X (0, 0) band near 306.7 nm.

- Other reactions contribute to the OH time profile, especially CH_3 + OH.

- Rate coefficient determined by fitting to detailed model (GRI-Mech – see Wednesday), with addition of acetone chemistry, deriving from dissociation of OH precursor (t-butylhydroperoxide). Detailed uncertainty analysis
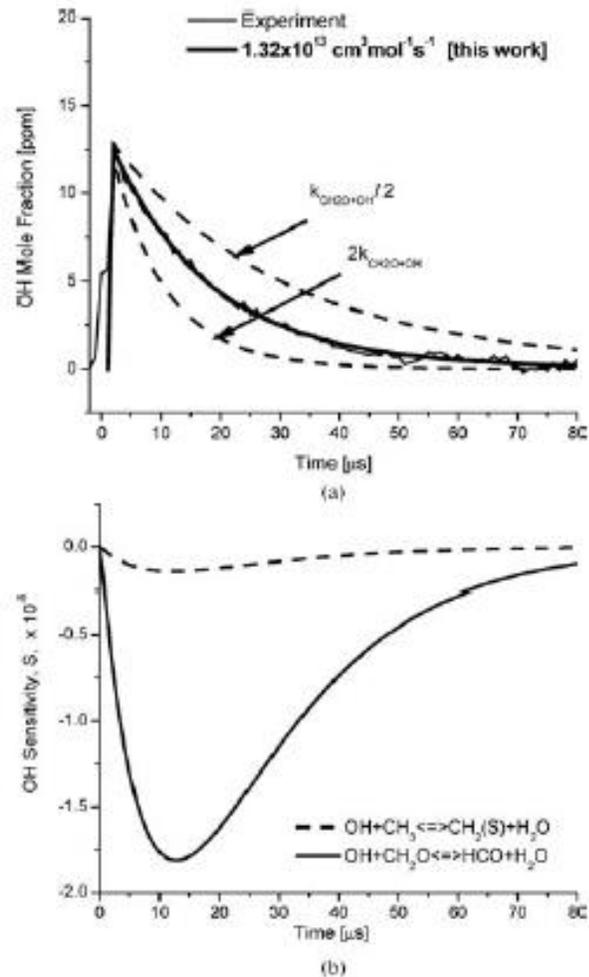
Determination of *k* and uncertainty analysis

Figure 2 (a) OH concentration time history. 13.25 ppm TBHP, 80 ppm $(CH_2O)_3$, Ar; initial reflected shock conditions: 1229 K, 1.64 atm. (b) Sensitivity analysis. 13.25 ppm TBHP, 80 ppm $(CH_2O)_3$, Ar; initial reflected shock conditions: 1229 K, 1.64 atm. $S = (dX_{OH}/dk_i)(k_i)$, where k_i is the rate constant for reaction i.
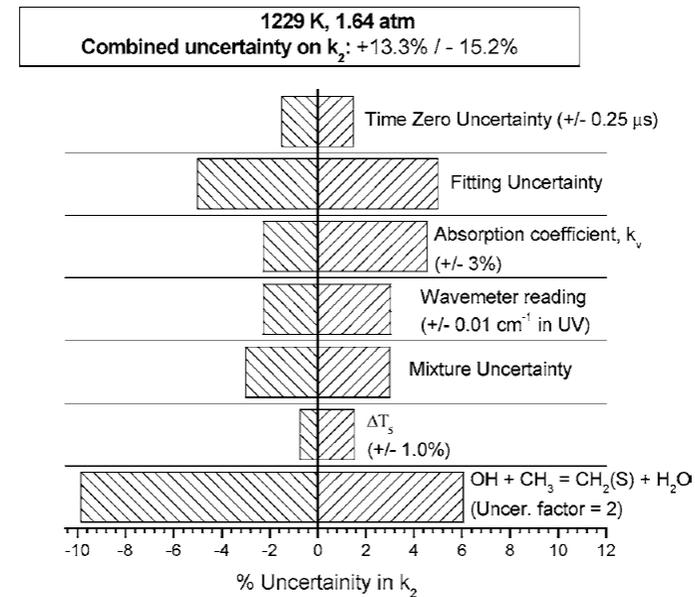

Figure 3 Uncertainty analysis for rate coefficient of $CH_2O + OH = HCO + H_2O$. Initial reflected shock conditions: 1229 K, 1.64 atm; individual error sources were applied separately and their effect on the rate of reaction (2) was determined. Uncertainties were combined to yield an overall uncertainty estimate for k_2.
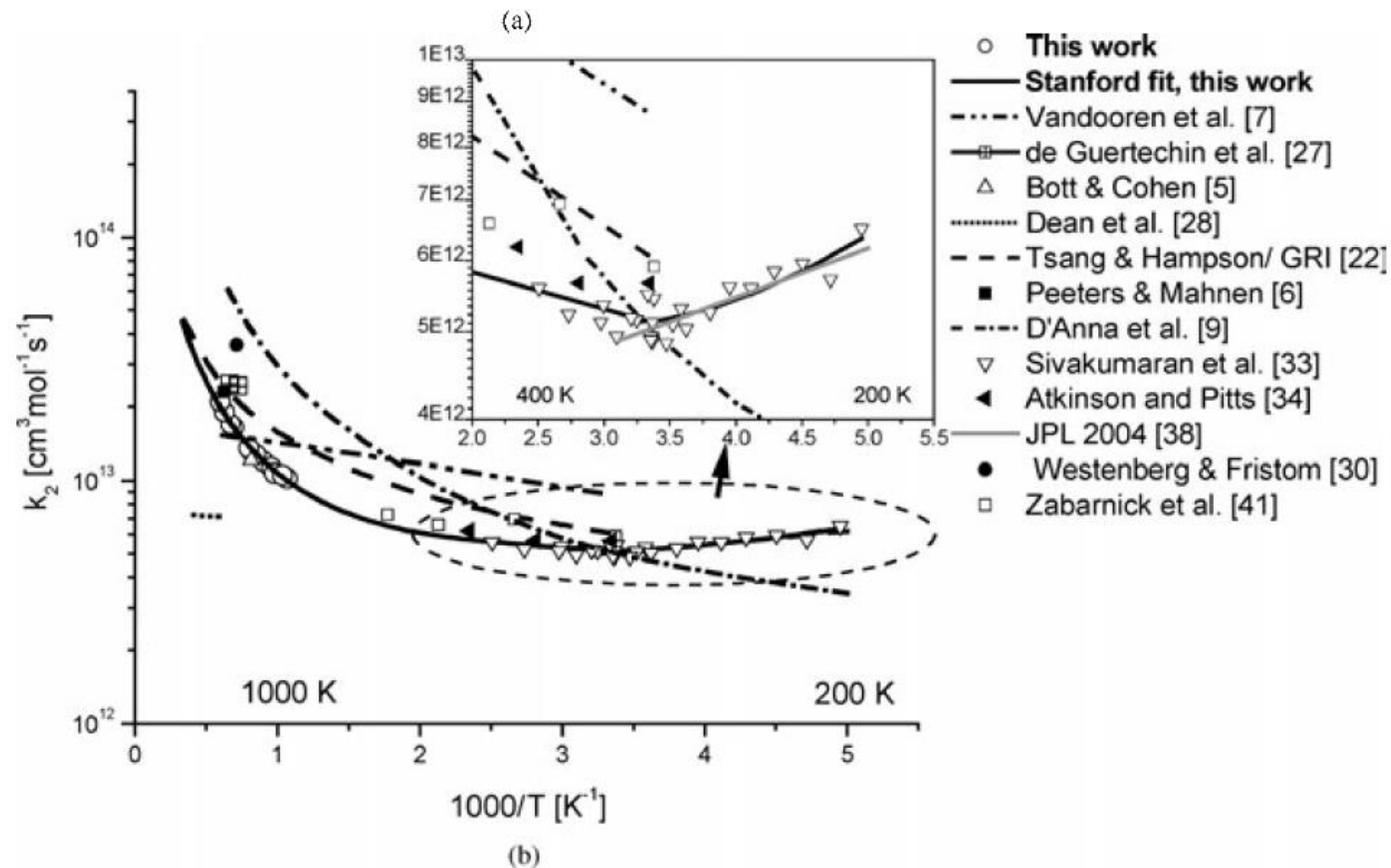
Arrhenius plot for OH + HCHO

Figure 7 (a) Arrhenius plot for $CH_2O + OH = HCO + H_2O$ at high temperatures (800–2500 K). (b) Arrhenius plot for $CH_2O + OH = HCO + H_2O$ at all temperatures (200–2500 K) and low (200–500 K) temperatures.

- $k_2 = 7.82 \times 10^7 T^{1.63} \exp(531/T) / cm^3\ mol^{-1}\ s^{-1}$

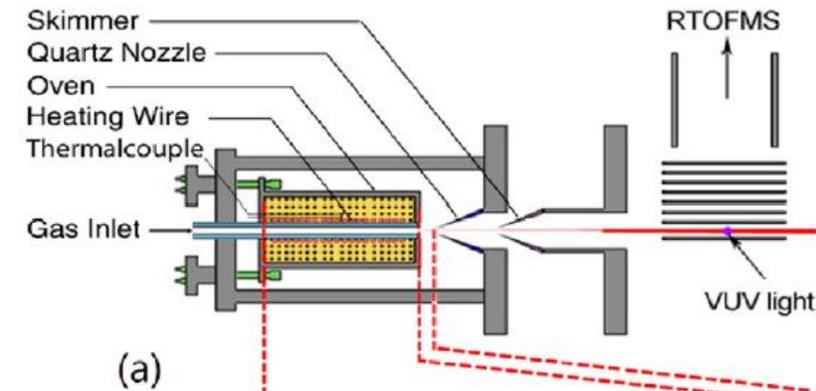# Flow tubes for elementary reactions and whole systems

Combined flow tube and pulsed photolysis: O + OH

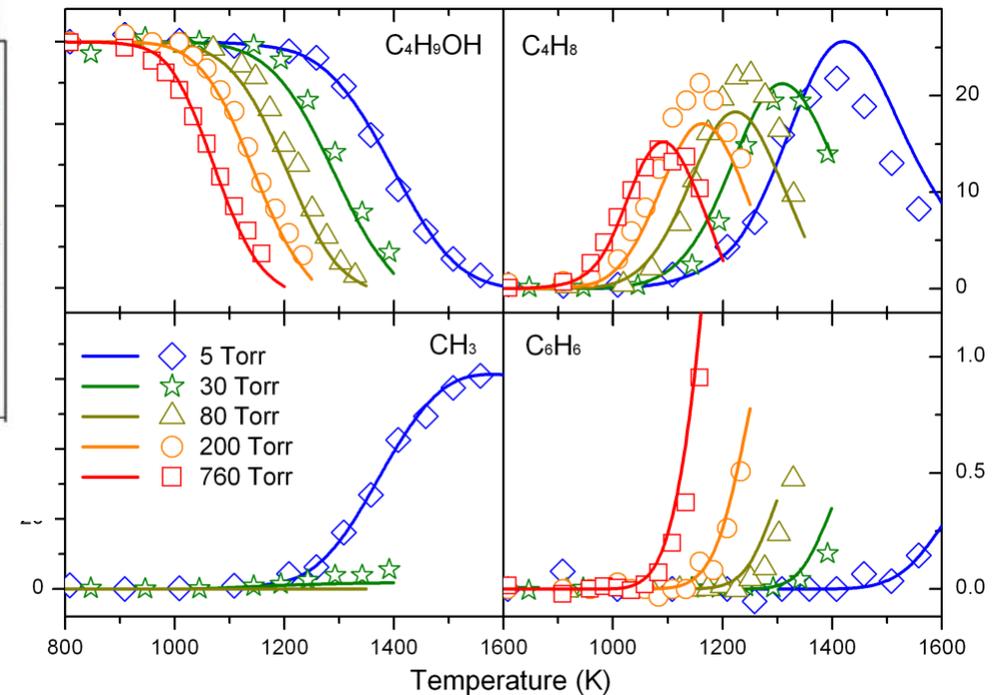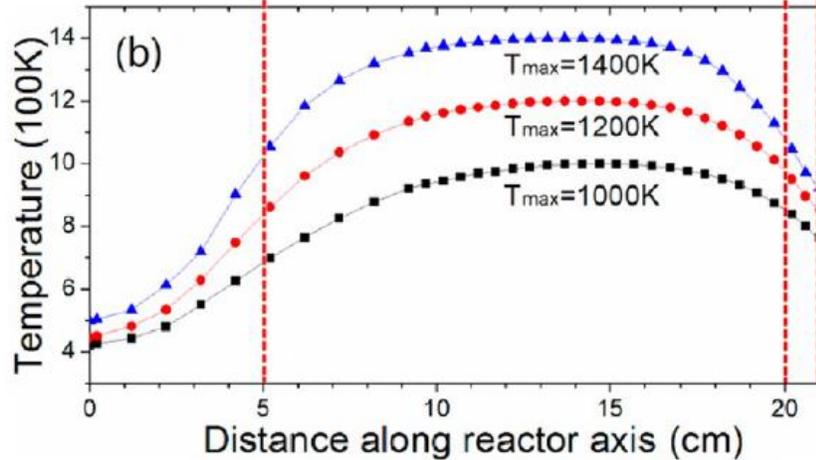Howard and Smith, J. Chem. Soc FaradayTrans. 2, 1981,77,997-1008
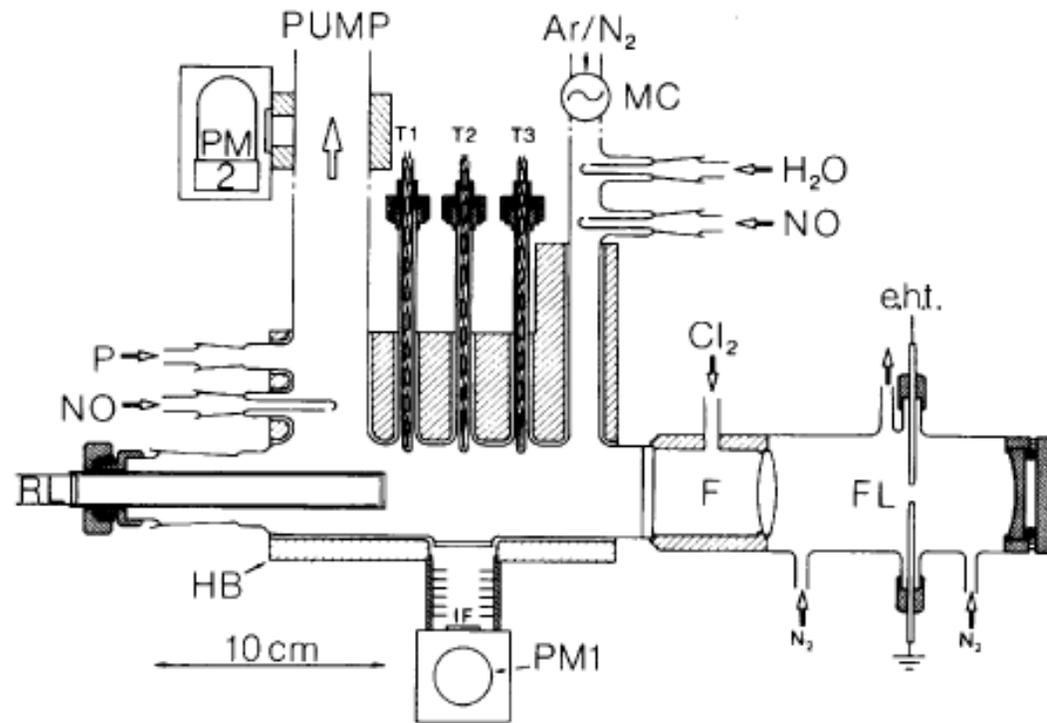
- O generated in discharge, OH by pulsed photolysis, with [O]>> [OH]. [O] generated from N + NO and concentration determined by titration.

Pyrolysis of butanol using molecular beam sampling from a plug flow reactor

Cai et al. (Energy & Fuels, 26, 5550-5568 (2012))
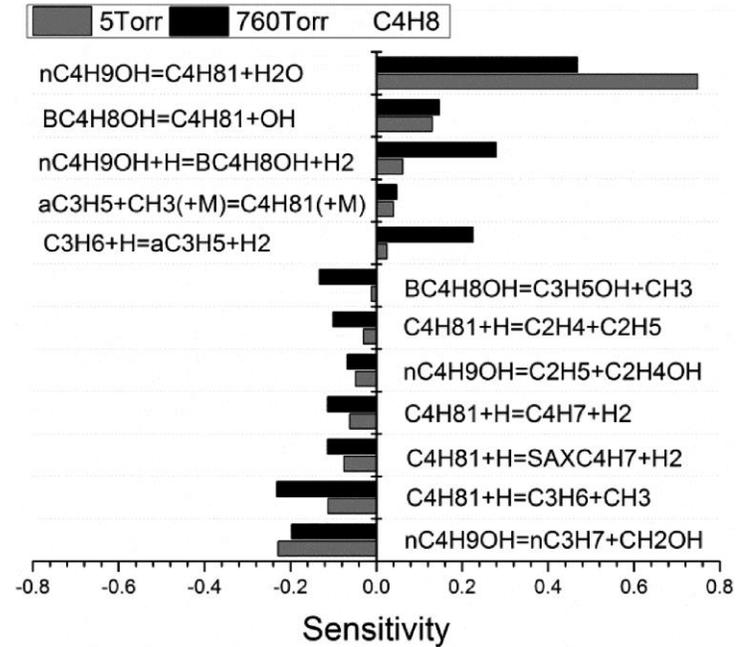
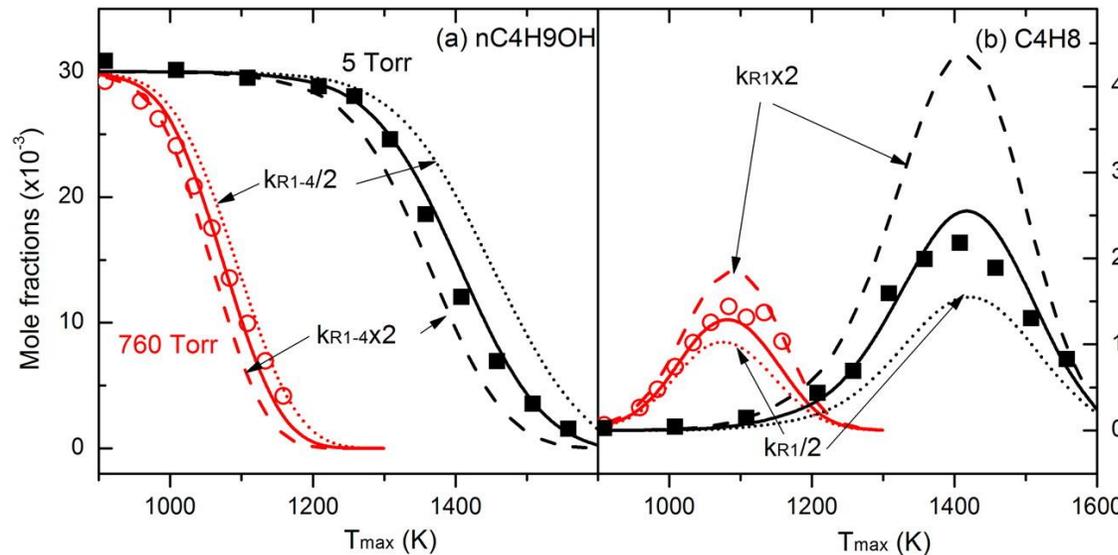# Use of species concentrations in flow reactor to determine rate coefficients: butanol dissociation

Cai et al. (Energy & Fuels, 5550-5568 (2012))

C_4H_8 sensitivity
T_{max} = 1450 K under 5 Torr (gray) and
T_{max} = 1100 K under 760 Torr (black)

Experimental mole fraction profiles (symbols) and modeling results (lines) of nC_4H_9OH pyrolysis at 5 and 760 Torr.

Deconvolution of photoionization curves in a flow tube study of cyclopentene oxidation

J. Phys. Chem. A 2008, *112,* 13444–13451
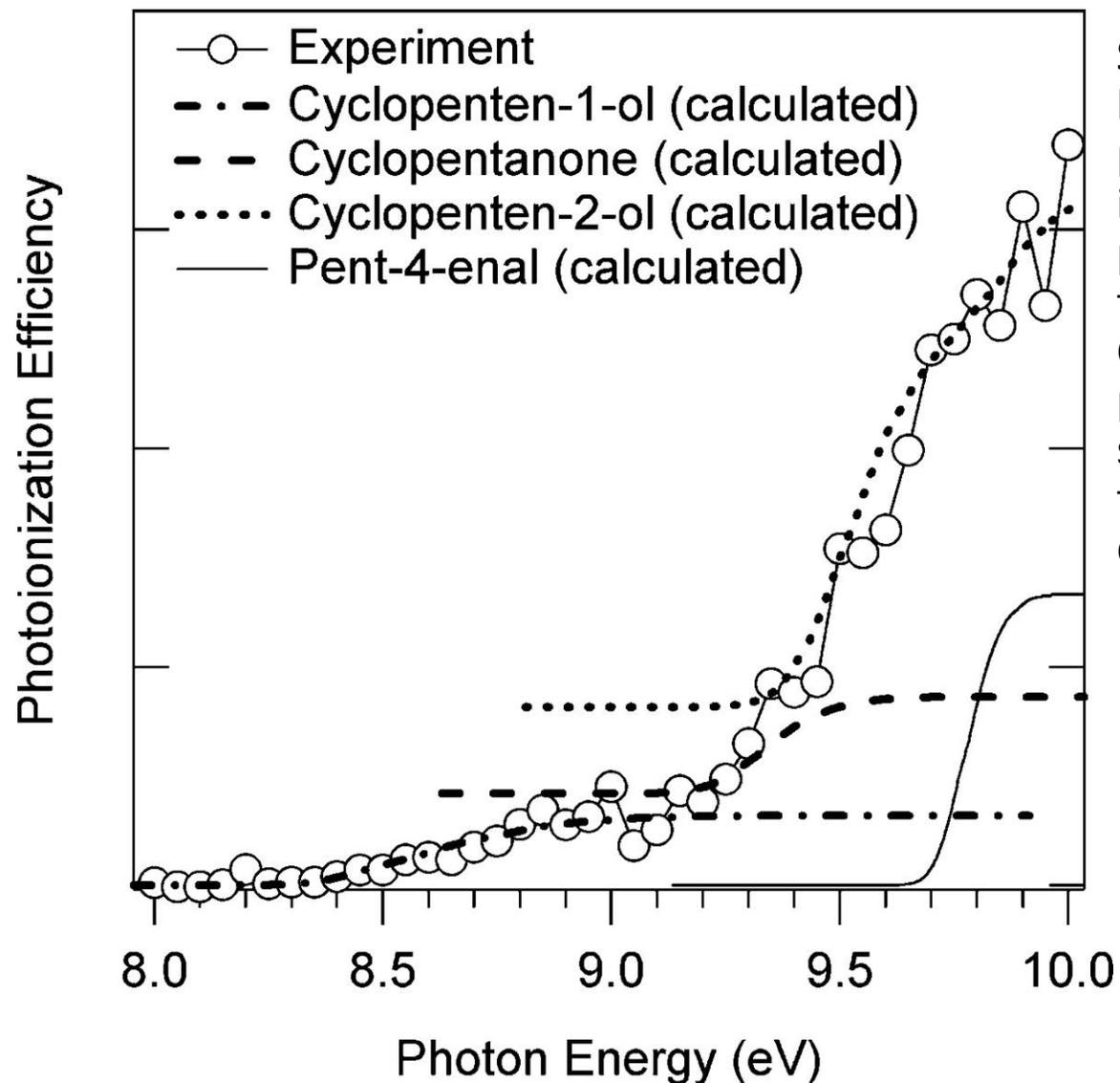
Schematic decomposition of the best fit to the experimental photoionization efficiency spectrum into the substituent calculated photoionization efficiency curves of the three isomers: $1\text{-}c\text{-}C_5H_7OH$, $c\text{-}C_5H_8O$, and $2\text{-}c\text{-}C_5H_7OH$. The isomeric photoionization efficiency curves are scaled by their weighting in the fit to the overall spectrum and vertically displaced for clarity.

Static reactors: Early studies of alkane oxidation kinetics and mechanism by Baldwin, Walker and co-workers

- The techniques rely on end product analysis using gas chromatography. Three techniques were used:
    - Addition of small amounts of alkane, RH, to a slowly reacting $H_{2\,+}$ OH mixture at ~ 750 K allowed measurements of, e.g. OH, H, HO_2 + RH. H_2 + O_2 provides a well-controlled environment containing the radicals. (JCS Faraday Trans 1., 1975, 71, 736)
    - Oxidation of aldehydes (550 – 800 K). Aldehydes act as a source of alkyl radicals, e.g. 2-C_3H_7 from 2-C_3H_7CHO (JCS Faraday Trans 2., 1987, 83, 1509)
    - Decomposition of tetramethylbutane (TMB) in the prsence of O_2. System acts as a source of $HO_{2.}$ (JCS Faraday Trans 1., 1986, 82, 89)

Interaction of elementary reactions in $H_2 + O_2$

- There are three ignition (explosion) limits. In each case, there is a competition between a termination reaction (removing radicals, decelerating the rate) and a branching reaction (accelerating the rate)

- First limit – competition between termination at the wall e.g. H → wall (rate ↑ as pressure ↓) and $H + O_2 \rightarrow OH + O$.

- Second limit – competition between $H + O_2 + M \rightarrow HO_2 + M$ (rate ↑ as pressure ↑) and $H + O_2 \rightarrow OH + O$. HO_2 is an unreactive radical and reacts mainly by $HO_2 + HO_2 + M \rightarrow H_2O_2 + M$.

- Third limit – H_2O_2 dissociates generating OH radicals ($H_2O_2 + M \rightarrow 2OH$) and propagation and branching recommence
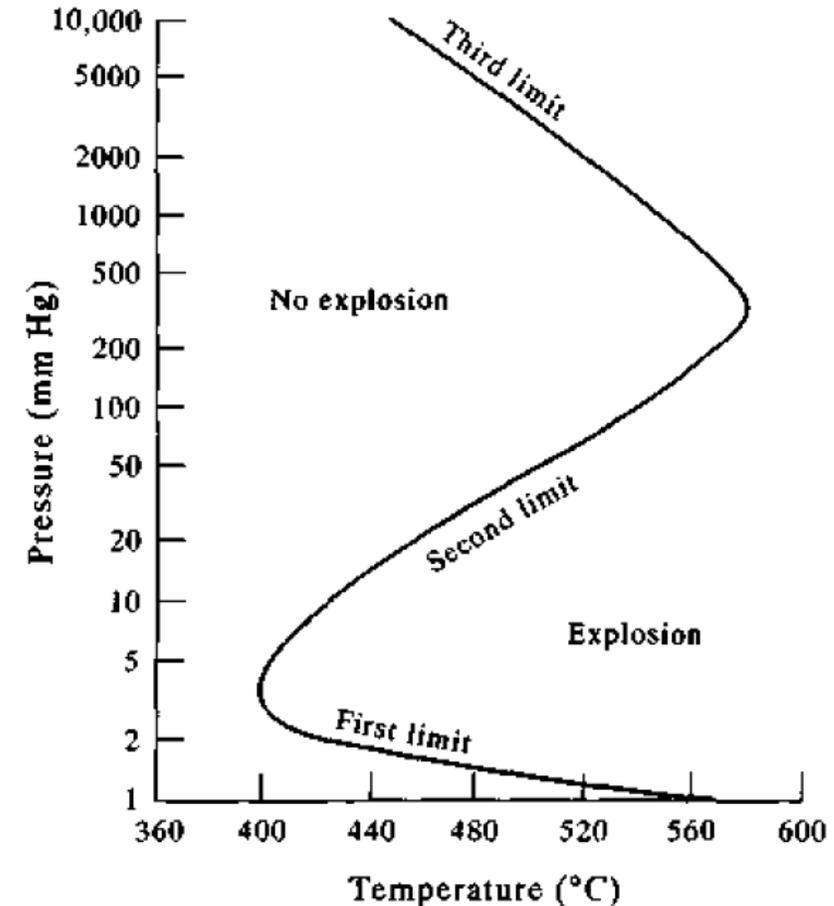
Hydrogen oxygen system

- Review by Miller et al. (Proc Comb. Inst., 2005, 30, 45-88)

- Slide shows sensitivities for ignition delay times (8% H_2, 2% O_2, 90% Ar, 1 bar).

- Note the significance of the $H + O_2$ branching step, the termination step $H + O_2 + M$ and the $H + HO_2$ steps

H + O$_2$ → OH + O
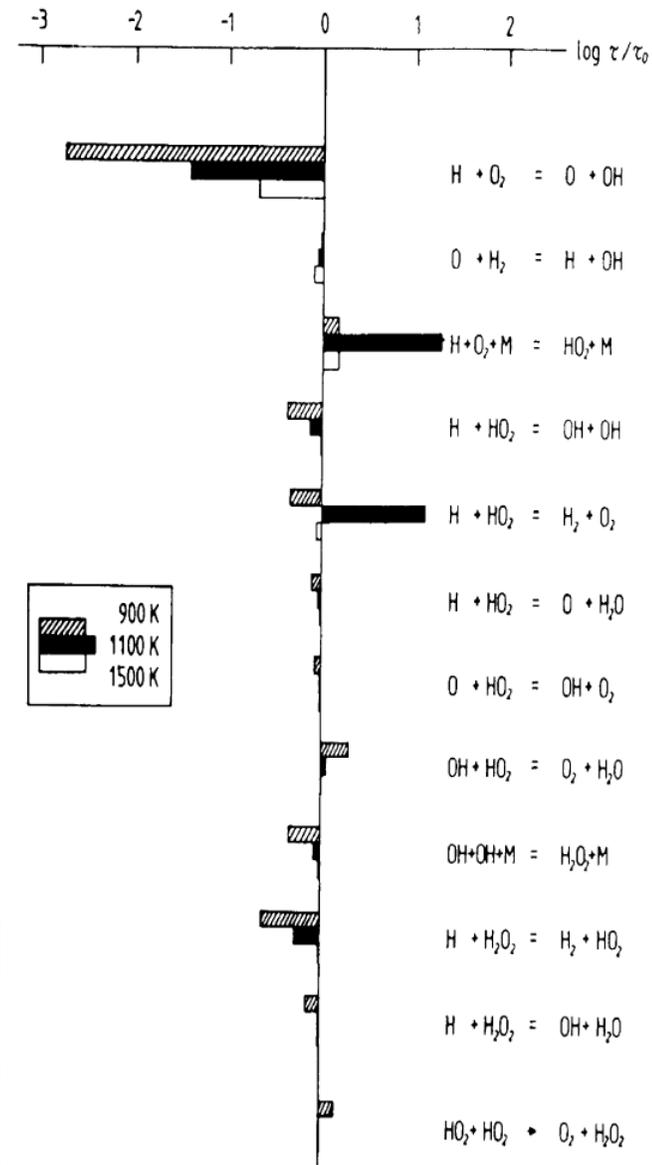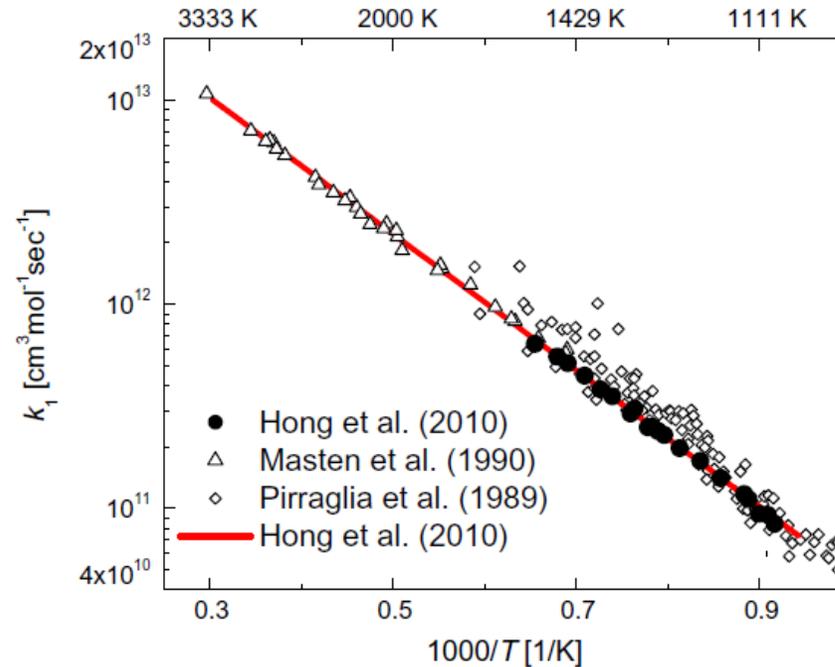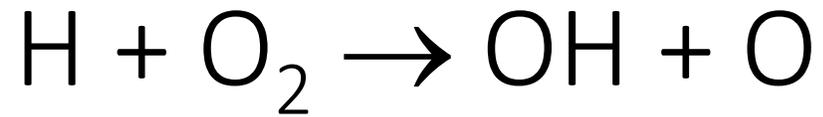
- From Hong et al., shock tube measurements. Comb Flame 2011, 158,633, $k = 1.7 \times 10^{-10} \exp(-7670/T)$ (1100 – 3370 K). Uncertainty ± 10%.

- See Burke et al. Int J Chem Kinet, 2012, 44, 444, who support the rate coefficient

- See discussions on evaluation in later lectures.

Reverse reaction: O + OH $\rightarrow$ H + O$_2$

- Studied 150 – 500 K, mainly by discharge flow / laser flash photolysis.

- Not of great importance in combustion, but provides additional information on reverse reaction through thermodynamics

- k = 2.00x10^{-10} T$^{-0.352}$ exp(113/T) cm^3 molecule^{-1} s^{-1} over the range 250–3000 K.

- Δlog k = ± 0.2 over the range 250–3000 K.

O + OH $\rightarrow$ O$_2$ + H

× Del Greco and Kaufman 1962
⁎ Clyne 1963
● Kaufman and Del Greco 1963
○ Kaufman 1964
■ Westenberg and DeHaas 1965
□ Breen and Glass 1970
▲ Westenberg *et al* 1970
△ Campbell and Handy 1977
▼ Howard and Smith 1980
▽ Lewis and Watson 1980
◆ Howard and Smith 1981
◇ Brune *et al* 1983
⁎ Keyser 1983
– – Smith and Stewart 1994

—— This Evaluation
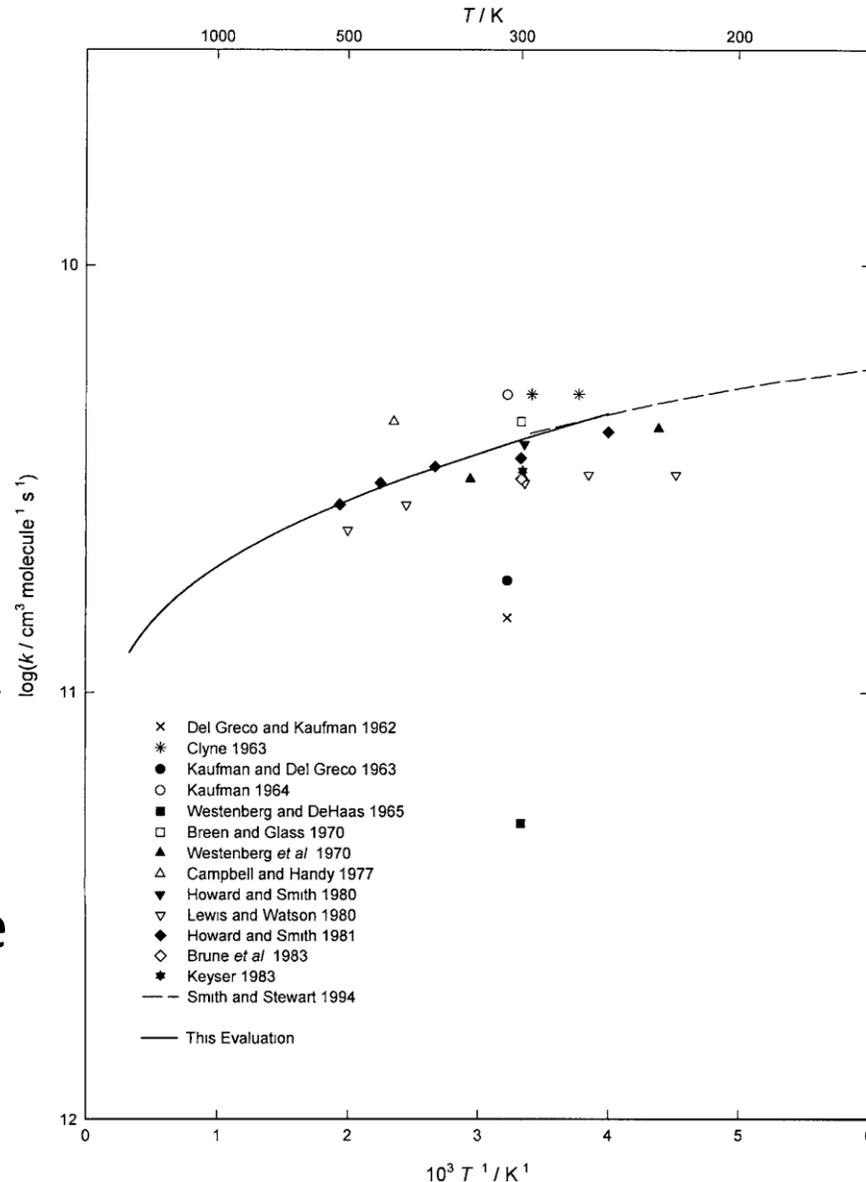
Second branching step
$O + H_2 \rightarrow OH + H$

- Sutherland et al. (21st Symp(Int) Comb, 1986, 929). Used flash photolysis, monitoring O by resonance fluorescence, and shock tube, generating O by flash photolysis of NO and monitoring by ARAS. ()

- Davidson and Hanson (Comb and Flame, 1990, 82, 445) used shock tube, generating O by laser flash photolysis of NO and by pyrolysis of N_2O. O monitored by ARAS
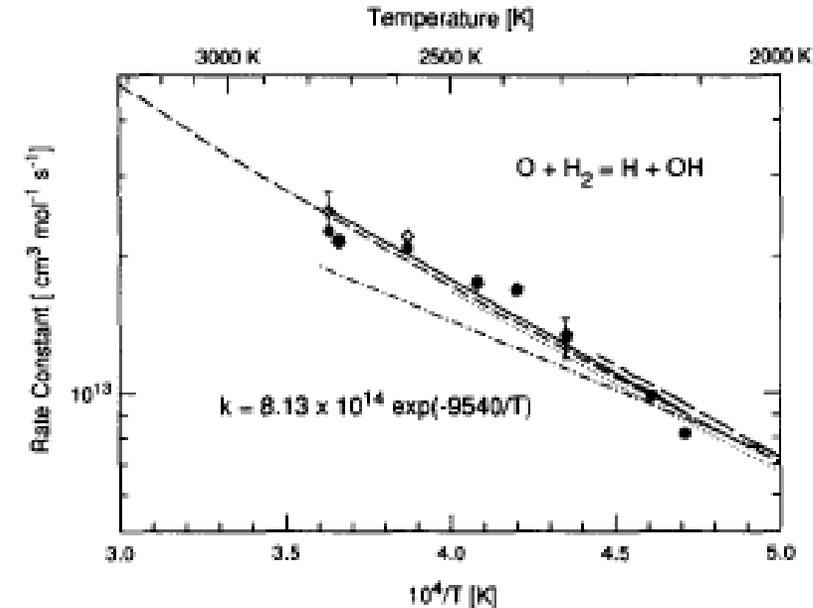

Fig. 2. Arrhenius diagram: $O + H_2 \rightarrow OH + H$. Filled circles—data derived from photolysis method. Open diamonds—data derived from pyrolysis method. Error bars represent ±10%. Solid line—best fit to present data. Dotted line—Sutherland et al. [8]. Dashed line—Nataranjan and Roth [9]. Dot-dashed line—Pamidimukkala and Skinner [10]. Long-dashed line—Shin et al. [11].

H + O$_2$ + M → HO$_2$ + M

- Termination step at lower T, converting reactive H into less reactive HO$_2$. Acts as a route to branching through formation of H$_2$O$_2$ through HO$_2$ + HO$_2$ (and HO2 + RH in hydrocarbon combustion)

- Reaction is at the third order limit except at higher pressures.

- Michael et al. J. Phys. Chem. A 2002, 106, 5297-5313 used flash photolysis at room T for a wide range of third bodies, and a shock tube at higher T for Ar,. O$_2$ and N$_2$. Showed that H$_2$O is an unusually effective third body.

- Detailed analysis of collision frequencies and energy transfer parameters.
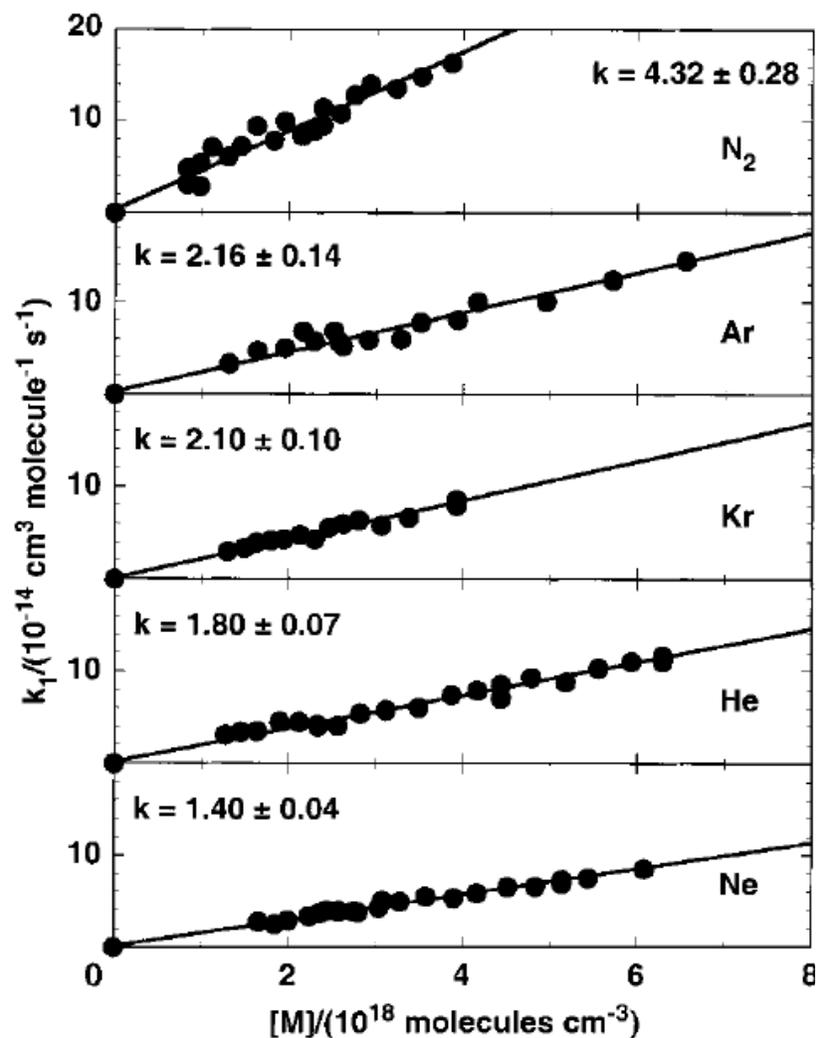
H + O$_2$ + M → HO$_2$ + M

Units of k: 10^{-32} cm^6 molecule^{-2} s^{-1}
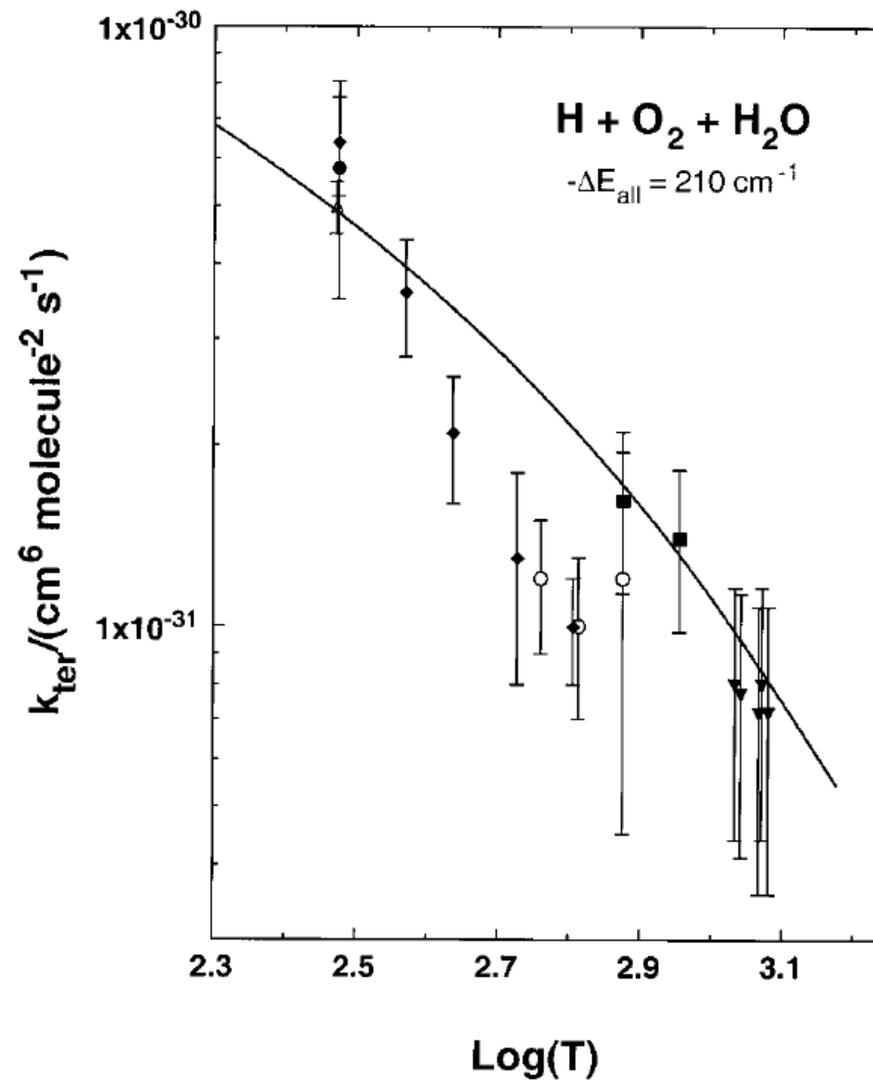
High pressure pulsed photolysis / flow reactor
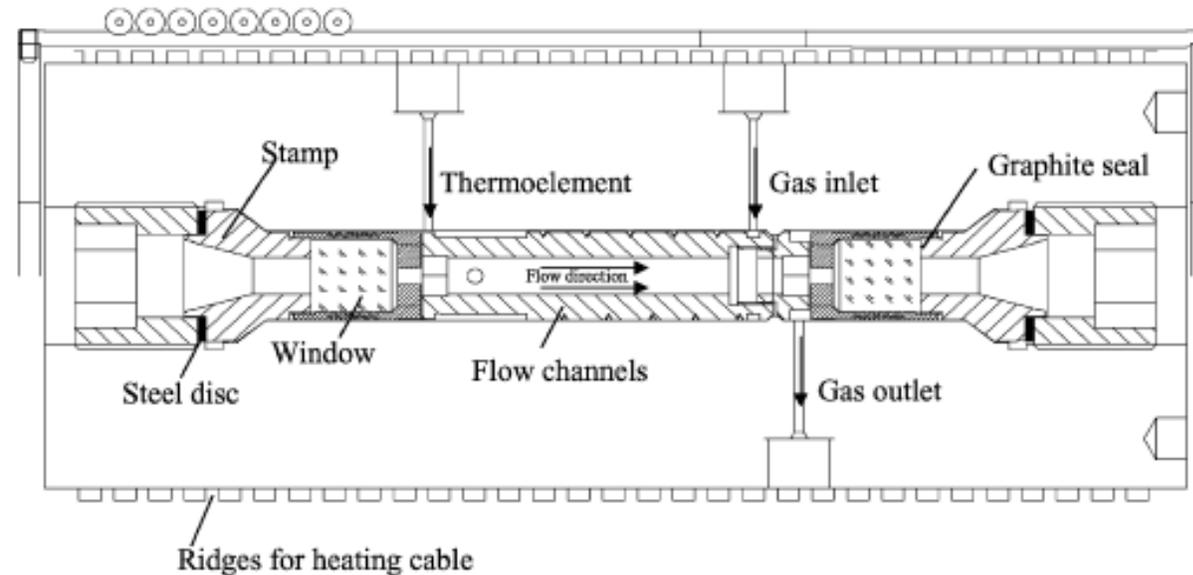
- H + O$_2$ + M → HO$_2$ + M, 300 – 900 K, 1.5 – 950 bar (!)

- H from photolysis of NH$_3$ at 193 nm

- HO$_2$ detected by absorption spectroscopy at 230 nm.

- At these higher pressures, the reaction moves into the fall-off region

H + O$_2$ + M → HO$_2$ + M
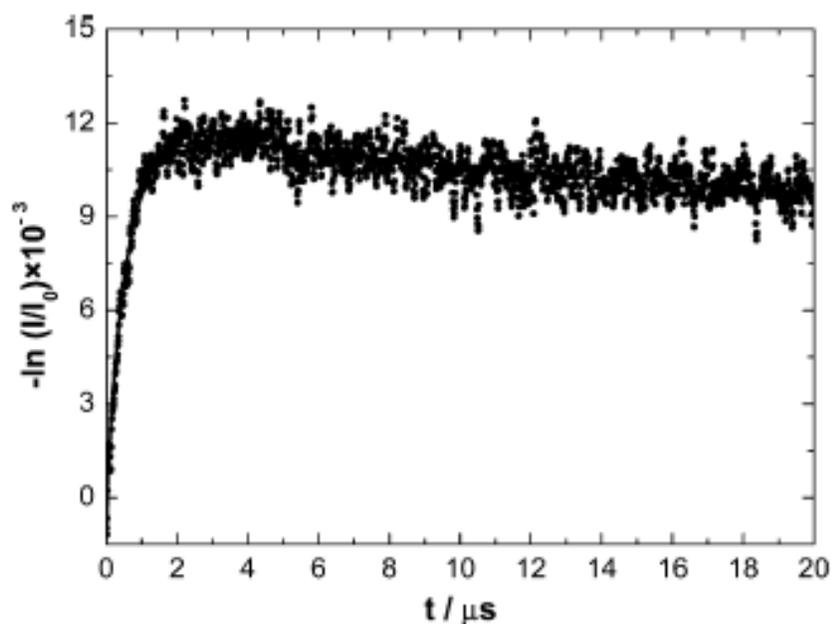
Fig. 2 Absorption–time profile of HO$_2$ (λ = 230 nm, T = 600 K, p = 300 bar, M = N$_2$).
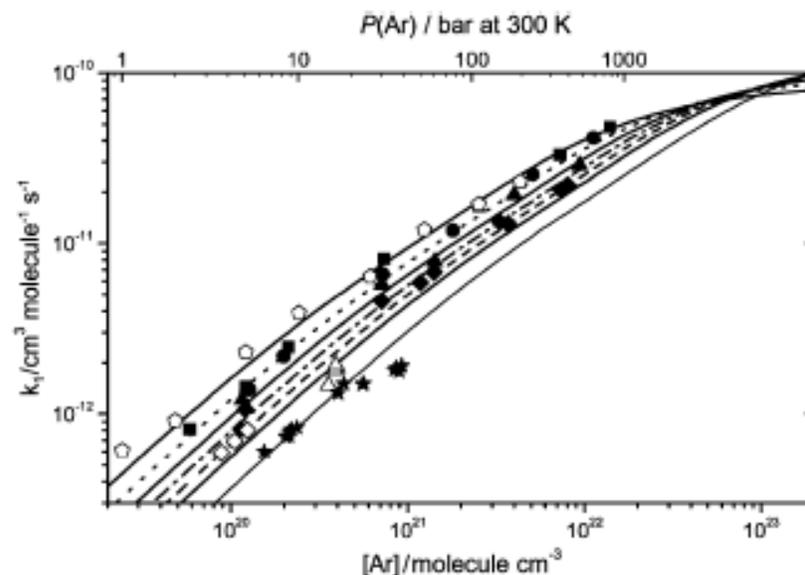
Fig. 5 Falloff curves for the recombination H + O$_2$ (+Ar) → HO$_2$ (+Ar) (representative upper pressure scale for 300 K; T/K = 300 (■), 400 (●), 500 (▲), and 600 (♦) from this work; 300 (⬡, ref. 19), 820 (◇, ref. 20), 1200 (★, ref. 22), and 1325 (△, ref. 21); the fitted curves at left from top to bottom are for T/K = 300, 400, 500, 600, 700, 820, and 1200, resp.).

H + O$_2$ + M → HO$_2$ + M

- Data for different third bodies and temperatures can be rationalised and placed on the same plot using reduced falloff curves. Requires calculation of high pressure limiting rate coefficient (that isn't accessible to experiment for this reaction.)
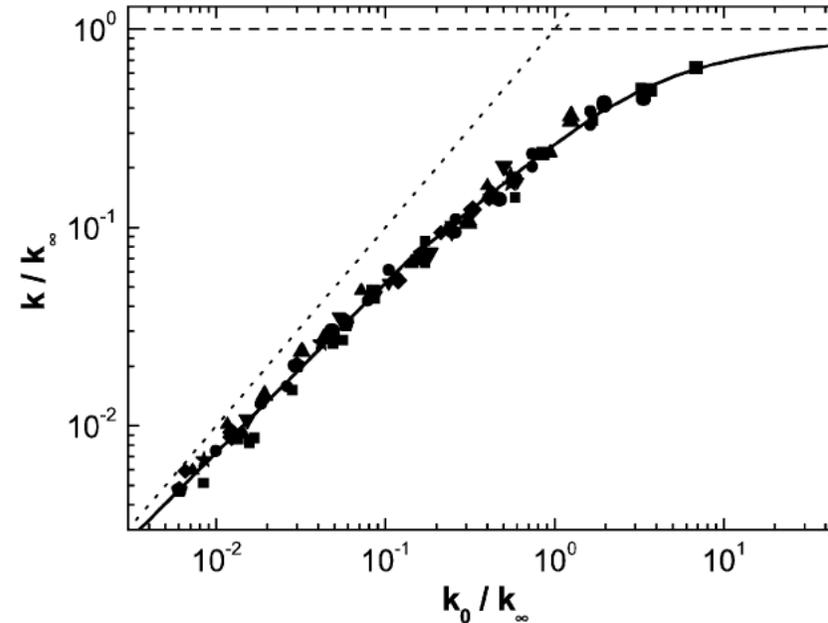
Fig. 7 Doubly reduced falloff curves for the recombination H + O$_2$ (+M) → HO$_2$ (+M) in the bath gases M = He, Ar, and N$_2$ (experimental points from this work from Tables 1–3; T/K = 300 (■), 400 (●), 500 (▲), 600 (▼), 700 (♦), 800 (★), and 900 (⬟), see text).

H + O$_2$ + M → HO$_2$ + M

Most recent evaluation: Burke et al, Int J Chem Kinet 2012, 44, 444
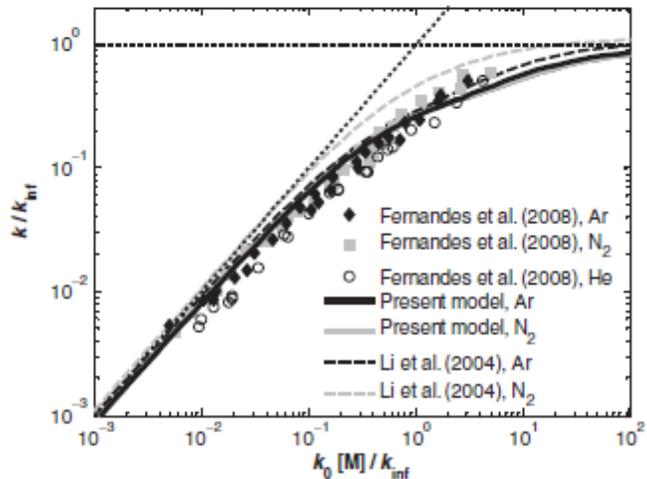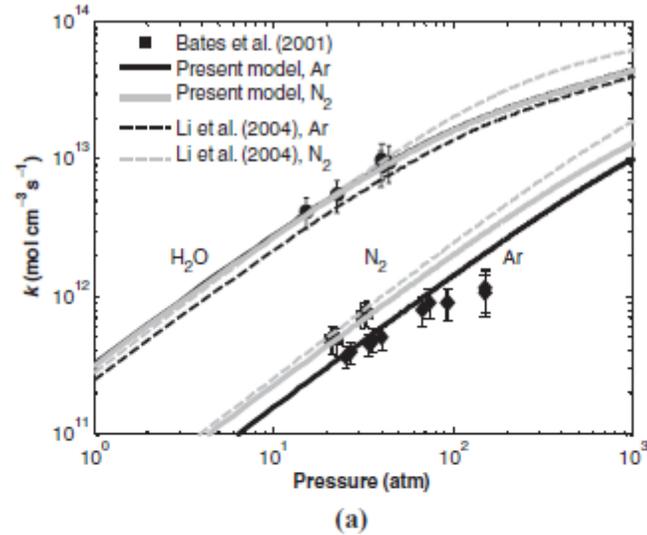
- See paper for detailed discussion of Troe parameters (next slide), uncertainties etc.

Pressure dependent association reactions: simple theory

$$A + B \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} AB^* \xrightarrow{k_s[M]} AB.$$

$$k = \frac{k_a \, k_s[M]}{k_{-a} + k_s[M]}$$

As $[M] \to \infty, k \to k_a = k^\infty$

As $[M] \to 0, k \to \dfrac{k_a k_s[M]}{k_{-a}} = k_0[M]$

$$k = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]}$$

Similar treatment for dissociation reactions

- This is the Lindemann-Hinshelwood model of pressure dependent unimolecular reactions.

- The treatment is an approximation because (i) k_{-a} depends on the energy of AB* (ii) deactivation of AB* takes place in a number of steps.

- These have the effect of *broadening* the fall-ff curve (k vs [M]). These effects have been incorporated in a fitting procedure developed by Troe that is widely used in parameterising rate coefficients for use in combustion modelling

Troe Fitting

Need to represent k(T,P) for Global Models

Standard is Troe Fitting

$$k(T,p) = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]}F \qquad \log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[\dfrac{\log_{10}(p*) + c}{N - d\left(\log_{10}(p*) + c\right)}\right]^2}$$

$$p* = k_0[M]/k^\infty \qquad d = 0.14$$

$$c = -0.4 - 0.67\log_{10} F_{cent} \qquad N = 0.75 - 1.27\log_{10} F_{cent}$$

Fit k_0 & k^∞ to modified Arrhenius $\quad k_0 = A_0 T^{n_0} \exp(-E_0/T)$

Fit F_{cent} to:

$$F_{cent} = (1-a)\exp\left(-T/T^{***}\right) + a\exp\left(-T/T^*\right) + \exp\left(-T^{**}/T\right)$$

HO$_2$ + HO$_2$ $\rightarrow$ H$_2$O$_2$ + O$_2$

- < 800 K. Flash photolysis, absorption spectroscopy

- Open circles: shock tube, absorption spectroscopy (Kappel et al, Phys Chem Chem Phys, 2002, 4, 4392)

- Reference 5: Hippler et al. J Chem Phys 1990, 93, 1755

- Significant disagreement for T > 1000 K

- Burke et al. 'Difficult to discern which, if any, (of the high T) determinations is reliable.' More measurements needed under combustion conditions.
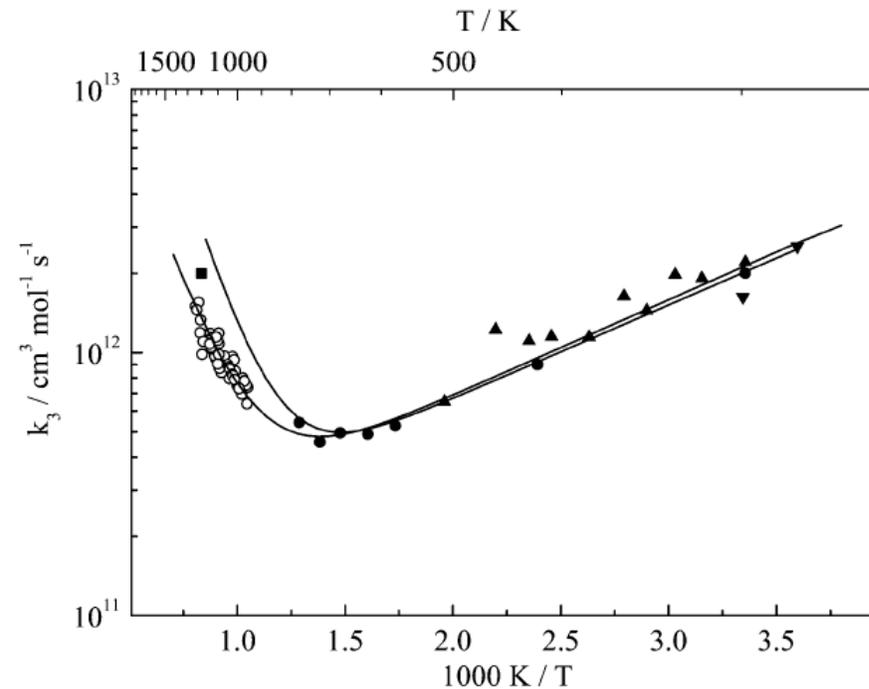

Fig. 10 Rate constants k_3 (■: ref. 2, ▲: ref. 35, ▼: ref. 36, ●: ref. 37, ○ and lower line: this work, upper line: ref. 5).

H$_2$O$_2$ + M $\rightarrow$ 2OH + M
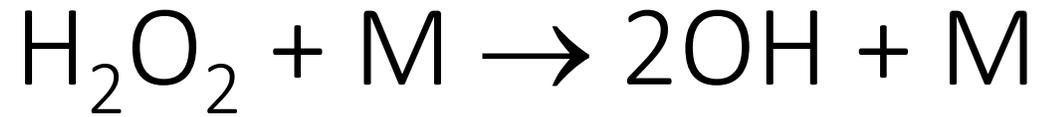
- Troe, Combustion and Flame 2011, 158, 594–601 The thermal dissociation/recombination reaction of hydrogen peroxide H$_2$O$_2$=2OH Analysis and representation of the temperature and pressure dependence over wide ranges.

- Reaction is far from the high pressure limit. To obtain a representation of k(T,p), Troe used the statistical adiabatic channel model to calculate k∞, using an ab initio surface (Phys. Chem. Chem. Phys. 10 (2008) 3915; J. Chem. Phys. 111 (1999) 2565.)

- An important aspect of this work was the use of thermodynamics to relate forward and reverse reactions, using the revised enthalpy of formation of OH – see lecture on thermodynamics

Association reaction OH + OH + M = H2O2 + M

- Flash photolysis coupled with saturated LIF.
- Use pressure dependence to separate from O + H_2O channel
- Also problems with secondary reactions (see paper)
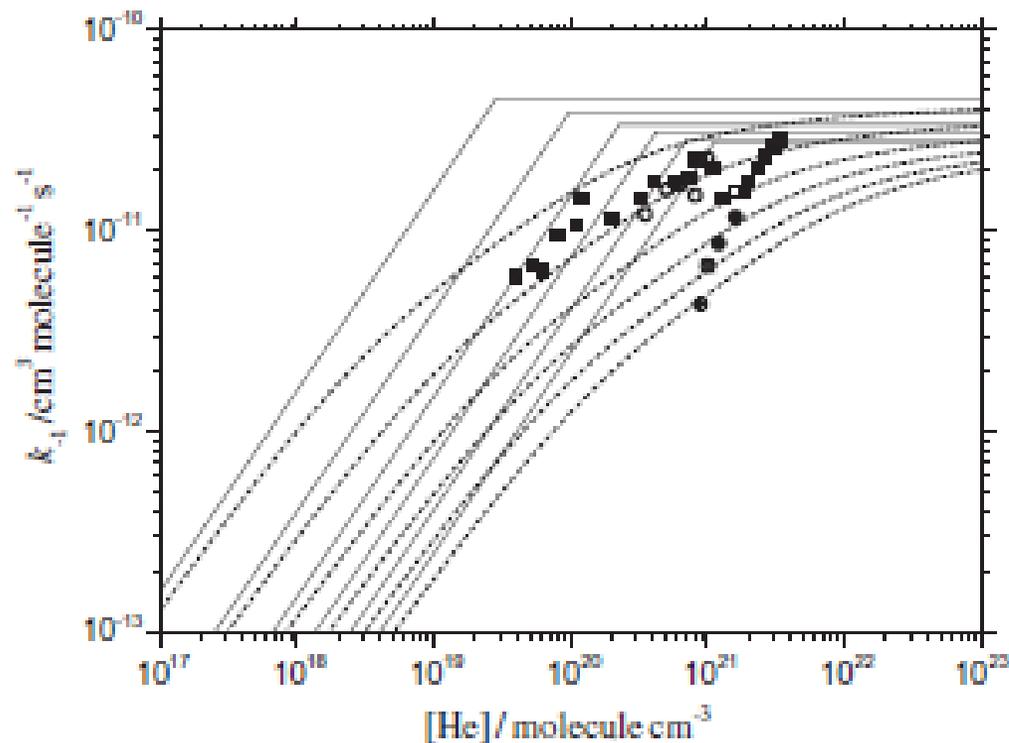
Reaction is second order in radical, so absolute OH Concentration is needed

Fig. 3. Experimental recombination rate coefficients k_{-1} and their modelled falloff representation (M = He, experimental points from Refs. [30,31] at T/K = 210 (○), 298 (■), 406 (□), 510 (●), 614 (⊙), and 694 (⊕); full lines = modelled limiting low and high pressure rate coefficients from Section 5 of this work; dashed lines = falloff representation by Eq. (3.3) with F_c = 0.37 and N = 1.32).

Dissociation reaction

Overall reaction

- Flow reactor and static studies at lower T and shock tube measurements above 950 K (see below)
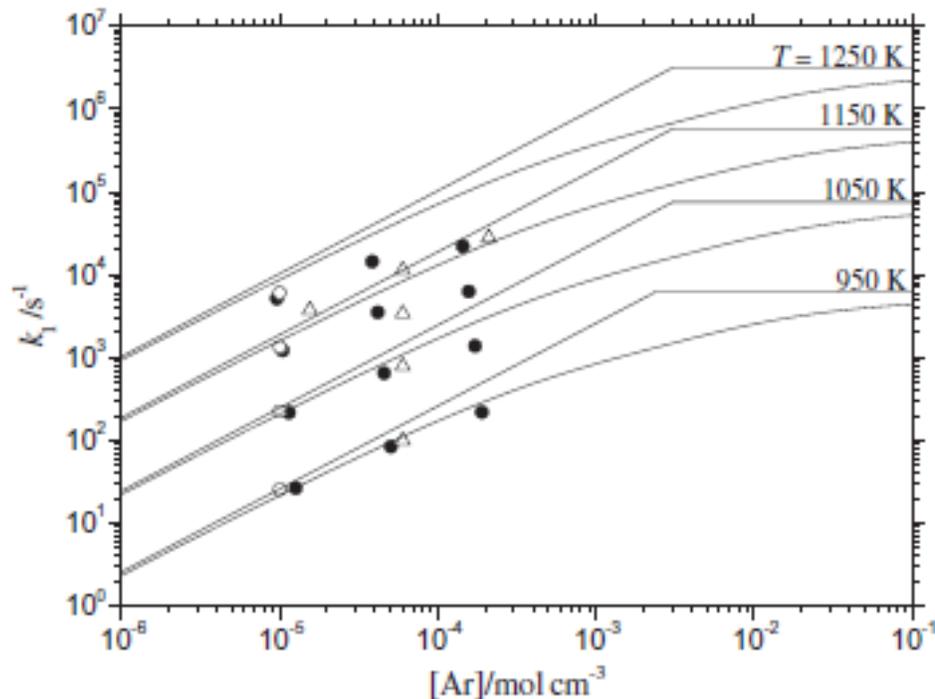
- Dissociation and association data fitted to Troe expression (see earlier) using theoretical high pressure limit and equilibrium constant

H$_2$O$_2$ dissociation
Hong et al. Comb Flame 2011, 158, 633

- Data refer to low pressure limit. Used shock tube with laser absorption detection of H$_2$O and OH
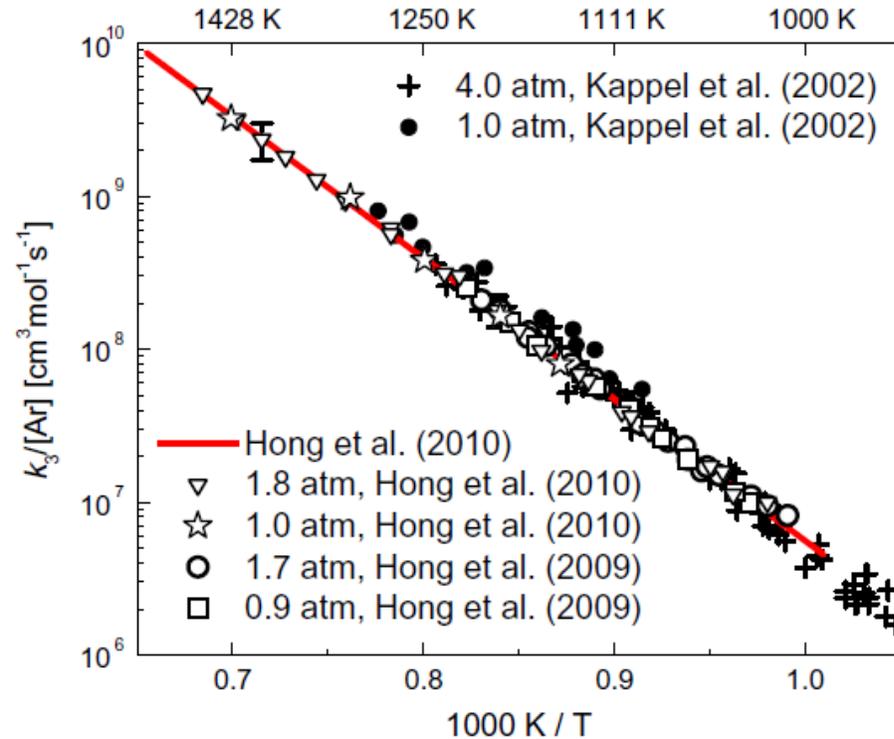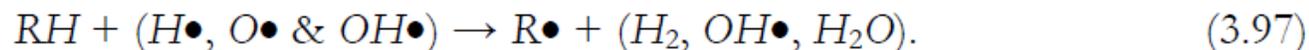
Some important reaction sequences in combustion

3.2.8 Higher Alkane Oxidation at High Temperatures

The high-temperature oxidation of a straight chain hydrocarbon is quite easy to understand. When free radicals are abundant, their reactions with an alkane are exclusively the H-abstraction reactions, i.e.,

$$RH + (H\bullet, O\bullet \& OH\bullet) \rightarrow R\bullet + (H_2, OH\bullet, H_2O). \tag{3.97}$$

The alkyl radicals usually decompose thermally and rapidly. Take propane as an example. The initial H-abstraction reaction may lead to the formation of the *n*-propyl radical,

$$CH_3–CH_2–CH_3 + (H\bullet, O\bullet \& OH\bullet) \rightarrow CH_3–CH_2–CH_2\bullet + (H_2, OH\bullet, H_2O). \tag{3.98}$$
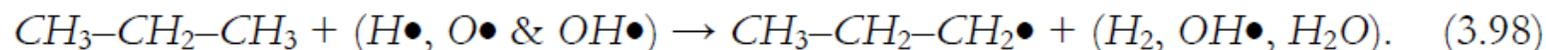
The resulting *n*-propyl radical will largely decompose following the β-scission rule, i.e.,

$$CH_3–CH_2–CH_2\bullet \ (+M) \rightarrow CH_3\bullet + C_2H_4 \ (+M), \tag{3.99}$$
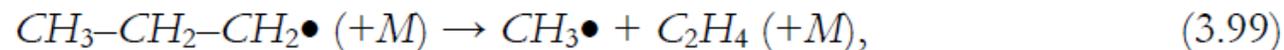
to yield the methyl radical and ethylene. In the case of *i*-propyl, the products of the above sequence of reactions would be propene and the $H\bullet$ atom,

$$CH_3–CH_2–CH_3 + (H\bullet, O\bullet \& OH\bullet) \rightarrow CH_3–CH\bullet–CH_3 + (H_2, OH\bullet, H_2O). \tag{3.100}$$

$$CH_3–CH\bullet–CH_3 \ (+M) \rightarrow H\bullet + C_3H_6 \ (+M), \tag{3.101}$$
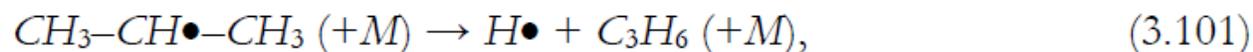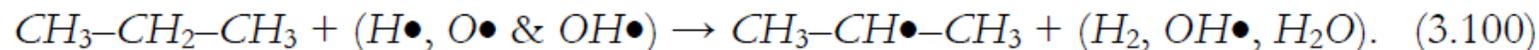
For T>1000 K, fuel radicals rapidly β-scission to alkenes plus smaller radicals.
Main products are ethane, propene, methane, H2

Another example is the *n*-octyl radical.

$$CH_3-CH_2\!\!\nrightarrow\!\! CH_2-CH_2\!\!\nrightarrow\!\! CH_2-CH_2\!\!\nrightarrow\!\! CH_2-CH_2\bullet \ (+M)$$
$$\rightarrow H\bullet + 4\ C_2H_4\ (+M). \tag{3.104}$$
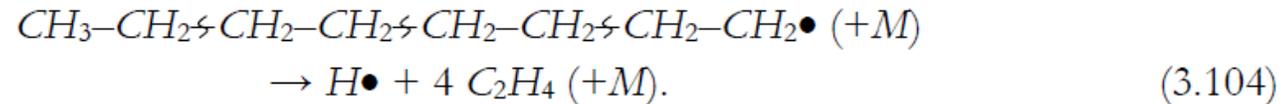
The various *i*-octyl radicals do make things complicated though, e.g.,

$$CH_3\!\!\nrightarrow\!\! CH_2-CH_2\!\!\nrightarrow\!\! CH_2-CH_2\!\!\nrightarrow\!\! CH_2-CH\bullet-CH_3\ (+M)$$
$$\rightarrow CH_3\bullet + 2\ C_2H_4 + C_3H_6\ (+M) \tag{3.105}$$

$$CH_3-CH_2\!\!\nrightarrow\!\! CH_2-CH_2\!\!\nrightarrow\!\! CH_2-CH\bullet-CH_2\!\!\nrightarrow\!\! CH_3\ (+M)$$
$$\rightarrow H\bullet + 2\ C_2H_4 + C_4H_8\ (+M) \tag{3.106a}$$

or

$$\rightarrow CH_3\bullet + C_7H_{14}\ (+M). \tag{3.106b}$$
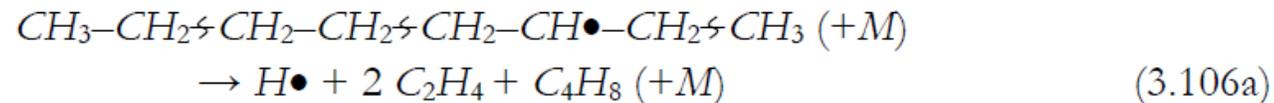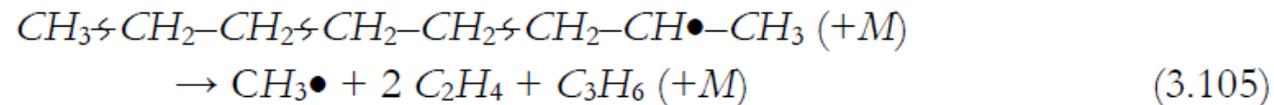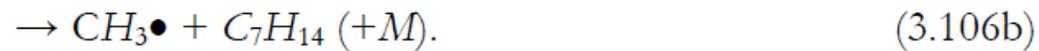
3.2.9 The Oxidation of Ethylene and Other Alkene Compounds

Although very few alkene compounds are present in real fuels, the oxidation of alkene is important to combustion chemistry. In general, alkenes are major intermediates of combustion. They are often formed as the result of β-scission reactions of larger alkyl radicals. In addition, under the fuel rich condition, the oxidation of methane also leads to ethylene formation through the recombination of the methyl radicals,

$$CH_3\bullet + CH_3\bullet \; (+M) \rightarrow C_2H_6 \; (+M) \tag{3.111}$$
$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_5\bullet + H\bullet \tag{3.112}$$
$$C_2H_6 + (H\bullet, O\bullet \; \& \; OH\bullet) \rightarrow C_2H_5\bullet + (H_2, OH\bullet, H_2O) \tag{3.113}$$
$$C_2H_5\bullet \; (+M) \rightarrow C_2H_4 + H\bullet \; (+M). \tag{3.114}$$
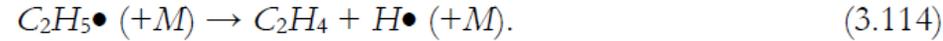
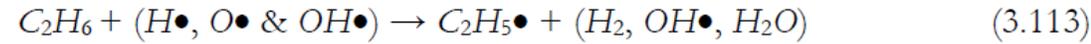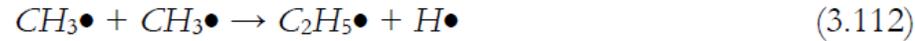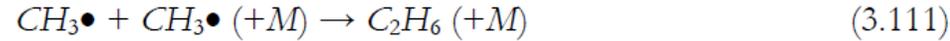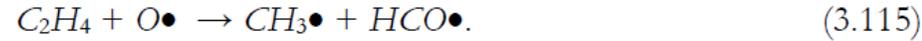Unlike the single σ C–C and C–H bond in alkanes, the π bond in ethylene is susceptible to attack by the $O\bullet$ atom,

$$C_2H_4 + O\bullet \rightarrow CH_3\bullet + HCO\bullet. \tag{3.115}$$

In addition, the H-abstraction of C_2H_4 by the $H\bullet$ and $OH\bullet$ radical leads to the formation of the vinyl ($C_2H_3\bullet$) radical,

$$C_2H_4 + (H\bullet \; \& \; OH\bullet) \rightarrow C_2H_3\bullet + (H_2 \; \& \; H_2O), \tag{3.116}$$
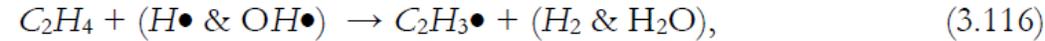
which is oxidized through

$$C_2H_3\bullet + O_2 \rightarrow CH_2O + HCO\bullet \tag{3.117}$$
$$C_2H_3\bullet + O_2 \rightarrow CH_2CHO\bullet + O\bullet \tag{3.118}$$
$$CH_2CHO\bullet \; (+M) \rightarrow CH_3O\bullet + CO \; (+M). \tag{3.119}$$

103
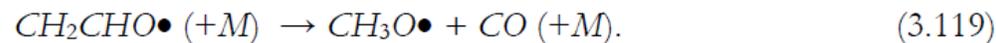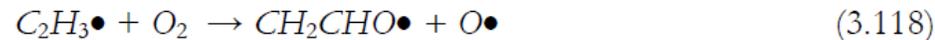
If enough O2 present, C2H3 burns. Otherwise…

Under the fuel rich conditions, the lack of sufficient molecular oxygen means that reactions (3.117) and (3.118) would be quite slow. Therefore the vinyl radical undergoes thermal decomposition to yield acetylene,

$$C_2H_3\bullet\ (+M)\ \rightarrow\ C_2H_2 + H\bullet\ (+M). \tag{3.120}$$
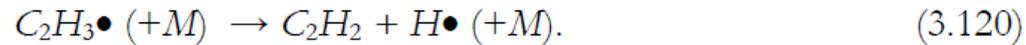
Thermodynamically acetylene is always favored as an end product, in addition to CO and solid carbon, under the fuel rich combustion of hydrocarbon fuels.

Much of the carbon in normal fuels forms C2H4 and then C2H3.
If enough O2 is present it burns cleanly. If not, it probably forms C2H2.

A build-up of C_2H_2 is likely to lead to soot formation.

Soot is very toxic, leading to the premature deaths of tens
of thousands of people each year.

So C_2H_3 is at a critical branch point in fuel chemistry…

Fuel Rich vs. Fuel Lean

- If system is fuel lean, at equilibrium almost all the carbon will be in form of CO2.

- If the system is fuel rich, even if we consume all the O2 we will have some CO or H2 or unburnt fuel left over. But if O:C ratio is greater than 1:1 we would not normally make soot at equilibrium (but maybe we would form it kinetically).

- If O:C ratio is less than 1:1, almost all the O atoms will end up as CO at equilibrium. In this case, the final temperature will be much lower than in normal combustion (normally CO burning to CO2 and H2 burning to H2O release a lot of energy as heat).

- In this very rich case, we have C atoms left over after all the O atoms are gone. These are likely to end up as soot at equilibrium.

Table 3.3 Primary Sources of Air Pollutants

Pollutant	Combustion sources	Other sources	Major effects
HC	Gasoline engines Incineration Fires	Fuel evaporation Organic solvents	Photochemical smog Reduced combustion efficiency Green house effects
CO	Gasoline engines	Industrial process	Toxic, lethal at high dosages photochemical smog
NO_x	Motor vehicles	Chemical processes	Photochemical smog Acid rain Respiratory illness Skin and eye irritation
SO_x	Electricity generation Industrial boilers	Chemical processes	Acid rain Respiratory illness
Particulates (soot)	Electricity generation Diesel engines		Global climate Toxic (skin cancer) Respiratory illness
CO_2	All hydrocarbon combustion	Deforestation	Green house effects

In general, acid rain problem is more severe in the eastern part of the U.S where the Ph level of rain water is around ~ 4.5. In some regions, a Ph level of 3 is common. The principal cause is coal combustion.
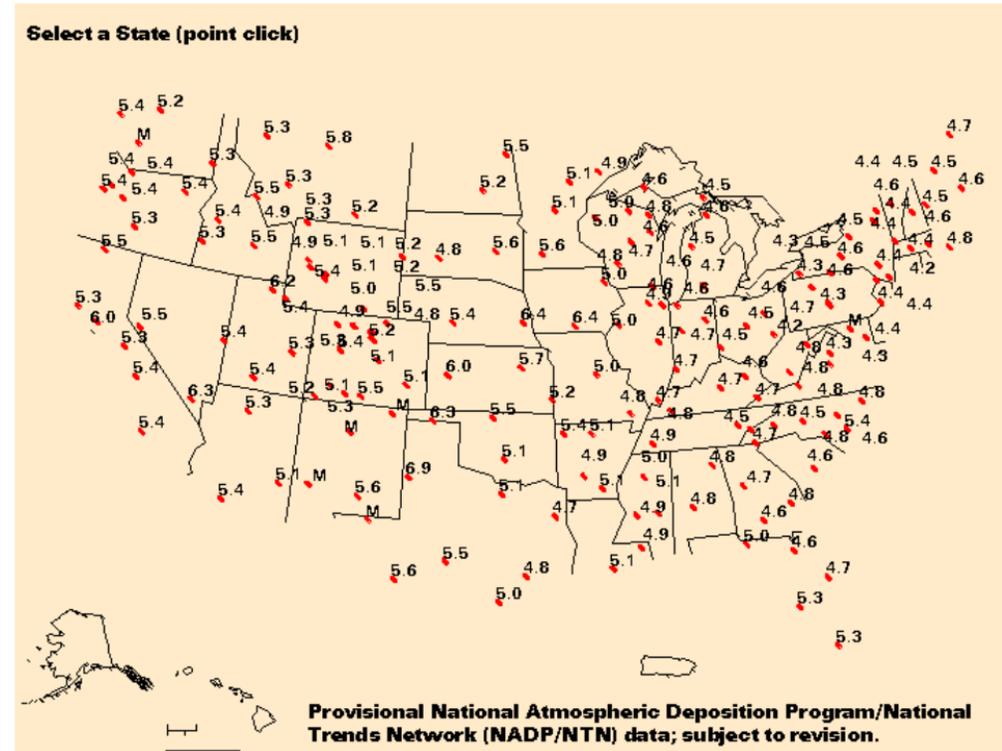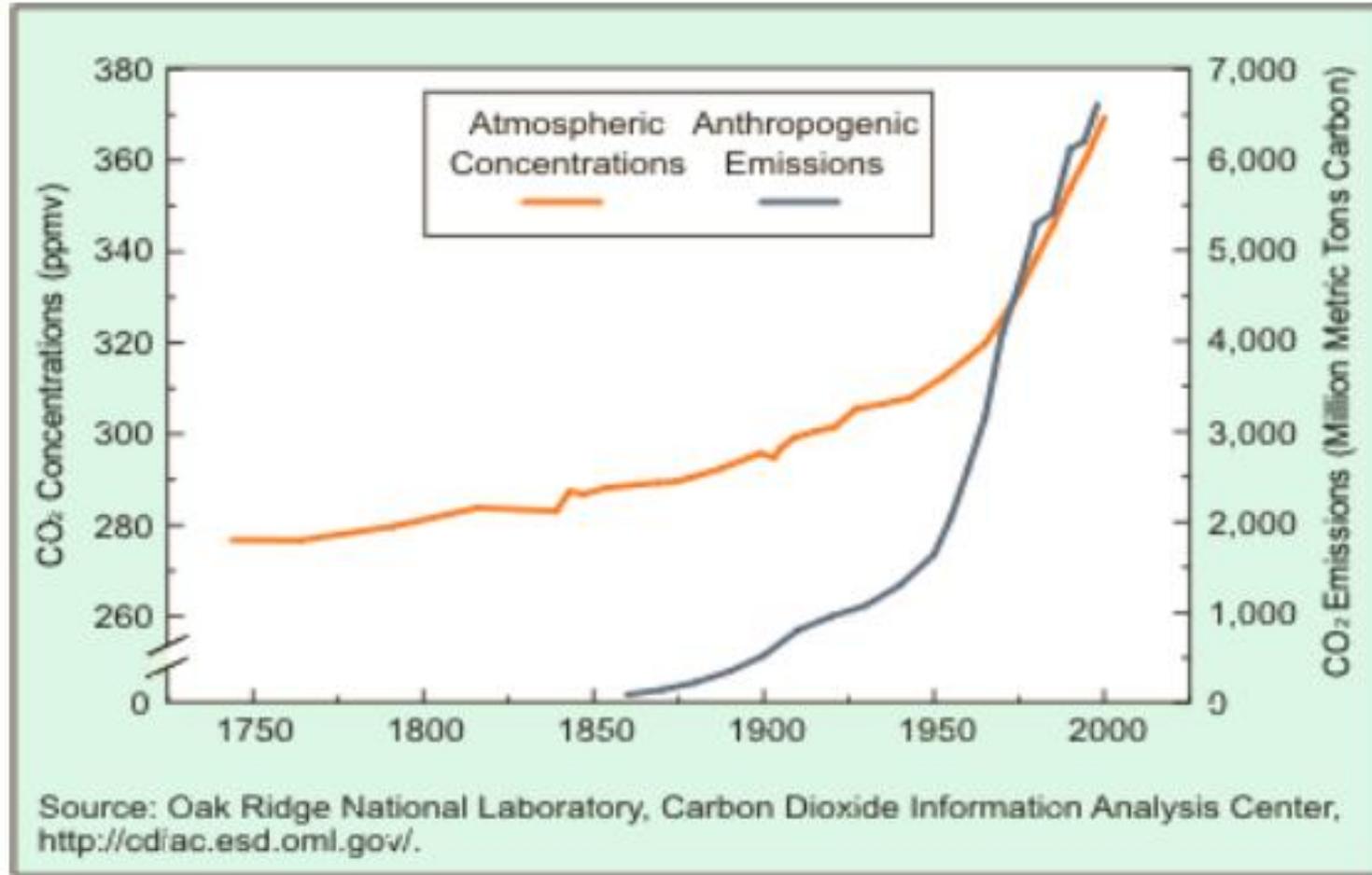
Acid Rain
from SOx
and NOx
Mostly from
Coal combustion

In 2001, most
Rainwater in
Eastern USA
had pH~4.5

SO_2 is toxic to
humans.

NOx drives
Photochemical
Smog reactions
(urban air pollution)

Figure 3.10. pH of Precipitation for November 26, - December 23, 2001 (taken from http://water.usgs.gov/nwc/NWC/pH/html/ph.html)

Acid rain causes acidification of lakes and streams and contributes to damage of trees at high elevations (for example, red spruce trees above 2,000 feet) and many sensitive forest soils. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation's cultural heritage. Prior to falling to the earth, SO_2 and NO_x gases and their particulate matter derivatives, sulfates and nitrates, contribute to visibility degradation and harm public health.

http://www.epa.gov/air/topics/comeap.html

Humans are dumping a lot of CO_2 into atmosphere. Driving [CO_2] to much higher-than-normal levels. Stopping this is Huge technical challenge for combustion scientists.

Source: Oak Ridge National Laboratory, Carbon Dioxide Information Analysis Center, http://cdiac.esd.oml.gov/.

Historically, perfect agreement between [CO2] and T, as expected from greenhouse effect calculations.
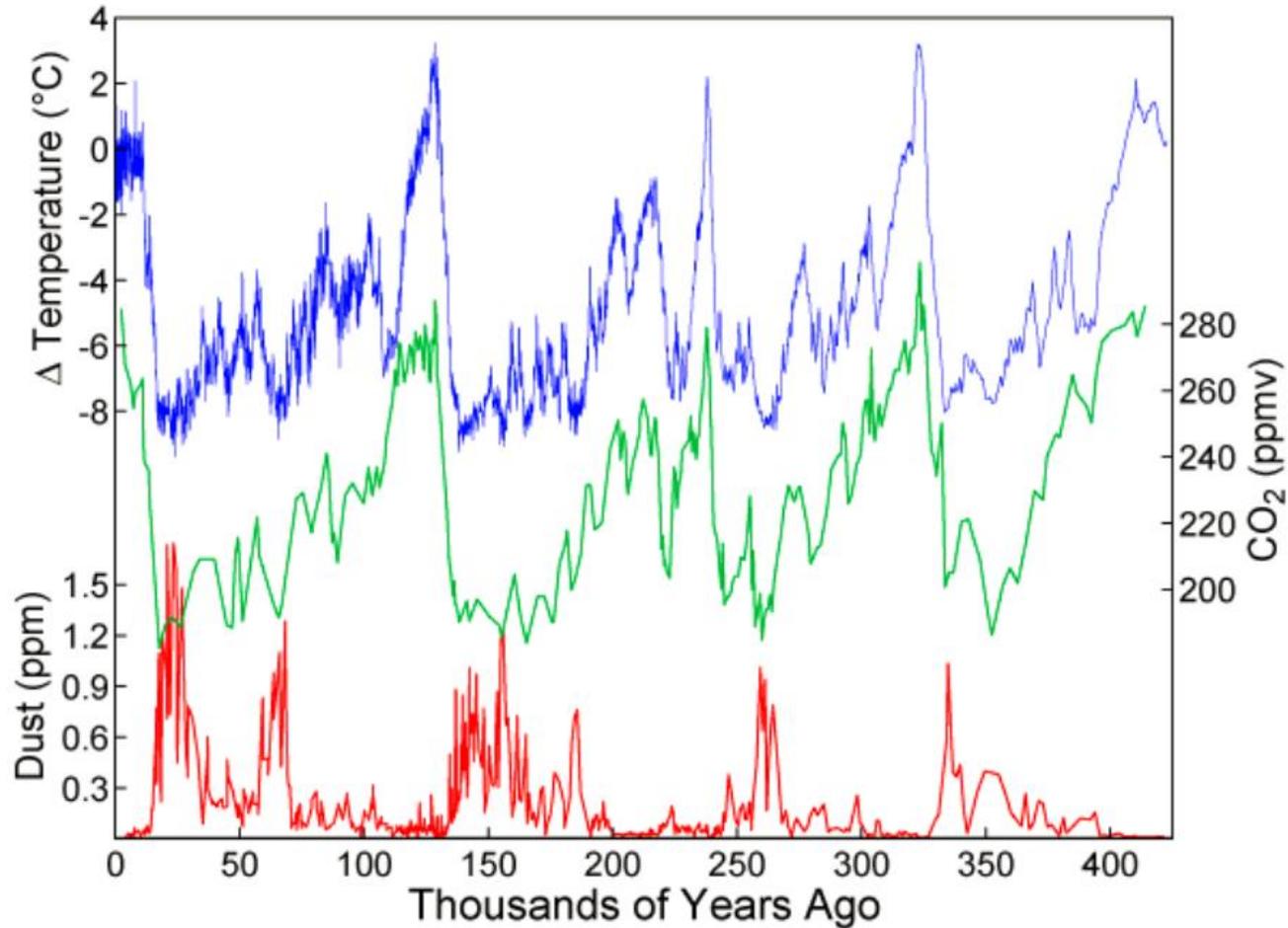

Figure 3.12 Variation of temperature (top), CO_2 (middle), and dust (bottom) levels over the last 400,000 years (adapted from http://en.wikipedia.org/wiki/Image:Ice_Age_Temperature.png).

We'll Run out of Atmosphere Before we Run out of Carbon…

- Financial Times, last week noted
- Climate scientists calculate we can put X gigatons of carbon as CO2 into atmosphere before causing huge climate disruption
- Most of the world's governments agree with that assessment
- Fuel companies have identified Y gigatons of fossil fuel carbon underground, called "proven reserves". Investors value fuel companies based on their proven reserves. Y > X.
- So either we will burn the proven reserves, justifying the stock price, but wrecking the climate… or
- A lot of investors (e.g. pension funds) have purchased fossil carbon that can never be burned….someone is going to lose a lot of money (maybe your pension?)
- ***Humans are inconsistent***: we want to maintain the climate, but we also want to burn fuel to travel and for electricity, and we are willing to pay a lot of future fuel.

Summary of Part 1: Overview, Chem Basics

- Fuels are both Boon and Bane
  - Fuels especially Oil are fantastic cheap-to-produce high-density energy carrier
  - Current system not sustainable, esp. greenhouse and human health
  - Challenge to come up with effective, affordable, less harmful alternative fuels (or alternative energy storage methods) suitable for transportation
- Fuel Combustion Chemistry is Tricky (not Arrhenius single step!!)
  - e.g. $H+O_2 = OH + O$ vs. $H+O_2+M = HO_2+M$ gives weird T,P dependence
  - Need to look into details to understand why fuels behave differently
- Many clever (tricky) methods for experimentally measuring rates
  - But you cannot measure everything…
- Part 2: Intro to Thermochemistry and Rate Theory