

Syllabus and References for Lectures on Reaction Kinetics and Modelling Chemical Processes in Combustion,

Prof. Alison Tomlin, Cambridge, July 2019.

Syllabus

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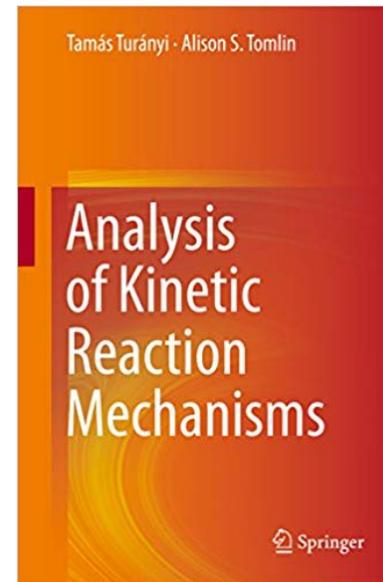
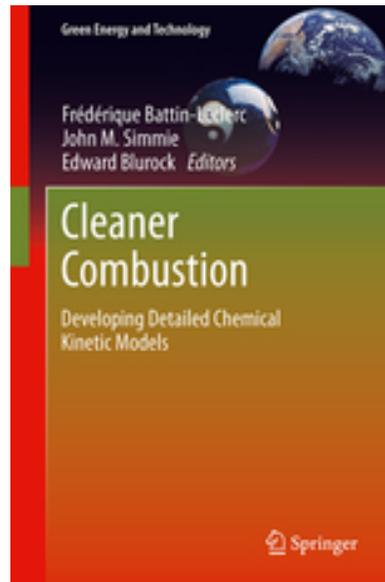
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Reaction Kinetics and Modelling Chemical Processes in Combustion

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MODELLING FUNDAMENTALS



- ***Cleaner Combustion Developing Detailed Chemical Kinetic Models***, Editors: **Battin-Leclerc, Frédérique**, **Simmie, John M.**, **Blurock, Edward** (Eds.), Springer, 2013.
- ***Analysis of Kinetic Reaction Mechanisms***, Tamás Turányi, Alison S. Tomlin, Springer, 2015.
- + List of references provided with syllabus.

What is the purpose of a model?

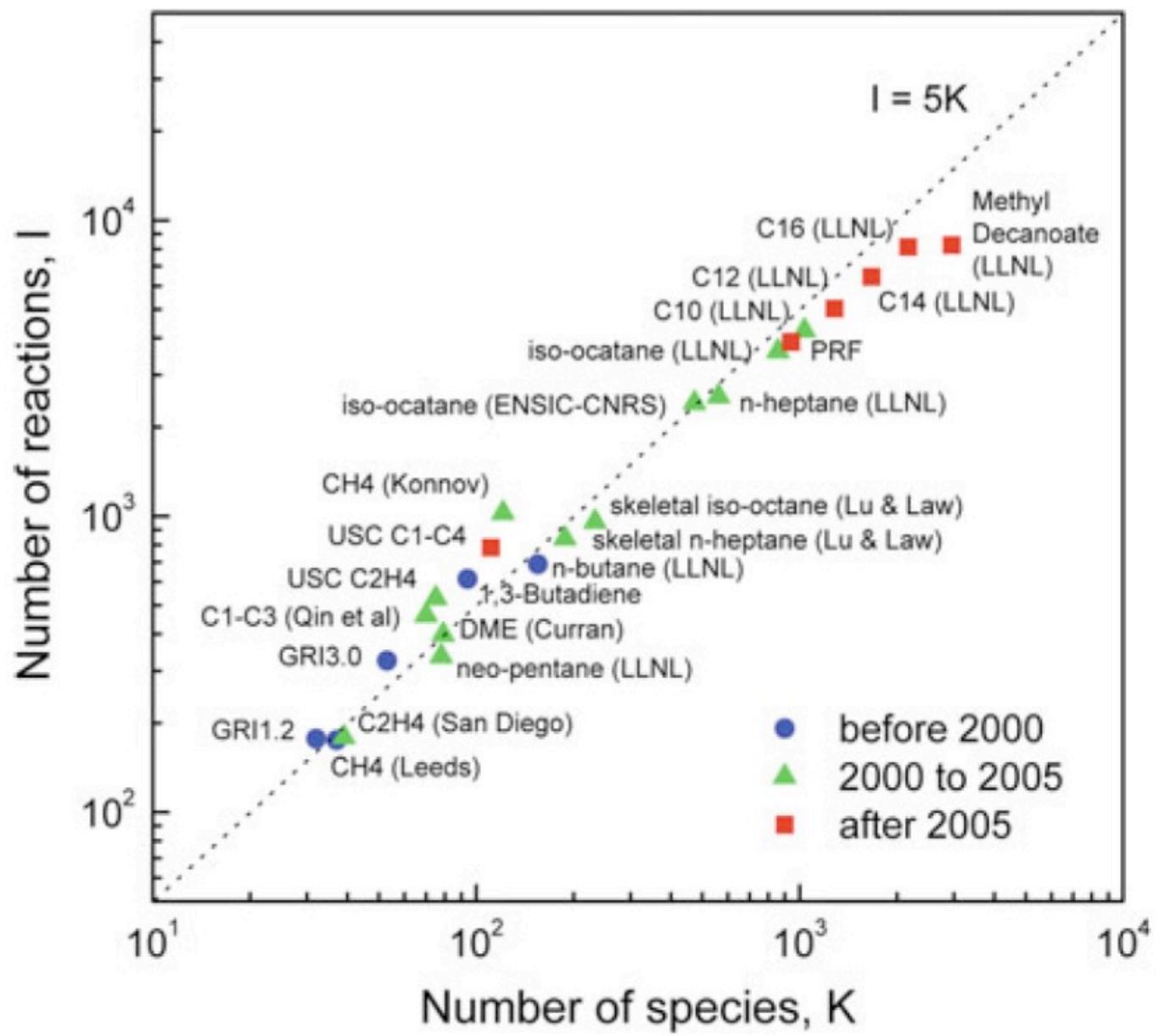
- A model is an *interpretation* and an *approximation* of physical reality.
- A construction which helps us to understand the governing principles behind physical/chemical phenomena we are trying to describe.
- We also need it to make predictions about physical behaviour.
 - means telling us *things we do not yet know or have not yet measured*.
 - **potentially saving time and money performing experiments.**
- Therefore a model needs to be **general enough to predict** across a wide range of conditions (temperatures, pressures, equivalence ratios).
- Not easy to achieve when data sets used in **model evaluation** are time consuming and expensive to obtain.
- There is only one physical reality, but there can be a **large number of models** representing it.
- We might expect that the more fundamental the model, the closer it might become to reality. **Is this true?**

Historical development of combustion models

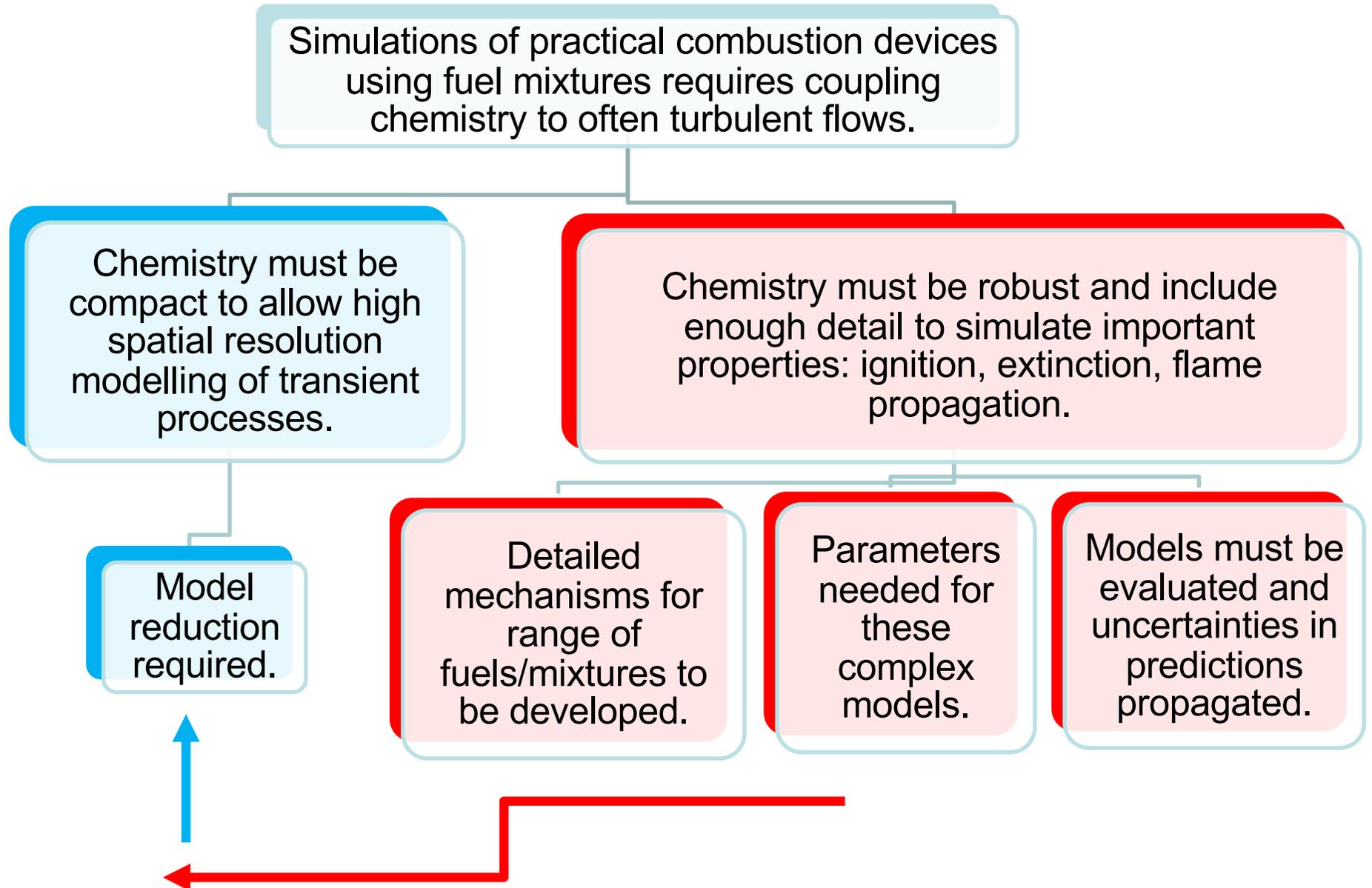
(Blurock & Battin-LeClerc, Cleaner Combustion, 2013)

- The more complex the model, the larger number of parameters it contains; a lot of work has to be done to quantify them.
- In combustion, tendency for models to become more and more complex as our understanding of fundamental processes improves.
- Semenov's theory of chain mechanisms and thermal explosions (Semenov 1935, 1958) was really the start of the modern science of combustion including **detailed reaction chemistry**.
- Nowadays a mechanism describing a complex bio-fuel may have 10 thousand reactions.
- To model a real combustion device **chemical kinetics** needs to be **coupled** to descriptions of **laminar or turbulent flows**.

Lu & Law
(2009)



Narrative of lectures...in reverse...



Overview

- Section 1 - Reaction kinetics basics
- Section 2 – Ignition phenomena and low, intermediate and high temperature chemistry, validation through experiment
- Section 3 – Laminar flames, burning velocities and flame speeds
- Section 4 – Model uncertainties and sensitivity analysis
- Section 5 – Chemical model reduction.

SECTION 1

REACTION KINETICS BASICS

1.1 Chemical mechanism structure

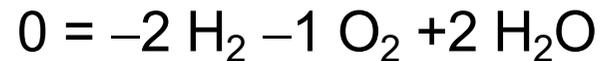
- The ***overall reaction equation*** for a chemical process can be described by a single stoichiometric equation. The stoichiometric equation defines the molar ratio of the reacting species and the reaction products.



- In real systems reactants reacting with each other forming products immediately, is very rare.
- In most cases, ***intermediates are produced*** which react with each other and the reactants, with the final products formed at the end of many coupled reaction steps.
- Each individual step is called an ***elementary reaction***. Within elementary reactions, there is no macroscopically observable intermediate between the reactants and the products.



- Reaction stoichiometry 2:1:2 describes ratio of hydrogen, oxygen, water molecules.
- By re-arranging, all terms can be shifted to the right hand side:



- Any multiple of this equation is also true.
- If we denote the formulae of the chemical species by the vector $\mathbf{A} = (A_1, A_2, A_3)$, and the corresponding multiplication factors by vector $\mathbf{v} = (v_1, v_2, v_3)$. In this case $A_1 = \text{„H}_2\text{“}$, $A_2 = \text{„O}_2\text{“}$, $A_3 = \text{„H}_2\text{O“}$, and $v_1 = -2$, $v_2 = -1$, $v_3 = +2$. The corresponding general stoichiometric equation is:

$$0 = \sum_{j=1}^{N_S} v_j A_j$$

where N_S is the number of species.

- The general stoichiometric equation of any chemical process can be defined in a similar way, where v_j is the stoichiometric coefficient of the j -th species, and A_j is the formula of the j -th species in the overall reaction equation.

Stoichiometric conditions and equivalence ratio

- Under stoichiometric conditions just enough oxidiser is available to completely burn the fuel to form CO₂ and H₂O.
- E.g. for methane and propane:



- For any general condition we can also define the Air/Fuel ratio – AFR, or the Fuel/Air ratio FAR.

$$\text{AFR} = \frac{m_{air}}{m_{fuel}}, \quad \text{FAR} = \frac{1}{\text{AFR}}$$

- The fuel-air equivalence ratio ϕ defines the actual conditions relative to the stoichiometric ones.

$$\phi = \frac{m_{fuel}/m_{ox}}{\left(m_{fuel}/m_{ox}\right)_{stoich}}$$

- $\phi = 1$ stoich; $\phi < 1$ lean; $\phi > 1$ rich.

Time dependence

- The time dependant behaviour of an *isothermal chemical system* for the simplest practical case of one or more reactants reacting in a **well-mixed** vessel to form one or more products over time can be described as:

$$r = \frac{1}{\nu_j} \frac{dY_j}{dt}.$$

r is the reaction rate and Y_j is the mass or molar concentration of the j -th species.

- Within a narrow range of concentrations, the reaction rate r can always be approximated by the following equation:

$$r = k \prod_{j=1}^{N_S} Y_j^{\alpha_j}$$

where the positive scalar k is the reaction rate coefficient, the exponents α_j are positive real numbers or zero, the operator \prod means that the product of all terms behind it should be calculated.

- k is independent of concentrations, but may depend on T , P , and the quality and quantity of the nonreactive species present (for example an inert dilution gas or solvent). Hence the term **rate coefficient** is preferred to rate constant.

Reaction order

The exponent α_j is called the reaction order with respect to species A_j . The sum of these exponents:

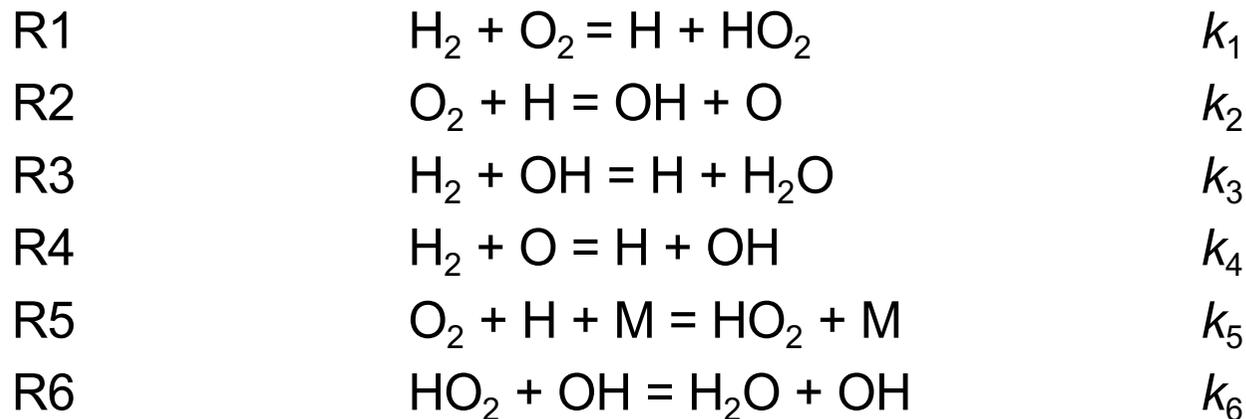
$$\alpha = \sum_{j=1}^{N_s} \alpha_j$$

is the overall order of reaction.

In the case of a global reaction equation such as $2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O}$, the order is not usually equal to the stoichiometric coefficient ν_j since there are intermediate steps in the system. For elementary reactions, the reaction order and the stoichiometric coefficient are commonly mathematically the same.

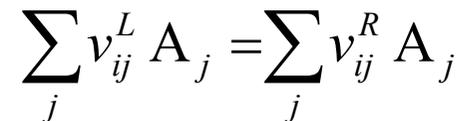
Importance of intermediates

- **Intermediates** are formed within most reaction systems.
- Hence to define the time dependant dynamics of a system accurately, a reaction model should include steps where such intermediates are formed from reactants and then go on to form products.
- E.G. detailed reaction mechanisms for the oxidation of hydrogen contain both the reactants (H_2 and O_2), the product (H_2O), and several intermediates (H , O , OH , HO_2 , H_2O_2), in the 30-40 total reaction steps.
- Critical steps are:



1.2 Stoichiometry

- Each elementary reaction step can be characterized by the following stoichiometric equation:



- The stoichiometric coefficients on the left hand side (v_{ij}^L) and the right hand side (v_{ij}^R) of an elementary reaction step should be distinguished.
- The stoichiometric coefficient belonging to species i in a reaction step can be obtained from the equation:
$$v_{ij} = v_{ij}^R - v_{ij}^L$$
- v_{ij}^L should be positive integers, while v_{ij}^R are integers for elementary reactions and can be positive or negative, integers or real numbers. Therefore, the overall stoichiometric coefficients can also be any numbers (positive or negative; integers or real numbers).

1.3 Rate equations for basic reactors

- The *kinetic system of ordinary differential equations (ODEs)* defines the relationship between the production rates of the species and rates of the reaction steps r_i :

$$\frac{dY_j}{dt} = \sum_i^{N_R} \nu_{ij} r_i; \quad j = 1, 2, \dots, N_S \quad \text{or in vector form} \quad \frac{d\mathbf{Y}}{dt} = \mathbf{v}\mathbf{r}$$

i.e number of equations equates to number of species.

- For most mechanisms eqns are coupled and must be solved simultaneously.
- In adiabatic systems or systems with a known heat loss rate, usually temperature is added as $(N_S+1)^{\text{th}}$ variable. The differential equation for the rate of change of temperature in a closed spatially homogeneous reaction vessel is given as:

$$C_p \frac{dT}{dt} = \sum_{i=1}^{N_R} \Delta_r H_i^\ominus r_i - \frac{\chi S}{V} (T - T_0)$$

T - temperature of the system, T_0 - ambient temperature, C_p - constant pressure heat capacity of mixture, $\Delta_r H_i^\ominus$ is the standard molar enthalpy of reaction step i , S and V are the surface and the volume of the system, respectively, and χ - heat transfer coefficient between the system and surroundings.

Initial value problem

- The kinetic system of ODEs and its initial values together provide the following initial value problem:

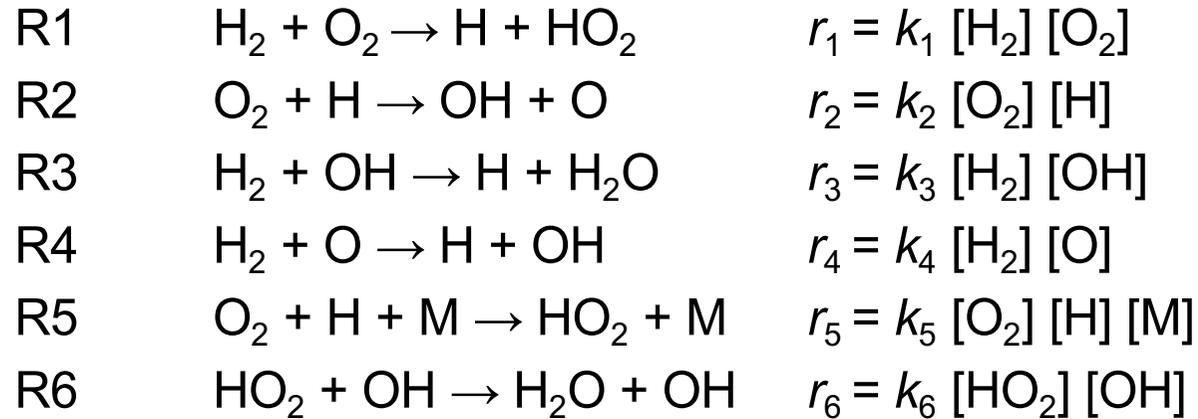
$$\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y}, \mathbf{k}) \quad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

- With the associated **Jacobian matrix** and normalised Jacobian:

$$\mathbf{J} = \frac{\partial \mathbf{f}(\mathbf{Y}, \mathbf{k})}{\partial \mathbf{Y}} = \left\{ \frac{\partial f_i}{\partial Y_j} \right\} \quad \tilde{\mathbf{J}} = \left\{ \frac{Y_j}{f_i} \frac{\partial f_i}{\partial Y_j} \right\}$$

- Reaction kinetic simulations frequently include the solution of partial differential equations, PDEs, that describe effects of chemical reactions, mass and thermal diffusion, convection and turbulence. In these PDEs f is the so called ***chemical source term***.
- Explicit numerical methods used to solve such initial value problems generally manipulate Jacobian matrix and hence **effort scales as N_s^2** .
- Reducing species numbers from a mechanism can therefore save a lot of computational time. **See later.**

Example



$$\frac{d[\text{H}]}{dt} = +1r_1 - 1r_2 + r_3 + 1r_4 - 1r_5 + 0r_6$$

$$\frac{d[\text{H}]}{dt} = k_1 [\text{H}_2] [\text{O}_2] - k_2 [\text{O}_2] [\text{H}] + k_3 [\text{H}_2] [\text{OH}] + k_4 [\text{H}_2] [\text{O}] - k_5 [\text{O}_2] [\text{H}] [\text{M}]$$

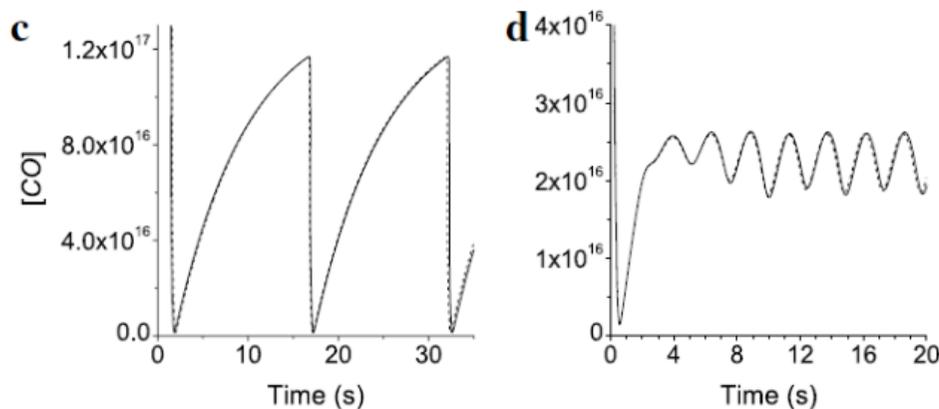
$$\frac{d[\text{H}_2\text{O}]}{dt} = k_3 [\text{H}_2] [\text{OH}] + k_6 [\text{HO}_2] [\text{OH}] \quad \textit{Etc.}$$

Closed vs. open systems

- In a **closed vessel**, system would tend towards a **final equilibrium point**.
- In an open vessel e.g. a continuously stirred tank reactor, CSTR, fresh reactants can be flowed into the vessel and products flow out. The system has a residence time t_{res} and can tend towards a non-equilibrium steady-state concentration or even a limit cycle or chaotic attractor.
- The system of ODEs is now modified to include inflow and outflow terms:

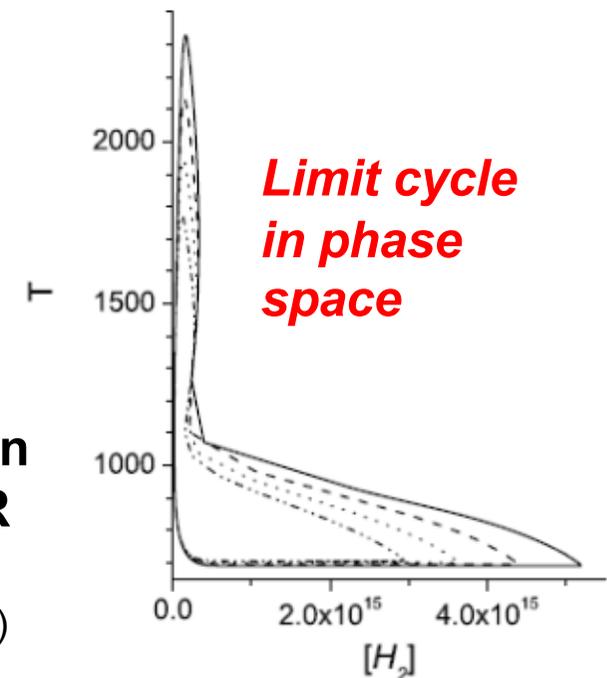
$$\frac{dY_j}{dt} = \left(\frac{Y_i^0 - Y_i}{t_{res}} \right) + \sum_i^{N_R} \nu_{ij} r_i; \quad j = 1, 2, \dots, N_S$$

$$C_p \frac{dT}{dt} = \sum_{i=1}^{N_R} \Delta_r H_i^\ominus r_i - \left[\frac{\chi S}{V} + \frac{C_p}{t_{res}} \right] (T - T_0)$$



Oscillations in wet CO CSTR system

(Brad et al., 2007)



PARAMETERISATION OF RATE COEFFICIENTS FOR USE IN COMBUSTION MODELS

1.4 Temperature dependence of rate coefficients

- Arrhenius argued that for reactants to transform into products, they must first acquire a minimum amount of energy, called the activation energy E .
- Consider the chemical reaction between two molecules, A and B, and the associated **potential energy changes** during the reaction.
- Reaction begins when the two molecules **collide** and interact, changing shape and exchanging atoms, momentum and energy.
- In this **transition state**, the potential energy (PE) of the reaction reaches a maximum, and a small energy increase pushes the reaction in the direction of the products formed, wherein the potential energy falls.
- **This maximum PE can be described by the activation energy E .**
- At an absolute temperature T , the fraction of molecules that have a kinetic energy greater than E can be calculated from statistical mechanics.
- The **Maxwell–Boltzmann (MB) distribution** describes particle speeds in idealised gases where the particles (in this case actually gases) move freely inside a stationary volume without interacting with one another, except for brief collisions in which they exchange energy and momentum with each other or with their thermal environment, assuming thermodynamic equilibrium has been reached.

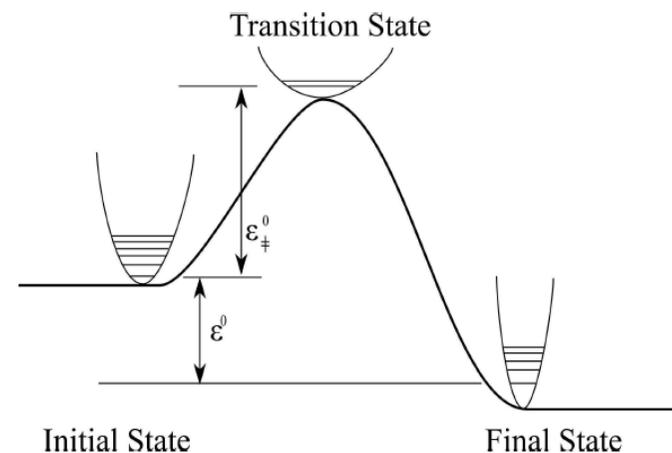
Temperature dependence of rate coefficients

- The calculations for reaction rate coefficients involve an energy averaging over an MB distribution with E as lower bound.
- By assuming a Boltzmann distribution, we know that the fraction of collisions which will have a kinetic energy high enough to pass over this potential barrier is given by: $e^{-E / RT}$.
- **Collision theory**, developed by Max Trautz and William Lewis in the years 1916–18 suggests that molecules react if they collide with a relative kinetic energy along their **lines-of-centre** that exceeds E .
- Hence both energy and orientation are important.
- Only a small percentage of total collisions have sufficient energy and appropriate orientations to form products.
- Formulation leads to an expression very similar to the Arrhenius equation which is given by:

$$k = AT^n \exp(-E / RT)$$

Temperature dependence of rate coefficients

- If the reaction between two molecules is an elementary one, occurring in a single step, A is related to the frequency of collisions between the reacting molecules.
- If E was zero, k would be equal to A , which means that the reaction would occur every time a collision occurred between the reactant molecules.
- This is the case for reactions in which no chemical bond is broken, such as the combination of atoms. **Not all reactions have an activation energy....**
- **Transition state theory** assumes quasi-equilibrium between reactants and activated transition state complexes.
- In transition-state theory, the **activated complex** is considered to have been formed in a **state of equilibrium** with the atoms or molecules in the initial state or to thermalize rapidly. Therefore its statistical and thermodynamic properties can be specified (**see later for challenges to this assumption**).

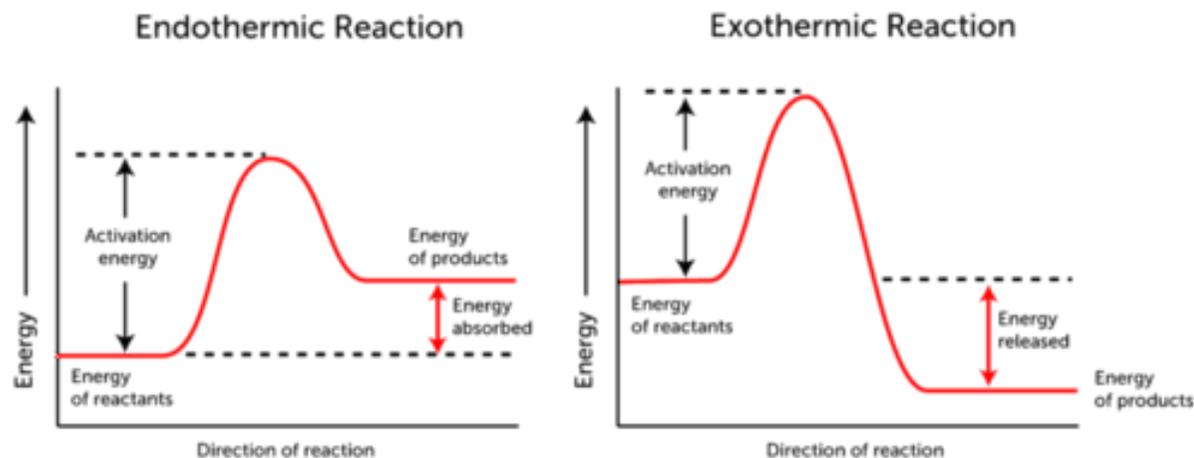


Temperature dependence of rate coefficients

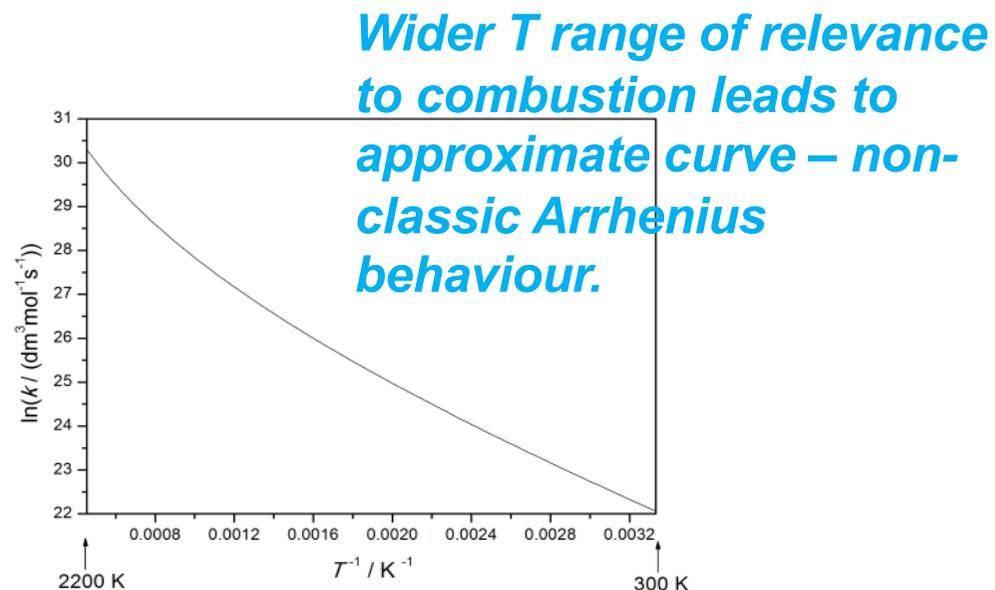
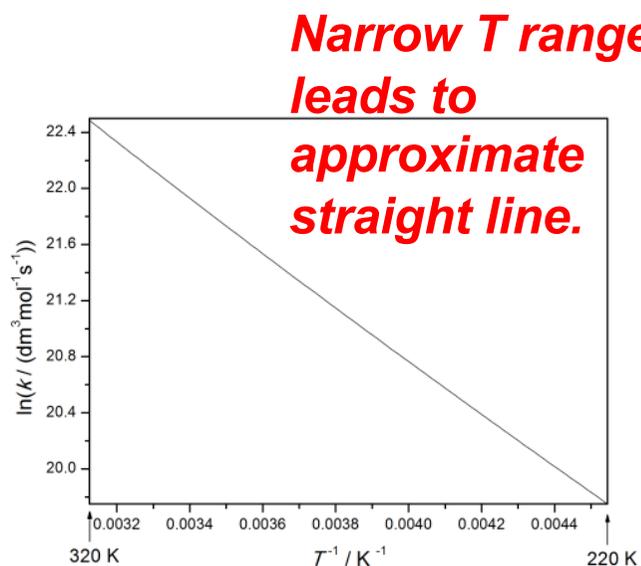
- Due to more limited ranges of T in liquid phase and in atmospheric kinetics the temperature dependence of rate coefficient k is usually described by the classic Arrhenius equation:

$$k = A \exp(-E / RT)$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant and T is temperature. The dimension of quantity E/R is temperature and therefore E/R is called the activation temperature.



If the temperature dependence of the rate coefficient can be described by the original Arrhenius equation, then plotting $\ln(k)$ as a function of $1/T$ (Arrhenius plot) gives a straight line. The slope of this line is $-E/R$, and the intercept is $\ln(A)$.



Arrhenius plot of the temperature dependence of the rate coefficient of reaction $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$. (a) temperature range 220 K to 320 K; (b) temperature range 300 K to 2200 K.

- In high temperature gas phase kinetic systems, such as combustion and pyrolytic systems, the temperature dependence of the rate coefficient is usually described by the modified Arrhenius equation:

$$k = AT^n \exp(-E / RT) \quad \text{or} \quad k = BT^n \exp(-C / RT)$$

to distinguish that B is not the same as the classic A -factor.

- This form means that the **activation energy changes with temperature** and can be calculated from the slope of the curve, i.e. the derivative of the temperature function with respect to $1/T$.

- The temperature dependent activation energy is given by:

$$E_a(T) = -R \left(\frac{d \ln \{k\}}{d(1/T)} \right) = -R \left(\frac{d(\ln \{B\} + n \ln \{T\} - C/RT)}{d(1/T)} \right) = -R \left(\frac{d \left(\ln \{B\} - n \ln \left\{ \frac{1}{T} \right\} - C/RT \right)}{d(1/T)} \right) = nRT + C$$

- Another type of unusual temperature dependence is when there are two different routes from the reactants to the products leading to non-Arrhenius behaviour. In such cases the temperature dependence of the reaction step in a wide temperature range is sometimes described by the sum of two Arrhenius expressions.
- E.g. $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$ (Burke et al., 2013) with expressions:

$$k_4(T) = 1.93 \times 10^{20} T^{-2.49} \exp(-294K/T) + 1.21 \times 10^9 T^{1.24} \exp(658K/T) \text{ [cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{]}$$

Declared as duplicate reaction

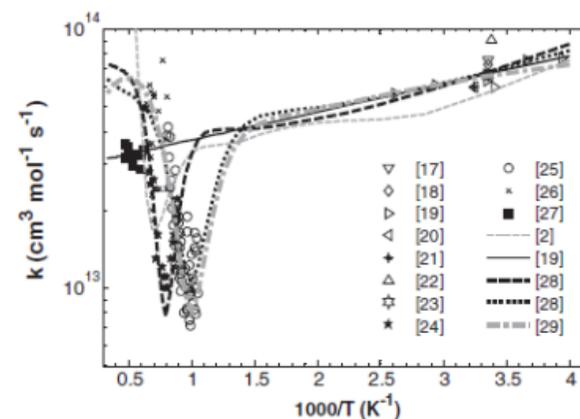
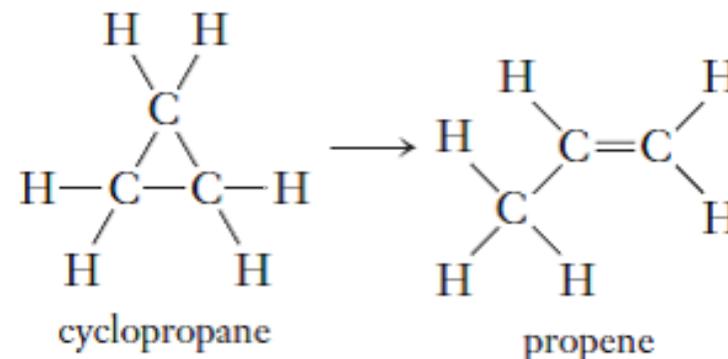


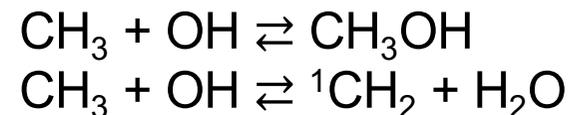
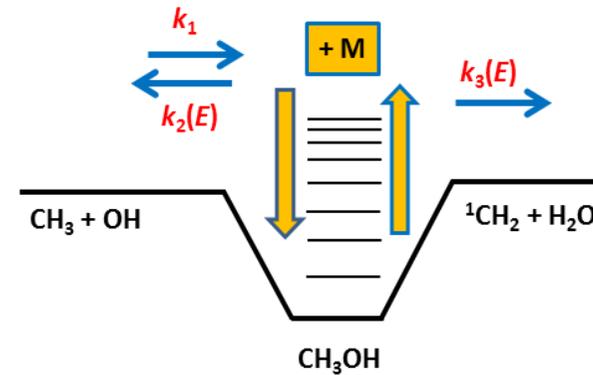
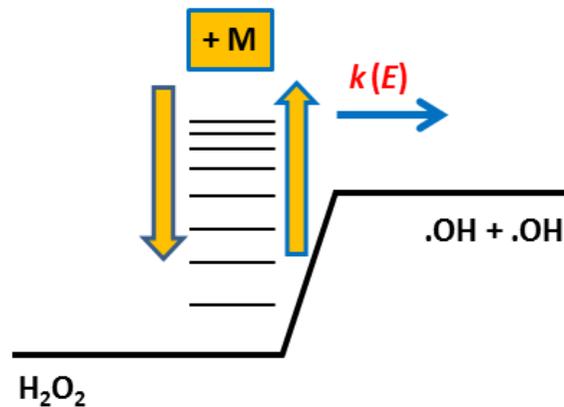
Fig. 1. Rate constants for $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$ (R4). Symbols represent experimental determinations [17–27], and lines represent proposed rate constant expressions [2,19,28,29] as indicated in the legend.

1.5 Pressure dependent rate coefficients

- The rate coefficients of thermal decomposition or isomerization reactions of some small organic molecules have been found to be pressure dependent at a given temperature.
- A model reaction was the **isomerization of cyclopropane** yielding propene. The rate coefficient was found to be first-order and pressure independent at high pressures, whilst second-order and linearly dependent on pressure at low pressures.
- Interpreted by Lindemann (1922) and Hinshelwood (1926) by assuming that the molecules of cyclopropane (C) are colliding with any of the other molecules present in the system (“third body”, denoted by M) producing rovibrationally excited cyclopropane molecules (C*).
- These molecules can then isomerize (transform into another molecule with the same atoms but with a different arrangement) yielding propene (P), or further collisions may convert the excited cyclopropane molecules back to non-excited ones: $C + M \rightleftharpoons C^* + M$ and $C^* \rightarrow P$.



- Later shown that collisions create excited reactant species having a wide range of rovibrational energies. Cyclopropane molecules can move up and down an energy ladder and rate coefficient depends on energy of excited reactant.
- This example not of high practical significance but there are many other similar *unimolecular reactions* of importance in combustion.
- Decomposition of H_2O_2 is important in combustion of hydrogen, wet CO and hydrocarbons.
- Due to collisions with any species present in mixture, the rovibrational energy level of H_2O_2 can move up and down on the energy ladder. Molecules having an energy level higher than a threshold can decompose to the OH radical and the rate of decomposition is energy dependent.



Fall-off

- At intermediate pressures the reaction rate of unimolecular reactions is neither second-order nor first-order. The apparent first-order rate coefficient in this pressure region (“**fall-off region**”) can be calculated using the Lindemann approach (Pilling & Seakins, 1995).
- Arrhenius rate parameters are required for both the low- and high-pressure limiting cases, and the Lindemann formulation blends them to produce a pressure-dependent rate expression.
- The low-pressure rate coefficient is given by the expression:

$$k_0 = A_0 T^{n_0} \exp\left(\frac{-E_0}{RT}\right)$$

and the high-pressure rate coefficient by the expression:

$$k_\infty = A_\infty T^{n_\infty} \exp\left(\frac{-E_\infty}{RT}\right)$$

the apparent first-order rate coefficient at any pressure can be calculated by:

$$k = k_\infty \left(\frac{P_r}{1 + P_r}\right) F$$

- In the equation above $F = 1$ in the Lindemann approach and the reduced pressure P_r is given by:

$$P_r = \frac{k_0[M]}{k_\infty}$$

where $[M]$ is the third body concentration.

- When calculating the effective concentration of the third body, the **collision efficiencies** m_{y_i} should also be taken into account:

$$[M] = \sum_i m_{y_i} [Y_i]$$

- In the example the effective $[M]$ is calculated by Metcalfe et al. (2013) as:

$[M] = 5.00 [H_2O] + 5.13 [H_2O_2] + 0.8 [O_2] + 2.47 [H_2] + 1.87 [CO] + 1.07 [CO_2] + 0.67 [Ar] + 0.43 [He] +$ the sum of the concentrations of all other species.

- Since N_2 is a commonly used “bath gas” within experiments, it often makes up the majority of the colliding species concentrations.
- N_2 is therefore assumed to have unit collision efficiency and those of the other species are compared against it.

- In $\text{H}_2\text{O}_2 (+\text{M}) \rightleftharpoons 2 \text{OH} (+\text{M})$, species with similar molecular energy levels to rovibrationally excited H_2O_2 (like H_2O_2 and H_2O) have large collision efficiencies, while noble gases have typically small collision efficiencies.
- General trend is that larger molecules with more excitable rovibrational frequencies have larger collision efficiency factors.
- Few measurements have specifically address third body efficiency factors and these values contribute to **model uncertainties**.
- Third body efficiency factors can also be considered as temperature dependent (Baulch et al., 2005), but an approximate parameterisation is hindered by the ***lack of appropriate experimental data***.
- Jasper (2015) recently published ***a theoretical study*** of third body efficiencies using theoretical methods for hydrocarbon collisions - linear, branched, and cyclic alkanes, alkenes, and alkyl radicals - with $\text{M} = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{H}_2, \text{N}_2, \text{O}_2$. Trends were extracted with respect to chemical structure and number of C atoms.
 - **Could be a way forward for determining more accurate values.**

Troe formulation

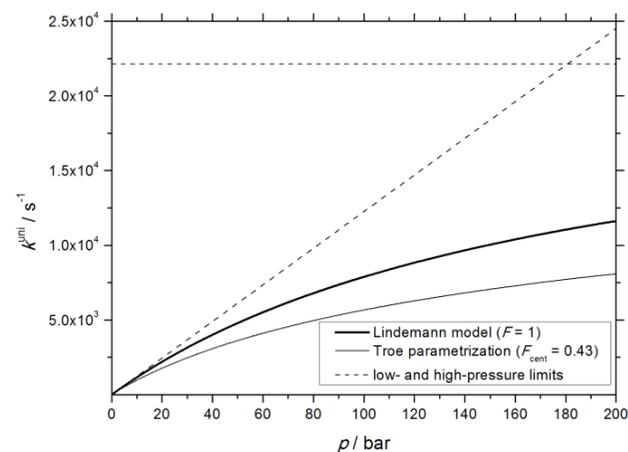
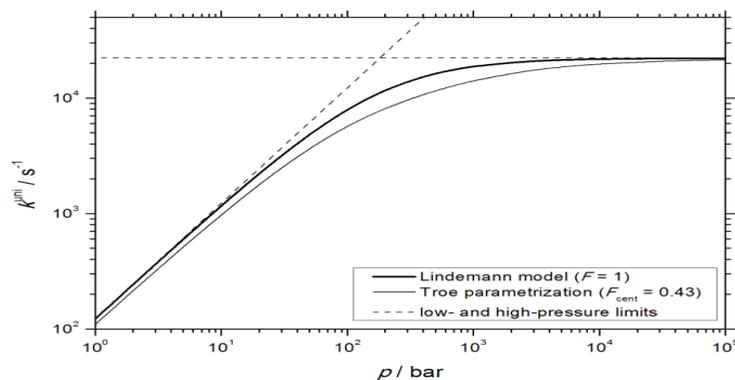
Lindeman equation can be improved by the application of the pressure and temperature dependent parameter F . In the Troe formulation (Gilbert et al., 1983), F is represented by a more complex expression:

$$\log F = \log F_{\text{cent}} \left[1 + \left[\frac{\log P_r + c}{n - d(\log P_r + c)} \right]^2 \right]^{-1}$$

with $c = -0.4 - 0.67 \log F_{\text{cent}}$, $n = -0.75 - 1.271 \log F_{\text{cent}}$, $d = 0.14$ and

$$F_{\text{cent}} = (1 - \alpha) \exp\left(-\frac{T}{T^{***}}\right) + \alpha \exp\left(-\frac{T}{T^*}\right) + \exp\left(-\frac{T^{**}}{T}\right)$$

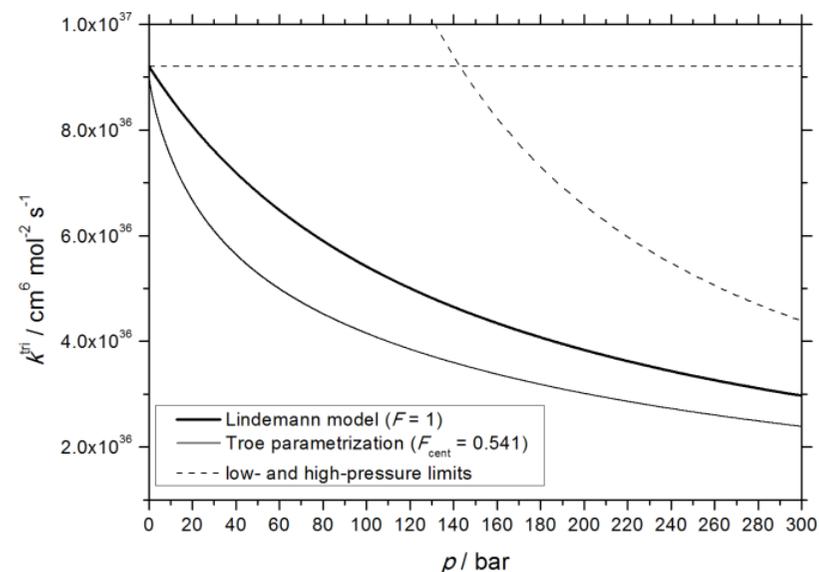
so that four extra parameters α , T^{***} , T^* , T^{**} must be defined in order to represent the fall-off curve.



The change of the apparent first-order rate coefficient k_{uni} with pressure for reaction $\text{H}_2\text{O}_2 \rightleftharpoons 2\text{OH}$ at temperature $T=1000$ K using bath gas N_2 (Troe, 2011).

Pressure dependence of bimolecular reactions

- *Complex-forming bimolecular reactions* may also be pressure dependent due to the complex losing extra energy in collisions leading to thermal equilibration.
- An example is the reaction of $\text{CH}_3 + \text{OH}$ forming the CH_3OH complex. With the main products the stabilization product CH_3OH and decomposition products $\text{CH}_2 + \text{H}_2\text{O}$.
- The Troe formulation accurately represents the fall-off region for single-well PE surfaces (Venkatech et al., 1997).
- For more complicated elementary reactions with **multiple wells**, differences between theoretically calculated rate coefficient and the best Troe fit can be as high as 40%.
- This has led to the so called “log p” formalism (see e.g. (Zádor et al., 2011)):



Ln P and Chebyshev polynomial formulations

- Here k is the rate coefficient belonging to pressure p , while the (p_i, k_i) pairs are a series of tabulated rate coefficients, defined by Arrhenius parameters, belonging to different pressures. Hence this is an **interpolation method** which is linear in $\ln p$.

$$\ln k = \ln k_i + (\ln k_{i+1} - \ln k_i) \frac{\ln p - \ln p_i}{\ln p_{i+1} - \ln p_i}$$

- Chebyshev polynomials can also be used for fitting the pressure dependence of rate coefficients, but **care** must be used **when extrapolating** them outside of the ranges over which they were fit. For details see Venkatech et al. (1997).

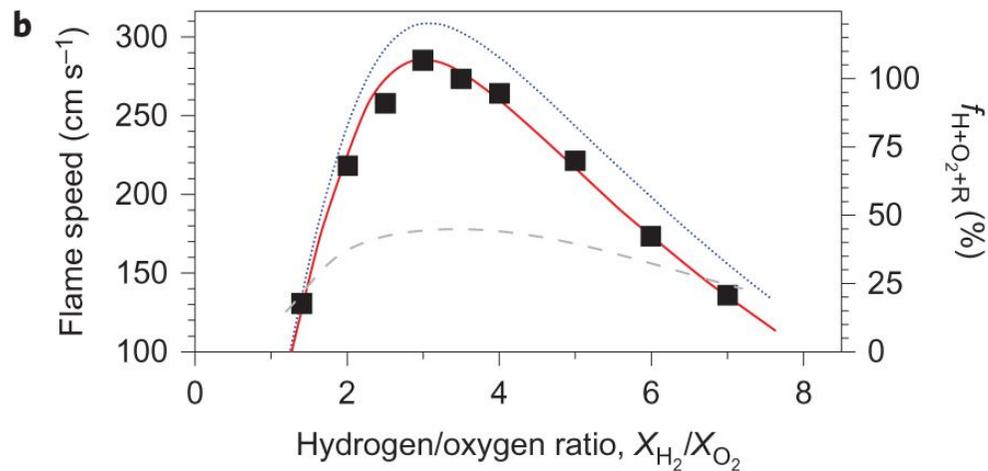
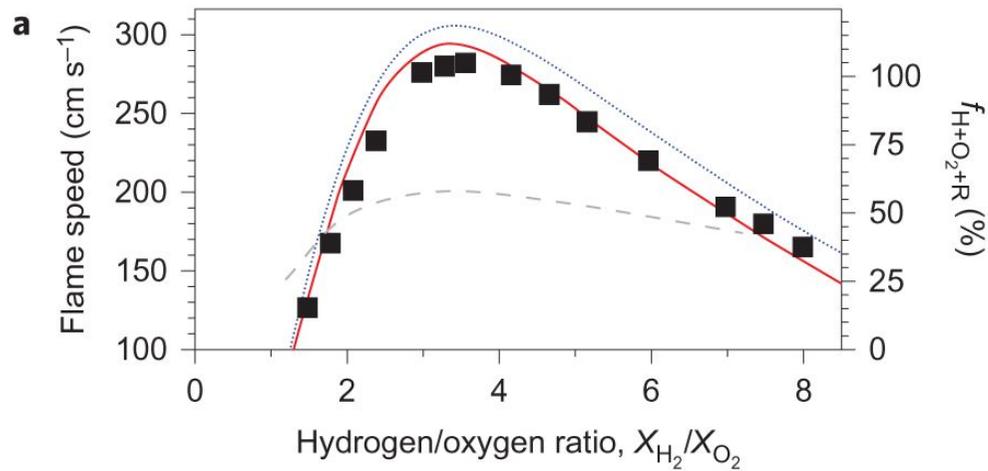
$$\log k(\tilde{T}, \tilde{P}) \approx \sum_{i=1}^N \sum_{j=1}^M a_{ij} \varphi_i(\tilde{T}) \varphi_j(\tilde{P}).$$

$$\varphi_i(x) = \cos[(i-1) \arccos(x)]; \quad i = 1, 2, \dots,$$

*Both formulations supported by **Chemkin and Cantera** if coefficients are provided within mechanisms.*

1.6 Non Boltzmann kinetics

- Chemical activation can occur due to exothermic or endothermic reactions occurring faster than heat/energy transfer, causing the reacting molecules to have non-thermal energy distributions (non-Boltzmann distribution).
- Can result in “chemically termolecular” reactions of potential importance to combustion predictions. Involve reactive collisions occurring on same time-scales as thermalisation (equilibration)
 - Typically gas phase termolecular reactions taught not to exist in standard Phys. Chem. texts.
- Here, three reactants involved in bond breaking and forming products i.e. $R + X + Y = \text{products}$, not, $R + X (+M) = RX (+M)$ (Burke & Klippenstein, 2017). They give the example: $H + O_2 + R$, as well as $H + O_2 + M = HO_2 + M$ followed by $HO_2 + R$.
- Termolecular reactions recently studied, by Barbet et al. (2019).
- Examples given that may be important for flame speeds include:
- $H + N_2 + O = NH + NO$, $H + CO + H = H_2 + CO$, and $H + C_2H_2 + O_2/OH/H$.
- Increasing the pressure increases the heat transfer rate between the reacting molecules and the rest of the system, reducing this effect.
 - How important are such reactions for modelling practical systems? Yet to be fully determined.
 - May be important for interpreting low pressure measurements.



Results shown for hydrogen–air mixtures at atmospheric temperature and pressure **(a)** and hydrogen–oxygen flames diluted with helium at atmospheric temperature for a pressure of 5 atm and $X_{\text{O}_2}/(X_{\text{O}_2} + X_{\text{He}}) = 0.08$ **(b)**.

Symbols experimental;
 blue dotted lines indicate results from simulations where $\text{H} + \text{O}_2 + \text{R}$ reactions were not included;
 red solid lines indicate results from simulations where $\text{H} + \text{O}_2 + \text{R}$ reactions were included.

The peak fraction of total $\text{HO}_2 + \text{R}$ reaction flux through $\text{H} + \text{O}_2 + \text{R}$, $f_{\text{H}+\text{O}_2+\text{R}} = \omega_{\text{H}+\text{O}_2+\text{R}}/(\omega_{\text{H}+\text{O}_2+\text{R}} + \omega_{\text{HO}_2+\text{R}})$, is also indicated with a thin grey dashed line.

Burke & Klippenstein, 2017

1.7 Basic thermodynamic quantities

Enthalpy

- Enthalpy comprises a system's internal energy: the energy required to create the system, plus the amount of work required to make room for it by displacing its environment and establishing its volume and pressure: $H = U + pV$.
- The total enthalpy of a system cannot be measured directly, the **enthalpy change** of a system is measured instead e.g. the enthalpy change during a reaction.

Enthalpy of reaction

- Enthalpy of formation for a species can be expressed as a polynomial function of temperature.
$$\frac{H^\circ}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$
- The enthalpy of reaction can be calculated by summing the enthalpies of the reactants and products of the reaction at a given temperature:

$$\frac{\Delta H_j^\circ}{RT} = \sum_{i=1}^I v_{ij} \frac{H_i^\circ}{RT}$$

where $(\Delta_r H_j^\circ) < 0$ for an exothermic reaction where heat flows from the system at constant pressure and overall enthalpy decreases and $(\Delta_r H_j^\circ) > 0$ for an endothermic one.

Basic thermodynamic quantities

Entropy:

- Related to the number Ω of microstates that are consistent with the macroscopic quantities characterising a system (e.g. V, p, T)
- Under the assumption that each microstate is equally probable, the entropy S is the natural logarithm of the number of microstates, multiplied by the Boltzmann constant k_B , $S = k_B \ln \Omega$.
- The **second law of thermodynamics** states that the entropy of an isolated system never decreases. Such systems spontaneously evolve towards **thermodynamic equilibrium**, the state with **maximum entropy**.
- In an open system where heat, work and mass can flow across the system boundaries:

$$\frac{dS}{dt} = \sum_{k=1}^K \dot{m}_k \hat{S}_k + \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

rate of entropy production within system.

net rate of entropy flow due to flows of mass into and out of system (\hat{S} = entropy per unit mass).

rate of entropy flow due to heat flow across boundary.

Basic thermodynamic quantities

Gibbs free energy: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; J in SI units under standard conditions.

$$\Delta G^\circ = \sum n \Delta G^\circ_f(\text{products}) - \sum m \Delta G^\circ_f(\text{reactants})$$

- Described by Gibbs as "available energy:"
 - the **greatest amount of mechanical work** which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies.
- A thermodynamic potential defining the maximum amount of **non-expansion work** that can be extracted from a thermodynamically closed system (one that can exchange heat and work with its surroundings, but not matter).
- In a completely **reversible process**, when a system transforms reversibly from an initial state to a final state, the decrease in Gibbs free energy equals the work done by the system to its surroundings, minus the work of the pressure forces.
 - Sign of standard free energy change ΔG° of a chemical reaction determines whether the reaction will tend to proceed in the forward or reverse direction.
- It is the thermodynamic potential that is minimized when a system reaches chemical equilibrium at constant pressure and temperature.

Basic thermodynamic quantities

Specific heat capacities:

- Specific heat capacities vary with T, P . $C = C(P, T)$.
- Expressed as values at:
 - Constant pressure C_p , where gas is allowed to expand performing work
 - Constant volume C_v , where gas is enclosed and pressure may change.
 - $C_v < C_p$
- At constant pressure heat capacity is equal to change in enthalpy divided by change in temperature $C_p = \frac{\Delta H}{\Delta T}$.

$$H_{Tf} = H_{Ti} + \int_{Ti}^{Tf} C_p dT$$

If we assume that C_p is independent of T this simplifies.

$$H_{Tf} = H_{Ti} + C_p(T_f - T_i)$$

1.8 Reversible reactions

- In theory, all thermal elementary reactions are reversible, which means that the reaction products may react with each other to re-form the reactants, denoted “ \rightleftharpoons ”.
- The use of irreversible reactions denoted by a single arrow “ \rightarrow ” means that either the reverse reaction has been neglected or that the reactions have been separated into forward and backwards rates.
- Forward rate expression given in Arrhenius or pressure dependent forms, and reverse rate is calculated from thermodynamic properties through the equilibrium constant:

$$k_{r_i} = \frac{k_{f_i}}{K_{c_i}}$$

Thermodynamic properties are evaluated at a given temperature (T), e.g. standard molar heat capacity (C_p^\ominus), enthalpy (H^\ominus) and entropy (S^\ominus). The standard molar reaction enthalpy ($\Delta_r H_j^\ominus$) and entropy ($\Delta_r S_j^\ominus$) can be calculated from the following equations:

$$\frac{\Delta S_j^\ominus}{R} = \sum_{i=1}^I \nu_{ij} \frac{S_i^\ominus}{R} \qquad \frac{\Delta H_j^\ominus}{RT} = \sum_{i=1}^I \nu_{ij} \frac{H_i^\ominus}{RT}$$

The equilibrium constant K in terms of normalised pressures is then obtained from:

$$\Delta_r G^\ominus = -RT \ln K \qquad K = \exp\left(\frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT}\right)$$

The equilibrium constant in concentration units K_c is related to the equilibrium constant in normalised pressure units K by the following:

$$K_c = K \left(\frac{p^\ominus}{RT}\right)^{\Delta \nu} \qquad \text{where } p^\ominus \text{ is the standard pressure and } \Delta \nu = \sum_i \nu_i \text{ is the sum of stoichiometric coefficients.}$$

So, knowing the thermodynamic properties of the species now allows the reverse rate constant to be calculated.

Representation in typical combustion models

Most models use 14 fitted polynomial coefficients - the NASA polynomials for each species (Burcat, 1984). Seven for $T_{\text{low}} - T_{\text{mid}}$ and seven for $T_{\text{mid}} - T_{\text{high}}$. Typical values are $T_{\text{low}} = 300 \text{ K}$, $T_{\text{mid}} = 1000 \text{ K}$ and $T_{\text{high}} = 5000 \text{ K}$.

$$\frac{C_p^\theta}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{H^\theta}{RT} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T}$$

$$\frac{S^\theta}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7$$

74-82-8

```
CH4 METHANE STATWT=1. SIGMA=12. IA=IB=IC=0.52410356 NU=2916.7,1533.295(2),
3019.491(3),1310.756(3) X11=-26 X12=-3 X13=-75 X14=-4 X22=-.4,X23=-9 X24=-20
X33=-17 X34=-17 X44=-11 ALFA1=.01 ALFA2=-.09 ALFA3=.04 ALFA4=.07 D0=1.10864E-4
HF298=-74.6+/-0.3 KJ HF0=66.63 kJ REF=TSIV 91 {HF298=-74.554+/-0.60 kJ REF=ATCT
C} MAX LST SQ ERROR CP @ 1300 K 0.54%.
```

```
CH4 ANHARMONIC g 8/99C 1.H 4. 0. 0.G 200.000 6000.000 B 16.04246 1
1.65326226E+00 1.00263099E-02-3.31661238E-06 5.36483138E-10-3.14696758E-14 2
-1.00095936E+04 9.90506283E+00 5.14911468E+00-1.36622009E-02 4.91453921E-05 3
-4.84246767E-08 1.66603441E-11-1.02465983E+04-4.63848842E+00-8.97226656E+03 4
```

1.9 Constructing Chemical Mechanisms - Manual

- Historically combustion mechanisms result from careful development work by experts.
- Begins with the selection of important species:
 - **reactants**
 - **products**
 - important **intermediates** necessary to predict production rates of key products or key quantities such as ignition behaviour or dynamic features such as oscillations.
- Types of reactions that can occur between these coupled groups of species then be specified along with appropriate thermochemical data.
- Over time, growing expertise led to **protocols** for different types of application.
- These indicate **reaction classes** for each category of important species.
- Typically, certain reaction classes are ignored if their rates are very slow compared to the overall time-scales of interest, they are too endothermic or they are too complex (e.g. too many bonds are broken or products produced (Yoneda, 1979; Németh et al., 2002)). Pathways to minor products also often ignored (Saunders et al., 2003a).

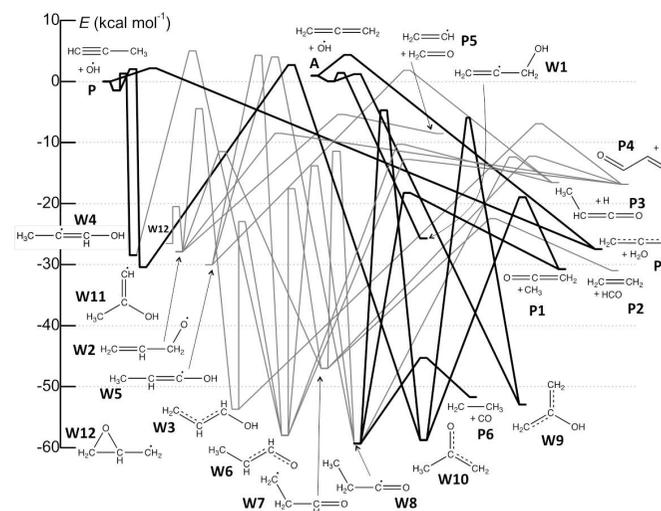
The concept of reaction classes

(Blurock, Battin-LeClerc, 2013)

- Developing detailed combustion mechanisms for the oxidation of fuels with a large number of carbon atoms presents some challenges in mechanism production philosophy.
- It is not possible to source the rate constants for such mechanisms exclusively from experiments/detailed theory.
- Estimates of reaction rate constants must come from general physical chemical principles based on fundamental kinetic studies for a smaller number of fuels.
- One way of encompassing these general principles into specific reactive properties is to define **reaction classes**.
- **Reaction classes** - kinetic generalisations that systematically embody analogies and physical principles a modeller uses to estimate rate constants where no specific evidence exists.
- Based on a local set of functional features around the reactive centre of a molecule that are significant when determining numeric value of rate constant.
- Used in both **automatic** and **manual generation** of reaction mechanisms e.g. n-hexadecane mechanism of Westbrook et al. (2009).

How to define reaction classes

- A reaction class has three sets of information:
 1. A pattern or rule to recognise within the chemical reactants (can be more than one) when the reaction class should be applied.
 2. A transformation of how the specific reactants are converted to products.
 3. The rate constants associated with the transformation.
- Generally built from years of chemical experience and intuition.
- May also be suggested by automatic computer codes designed to explore chemical pathways automatically for reactions that are relevant in gas phase chemical problems e.g. KinBot (Zador & Van De Vijver <https://www.osti.gov/biblio/1464498-kinbot>).
- KinBot uses a chemical network approach coupled with knowledge of the **potential energy surface** determined for the particular system.



Examples of high temperature reaction classes

(Sarathy et al., 2011)

1. Unimolecular fuel decomposition
2. H-atom abstraction from the fuel
3. Alkyl radical decomposition
4. Alkyl radical isomerization
5. H-atom abstraction reactions from alkenes
6. Addition of radical species O and OH to alkenes
7. Reactions of alkenyl radicals with HO_2 , CH_3O_2 , and $\text{C}_2\text{H}_5\text{O}_2$
8. Alkenyl radical decomposition
9. Alkene decomposition
10. Retroene decomposition reactions

Examples of Low Temperature Reaction Classes

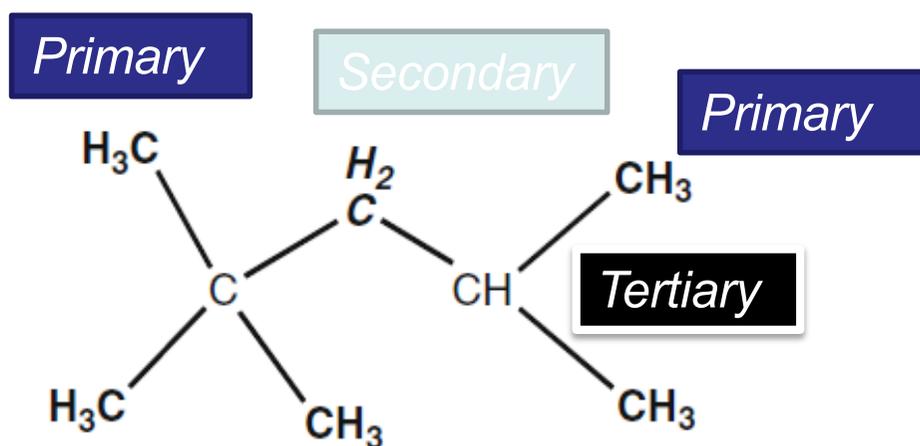
(e.g. RH any general alkane, Sarathy et al. 2011)

11. **Addition of O₂ to alkyl radicals (R + O₂ = ROO)**
12. R + ROO = RO + RO
13. R + HO₂ = RO + OH
14. R + CH₃OO = RO + CH₃O
15. **Alkyl peroxy radical isomerization (ROO = QOOH)**
16. Concerted eliminations (ROO = alkene + HO₂)
17. ROO + HO₂ = ROOH + O₂
18. ROO + H₂O₂ = ROOH + HO₂
19. ROO + CH₃O₂ = RO + CH₃O + O₂
20. ROO + ROO = RO + RO + O₂
21. ROOH = RO + OH
22. RO decomposition.
23. QOOH = cyclic ether + OH (cyclic ether formation)
24. QOOH = alkene + HO₂ (radical site beta to OOH group)
25. QOOH = alkene + carbonyl + OH (radical site gamma to OOH group)
26. **Addition of O₂ to QOOH (QOOH + O₂ = OOQOOH)**
27. **Isomerization of OOQOOH and formation of ketohydroperoxide and OH**
28. **Decomposition of ketohydroperoxide to form oxygenated radical species and OH**
29. Cyclic ether reactions with OH and HO₂
30. Decomposition of large carbonyl species and carbonyl radicals

*Typical low temperature
chain branching route for
alkanes*

Rate constants and functional groups

- Every chemical environment, meaning an atom and its bonding, has an effect on the neighbouring atoms and bonds.
- For example, a radical on a carbon atom is more energetically stable on a **tertiary** carbon atom than on a **primary** carbon atom which has the consequence that a **tertiary** hydrogen atom is more easily extracted from the carbon atom.



- Mechanisms for larger fuels can be built using this concept of reaction classes and populated by data based partly on experimental measurements or detailed theory calculations and partly on extrapolations of this data to larger and larger molecules using the concept of **functional groups**.

Use of functional groups: example of hydrogen atom abstraction from the fuel

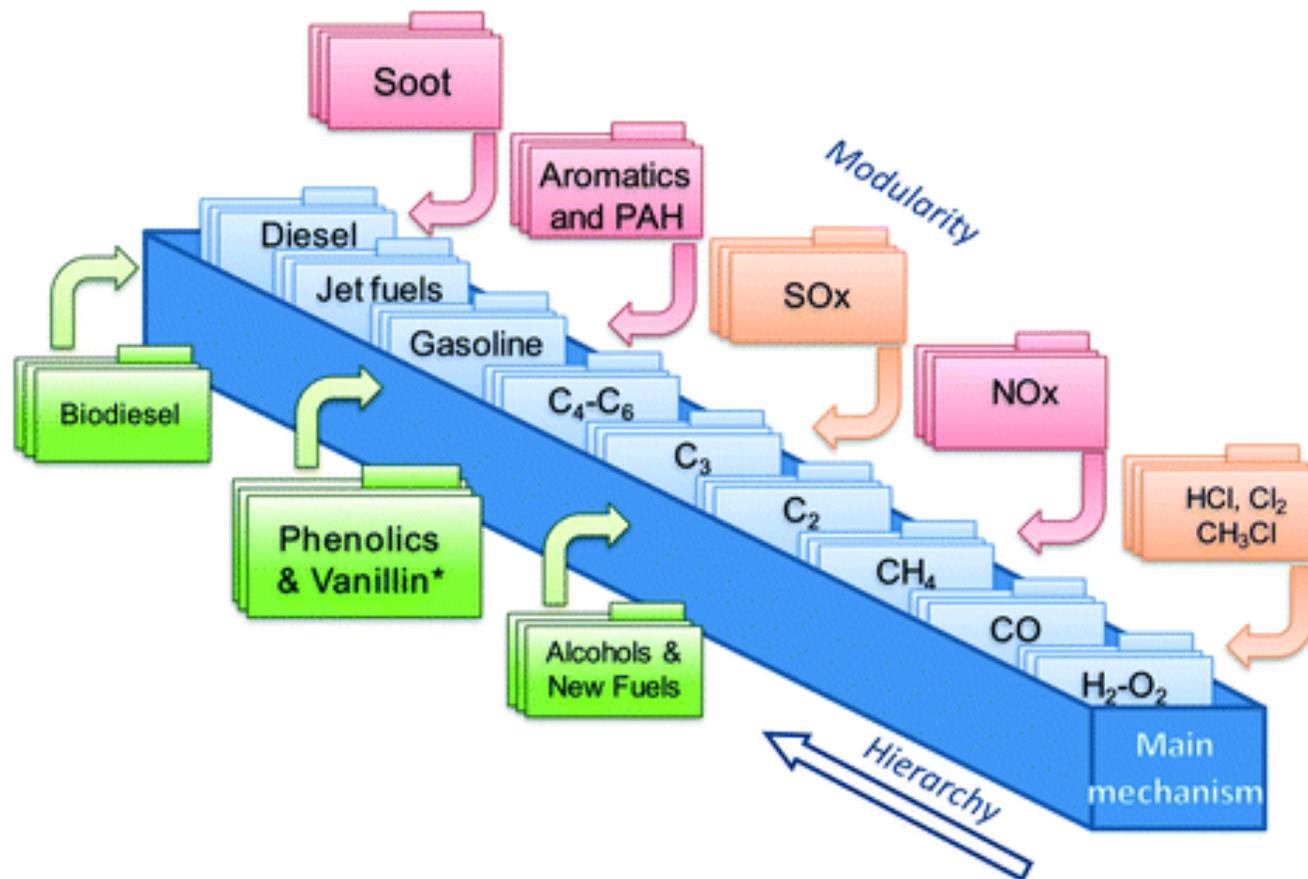
Table 2.1 Rate constants for alkylic hydrogen atom abstractions, expressed in the form $k = A T^b \exp(-E/RT)$, with the units cm^3 , mol, s, kcal, by hydrogen atoms which can be abstracted (Buda et al. 2005)

H-abstraction	Primary H			Secondary H			Tertiary H		
	lg A	b	E	lg A	b	E	lg A	b	E
O_2	12.84	0	ΔHr	12.84	0	ΔHr	12.84	0	ΔHr
$\cdot\text{H}$	6.98	2	7700	6.65	2	5000	6.62	2	2400
$\cdot\text{OH}$	5.95	2	450	6.11	2	-770	6.06	2	-1870
$\cdot\text{CH}_3$	-1	4	8200	11.0	0	9600	11.00	0	7900
$\text{HO}_2\cdot$	11.30	0	17000	11.30	0	15500	12.00	0	14000

The structure of reaction mechanisms

- Reaction classes can vary with temperature and hence size of required mechanism can be reduced by, e.g., restricting to low T classes (e.g. ignition problems), or high T mechanisms (e.g. flame propagation).
- Additional classification of sub-mechanisms can be based on:
 - **Hierarchical sub-mechanisms** based on size of reactants: within a given sub-mechanism, only species of a given size are consumed. Smaller products (produced but not consumed within this sub-mechanism) are consumed by sub-mechanisms 'lower' in the hierarchy.
 - **Primary**, **secondary**, and **base** mechanisms: a special case of the hierarchical structure.
 - The **primary mechanism** - reactions of initial reactants and directly derived radicals.
 - The **secondary mechanism** – consumes products of primary mechanism. It would be possible to define iteratively tertiary and even n-ary mechanisms, but in practice in most combustion models, secondary mechanisms are designed to lead to intermediate species, which are finally consumed in a **base mechanism**.
- **Pathways**: A chain of reactions or reaction classes. The remaining species at the end of this chain should be consumed by other sub-mechanisms.

Hierarchical development of mechanisms



The base mechanism

- Usually, a well-validated detailed mechanism of smaller species (e.g. up to C2-C4), which includes reactions taken from databases.
- Has usually been validated under the conditions being considered.
- Estimated rate constants are not usually used within base mechanisms, rather data is obtained from *measurements*, *theory calcs*, *evaluations* or even from *optimised mechanisms*.
- Likely to be known with **lower uncertainty** than the reaction pathways for the larger hydrocarbons.
- Needs to be updated frequently but often in larger mechanisms “legacy” mechanisms may still be present.
- Care needs to be taken when updating base mechanisms within larger schemes since other reaction steps may have been “tuned” based on the existing base scheme.
- Example:
 - Aramco mechanism (2.0
<http://www.nuigalway.ie/c3/aramco2/frontmatter.html>)

AramcoMech2.0

- A C1-C4 mechanism that has been developed in a hierarchical way 'from the bottom up'
 - starting with a H₂/O₂ sub-mechanism,
 - followed by a C1 sub-mechanism
 - grown to include larger carbon species such as ethane, ethylene, acetylene, allene, propyne, propene, n-butane, isobutane, isobutene, 1-butene and 2-butene, and oxygenated species including formaldehyde, acetaldehyde, methanol, ethanol, and dimethyl ether.
- Has been **validated against a large array of experimental** measurements including data from shock tubes, rapid compression machines, flames, jet-stirred and plug-flow reactors.

Primary and secondary mechanisms

- Primary mechanism represents reactions of the primary fuels and their derived radicals.
 - Usually kept in detail.
- Secondary mechanism consumes the products of the primary mechanism forming smaller species.
- In secondary mechanisms often simplifications are made even at the generation stage to keep the number of reactions as low as possible:
 - **Vertical reaction lumping** is applied so that reactants go directly to smaller products via one reaction step without passing through intermediates (*see later for methodology*).
 - **Species lumping** where parallel pathways of similar isomers are grouped (*see later*).
 - Reaction classes of **low importance** can be removed.

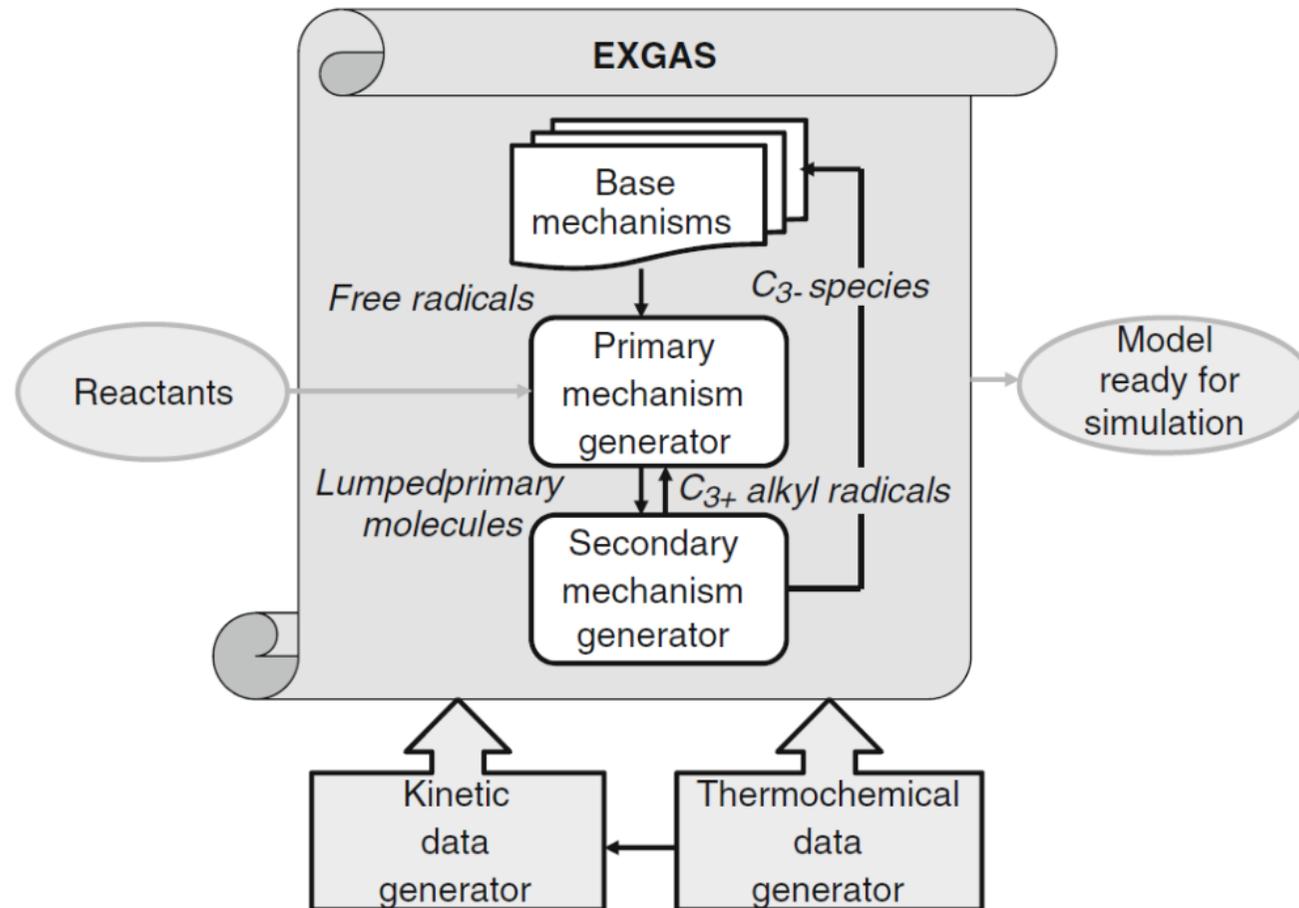
1.10 Automatic Reaction Generation Methods

- Several reasons why this is important for mechanisms describing the oxidation of larger and more complex fuels:
 - simply too large a task for a single human
 - humans make mistakes
 - the production of larger mechanisms has to be careful and systematic to generate what could be mechanisms with thousands of species and reactions
 - data for individual reactions is unlikely to be obtained from experiment/evaluation. Estimations based on Reaction Class rules will be required.
- **Why not use the help of a computer informed by decades of human knowledge?**

Principles of Automatic Generators

- Expert systems using a database of chemical principles to systematically and efficiently produce large detailed mechanisms (Blurock et al., 2013, Cleaner Combustion, p59-92).
- The developer or modeller determines which sub-mechanisms and reaction classes should be generated.
- Therefore the expert system is based on similar rules and reaction classes discussed earlier but these are now encoded rather than applied by hand.
- This should reduce errors and apply rules in a systematic way.
- If rate constants are changed for a whole class then should be easier to regenerate the mechanism.
 - EXGAS – Developed at CNRS Nancy (Côme et al., 1997).
 - RMG – Developed at MIT (Green et al., 2001; Van Geem et al., 2006).
 - REACTION – Developed by Ned Blurock (Blurock, 1995; Moreac et al., 2006).
 - MAMOX++ – Developed by Milan (Ranzi et al., 1995).

Example structure from EXGAS



Adapted from Warth et al. (1998)

Structure of an Automatic Generator

(Blurock, Cleaner Combustion 2013)

- **Generator engine.** The central module, interacting with all the other modules, which steers the generation process.
- **Species pool.** The molecules that, under each iteration, serve as input to the generator engine to produce the reactions and molecules (taken in a wide sense including both stable molecules and free-radicals) of the current iteration.
- **Molecule database.** The set of predefined molecules that could be used within the generation process.
- **Reaction class database.** Database containing information about each reaction class to be used in the generation process. Will vary according to fuel type.

Different AMG codes and specificities

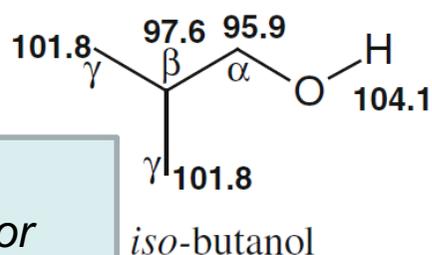
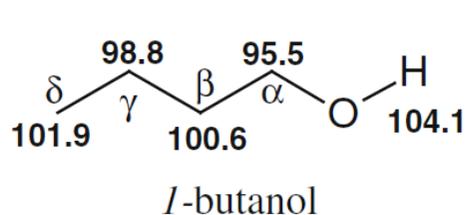
- **MAMOX ++**
 - Produces hierarchy of (highly) lumped mechanisms derived numerically from automatically generated detailed mechanisms.
- **EXGAS**
 - Has comprehensive reaction class database and large choice given to user for mechanism tailoring: e.g. low T vs high T , degree of lumping used etc.
- **RMG**
 - Uses a unique “generate and test” algorithm which generates a fundamental mechanistic step, estimates rate constants and then uses an “on-the-fly” reduction processes to determine whether the reaction should be included in the final mechanism.
 - Publicly distributed automatic generator of pressure-dependent reaction networks.
- **REACTION**
 - Uses concept of Reaction Pathways rather than exhaustive list of Reaction Classes.
 - Fundamental chemical information solely based on external databases so that it can be updated without modifying or recompiling the software.

Particular Challenges Posed by Biofuels

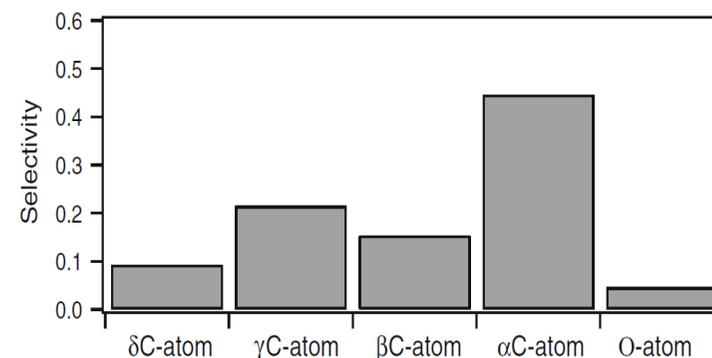
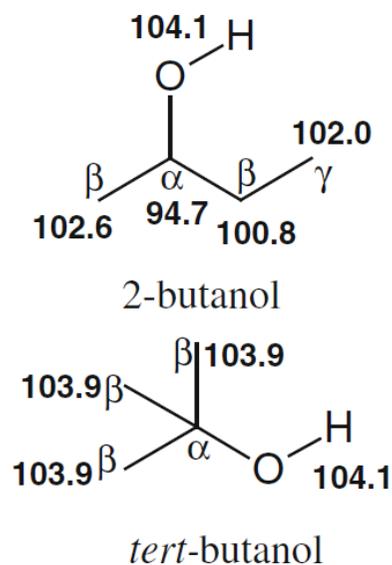
- **AMG codes initially based on alkanes.**
- Wide range of biofuels now being used for applications in vehicles e.g. as additives or in blends with gasoline and diesel.
- Most common examples include:
 - Alcohols e.g. ethanol, butanol isomers, methanol
 - Methyl Esters e.g. in biodiesel, furans, etc.
- **Molecules contain oxygen** and have **different functional groups** compared to e.g. alkanes.
- Modifications need to be made in terms of
 - Reaction classes
 - Relevant rate data for existing classes compared to alkanes, alkenes
 - Species present
- The existence of measured data for the reactions of such compounds is SCARSE!

Example of H abstraction Reactions

- We saw for alkanes that H abstraction rates were determined based on whether the H was attached to a primary, secondary or tertiary carbon atom.
- For oxygenated species there are more types of H atom.



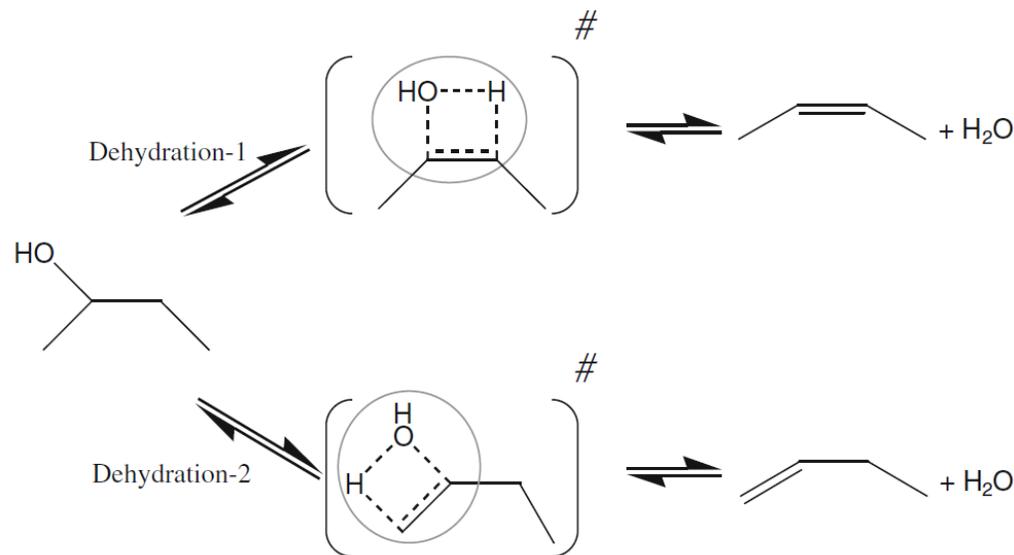
C-H bond energies for butanol isomers



Selectivities for abstraction by OH
(Frassoldati et al., 2012)

Molecular dehydration and dehydrogenation reactions for alcohols

- Reaction classes specific to alcohols forming water + alkene (Battin LeCelerc et al., Cleaner Combustion 2013).



Few direct measurements of rate constants available but shown to be sensitive for ignition delays in shock tubes for butanol isomers

Intramolecular dehydration reactions for 2-butanol

SECTION 2
Fundamental experiments
and ignition

Fundamental experiments and simulations

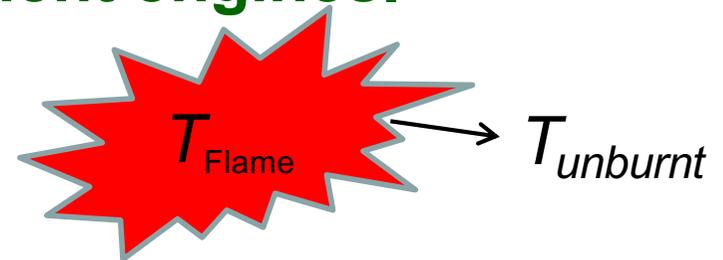
- Ultimately, we are working towards applying chemical kinetics models in the design of efficient, low pollution, practical combustors:
 - **Engines**
 - **Gas turbines**
 - **Boilers, fires, furnaces.**
- Validating models in such reactors is however, tricky, as chemistry is coupled to complex, often 3D flows.
 - *Too many sources of uncertainty, how to identify the main ones?*
- Hence, we use more simple reactors to limit flow complexity to:
 1. Learn about fundamental combustion properties e.g. ignition delay times, laminar burning velocities, flame temperatures, species profiles.
 2. Provide data for validation/evaluation of certain aspects of the models e.g. chemical source terms, by isolating these processes.

Ignition and auto-ignition – why are they important?

- **Auto-ignition in the wrong place can cause a range of hazards.**
 - Explosion hazards
 - Knocking in engines which causes physical damage to engine.
- **On the other hand, auto-ignition could be used in the design of new, more fuel efficient engines.**

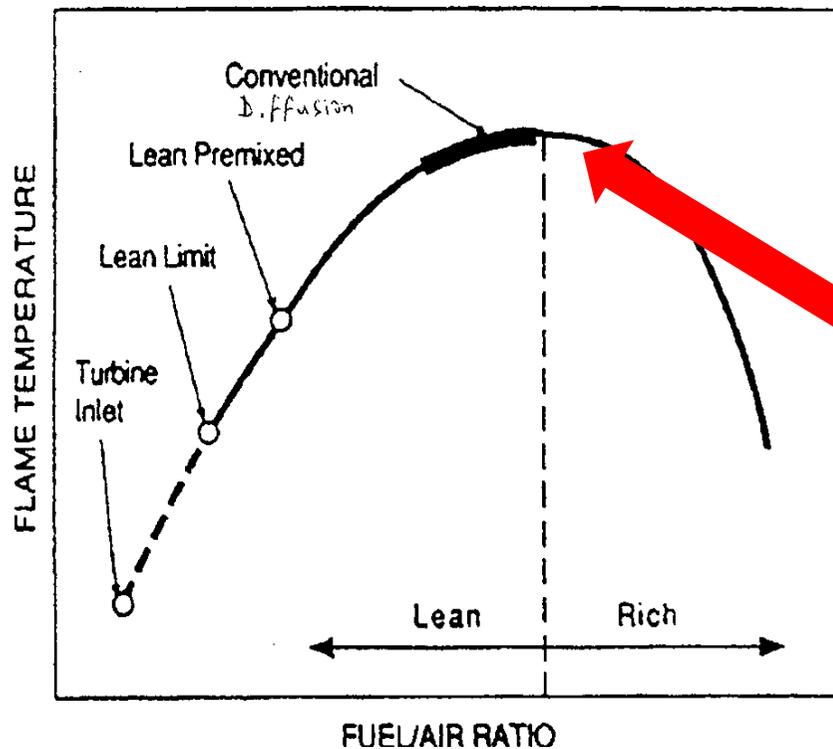
Ignition Condition:

- (1) Start reaction – gas, liquid, solid
- (2) The heat liberated by ignition must balance the heat loss to the surroundings.



2.1 Minimum Ignition Energy

Minimum Ignition Energy is the lowest energy of spark that can just ignite the material in air. Measured in Joules. Very important for safety applications. Tells us about the relative reactivity of different fuels under different conditions.

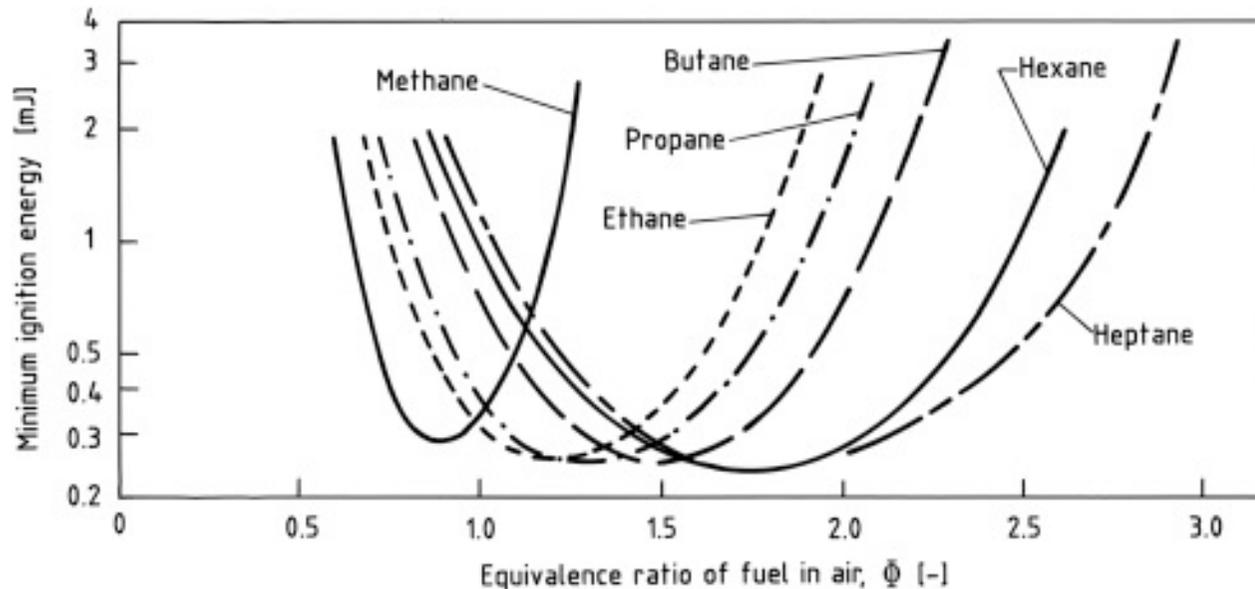


Every concentration has its minimum ignition energy.

The lowest/minimum ignition energy value usually occurs at near the stoichiometric combustion concentration which also has the highest flame temperature.

Heat generation rate is the key factor

MIE for gases and vapours: hydrocarbons

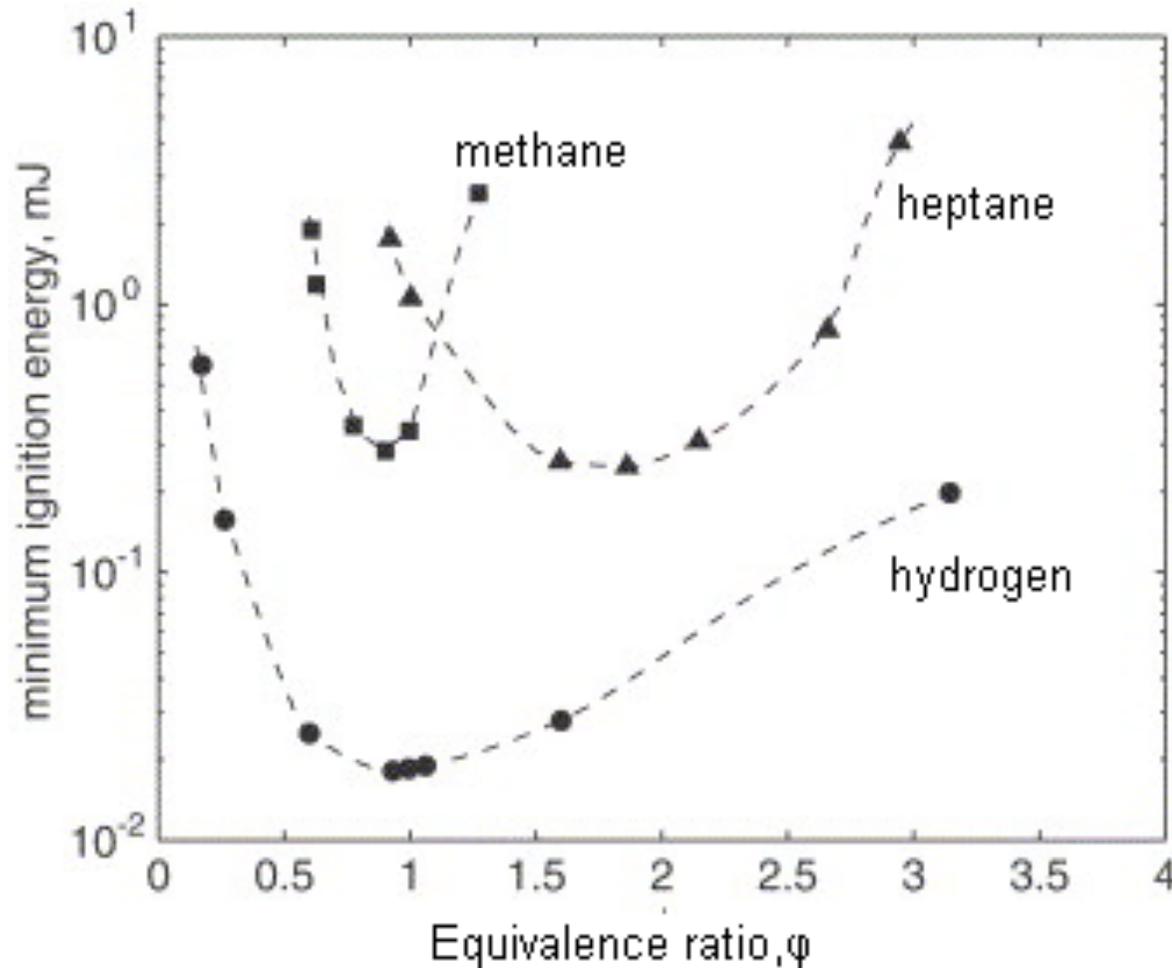


MIE increases near the lean and rich limits, but it is the minimum that is relevant to ignition safety.

MIE is 0.2-0.3 mJ for all HCs/air.

Note that the ϕ for MIE is rich for higher carbon number HCs. *In rich mixtures, oxygen diffuses preferentially into the reaction zone leading to local conditions that are closer to stoichiometric. The effect increases as the differential diffusion of fuel and oxygen increases.*

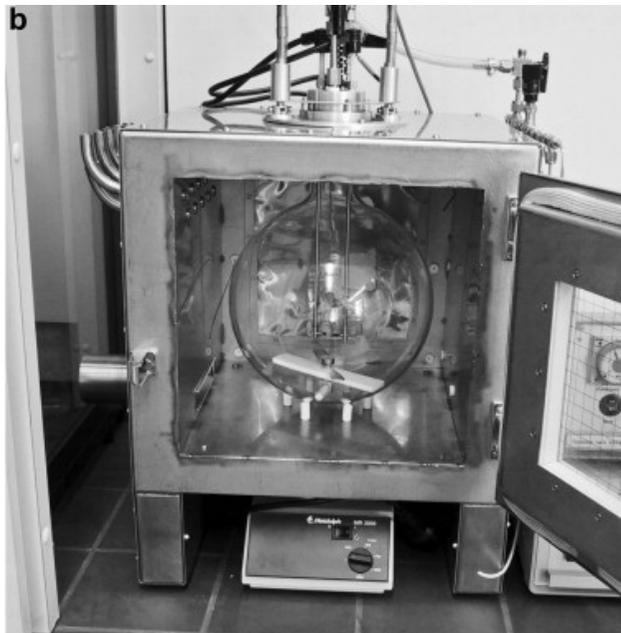
MIE for gases and vapours: hydrogen



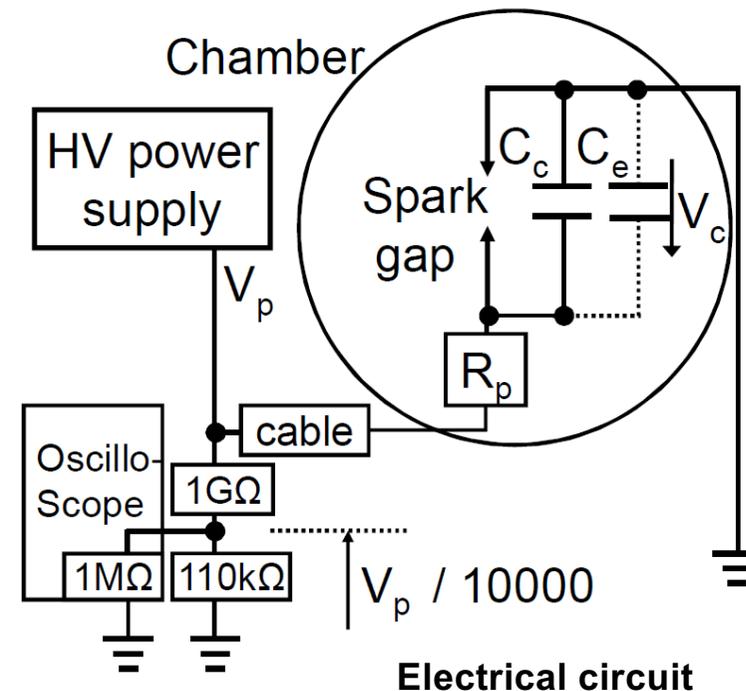
Hydrogen is a special case with very low MIE – implications for hydrogen economy.

Measuring minimum ignition energy

MIE is usually measured using high voltage capacitive sparks.



A stainless steel vessel is typically used



The capacitor with capacitance C is charged until a breakup voltage V is reached, when the charge stored in the capacitor is discharged in a test chamber filled with an explosive mixture. MIE is defined as the lowest discharge energy ($CV^2/2$) required for ignition.

MIE for aerosols and dust

- For dust the MIE is generally higher than for aerosols.

Gases/vapours: 0.001 – 1 mJ.

Aerosols: 0.1 - 10 mJ for SMD < 70 μm for diesel

Dust: 10 – 100 mJ.

- These are very low energy values. The MIE is a function of fuels and particle sizes for aerosols and dust.
- At the moment, little is known about nano-particles but metal particles like aluminium can have low MIE < 1 mJ.

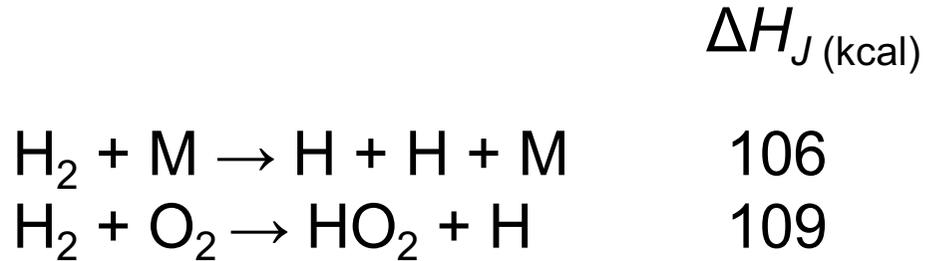
Dust is often ignited by electrostatic sparks of relatively low energy.

2.0 What is auto-ignition and what causes it?

- Combustion chemistry driven by chain reactions of reactive radicals.
- Progress of combustion depends on the balance of chain-branching and chain-terminating reactions.
- Auto-ignition, **the spontaneous ignition of a fuel-air mixture**, occurs when initially slow thermal reactions have a large enough chain-branching component to sustain and accelerate oxidation.
- Increasing radical concentrations and reaction rate build on themselves and eventually lead to a rapid **explosive rise in radical concentration**, oxidation rate, **and temperature** – ignition!
- Reactions typically release heat, increasing temperature of system, and at same time their rate is strongly dependent on temperature and pressure.

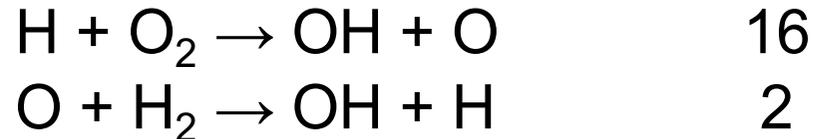
Example - auto-ignition of H₂/O₂ mixtures

Initiation reactions (generation of first radicals)



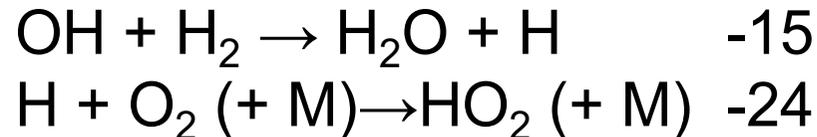
Require lots of heat

Chain branching (1 radical makes 2 radicals)



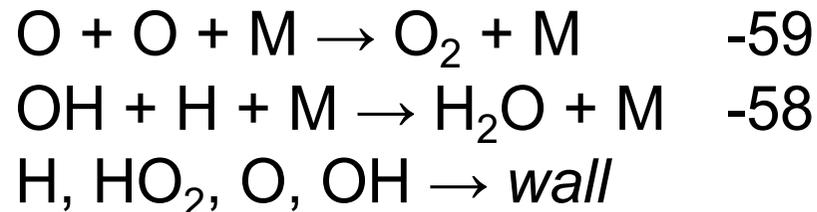
Require small heat

Chain propagation (conversion between radicals)



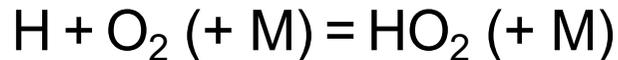
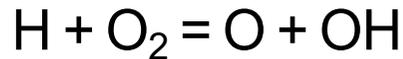
Produce heat

Termination (radicals are lost to form stable species)



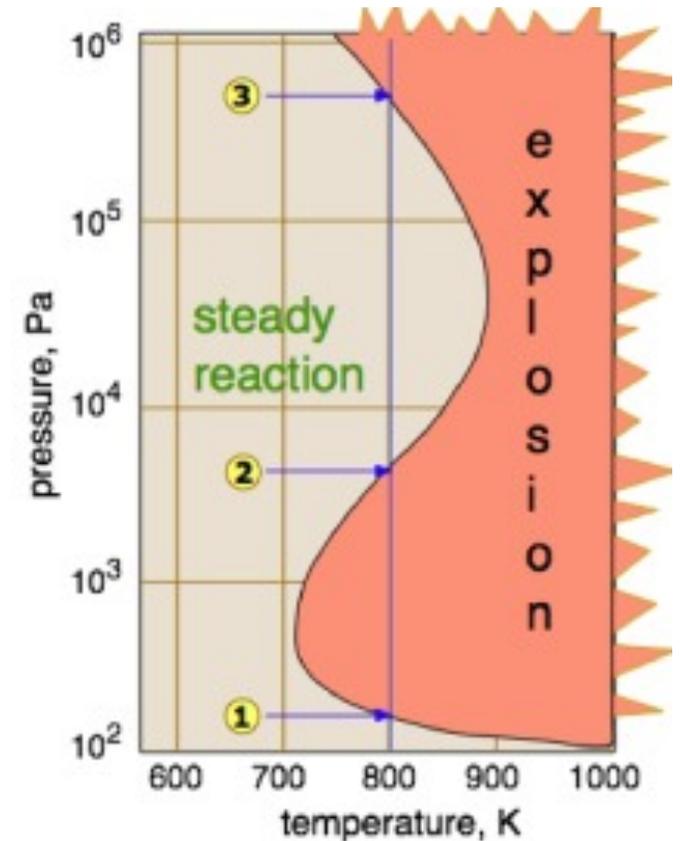
Produce heat

Hydrogen oxidation is controlled by the competition between chain-branching and pressure-dependent chain-propagation reactions:



leading to the 2nd limit of the hydrogen explosion diagram.

- At 800 K and low pressures, diffusion of H to the reactor walls dominates with no explosion.
- At $P \sim 160\text{--}5000$ Pa chain branching dominates leading to explosion.
- Above ~ 5000 Pa (~ 0.05 bar) $\text{H} + \text{O}_2 (+ \text{M}) = \text{HO}_2 (+ \text{M})$ competes with chain-branching reaction and no explosion occurs.
- Above ~ 5 bar HO_2 and H_2O_2 chemistry become important leading to the 3rd limit with branching due to HO_2 competing with wall termination of the radical.



Griffiths & Barnard, 1995

The Auto-ignition Temperature (AIT)

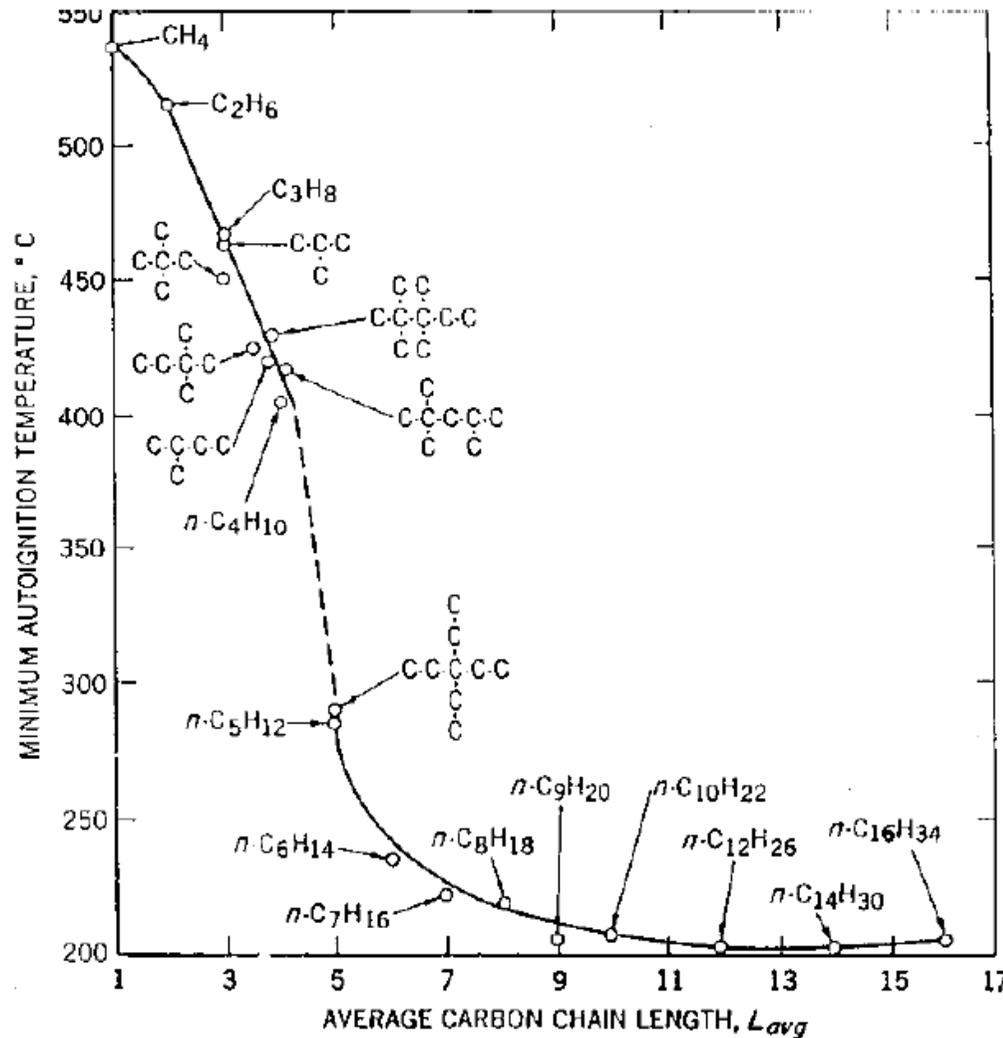
- The auto-ignition temperature is defined as:
 - the lowest temperature that a substance needs to be at to sustain combustion **without** the application of an **ignition source**.

Fuel	AIT °C	Flash point °C
Diesel	200	70
Hexane	233	-22
Kerosene JA1	250	37
Petrol	450	-20
Acetone	535	-18

- Note that there is no link between the auto-ignition temperature and the flash point.
- The **flash point** of a volatile material is the lowest temperature at which it can vaporise to form an ignitable mixture in air.



AIT of Paraffin hydrocarbons at atmospheric pressure



Both pressure and stoichiometry would also affect AITs.

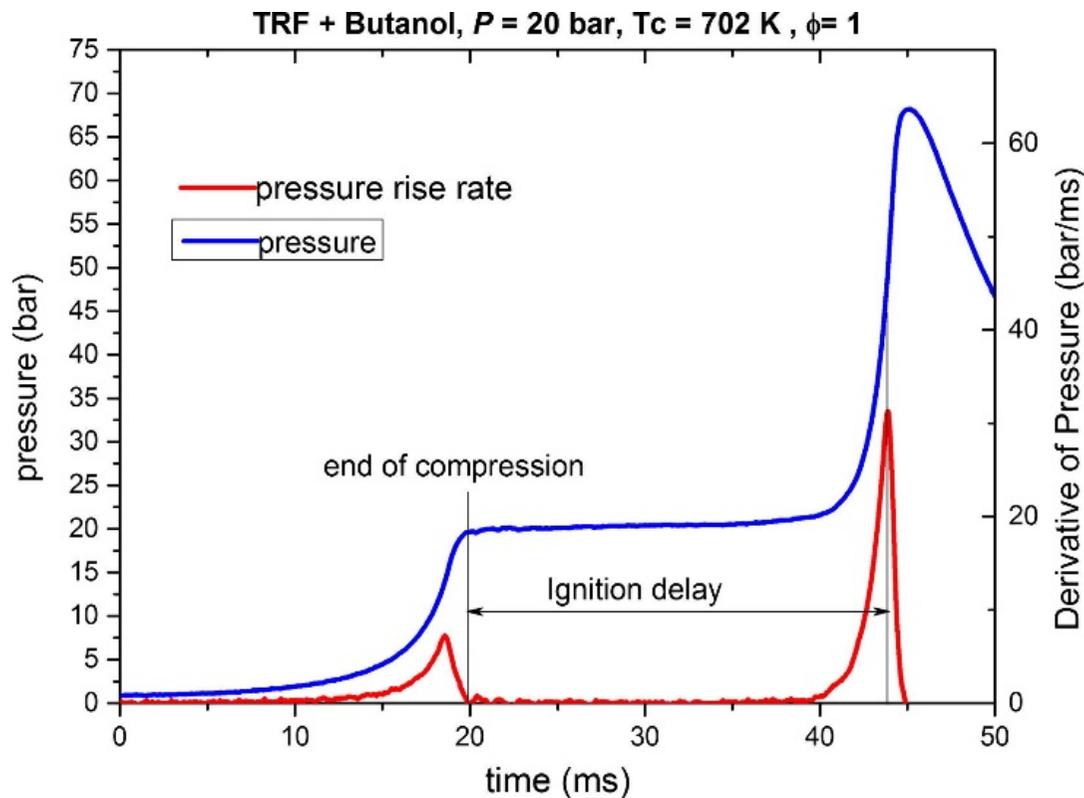
For many of the heavier **liquid hydrocarbons** the auto-ignition temperature is close to **200°C**

Applications of ignition studies

- Auto-ignition temperature and minimum ignition energy are key properties of fuels for **hazard applications**.
- Many explosions have occurred at fuel storage and fuel processing facilities and designs must seek to prevent this e.g. by limiting oxygen availability, providing flame arrestors etc.
- Another critical parameter is the ***ignition delay time, IDT***, for a fuel/air/oxygen mixture.
- Relevant to engine applications.

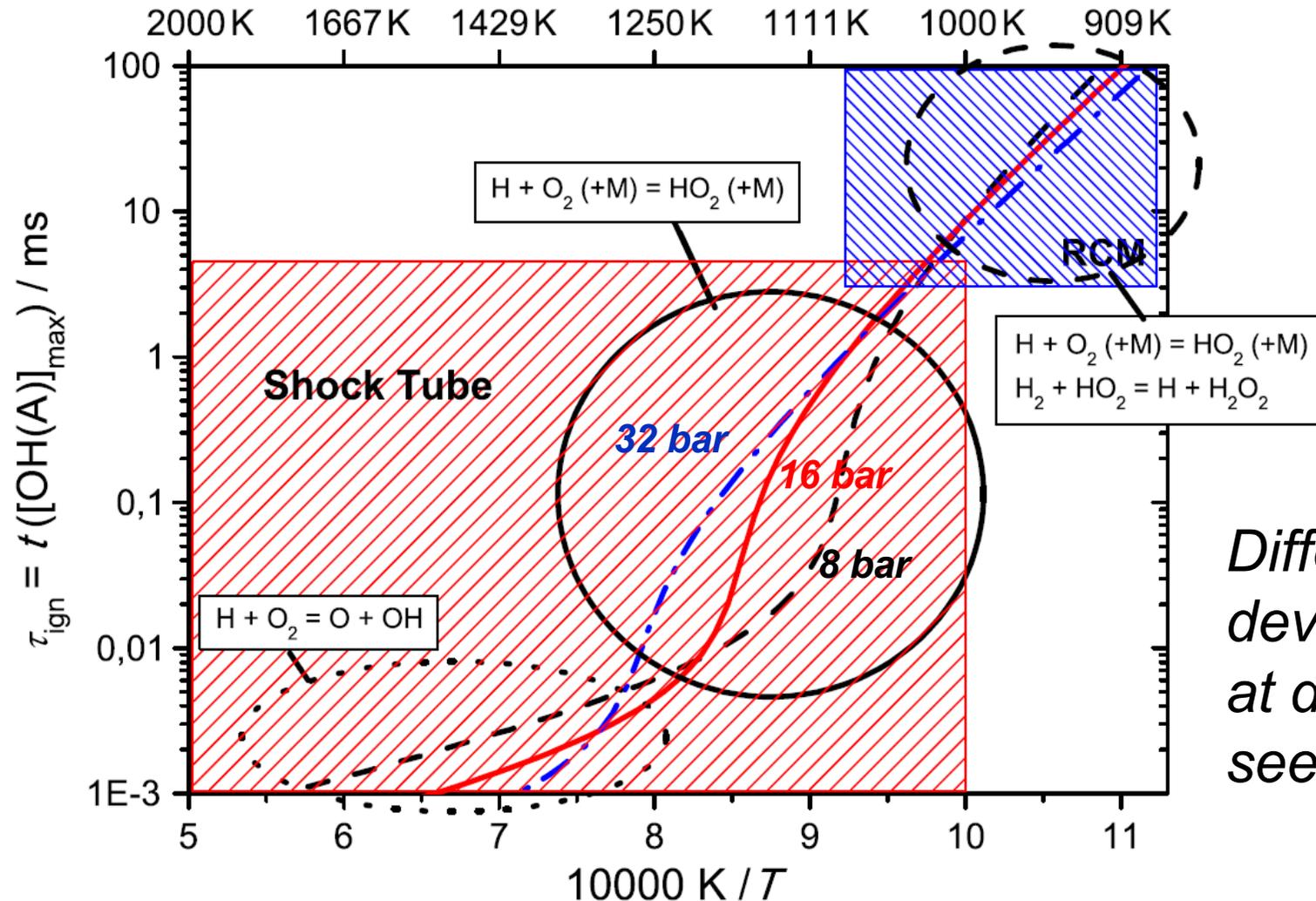
2.3 Ignition delay times

- As well as explosion characteristics we may also study the ignition delay of fuel/air/O₂ mixtures at different T, P .
- Tells us about reactivity and the ability of a fuel to auto-ignite e.g. under compression within a piston.



Example from single piston rapid compression machine
(Agbro *et al.*, 2017)

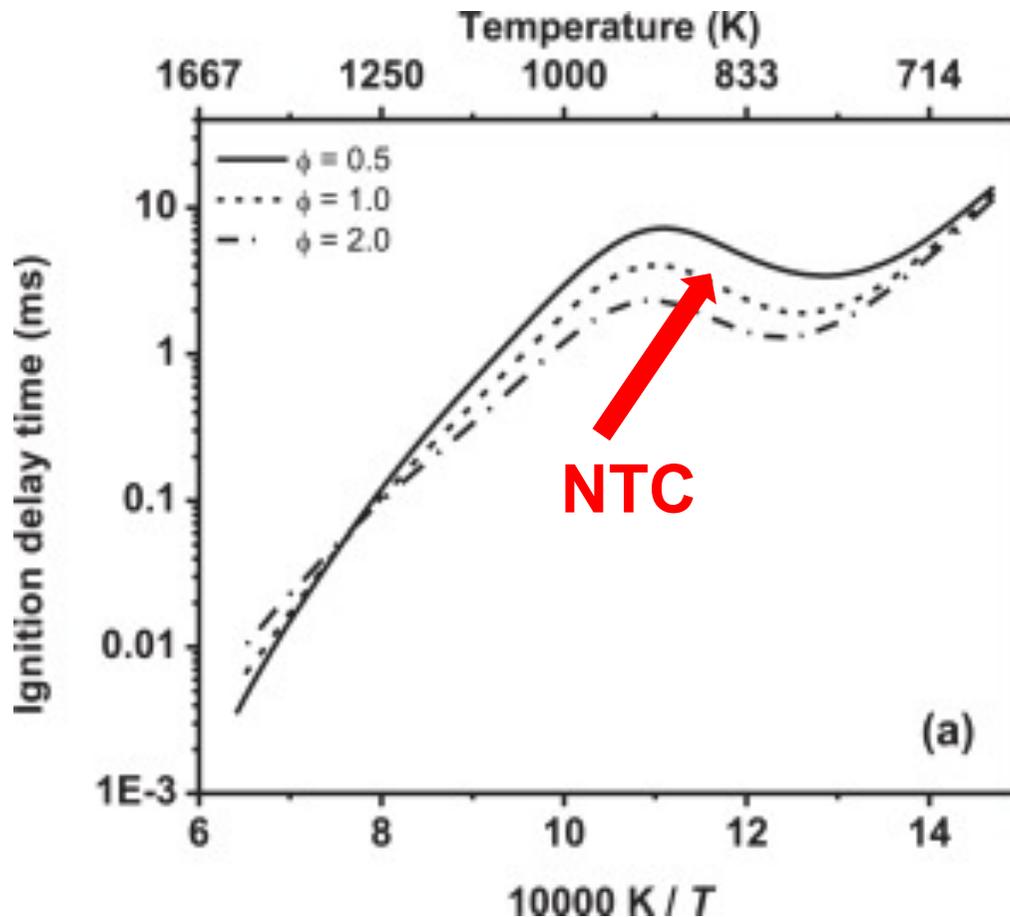
Impact of temperature and pressure on ignition delays for a mixture of 0.7 H₂ + O₂ + 3.76 Ar



Different devices used at different T, see later.

Ignition regimes for hydrocarbons

Model predicted ignition delay times for n-pentane oxidation in 'air' at 20 atm

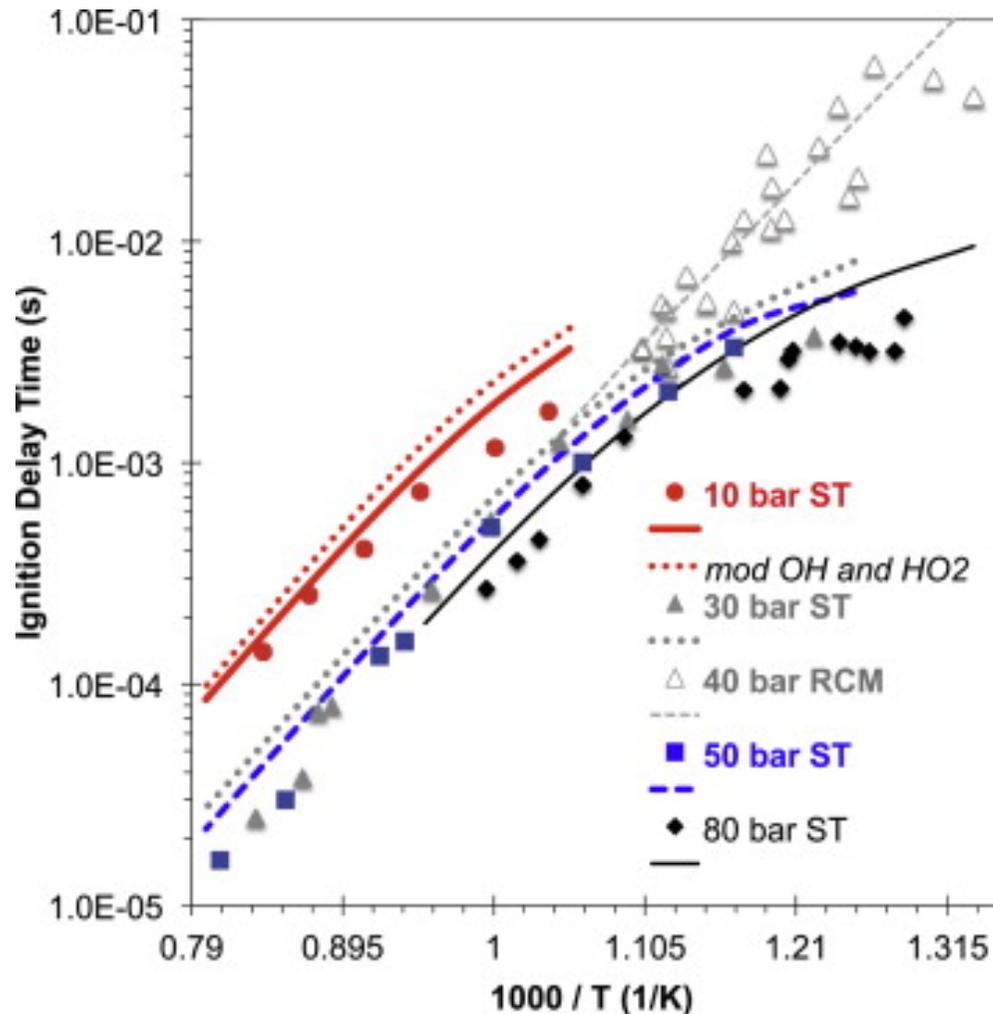


Data shows three distinct temperature ranges of reactivity:

- low (600–750 K)
- intermediate (900–1250 K)
- high temperatures (>1300 K).

Both low and high temperatures are included in the **negative temperature coefficient (NTC)** regime where ignition delays increase with increasing T .

Do all fuels show an NTC?



No, for example several of the smaller (lower C numbers) alcohol type fuels exhibit more Arrhenius type behaviour where $\log(\text{ignition delays})$ are closer to linear with respect to $1/T$.

As the chain length gets longer the alcohols behave more like alkanes (Sarathy et al., 2014).

Ignition delay times of *ethanol/air mixtures* at stoichiometric conditions (Sarathy et al., 2014)

Chemistry controlling different T regimes

- Main reaction classes

High temperature reaction classes

- H-atom abstraction (by O_2 , OH, H, HO_2 , etc.)
- Unimolecular decomposition
- Alkyl radical decomposition
- Alkyl radical isomerisation



Initiation

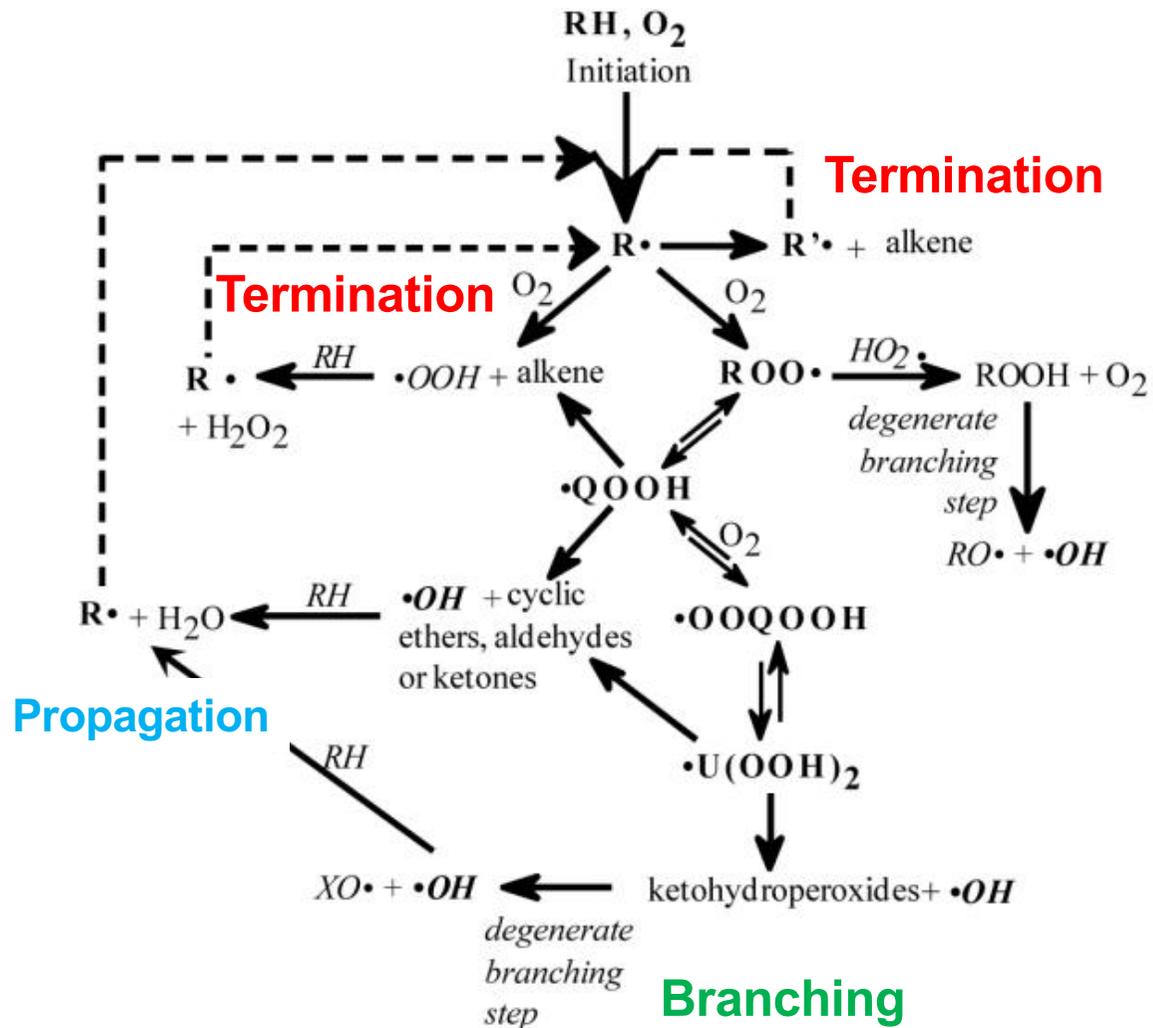
Low temperature reaction classes

- Addition of O_2 to alkyl radicals ($R+O_2=ROO$)
- $HO_2+ROO=ROOH+O_2$
- $ROOH=RO+OH$
- Alkyl peroxy radical isomerisation ($ROO=QOOH$)
- Addition of O_2 to $QOOH$ ($QOOH+O_2=OOQOOH$)
- Isomerisation of $OOQOOH$ to form ketohydroperoxide and OH
- $QOOH =$ cyclic ether + OH

*Promotes chain
branching*



Competition between branching and termination for generic alkane RH

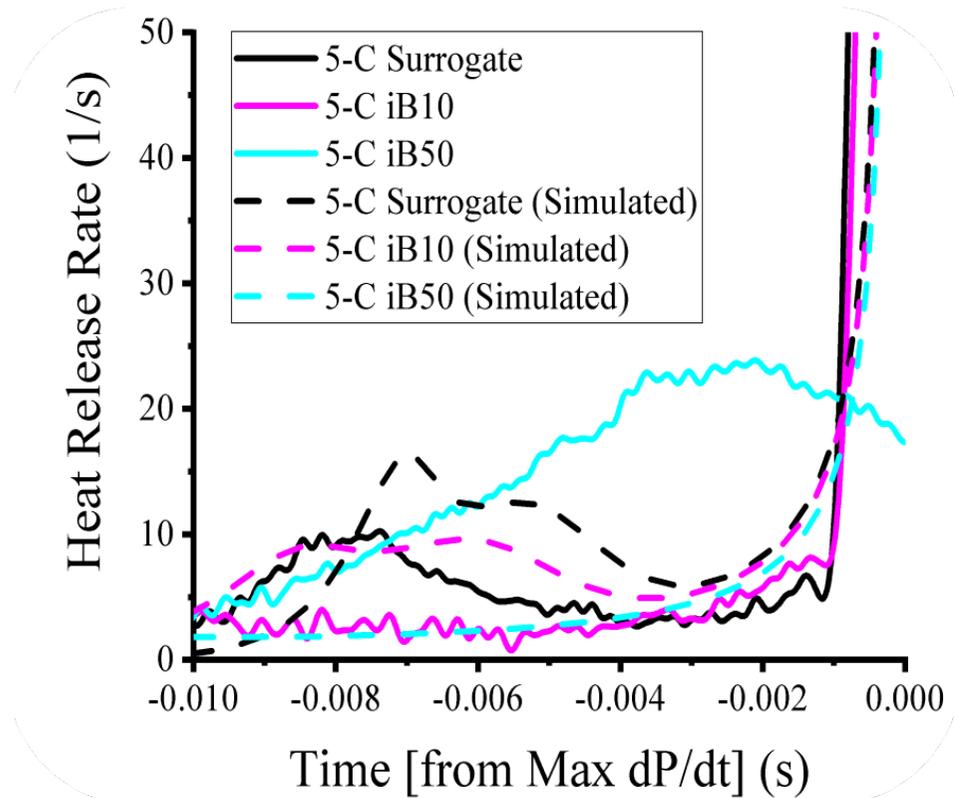


Depending on the T/P /stoichiometric conditions, either chain branching or termination can dominate, leading to ignition or not.

What causes the NTC?

- Key to reactivity is **fate** of **alkylperoxy RO₂ radicals** which undergo a number of reactions depending on *T* and *P*.
 - Most relevant for chain branching is isomerisation of RO₂ via internal hydrogen abstraction onto the oxygen radical site through a transition state ring resulting in formation of **hydroperoxyalkyl radical** (QOOH, where Q = R_{H-1}).
 - QOOH can undergo second O₂ addition with subsequent formation of OH + ketohydroperoxide, which again can form an additional OH.
- Branching**
- At lower temperatures RO₂ can reform original alkyl R + O₂ or can dissociate to produce an alkene + HO₂.
 - Formation of HO₂ and its fate is key to NTC. It is lower in reactivity than H and at intermediate temperatures can go on to form H₂O₂.
 - H₂O₂ is stable up to higher temperatures and hence its formation reduces overall radical pool, lowering reactivity increasing IDTs.
 - At higher temperatures H₂O₂ can decompose to form two OH radicals, thus increasing reactivity again.

Three stage heat release occurring at low T



- Michelbach, ECM, 2019 showed at 710 K gasoline surrogate showed three stage heat release in both experimental and simulated data from RCM.
- Sarathy et al. (2019) reported similar for n-heptane.
- **1st stage** dominated by low T chemistry $RO_2 \rightarrow QOOH$, $O_2 + QOOH$ and, $O_2QOOH \rightarrow$ ketohydroperoxide + OH .
- **2nd stage** dominated by hydrocarbon + HO_2 and H_2O_2 chemistry including $H_2O_2 \leftrightarrow 2OH$ followed by $H + O_2$ chain branching.

3rd stage dominated by small molecule chemistry e.g. $OH + HO_2 \rightarrow H_2O + O_2$, $CO + OH \leftrightarrow CO_2 + H$.

Ignition in engines

Both gasoline and diesel engines work through the ignition of fuel air mixtures:

Spark ignition – gasoline and air injected into small metal cylinders. A piston compresses the mixture, making it explosive, and it is then ignited by a small electric spark. The increase in pressure from the explosion pushes the piston down the cylinder which (through the crankshaft and gears) turns the wheels.

- Auto-ignition (i.e. chemically induced ignition) is usually **BAD** in an SI engine since it occurs **away from the normal flame front** and creates pressure waves which can damage the engine.
- This is called engine **KNOCK**.

Diesel – The air in the cylinder is compressed by factor ~ 20 . This generates heat. The fuel is then sprayed into the cylinder and ignites due to the temperature (~ 500 °C).



This photo of a badly damaged piston indicates the effects of long-term engine knock.

HCCI – homogeneous charge compression ignition engines

- An HCCI engine is a mix of both conventional [spark-ignition](#) and diesel compression ignition technology.
- Offers diesel-like high efficiency with lower NOx and particulate matter emissions.
- Fuel is **homogeneously mixed** with air in the combustion chamber with a very high proportion of air to fuel (lean mixture) and is compressed.
- As the engine's piston reaches its highest point (top dead centre) on the compression stroke, the **air/fuel mixture auto-ignites** from compression heat, much like a diesel engine.
- **Ignition delay important for HCCI since different fuel components within mixture can be used to control ignition timing.**

2.4 Validation data: Ignition delay time (IDT) measurements from RCM

IDT can be measured in a variety of experimental set-ups but of relevance to engines is the **rapid compression machine (RCM)** where IDT studied as function of equivalence ratio/thermodynamic conditions for different fuels and blends.

Single or dual piston machines operating at 600-1000 K, 1- 70 bar, with compressed temperatures depending on diluent used.

- Compression stroke followed by auto-ignition for reactive mixtures.
- Pressure rise captured by pressure transducers. Laser based piston location measurements used to determine volume changes.
- Some newer designs are able to perform rapid sampling of intermediates.



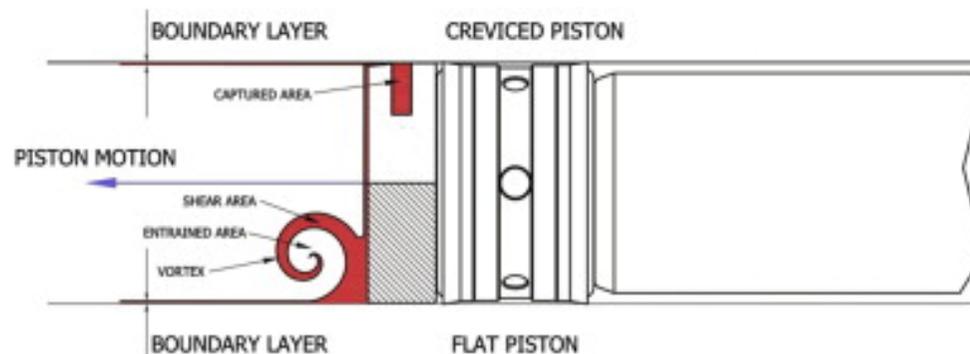
The Leeds RCM

Optimal RCM design features

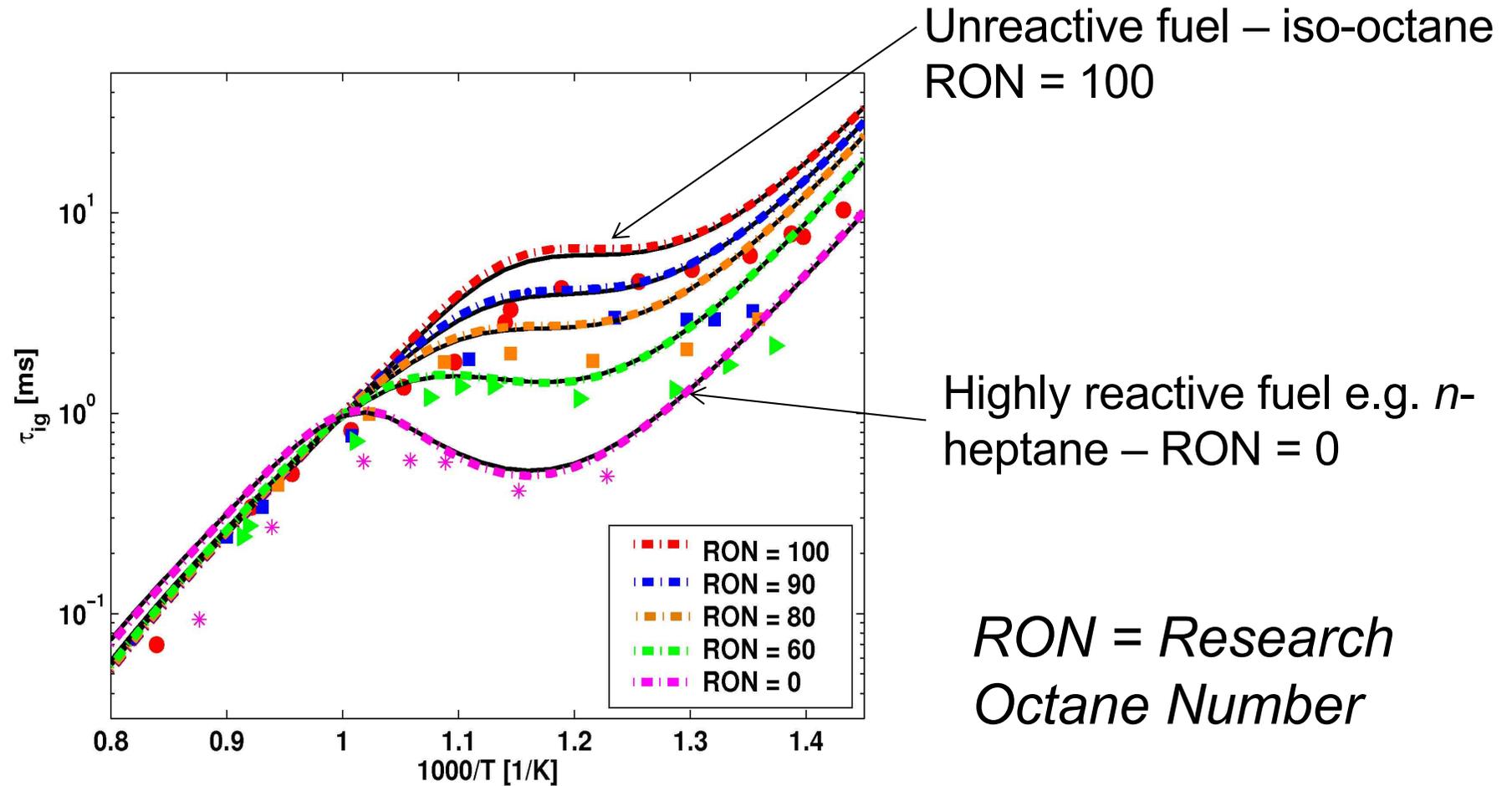
- Fast as possible compression time (10-70 ms) - adiabatic process.
- Constant as possible piston location at the end of compression - breaking and damping.

Issues:

- Cold boundary layer can be rolled up by piston, creating inhomogeneities (Lee & Hochgreb, 1998).
- Use of creviced pistons attempt to reduce this effect as does the use of twin-pistons creating symmetry (Sung & Curran, 2014).
- Optical diagnostics can be used to investigate inhomogeneities in RCM leading to hot-spots and pre-ignition.
- Inhomogeneities bigger issue for lower reactivity fuels and low T_s .
 - Methods to exclude pre-ignition profiles can be used.



Ignition delay measurements



Source: Stanford

RON and MON

- In an SI engine, efficient fuels are required but we do not want fuels that will create the potential for knocking.
- Historically the anti-knock quality is expressed by **octane numbers** by comparison to mixtures of *n*-heptane + iso-octane.
- The higher the octane number, the more compression the fuel can withstand before igniting.
- RON – Research Octane Number
 - *Determined by running the fuel in a test engine with a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of iso-octane and n-heptane. Low speed, milder driving.*
- MON – Motor Octane Number
 - *Determined at 900 rpm engine speed and not 600 rpm for RON using variable ignition timing.*

RON and MON have been useful measures of fuel tendencies to auto-ignite but cover specific conditions and not easily extrapolated to those of modern down-sized, boosted engines.



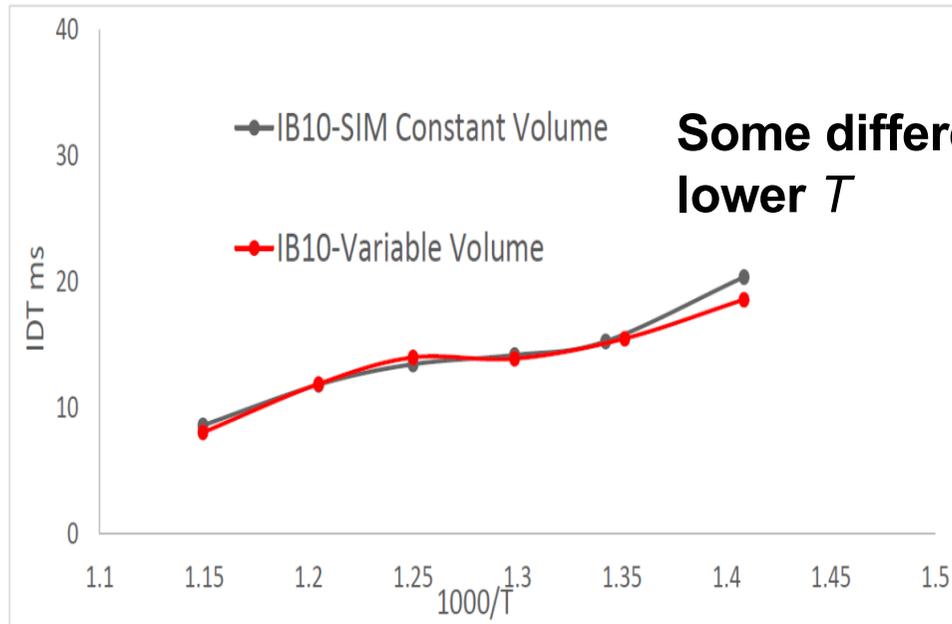
Modelling chemistry within the RCM

- If we can develop models that well represent fuels/mixtures across different temperatures and pressures, better detail for use in engine design.
 - RCM provides validation opportunities for such models.
- Most validation studies assume adiabatic core hypothesis.
 - Assumes a boundary layer exists along the walls of the combustion chamber and is the only location where heat loss to the walls occurs.
 - Used to determine temperature within chamber at end of compression.

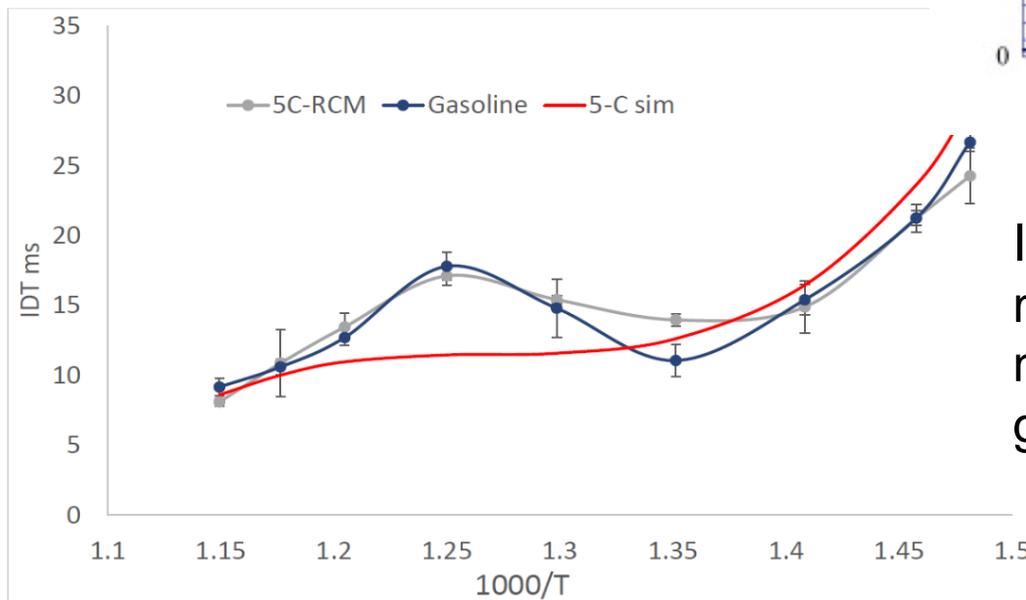
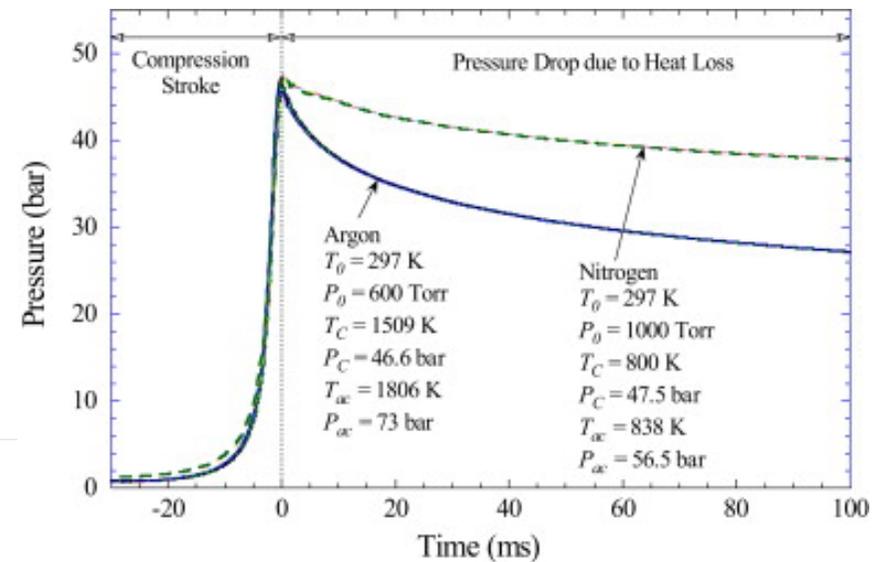
$$\frac{T_c}{T_i} = \left(\frac{P_c}{P_i}\right)^{\frac{\gamma-1}{\gamma}}$$

- γ is temperature dependent ratio of specific heats for the mixture
- Simplest modelling approach closed, constant volume, well mixed reactor - in reality heat losses occur during compression.
- Thus “***non-reactive***” data also obtained using mixture with thermodynamic properties as reactive condition but inert.
 - Achieved by replacing oxygen with nitrogen.
 - **Volume profile then used in subsequent modelling of reactive case.**

Constant vs. variable volume simulations



Sung & Curran, 2014



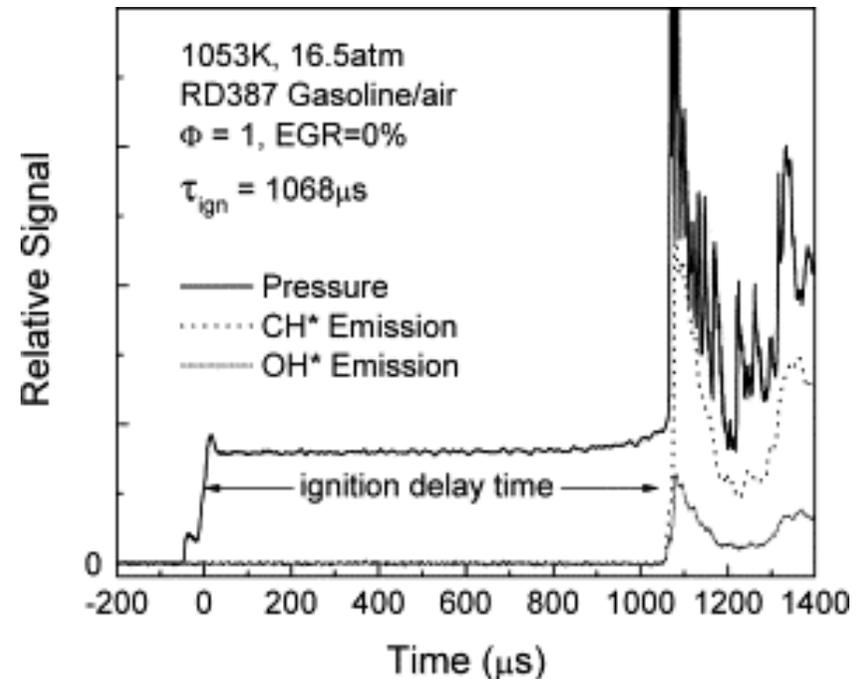
IDT data shows where chemical models are working and are not...e.g. this 5 component gasoline surrogate.

2.5 Validation data: shock tubes

- The shock tube is an almost idealised reactor consisting of long tube separated into two sections of different pressures e.g. by diaphragm.
- As **diaphragm ruptures** gases strive for equilibrium resulting in a normal shock wave which hits the end wall and causes a stagnation point as the wave reflects
 - the test location.
- Process very rapid occurring within micro-seconds
 - negligible heat loss holding temperatures/pressures constant at test location until the arrival of waves from the driver side.
- Non-idealised behaviour:
 - finite diaphragm breaking and shock formation time;
 - a boundary layer build up due to viscous effects behind moving incident shock waves
- Despite this repeatability usually good.
- Can be used for IDT measurement or for **species profiling**.

Validation data: IDT and species profiling from shock tubes, Ch 6 in Cleaner Combustion

- IDT - time interval between arrival of reflected shock wave and onset of ignition at test location determined by P measurements or CH^* and OH^* emission. (Gauthier et al., 2004)
- Low T measurements limited by available test time
 - interval between the arrival of the reflected shock at the observation port and the arrival at same location of a significant pressure disturbance from the predicted or measured reflected shock pressure.
- Not suitable for long IDTs.
- **Time-of-flight mass spectrometry** or multi-species optical diagnostics can be used for continuous sampling and species analysis.
- **Gas chromatography** used for product analysis at end of process.
- Species data allows for wider mechanism validation vs IDT.



2.6 Validation data: Species profiles from Jet Stirred Reactors (JSRs)

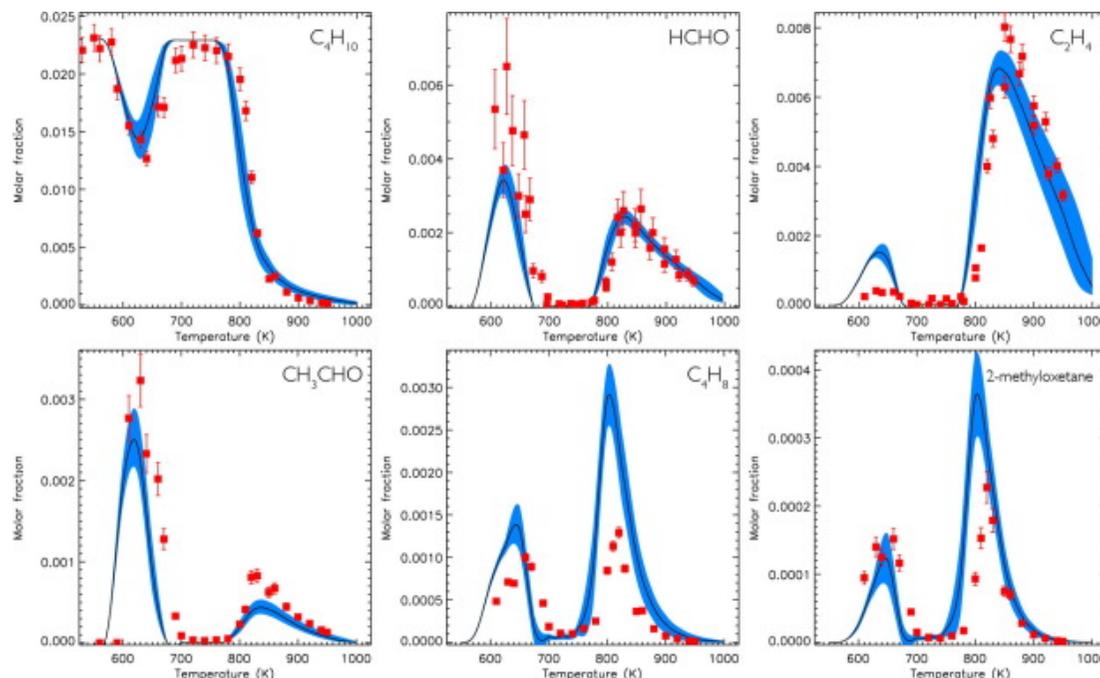
- Can more easily give information about reactants products and intermediates over a range of T when operated at steady state or under oscillatory conditions.
- Turbulent jets used for enhanced mixing in order to create **homogeneous reactor**.
- Preheating of mixture improves T homogeneity.
- Higher pressures can be achieved - quartz reactor encased in pressure resistant jacket.
- Modelled using well mixed open reactor equations with heat transfer - *shown earlier*.
- Usually operated **isothermally**.
- Heat losses, losses of radicals to walls and residence times are important physical parameters in models.
 - Radical wall losses reduced by use of fused silica vessels.



Species observations

- Coupled with species measurement systems including gas chromatography, IR spectrometry e.g. butane oxidation shown here. (Hébrard et al., 2015).
- Recent use of **synchrotron** vacuum UV photo ionisation mass spectrometry for detecting **intermediates** for the first time e.g. ketohydroperoxides/enols.

- Identification of intermediates helps to confirm reaction pathways.
- **Stringent test** of reaction mechanisms' ability to predict species in reaction chain



SECTION 3

LAMINAR FLAMES

Why should we understand flames?

- Flames are important in many practical situations and propagate in engines, gas turbines, domestic burners, boilers etc.
- The properties of flames for different fuels tell us about the fuel reactivity at higher temperatures and provide fundamental understanding of importance in device design.
- We must design burners safely and with low pollution emissions.



Flame propagation

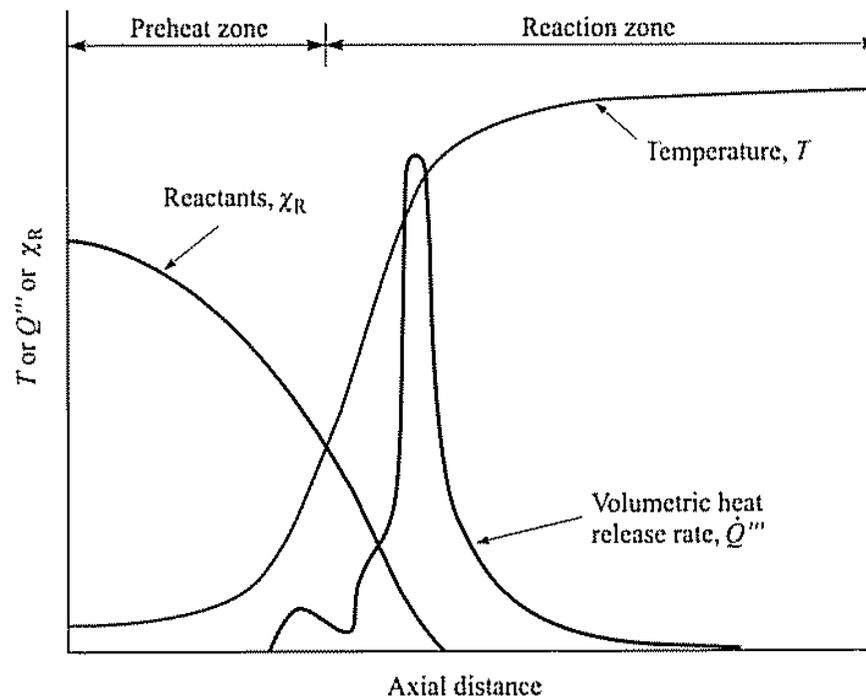
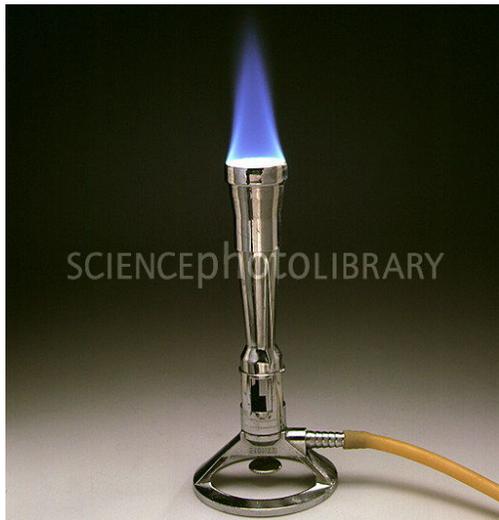
- Not all mixtures of fuel and air are capable of supporting or propagating a flame.
- Imagine a region in space containing fuel/air mixture is made up of lots of discrete (control) volumes.
- If an ignition source is applied to a volume then a flame will propagate if the energy transfer out of the control volume is sufficient to cause ignition in the next one.
- Clearly, **close to stoichiometric** conditions is where the **max. flame temperature** occurs and therefore the max. heat release.
- **Hence there is a correlation between the equivalence ratio for max. flame temperature and burning velocity.**

Flame types

- **Combustion can occur in flame or non-flame modes.**
- **Types of flames:**
 - **Premixed** flames where fuel and oxidizer are mixed before flowing into burner.
 - **Diffusion** (non-premixed) flames where oxidizer diffuses from atmosphere to flame edges.
- **Flames can be:**
 - Freely propagating e.g. in an explosion or in a spherical reaction vessel.
 - Burner stabilized as in a Bunsen flame, cooker, boiler.
- **Modes of combustion**
 - A discrete combustion wave that travels subsonically is called a **deflagration**.
 - Combustion waves may be also travel at supersonic velocities, called **detonation**.

Premixed flames

- Most familiar example is Bunsen flame with collar open allowing good pre-mixing of fuel and air.
- This is a burner stabilised flame – its stability depends on fuel/air flow rates.
- At high flow rates flames can experience **lift-off** or even **blow out**.
- **Flash back** can also occur in premixed flames if the burner nozzle size is too large to be able to quench the flame through heat transfer.



Flames at different flow velocities



Attached



lifted



lifted



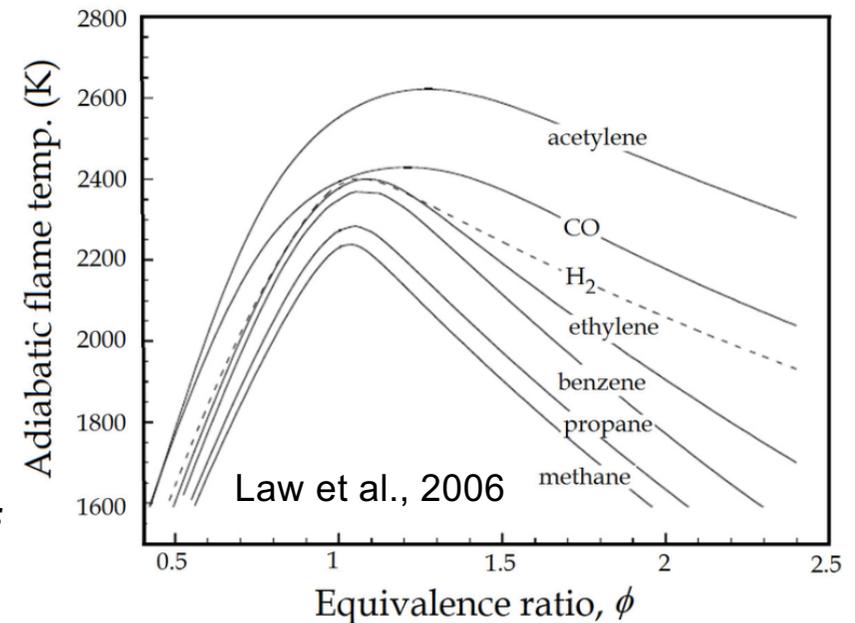
blow off

Fundamental properties of Flames: Adiabatic flame temperature (AFT)

Two types of **adiabatic flame temperature** depending on how the process is completed:

- 1. constant volume:** temperature that results from complete combustion without any work, heat transfer or changes in kinetic or potential energy.
- 2. constant pressure:** energy is utilised to change the volume of the system (i.e., generate work) leading to a lower temperature.

- Theoretically the **maximum adiabatic flame temperature** for a given fuel and oxidizer combination **occurs with a stoichiometric** mixture (correct proportions such that all fuel and all oxidizer are consumed).
- In practical systems the maximum flame temperature can occur on the rich side of stoichiometric for hydrocarbons due to preferential diffusion of O_2 into the flame zone and incomplete combustion.

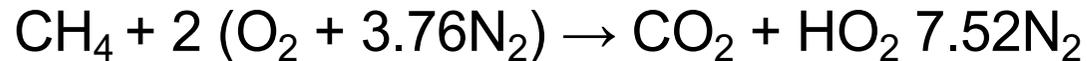


Calculation of AFT

- In reality heat transfer, incomplete combustion, and dissociation all result in lower temperature but provides a constant to compare fuels
- Simplest calculation is constant volume adiabatic flame temperature which is the maximum possible T .
 - No heat is lost and enthalpy stays constant, no work done.

$$H_{reac} = N_i h_{i,298} = H_{products} = N_j h_{j,Tad}$$

For example the stoichiometric combustion of methane in air:



Enthalpies, match and solve for T_{ad}

$$H_{react,298} = h_{CH_4} + 2h_{O_2} + h_{N_2}$$

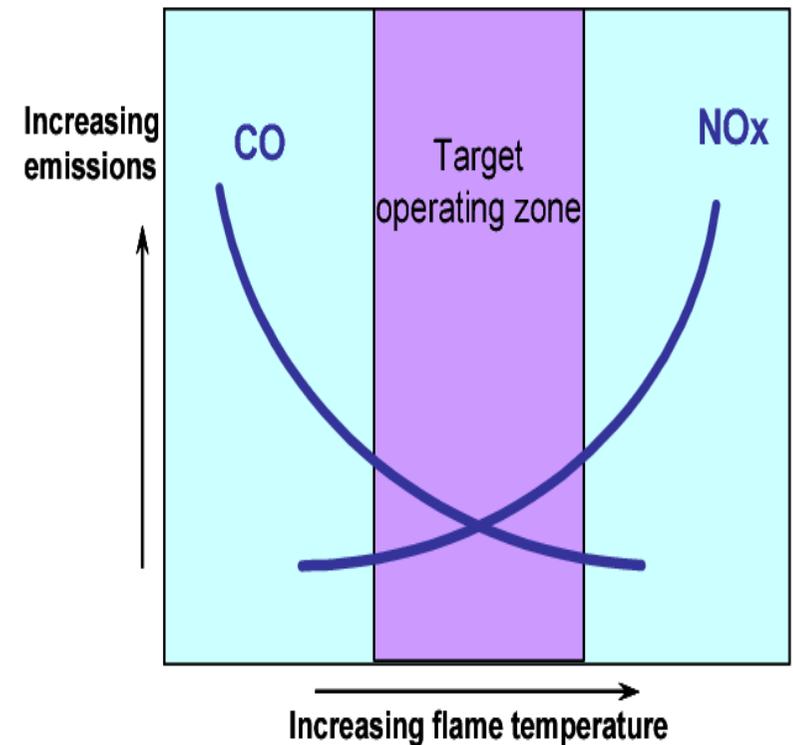
$$H_{prod,T_{ad}} = (h_{CO_2,298} + C_{P,CO_2} (T_{ad}-298)) \\ (h_{H_2O,298} + C_{P,H_2O} (T_{ad}-298)) \\ (h_{N_2,298} + C_{P,N_2} (T_{ad} - 298))$$

- We do not know T_{ad} and also C_p is a function of T – so needed to simplify to an average value to use this form of equation.
- Generally C_p could be expressed as NASA polynomial and iterative methods used to solve for T_{ad} .
- Incorporated into commonly available codes such as Chemkin, Cantera etc.
- Full tutorial:

<http://elearning.cerfacs.fr/combustion/n7masterCourses/adiabaticflametemperature/index.php>

Constant pressure adiabatic flame temperatures of typical fuels

Fuel	Oxidiser	Adiabatic flame T (°C)
Hydrogen (H ₂)	Oxygen	3200
Propane (C ₃ H ₈)	Oxygen	2526
Acetylene (C ₂ H ₂)	Air	2500
Hydrogen (H ₂)	Air	2254
Anthracite	Air	2180
Bituminous Coal	Air	2172
Gasoline	Air	2138
Light fuel oil	Air	2104
Kerosene	Air	2093
Ethanol	Air	2082
Toluene (C ₇ H ₈)	Air	2071
Propane (C ₃ H ₈)	Air	1980
Wood	Air	1980
Butane (C ₄ H ₁₀)	Air	1970
Methane (CH ₄)	Air	1963
Natural gas	Air	1960
Methanol (CH ₄ O)	Air	1949



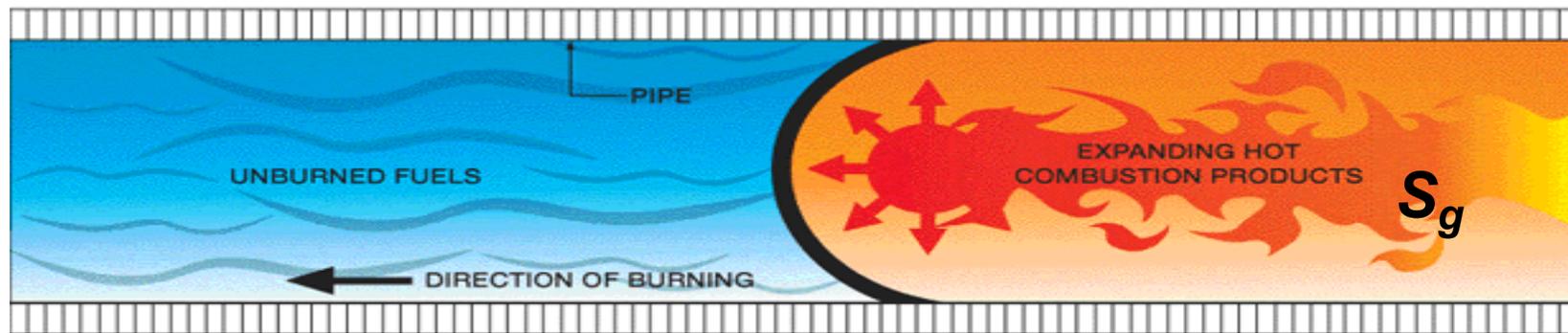
Fundamental properties of Flames:

Laminar Burning Velocity, LBV

- Laminar burning velocity is a physiochemical constant for a given combustible mixture, T , P , ϕ .
 - Velocity, relative to unburnt gas, with which a planar one dimensional flame travels along the normal to its surface into the mixture.
- Unfortunately, although its theoretical definition is simple, the same cannot said of its practical measurement .
- Burning velocity is a measure of how fast reactants are moving into the flame zone in a moving frame of reference.
 - E.g. in a spherically expanding flame.
 - The spherical flame has no heat losses and burns at the adiabatic flame temperature.
- Flame speeds are measured relative to a fixed point and are influenced by the expansion of burnt gases.

LBV vs flame speed

- In an explosion in a closed spherical vessel ignited by a spark, flame moves into unburnt gas at flame speed, S_s which is greater than the burning velocity S_L .
 - Due to expansion of burnt gases behind the flame front moving at speed S_g .

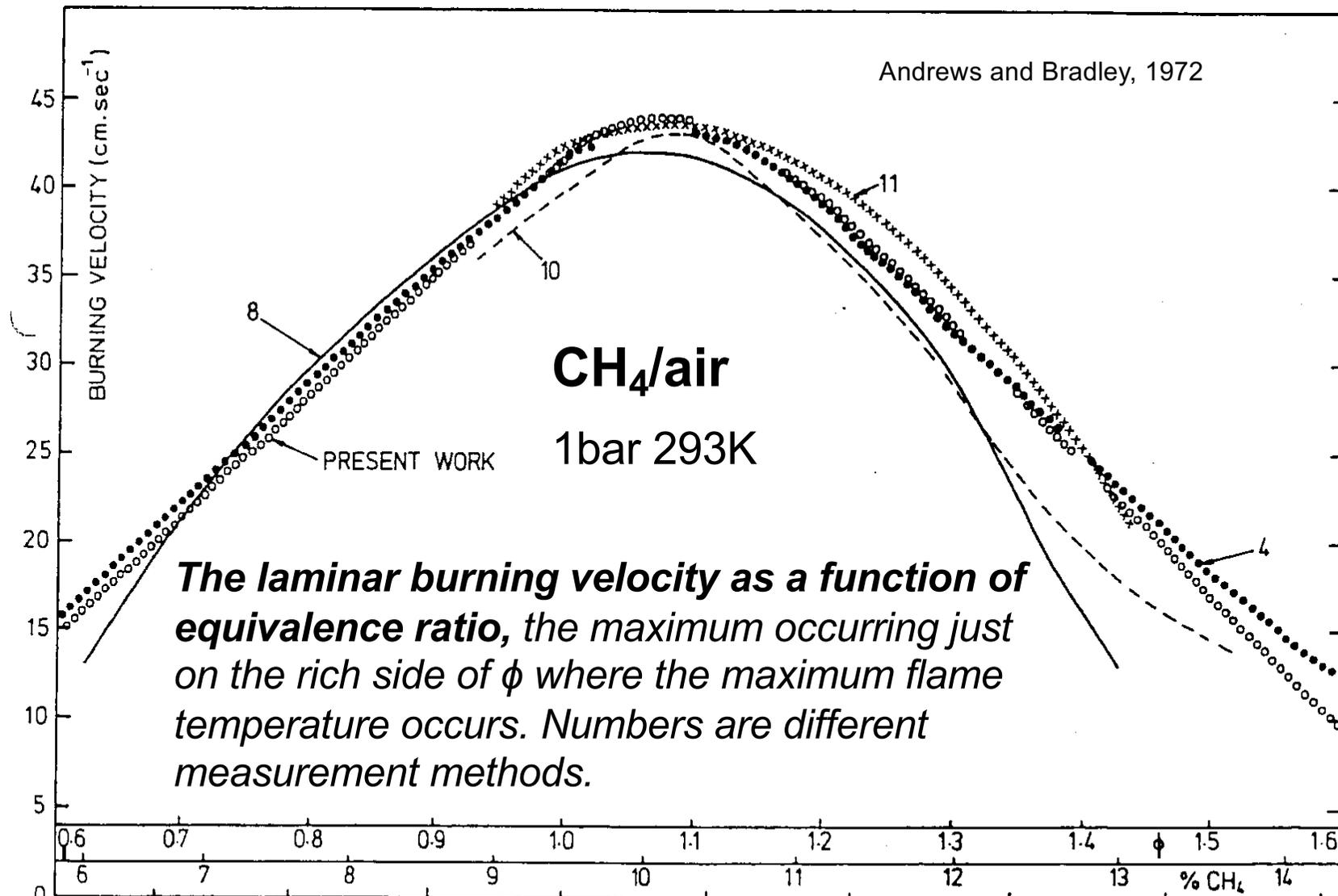


$$S_s = S_L + S_g$$

- For a stationary burner stabilised flat flame with no heat losses, the LBV is the velocity at which unburnt gases are supplied to the burner.



Effect of stoichiometry



Measuring burning velocity – conical flame

Using a laminar conical flame:

The minimum fuel speed normal to the flame surface
= Laminar burning velocity S_L

Laminar conical flame: $S_L = U_{\perp} = U_R \times \sin\theta$

$$U_R = S_L / \sin\theta$$

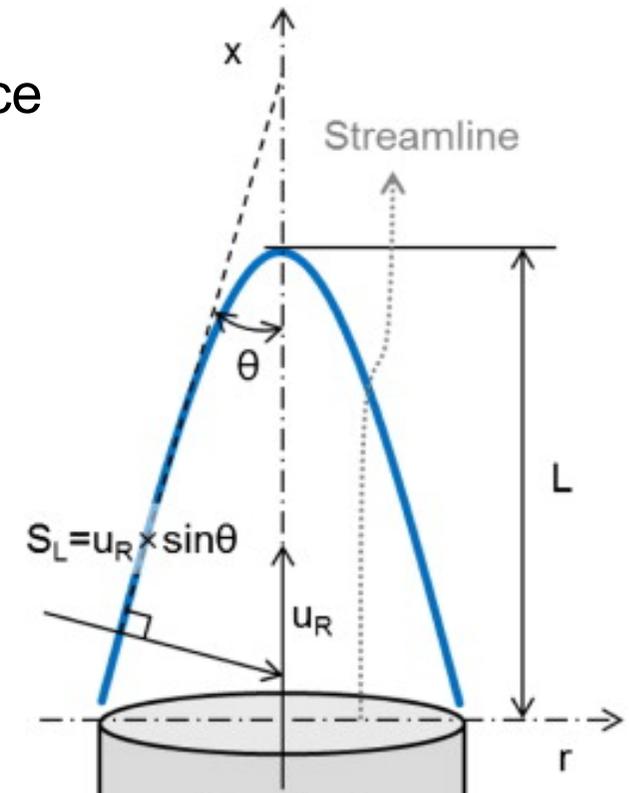
Typically $\theta \sim 30^\circ$:

For a stable flame: $U_R \geq 2 \times S_L$

*To measure S_L , need to measure min U_R
for stationary flame and θ .*

Difficulties in measuring angle/area.

Possible influences of stretch for differential
diffusion of reactant species.

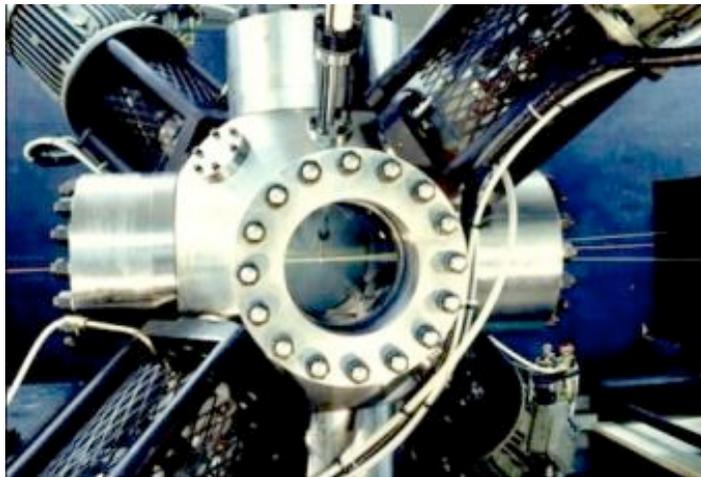


Bunsen burner

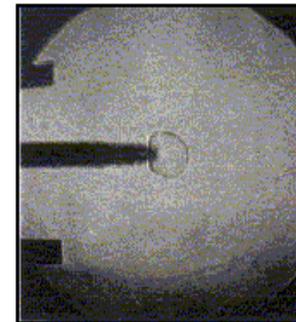


Measuring burning velocity - spherical bomb

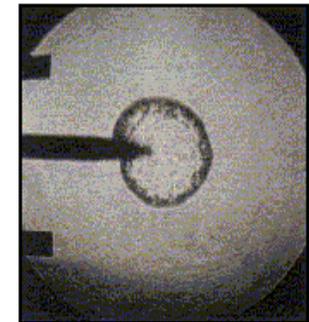
- S_L can also be measured in a constant volume spherical vessel.
- Pressure measurements or Schlieren photography can be used to evaluate burning velocities but requires interpolation.
- Instabilities, curvature and stretch cause measurement difficulties, particularly for pressure method.
- Can also be used for turbulent velocities by use of fans and at varying pressures.



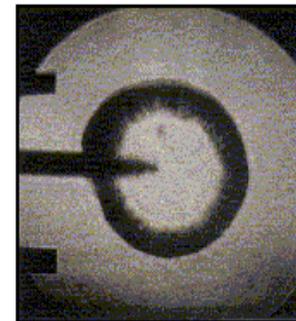
The bomb!



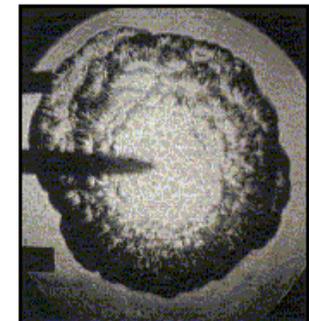
$t = 5\text{ms}$ $r_f = 9\text{ mm}$ (smooth)



$t = 11\text{ms}$ $r_f = 22\text{ mm}$ (cellular)



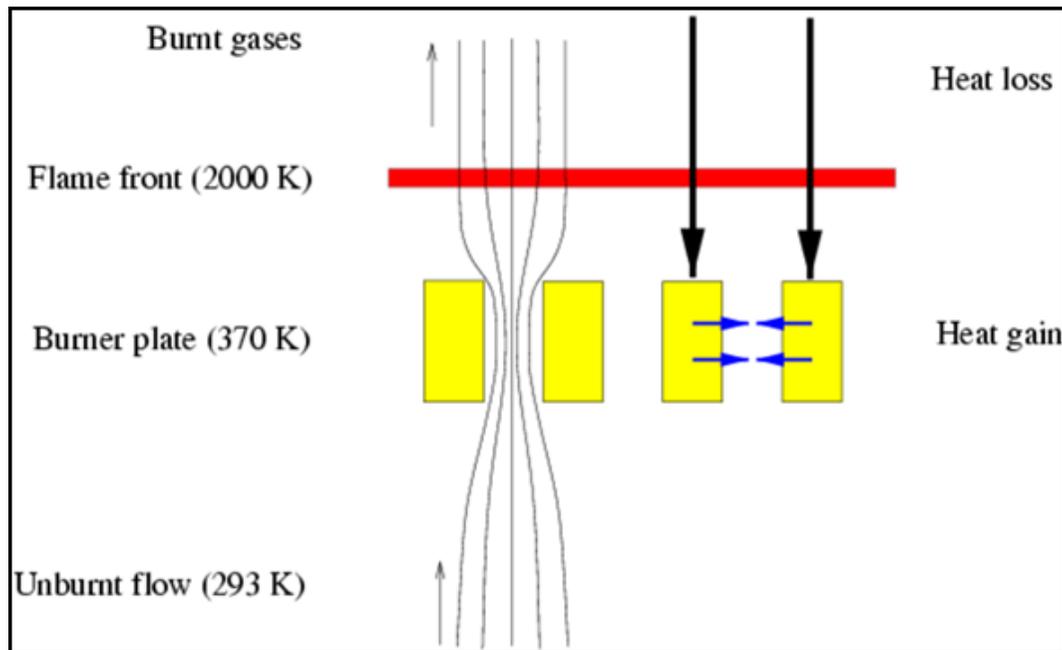
$t = 21\text{ms}$ $r_f = 35\text{ mm}$ (smooth)



$t = 38\text{ ms}$ $r_f = 53\text{ mm}$ (cellular)

Measuring burning velocity, flat flame burner

- Heat flux method is used by creating adiabatic conditions on a flat stable flame.

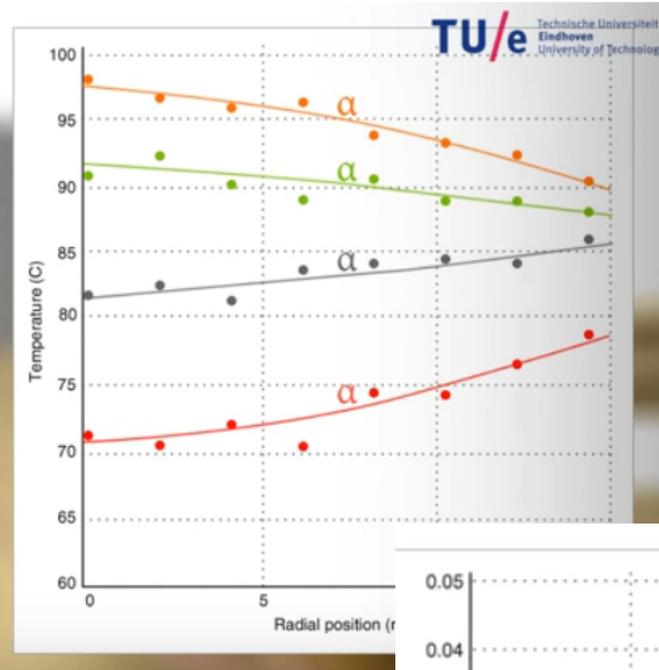
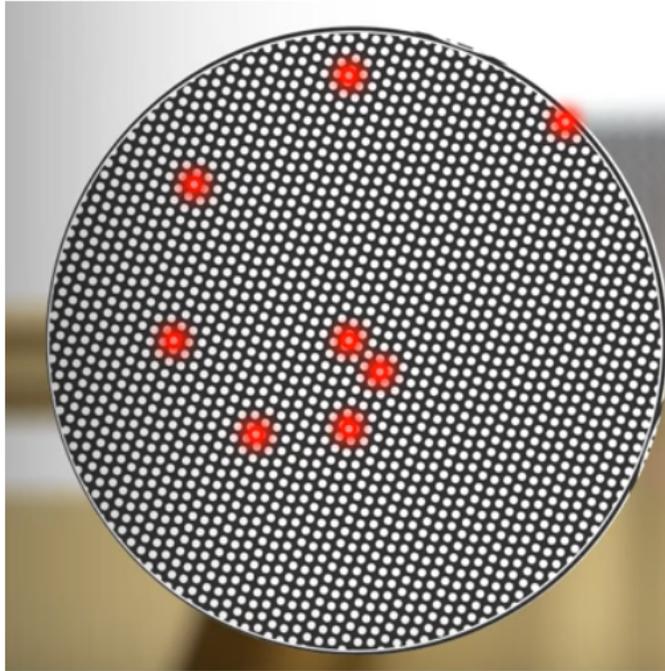


<http://cms.heatfluxburner.org/home/>

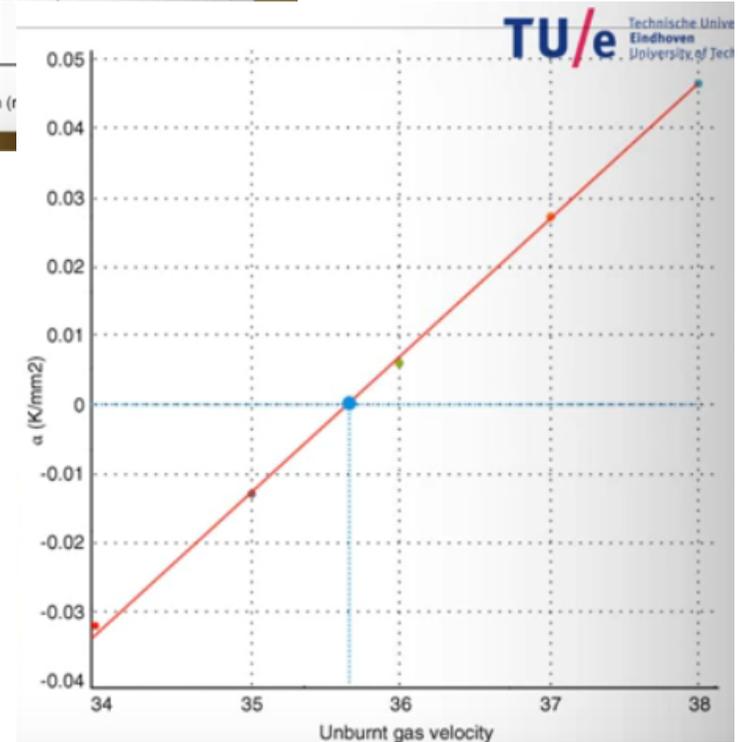
Measuring burning velocity – flat flame burner

- When gas inlet velocity $<$ laminar burning velocity, flame is stabilised on the burner.
 - As a result the heat loss of the flame to the burner plate is larger than the heat gain of the gas mixture from the burner plate.
- When unburnt gas velocity $>$ laminar burning velocity heat gain of gas from burner plate is larger than heat loss of flame.
- Both of these are non adiabatic situations.
- An **adiabatic** situation is found when there is no net heat loss to the burner, meaning heat loss and gain level each other off.
- In this case **laminar adiabatic burning velocity equals inlet velocity of the gas mixture**. T profile is flat across the flame.
- Various inlet gas velocities are tested T profile measured and interpolation used to obtain zero heat flux conditions.

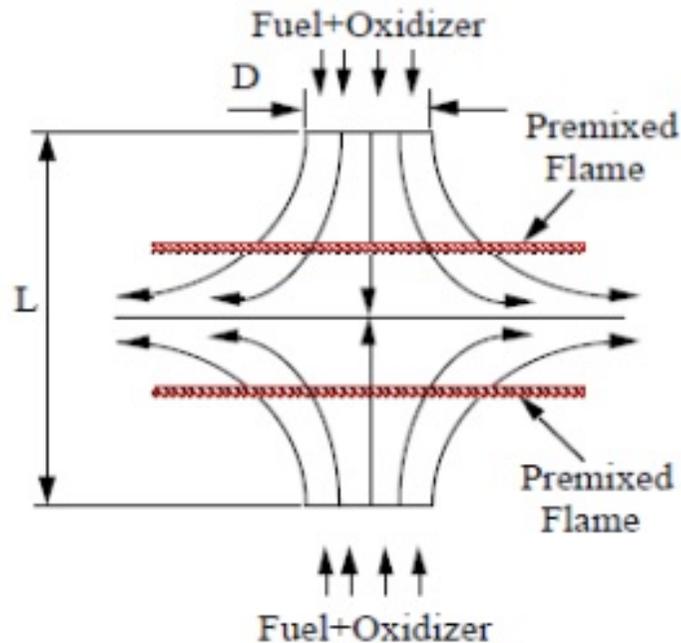
Interpolation method



T profiles taken at various unburnt gas velocities and interpolation used to find zero gradient profile corresponding to LBV.



Counterflow flames

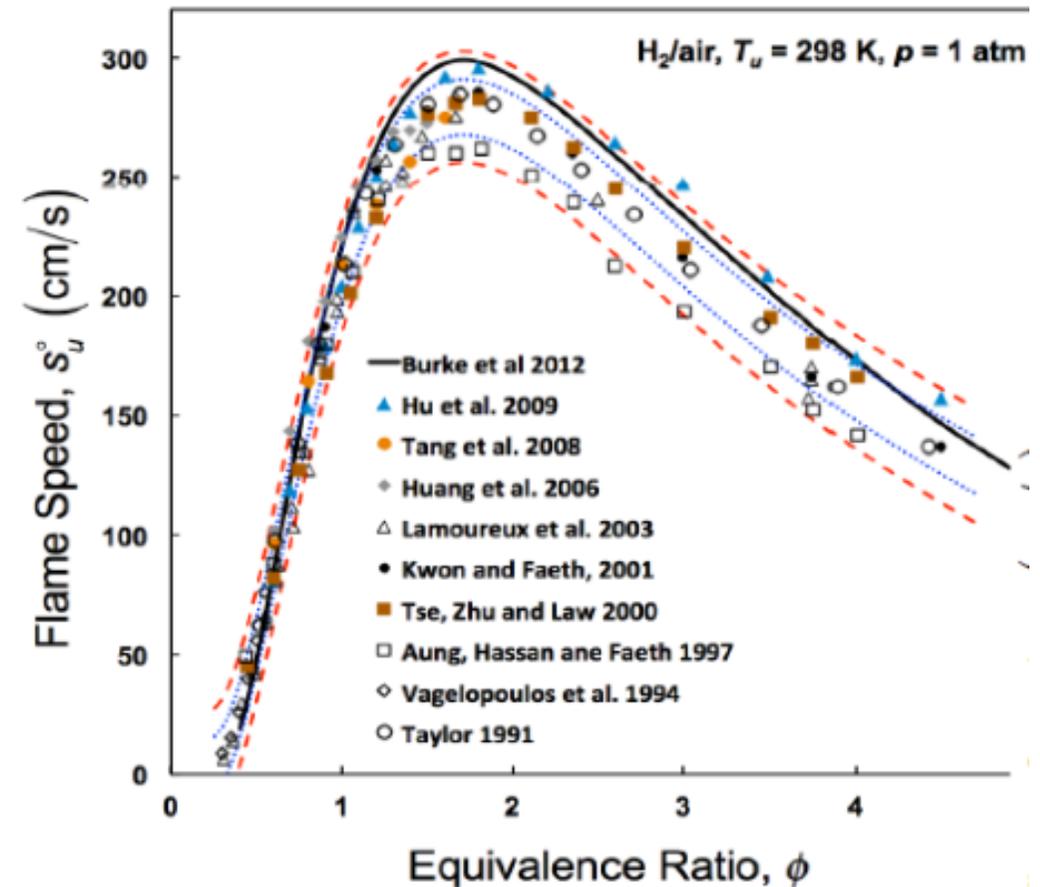


- Wu and Law, 1985 first used for LBV measurements demonstrating the influence of stretch.
- Stagnation flames achieved by:
 - impinging separate fuel and oxidizer streams
 - impinging two premixed streams
 - from a premixed stream impinging on a solid surface.
- Attractive as leads to flat flame assisting probing species and structure.
- Assumption that radial velocity varies linearly in the y or radial direction, leading to a simplification in which the fluid properties are functions of the axial distance only.

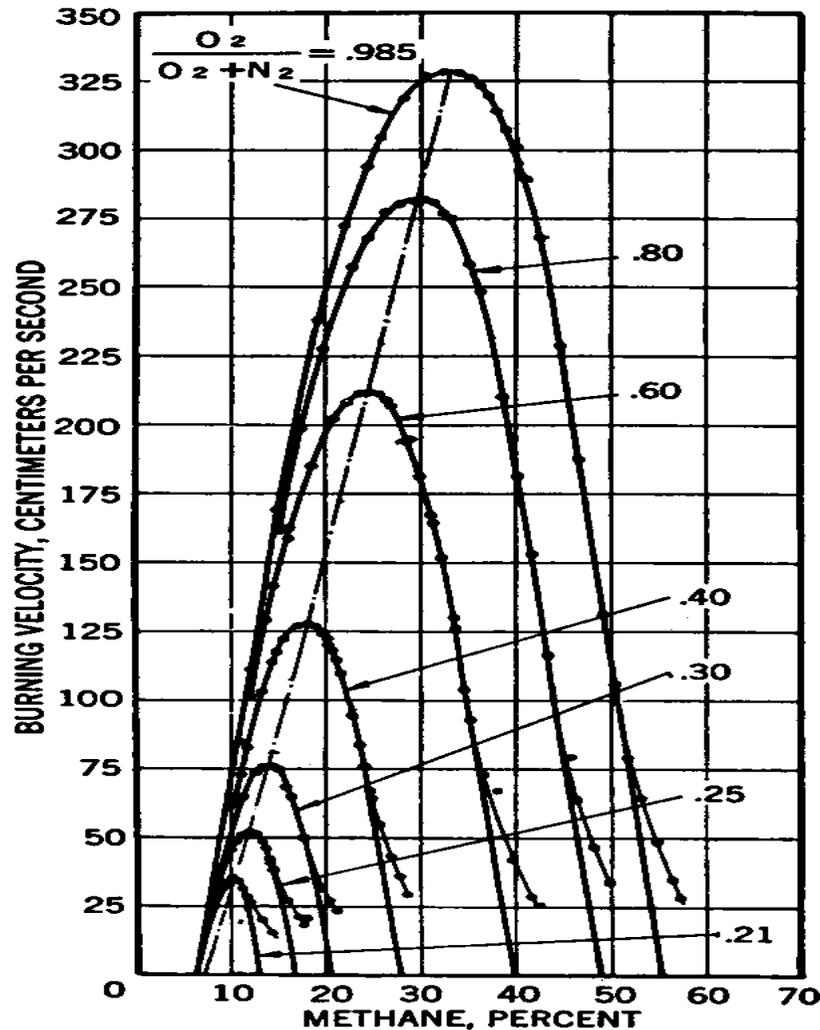
Uncertainties in LBV measurement

- **ALL** methods for LBV are not measuring directly & require interpretation.
- Measured values show **variability** between experiments.
- **Inherent level of uncertainty.**
- Coupling experiment with DNS may help interpretation.
- Recommend to read presentation by Egolfopoulos:

Towards Eliminating Apparatus Dependence and Approaching Extreme Engine-Relevant Conditions



Effect of oxygen and nitrogen



burning velocities of mixtures of methane, oxygen, and nitrogen at atmospheric pressure (Jahn).

Methane flame with varying amounts of O_2 and N_2 .

Note the Very wide Flammable Range with 100% O_2

S_L in oxygen is $\sim 10 \times S_L$ air

Measured flame speed – CH₄ and H₂

Andrews and Herath – 1986, Herath PhD., U. Leeds

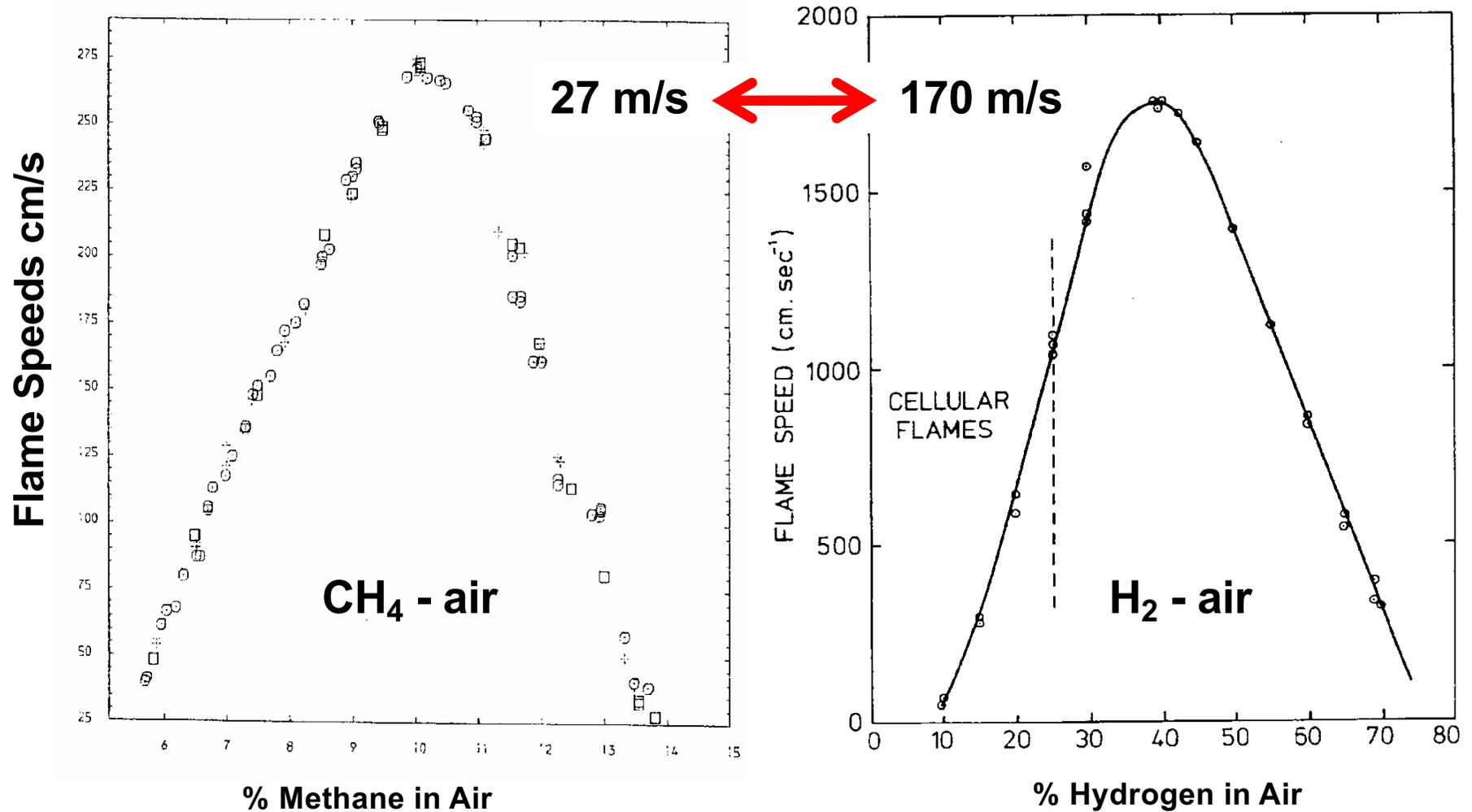


Fig. 8. Flame speeds for hydrogen-air at one atmosphere.

measured in a 0.5 m diameter by 0.5 m long closed vessel

Effect of initial temperature

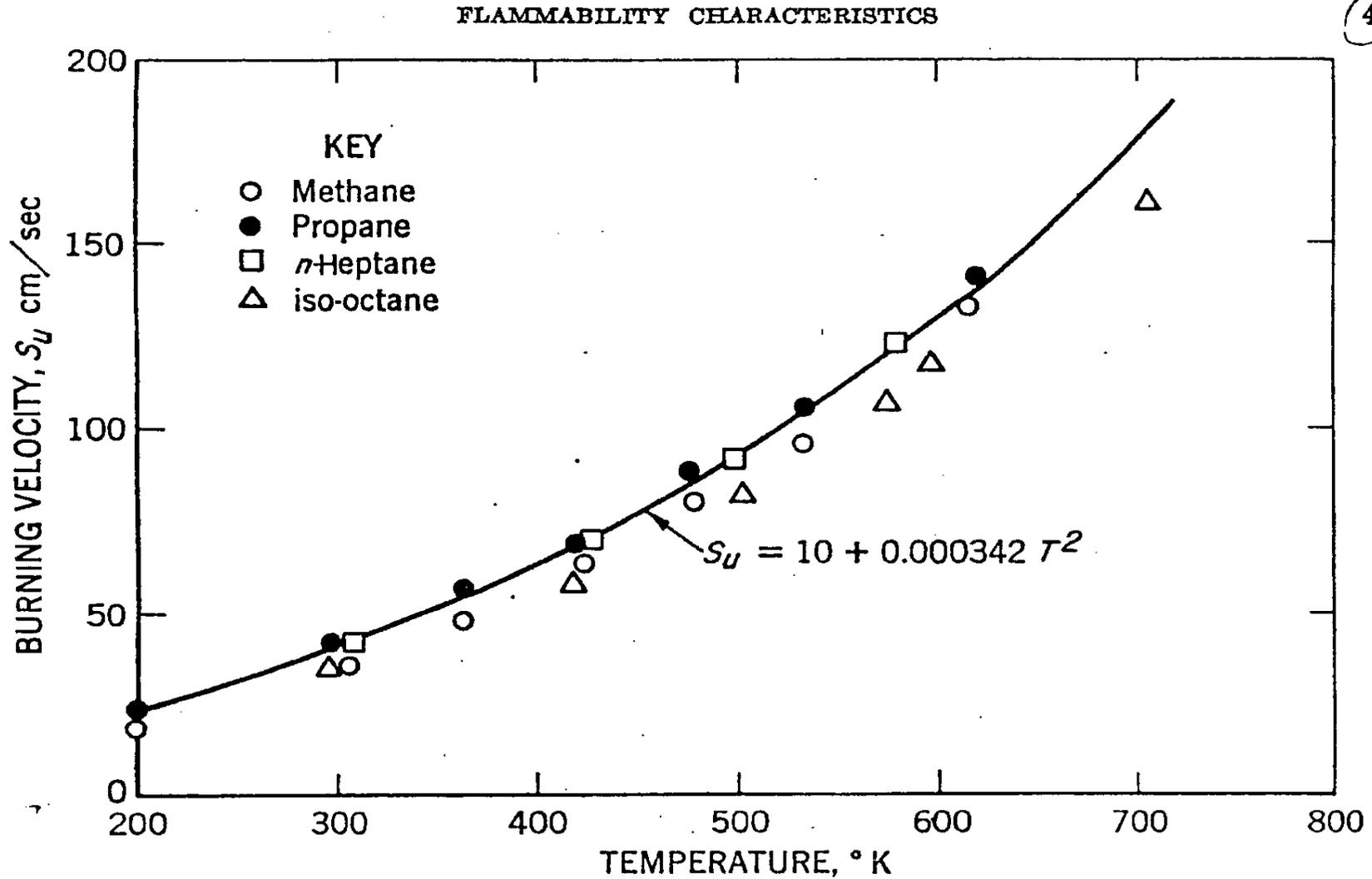


FIGURE 48.—Effect of Temperature on Burning Velocities of Four Paraffin Hydrocarbons in Air at Atmospheric Pressure.

Effect of pressure

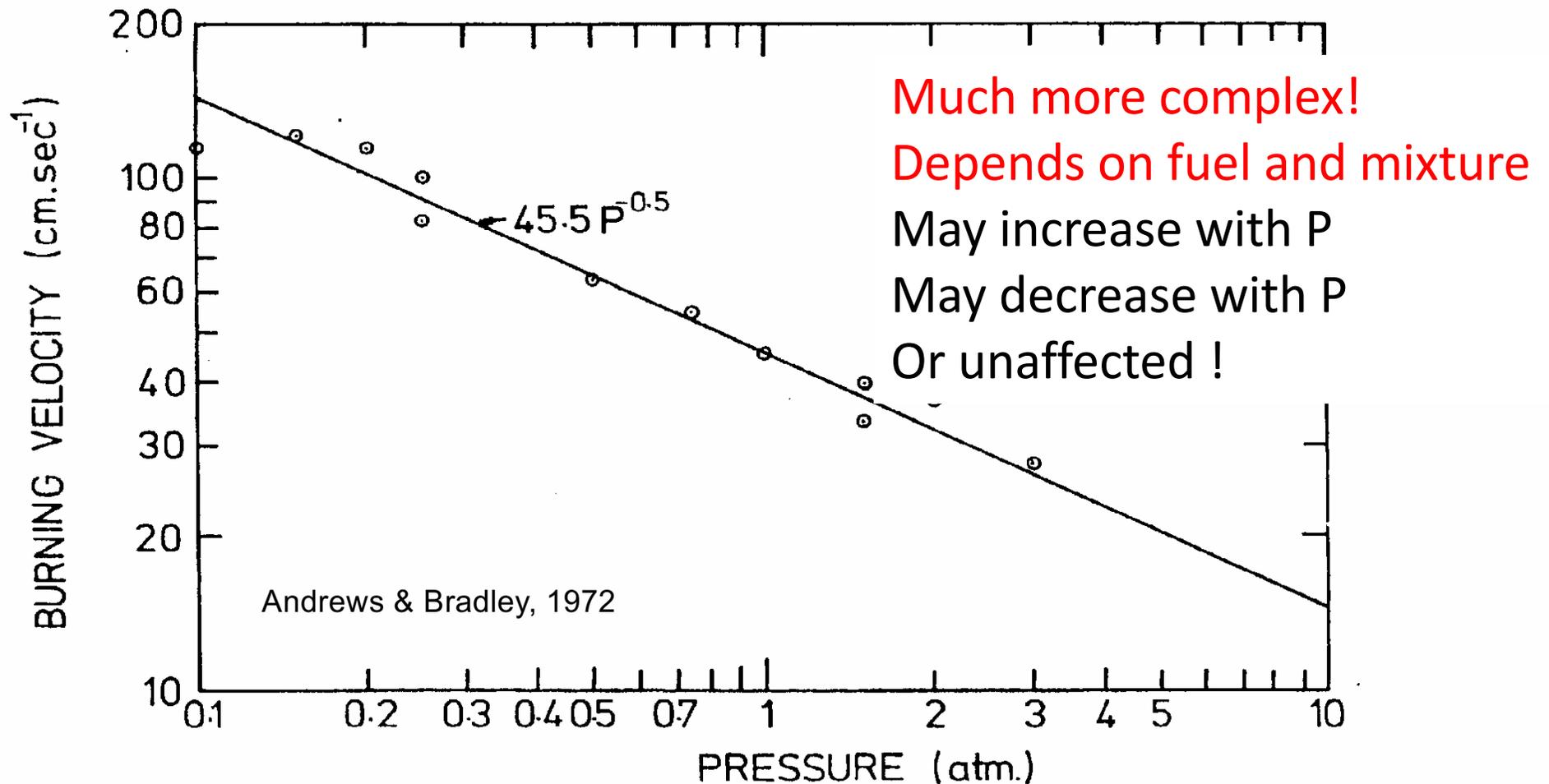


Fig. 11. Variation of burning velocity of 10% methane-air with pressure using double kernel technique.

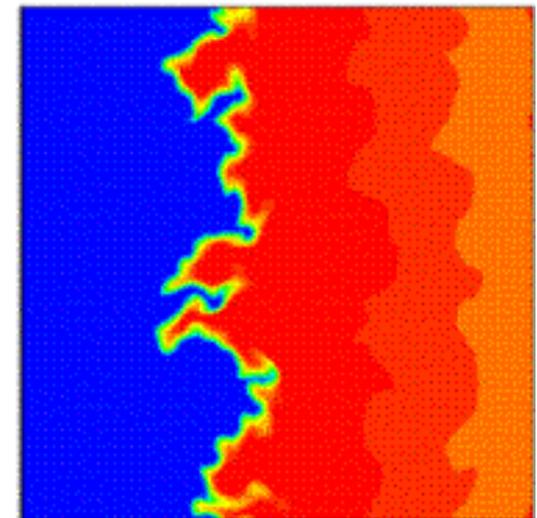
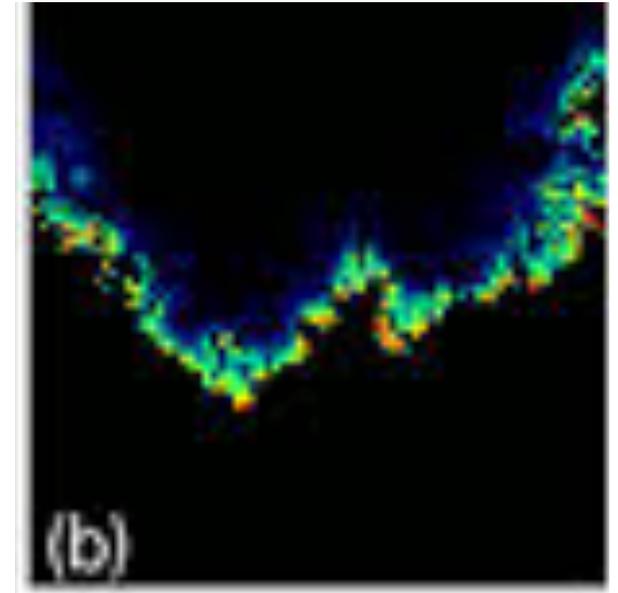
Effect of temperature and pressure - summary

- The influence of increasing T is to increase the burning velocity quite markedly. Corrections for temperature away from reference conditions have been proposed of the form: $S_L = S_{L0} (T/T_0)^\alpha$ where α can vary with P and ϕ .
- Most burning velocity data at elevated temperatures is given for mixtures near stoichiometric. However, the effects are very significant in near limit mixtures due to the **extension of flammability limits with temperature**.
- The influence of **pressure is more complex** and is not known for many compounds. Corrections for pressure have been proposed of the form: $S_L = S_{L0} (P/P_0)^\beta$ where β depends on the overall order of reaction and is -0.5 for first-order reactions.
- Nowadays some scepticism about the use of such simple correlations.

Turbulent flames

- A turbulent flame forms a connected but highly wrinkled thin surface that separates the reactants from the products.
- This flame surface is convected, bent, and strained by the turbulence and propagates (relative to the fluid) at a speed that can depend on the local conditions (surface curvature, strain rate, etc.).
- The gas expansion due to combustion makes the flame unstable.

<https://www.youtube.com/watch?v=0RdQWyqAUdg>



Effect of Reynolds number

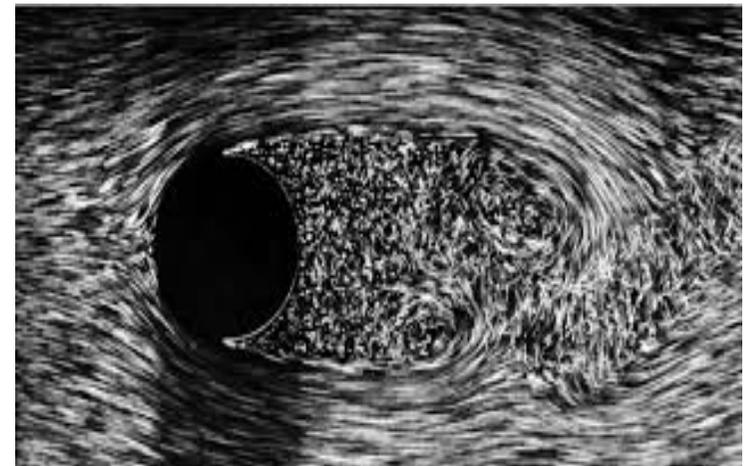
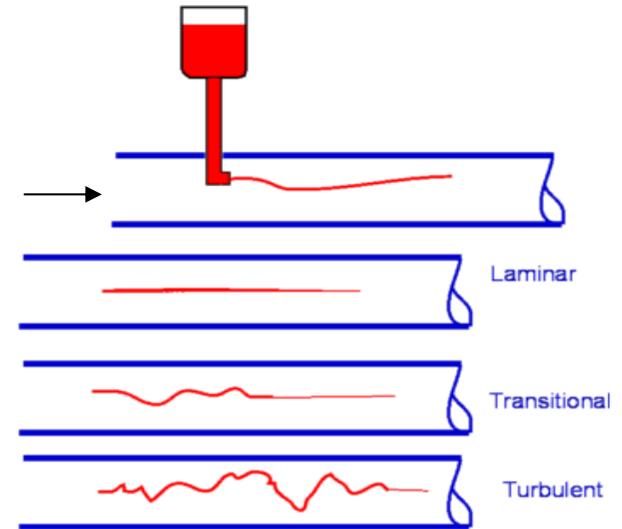
Reynolds number

$$Re = \frac{\rho v l}{\mu}, \mu / \rho \text{ is kinematic viscosity,}$$

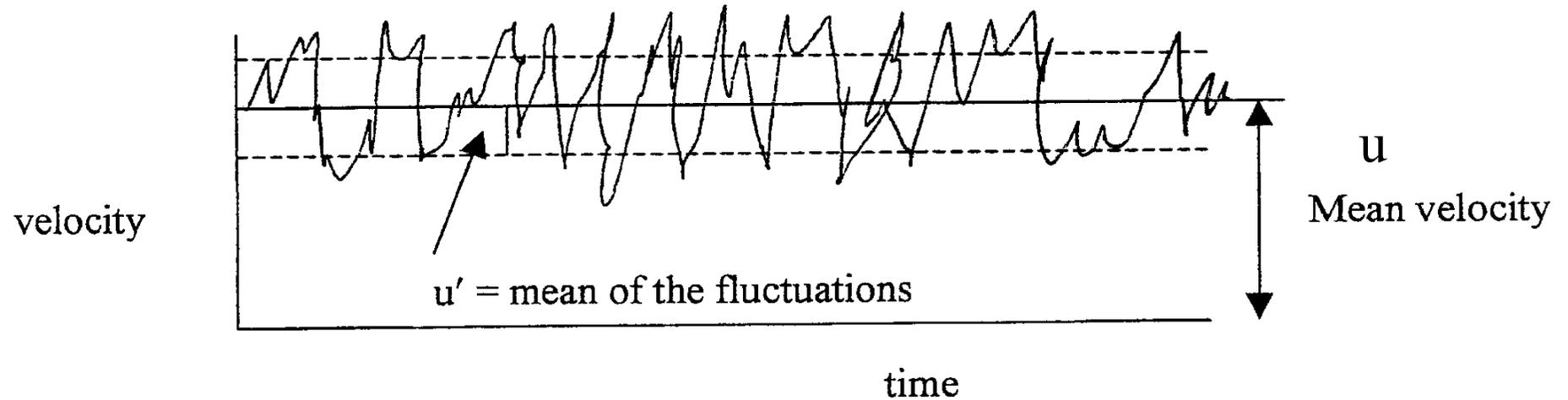
l is characteristic length scale

*Laminar flow turns turbulent
when $Re > \sim 2000$*

<https://www.youtube.com/watch?v=t5IJ3GXP190>



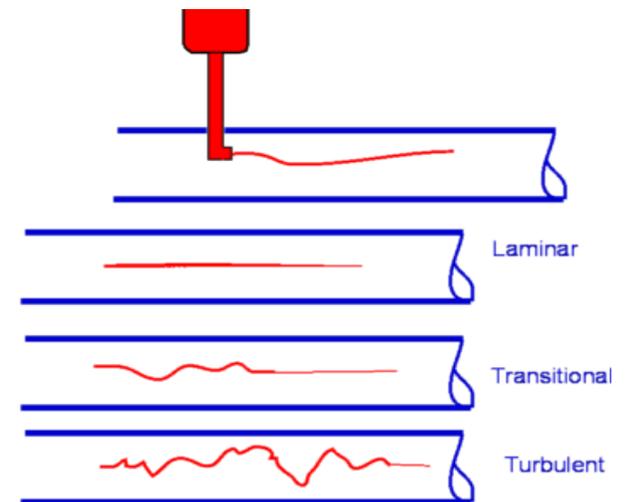
Effect of increasing Reynolds number



$$u' = \sqrt{\frac{1}{3}(u_x'^2 + u_y'^2 + u_z'^2)}$$

$$T.I. = \frac{u'}{u}$$

High turbulent intensity *T.I.* significantly influences burning velocity



Turbulent burning velocity S_T

This is still a research problem

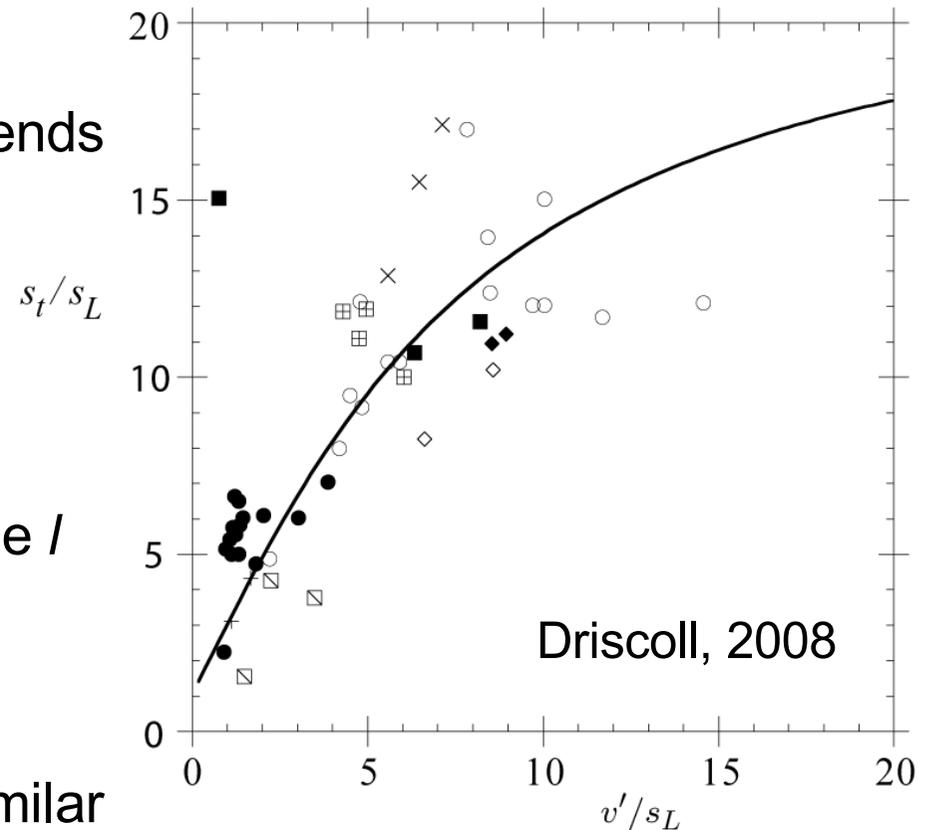
- Simple correlations suggest it depends on local turbulence

$$S_T/S_L = 1 + \alpha (u'/S_L)^n$$

$0.5 < n < 1.0, \sim 0.7$

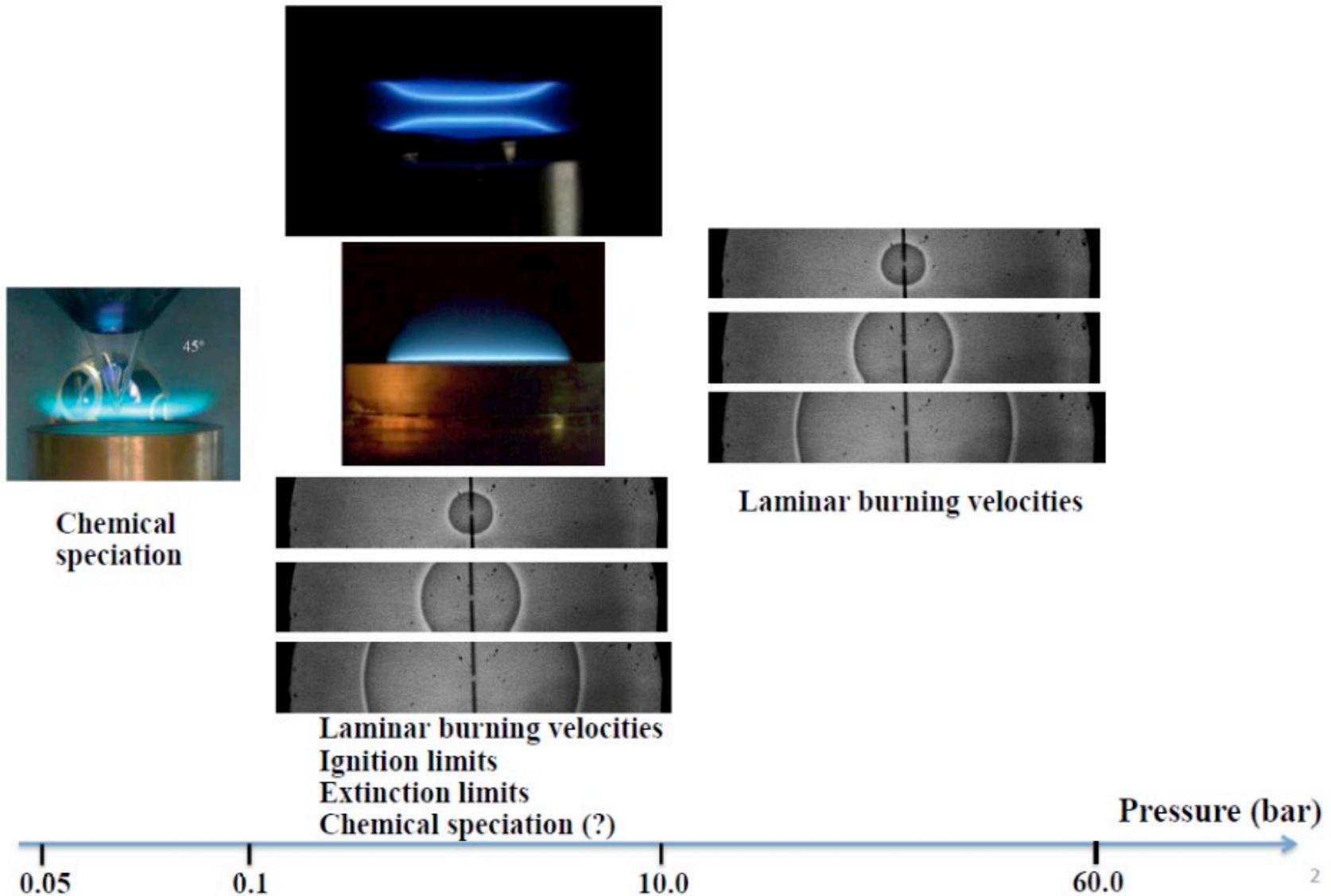
$\alpha = l/l_F$ i.e. ratio of integral length scale l to flame thickness l_F and is related to turbulence & fuel.

- For hydrocarbons. Most HC are similar and $\alpha = 2$ is a good fit to the data.
- As u' tends to zero S_T tends to S_L as expected.



Overall measurables in laminar flames,

Egolfopoulos, 2014



Laminar flame calculations

- Set-ups discussed attempt to achieve symmetries and hence can be modelled using 1D simulations – steady state equations.

Continuity: $\frac{d(\rho u)}{dx} = 0$ Equation of State $\rho = \frac{P\bar{W}}{RT}$

Species: $\dot{M} \frac{dY_i}{dx} = -\frac{d}{dx}(\rho A Y_i V_i) + A \dot{\omega}_i W_i$

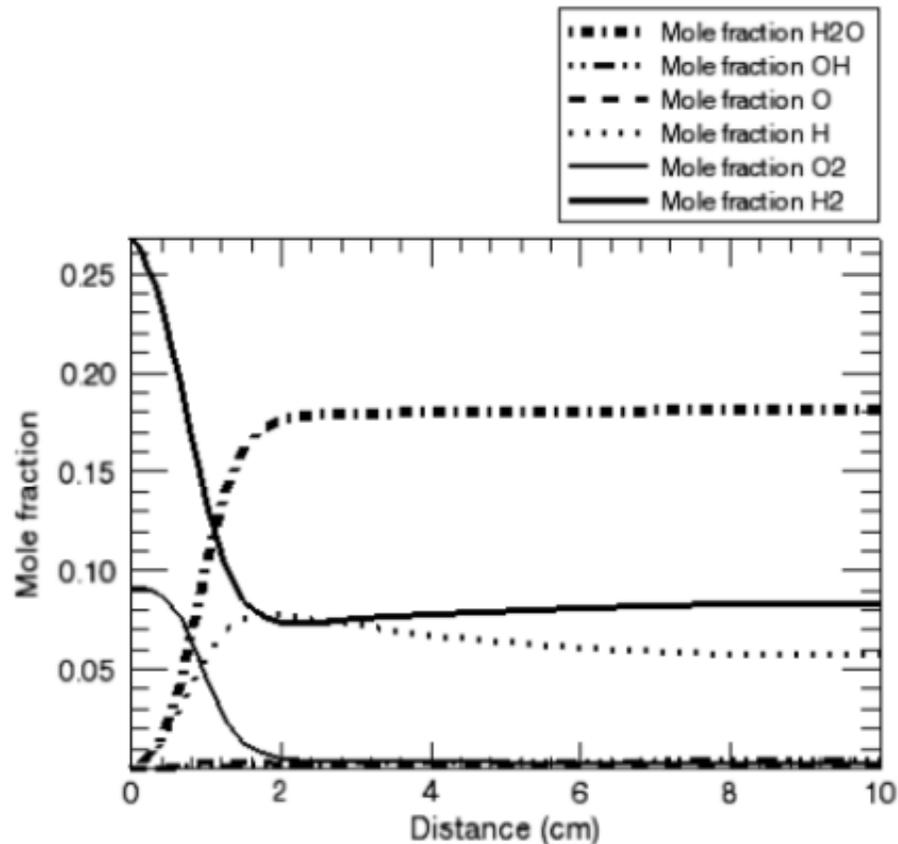
Energy: $\dot{M} \frac{dT}{dx} - \frac{1}{C_p} \frac{d}{dx} \left(\lambda A \frac{dT}{dx} \right) + \frac{A}{C_p} \sum_{i=1}^{N_s} \rho Y_i v_i C_{p,i} \frac{dT}{dx} + \frac{A}{C_p} \sum_{i=1}^{N_s} \dot{\omega}_i h_i W_i + \frac{A}{C_p} \dot{Q}_{rad} = 0$

x - spatial coordinate; \dot{M} - mass flow rate independent of x ; Y_i - mass fraction of i th species; u - velocity of fluid mixture; W_i - molecular weight of i th species; \bar{W} - mean molecular weight of mixture; λ - thermal conductivity of mixture; $C_{p,i}$ - constant pressure heat capacity of i th species; $\dot{\omega}_i$ - molar rate of production by chemical reaction of i th species per unit volume; h_i specific enthalpy of i th species; V_i - diffusion velocity of i th species; \dot{Q}_{rad} - heat loss due to gas and particle radiation; and A - cross-sectional area of the stream tube encompassing the flame (normally increasing due to thermal expansion) normalized by the burner area.

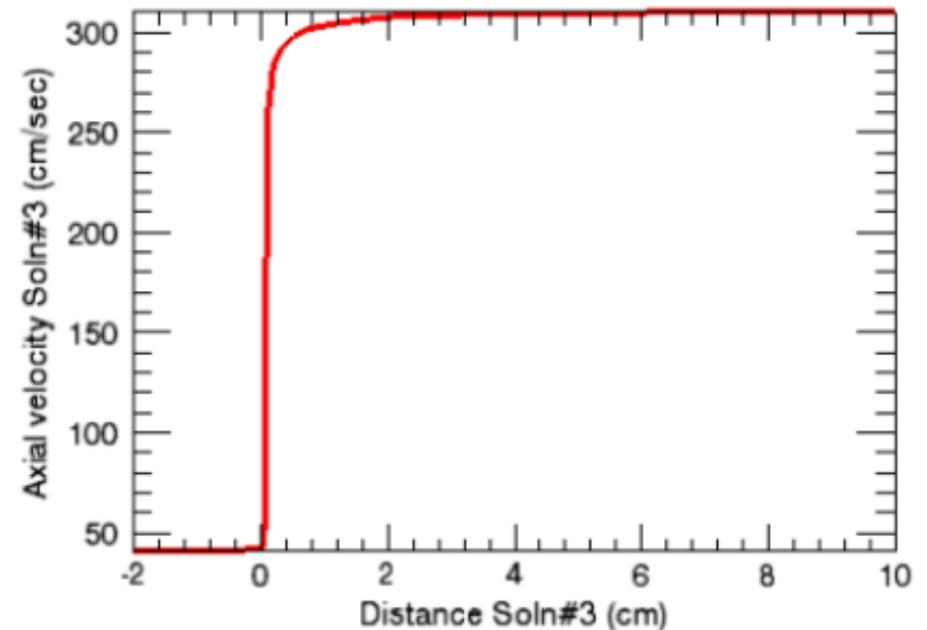
Laminar flame calculations

- In addition to reaction rate data previously discussed for homogeneous reactors we also now need:
 - **Thermal conductivities**
 - **Diffusion constants**
 - mixture-averaged formulas or a multicomponent diffusion model, Hirschfelder & Curtiss (1954). See also Chemkin theory manual.
 - **Gas and particle radiation models**, particularly if soot is present.
 - **Boundary conditions**
 - Vary depending on whether a burner-stabilized flame or an adiabatic freely propagating flame is being modelled, Hirschfelder and Curtiss.
 - For burner-stabilized flames \dot{M} is known constant, T and mass flux fractions are specified at cold boundary, and vanishing gradients are imposed at hot boundary.
 - For freely propagating flames \dot{M} is an eigenvalue to be determined.
 - Additional constraint required such as T at fixed point.
- Solved in typical codes using a ***finite difference*** approach.

Typical outputs from e.g. Chemkin, tutorial manual



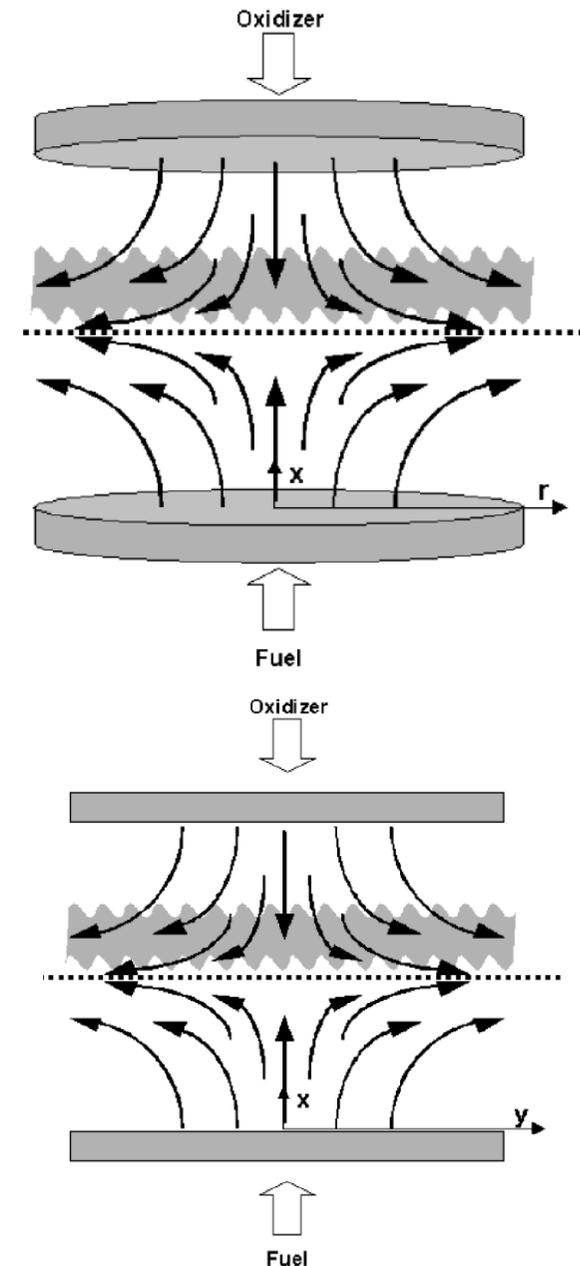
Species mole fractions for
burner stabilised flame



Flame speed calc for freely
propagating flame

Opposed flow stagnation flames

- 2 or 3 D flow is reduced mathematically to 1 D by assuming that radial velocity varies linearly in the radial direction, which leads to fluid properties being functions of axial distance only.
- One-dimensional models predict the species, T , and velocity profiles in the core flow between the nozzles (neglecting edge effects). Both premixed and non-premixed flames can be simulated.
- The **axisymmetric geometry** consists of two concentric, circular nozzles directed towards each other, producing an axisymmetric flow field with a stagnation plane between the nozzles.
- Similar effect with concentric linear nozzles producing a stagnated planar flame.
- When streams are premixed, two premixed flames exist, one on either side of stagnation plane.
- When one stream contains fuel and the other oxidizer, a diffusion flame is established.



Equations for stagnation flames

- ζ represents either the radial direction for the axisymmetric case, or the perpendicular direction for the planar case. $n = 3$ for axisymmetric case, $n = 2$ for planar case. Define variable transformations:

$$G(x) = \frac{-(\rho v \zeta)}{\zeta} F(x) = \frac{\rho u}{(n-1)} G(x) = \frac{dF(x)}{dx}$$

- Perpendicular momentum given by:

$$H - (n - 1) \frac{d}{dx} \left(\frac{FG}{\rho} \right) + \frac{nG^2}{\rho} + \frac{d}{dx} \left[\mu \frac{d}{dx} \left(\frac{G}{\rho} \right) \right] = 0$$

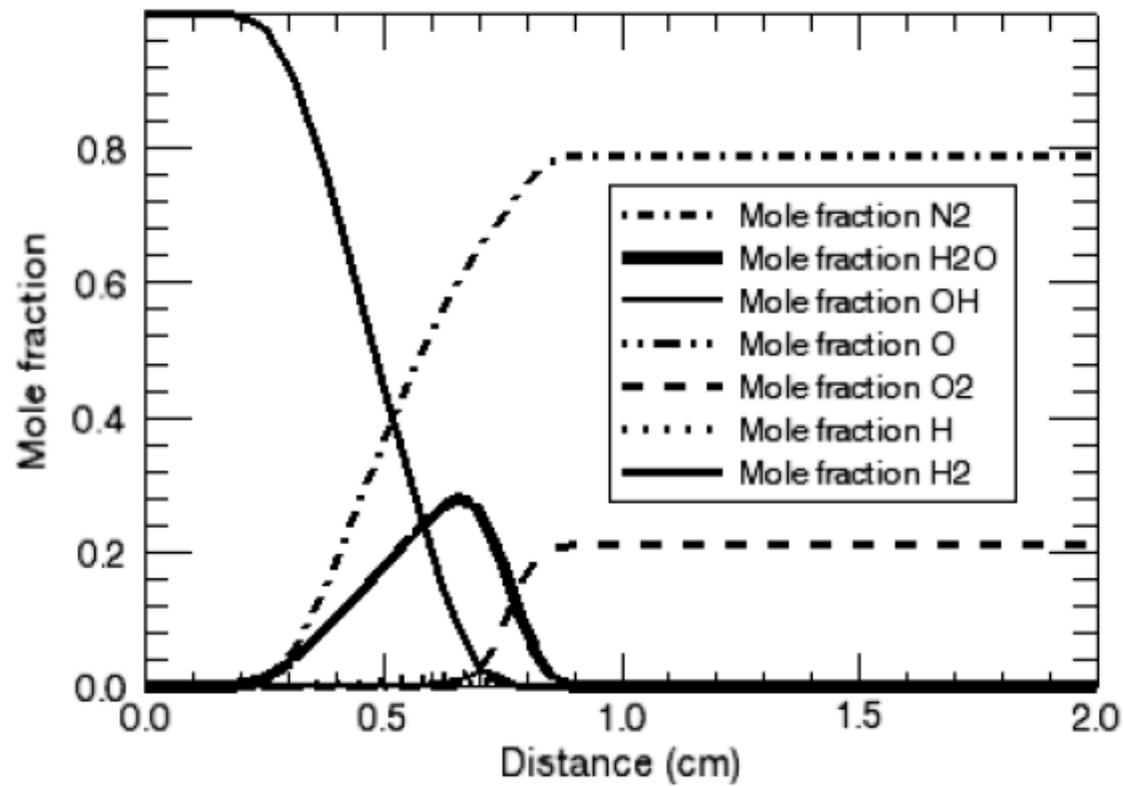
- Energy and Species conservation:

$$\rho u \frac{dT}{dx} - \frac{1}{C_P} \frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) + \frac{\rho}{C_P} \sum_i C_{P,i} Y_i V_i \frac{dT}{dx} + \frac{1}{C_P} \sum_i h_i \dot{\omega}_i + \frac{1}{C_P} \dot{Q}_{rad} = 0$$

$$\rho u \frac{dY_i}{dx} + \frac{d}{dx} (\rho Y_i V_i) - \dot{\omega}_i W_i = 0 \quad i = 1, \dots, N_S$$

Example

- Opposed flow hydrogen flame showing flame sitting on fuel side of stagnation plane.



Overview of validation studies

- Each type of experiment tests a chemical model in different ways and a general model should be applicable for all scenarios.
- Low T , **IDT** really mainly depends on predicting **relative rate of branching to termination routes**.
 - Could be predicted even with incorrect heat release or intermediate concentrations, so not a complete test.
 - However, most relevant to engine knock conditions.
- **LBV measurements** add high temperature targets for models of relevance to **flame extinction** and turbulent flame propagation within engines.
- **Speciation measurements** in flames and JSRs – particularly **intermediates** - add more stringent tests for mechanisms.
 - Often highlight missing pathways, or highly uncertain rate coefficients.
- In most cases, we are **much WORSE** at including **uncertainties for model** results than we are for experimental data.

Section 4

Model uncertainties, and sensitivity analysis

4.1

Sources of data for chemical models and their uncertainties

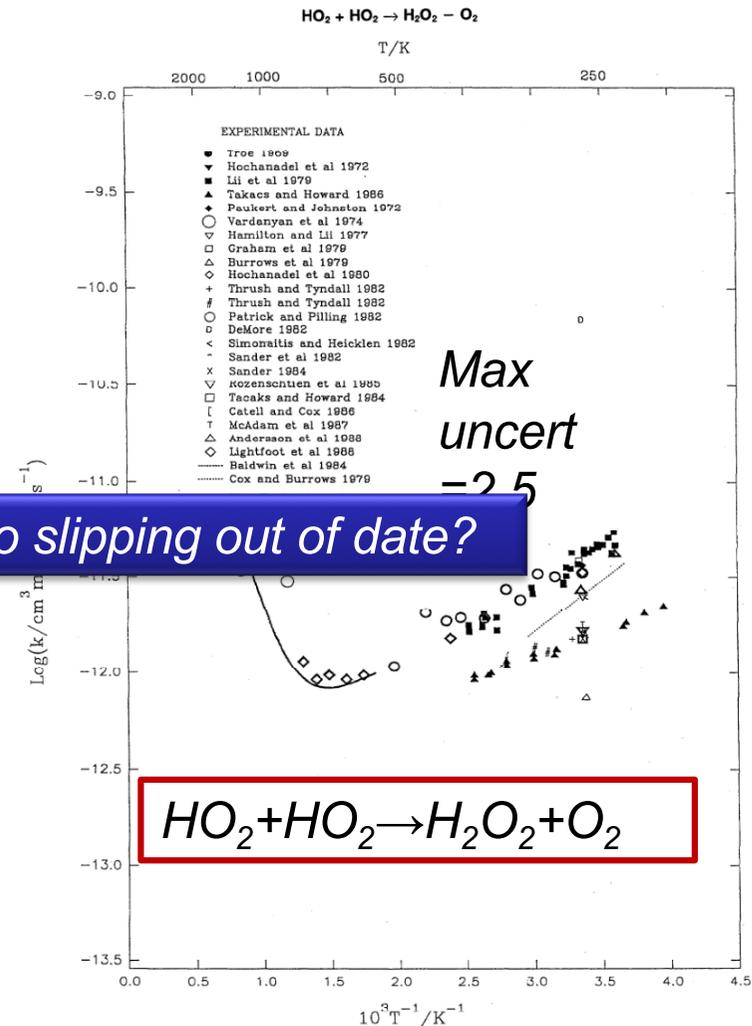
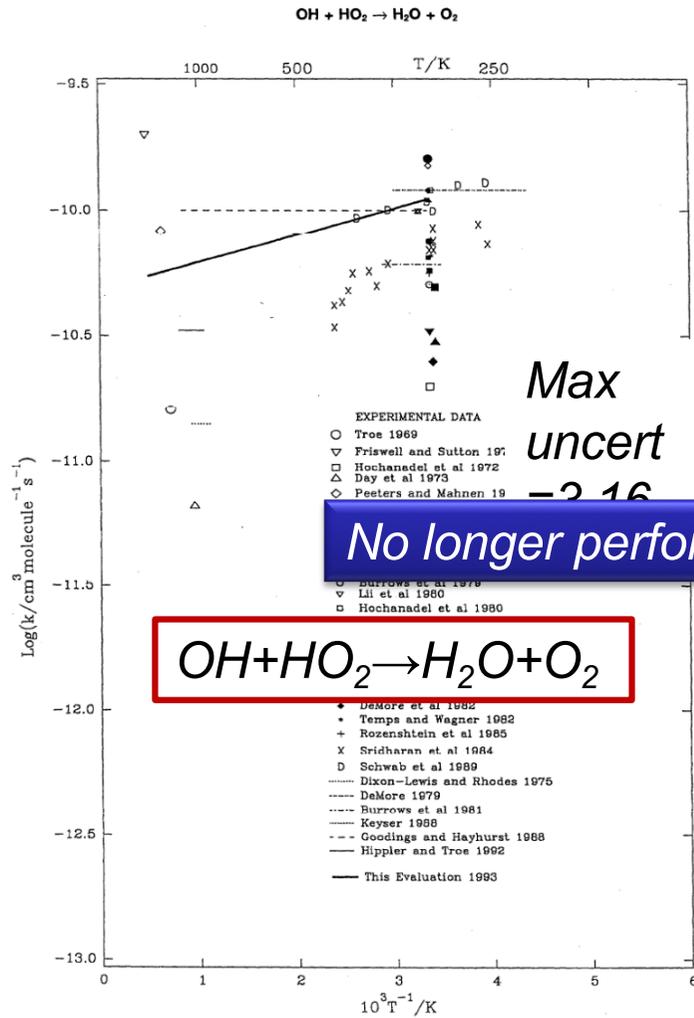
Sources of model input data and uncertainty information

- Kinetic evaluations (e.g. Baulch, Tsang, Atkinson).
- NIST data base.
- Output from theoretical studies.
- Trawling literature for individual papers on rate coefficients etc.....
 - Time consuming!
- Detailed statistical studies
 - Active tables for thermodynamic data (Ruscic and coworkers).
 - Optimisation studies for reaction mechanisms (Nagy and coworkers).
- What to do about estimated parameters?

Evaluated data (Baulch et al., 1994)

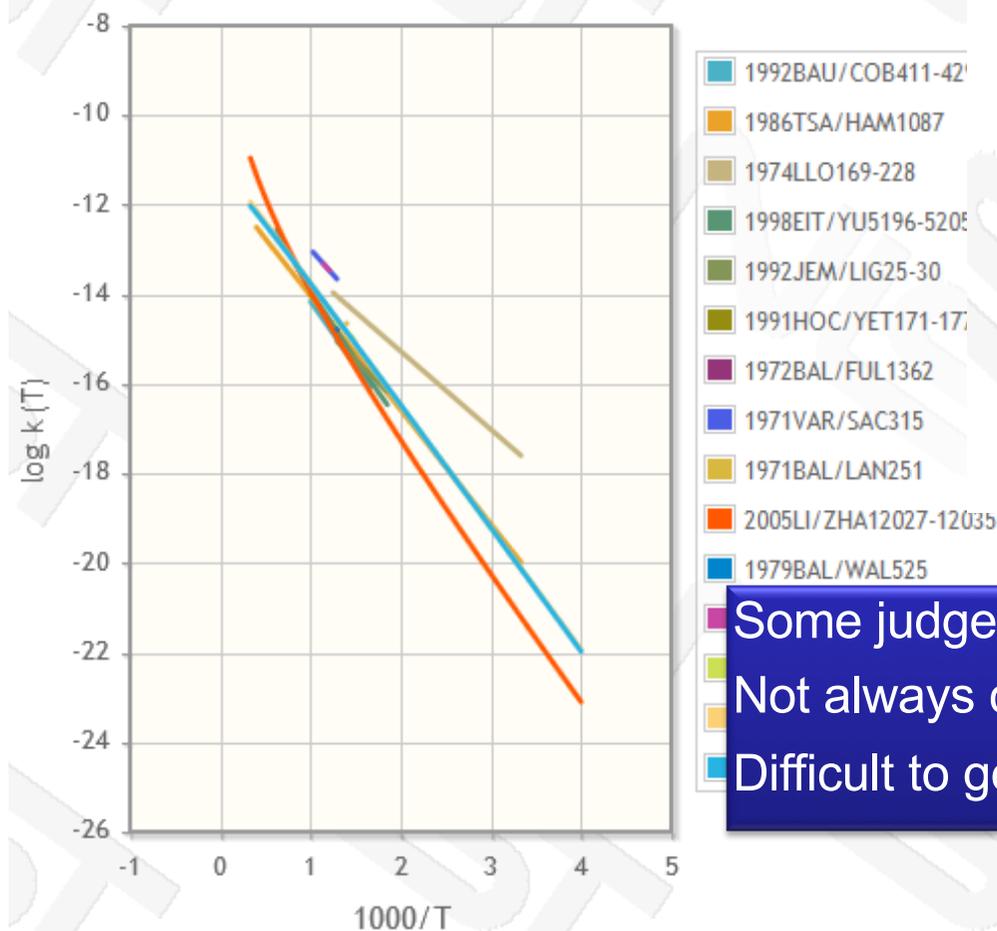
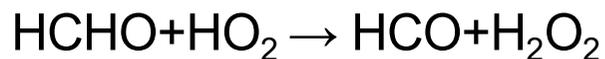
$\Delta \log k = \pm 0.2$ (300K) ± 0.5 (2000K)

$\Delta \log k = \pm 0.15$ (550-800K) ± 0.4 (1250K)



No longer performed so slipping out of date?

NIST data base



Fit of Arrhenius parameters to set:

Temperature range: 250 - 3000 K

Two-parameter fit:

$$k(T) = A \exp(-E_a/RT)$$

$$A = 9.25\text{E-}12 \text{ [cm}^3/\text{molecule s]}$$

$$E_a = 52.17 \text{ [kJ]}$$

$$\text{RMSD} = 4.3$$

Three-parameter fit:

$$k(T) = A(T/T_{\text{ref}})^n \exp(-E_a/RT)$$

$$A = 1.51\text{E-}11 \text{ [cm}^3/\text{molecule s]}$$

$$n = -0.3$$

$$T_{\text{ref}} = 298 \text{ [K]}$$

$$E_a = 53.48 \text{ [kJ]}$$

$$\text{RMSD} = 4.2$$

Some judgement has to be made about outliers
 Not always completely up to date
 Difficult to get temperature dependant uncertainties

Representations of Uncertainty

- Depends of level of knowledge about a particular parameter.
- If evaluation available then f value may be given.

$$f = \log_{10} \left(\frac{k^0}{k^{\min}} \right) = \log_{10} \left(\frac{k^{\max}}{k^0} \right) \quad \frac{k^{\max}}{k^0} = 10^f$$

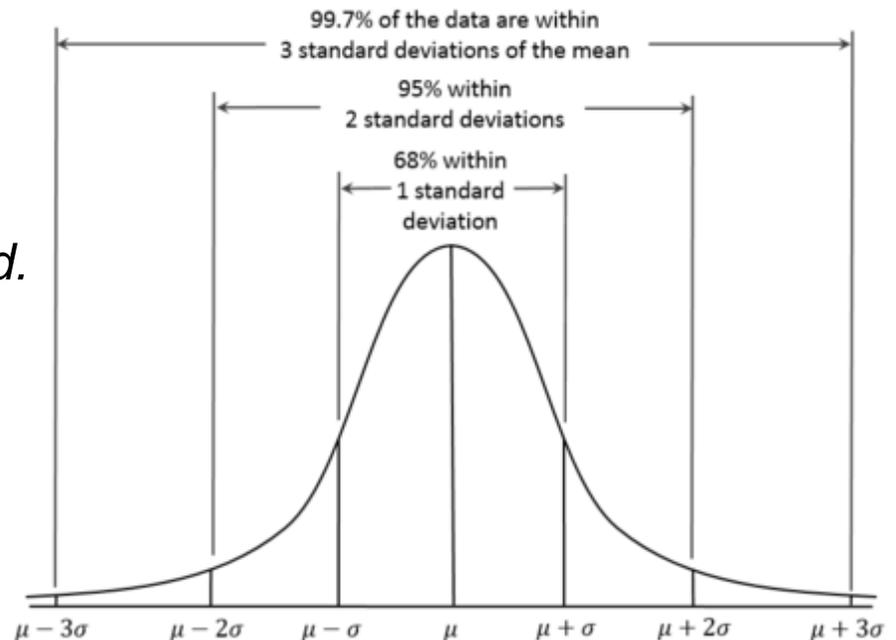
- k_0 recommended value of rate coefficient. k_{\min} , k_{\max} extreme values.

$$\sigma^2(\ln \{k\}) = ((f \ln 10)/m)^2$$

where m is the level of uncertainty suggested.

$m = 2$, 2σ deviation or 95 %ile,

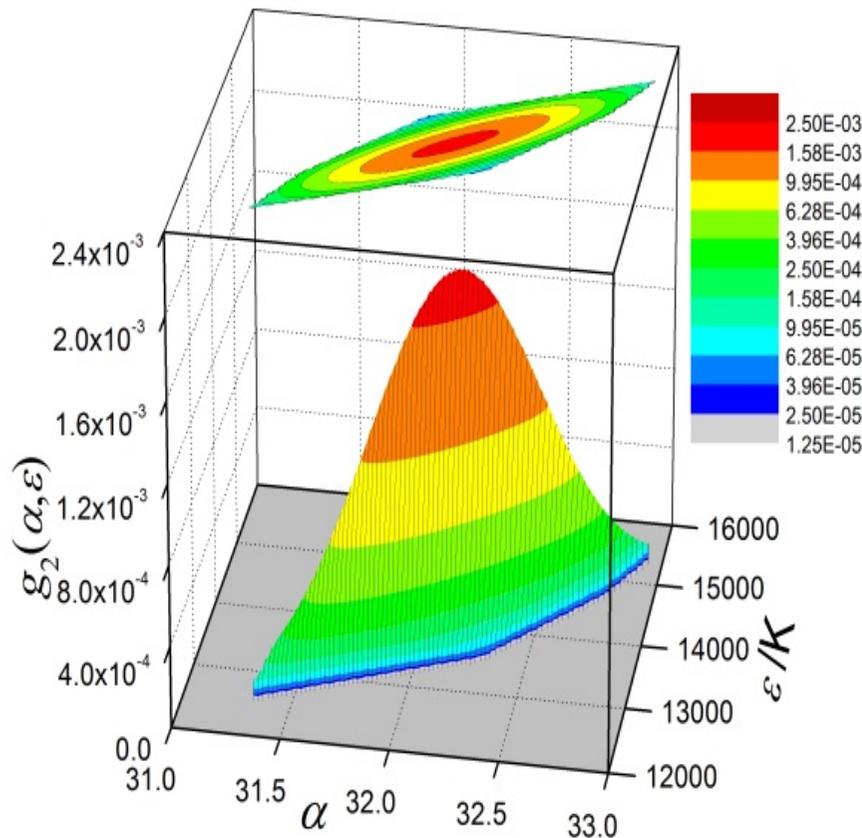
$m = 3$, 3σ deviation or 99.7 %ile



Examples of levels of uncertainty

uncertainty parameter f	multiplication factor of 3σ uncertainty limits	$\sigma(\log_{10} k)$	$\sigma(\ln k)$	multiplication factor of 1σ	multiplication factor of 2σ
0.1	1.26	0.03	0.08	1.09 (9%)	1.17
0.3	2.00	0.10	0.23	1.33 (33%)	1.67
0.5	3.16	0.17	0.38	1.72	2.44
0.7	5.01	0.23	0.54	2.34	3.67
0.9	7.94	0.30	0.69	3.31	5.63
1.0	10.00	0.33	0.77	4.00	7.00

Statistical methods

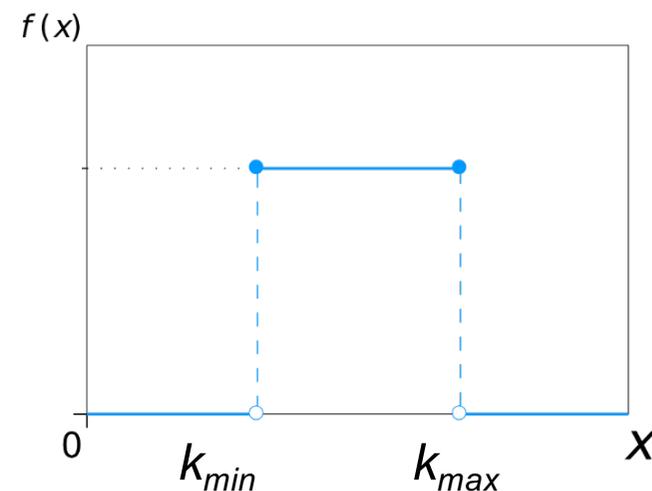


- All available current information on a system is used fit a joint pdf of parameters
 - e.g. 2,3 parameter Arrhenius
- Provides highly detailed data on parameter correlations etc.

For reaction kinetics has been carried out for only a few simple systems e.g. H_2 , wet CO oxidation, methanol (Nagy et al., 2011).

Estimated parameters

- For estimated parameters 10^f is likely to be a guesstimate e.g. factor of 2 or a factor of 5.
- A uniform distribution used since no probabilistic information likely to be available.
- In future – would be useful to provide estimates based on reaction classes from AMG packages like RMG etc.
 - What is the uncertainty for a particular reaction class based on available data?
 - How does the uncertainty change as e.g. the number of carbons grows?



Active Tables

- New paradigm to develop accurate, reliable, and internally consistent thermochemical values (such as enthalpies of formation, Gibbs energies of formation, bond dissociation energies, reaction enthalpies, etc.) for stable, reactive, and transient chemical species by utilizing to the fullest all available experimental measurements as well as state-of-the art theoretical data.
- ATcT is based on constructing, analysing, and solving the underlying Thermochemical Network (TN).
- Brings together both experimental and theoretical studies to reduce uncertainties in data (Burcat & Ruscic, 2005).

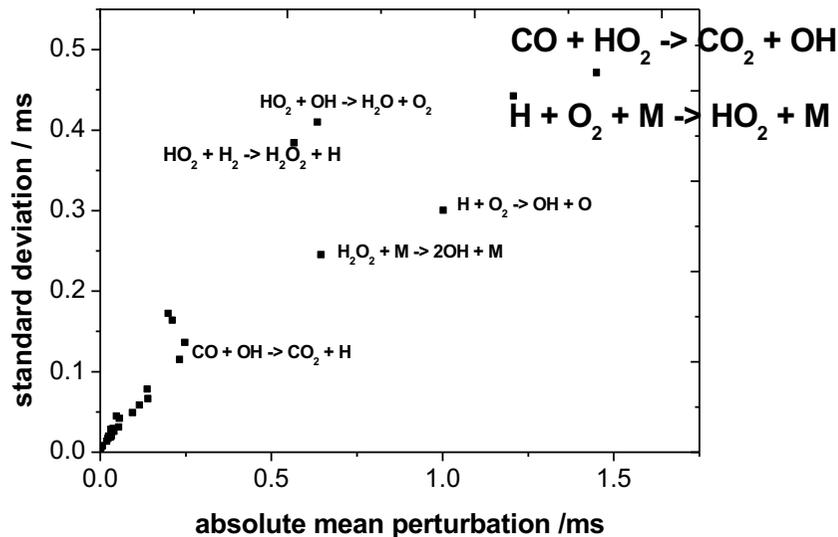
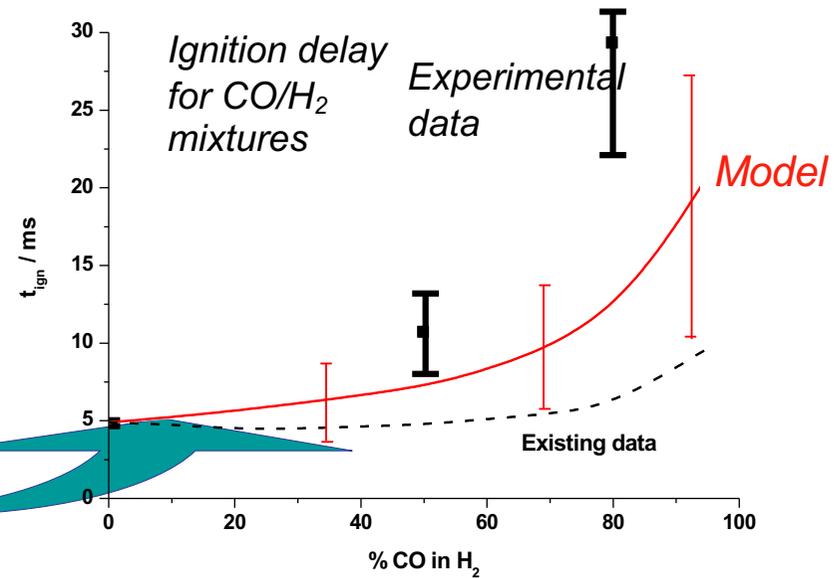
Species Name	Formula	$\Delta_f H^\circ(0\text{ K})$	$\Delta_f H^\circ(298.15\text{ K})$	Uncertainty	Units	Relative Molecular Mass	ATcT ID
Dihydrogen	H ₂ (g)	0	0	exact		2.01588 ± 0.00014	1333-74-0*0
Helium	He (g)	0	0	exact		4.0026020 ± 0.0000020	7440-59-7*0
Heptane	C ₇ H ₁₆ (l)	-201.46	-223.91	± 0.74	kJ/mol	100.2019 ± 0.0057	142-82-5*500
Octane	C ₈ H ₁₈ (l)	-226.61	-249.73	± 0.79	kJ/mol	114.2285 ± 0.0065	111-65-9*500
2,2,4-Trimethylpentane	(CH ₃) ₂ CHCH ₂ C(CH ₃) ₃ (l)	-224.4	-258.9	± 1.5	kJ/mol	114.2285 ± 0.0065	540-84-1*500

4.2 Sensitivity and uncertainty analysis

- **Uncertainty analysis**

(UA) estimates the overall predictive uncertainty of a model given the state/or lack of knowledge about its input parameters.

- UA puts error bars on predictions.

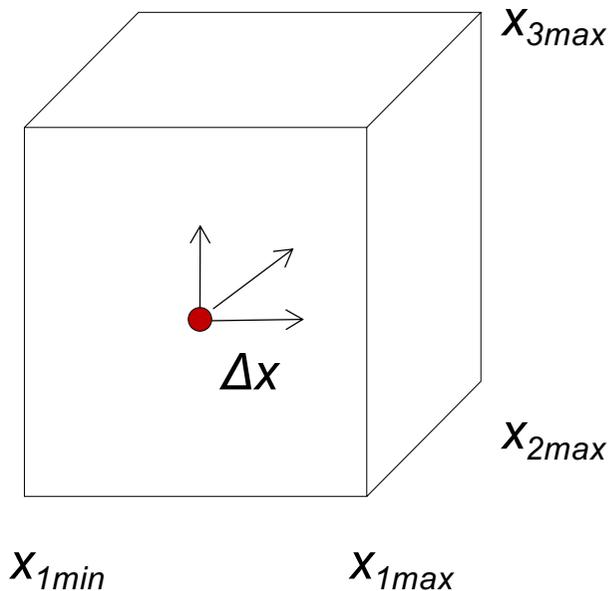


- **Sensitivity analysis (SA)**

determines how much each input parameter contributes to the output uncertainty (usually variance).

Local sensitivity coefficients

- *nominal values*



*Local
first-order
sensitivity
coefficient*

$$S_{ij} = \frac{\partial Y_i}{\partial x_j}$$

*Normalised
first-order
sensitivity
coefficient*

$$S'_{ij} = \frac{x_j}{Y_i} \frac{\partial Y_i}{\partial x_j}$$

Commonly incorporated into codes such as Chemkin, Cantera using finite difference methods.

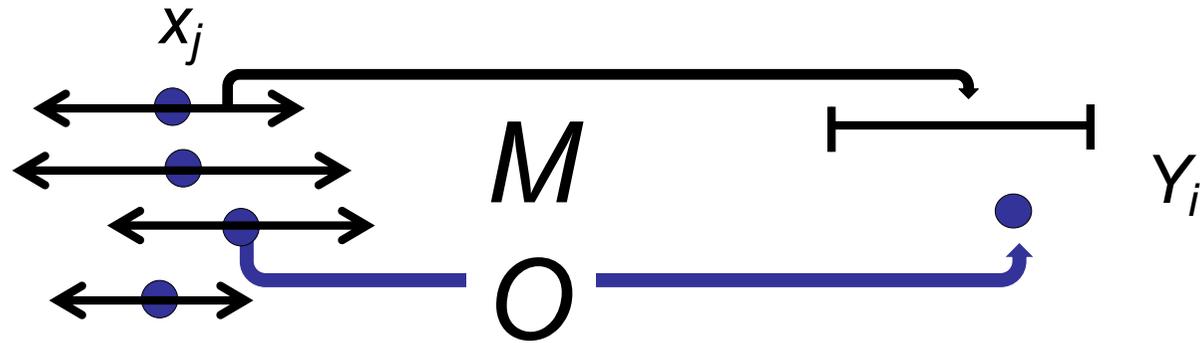
Contributions to uncertainty?

- Really we want to know, not just sensitivity, but also how much a parameter contributes to model uncertainty.
- Some parameters have **high sensitivity**, but are very **well quantified**.
- Others may have **lower sensitivity** but are **poorly known** and therefore drive potential errors in models.
- If $\sigma(x_j)$ are known – or estimated - then we can estimate overall uncertainty:

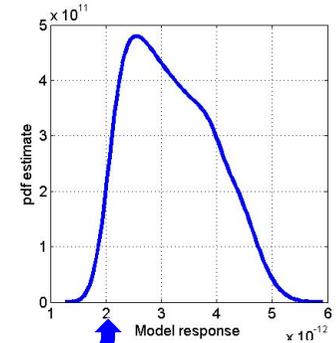
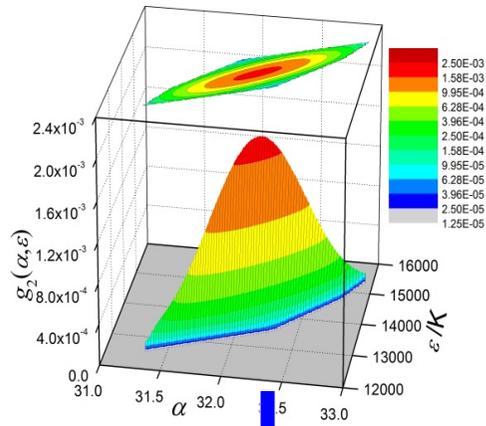
$$\sigma^2(\mathbf{Y}) = \sum_j (\mathbf{s}'_j)^2 \frac{\sigma^2(x_j)}{x^2_j}$$

- The **fractional contribution** of each parameter to this **uncertainty** can be estimated.
- Gives a better measure of parameter importance than S'_{ij} alone.
- Tells us how better quantification of each parameter could reduce overall modelling uncertainty.

Local vs global methods

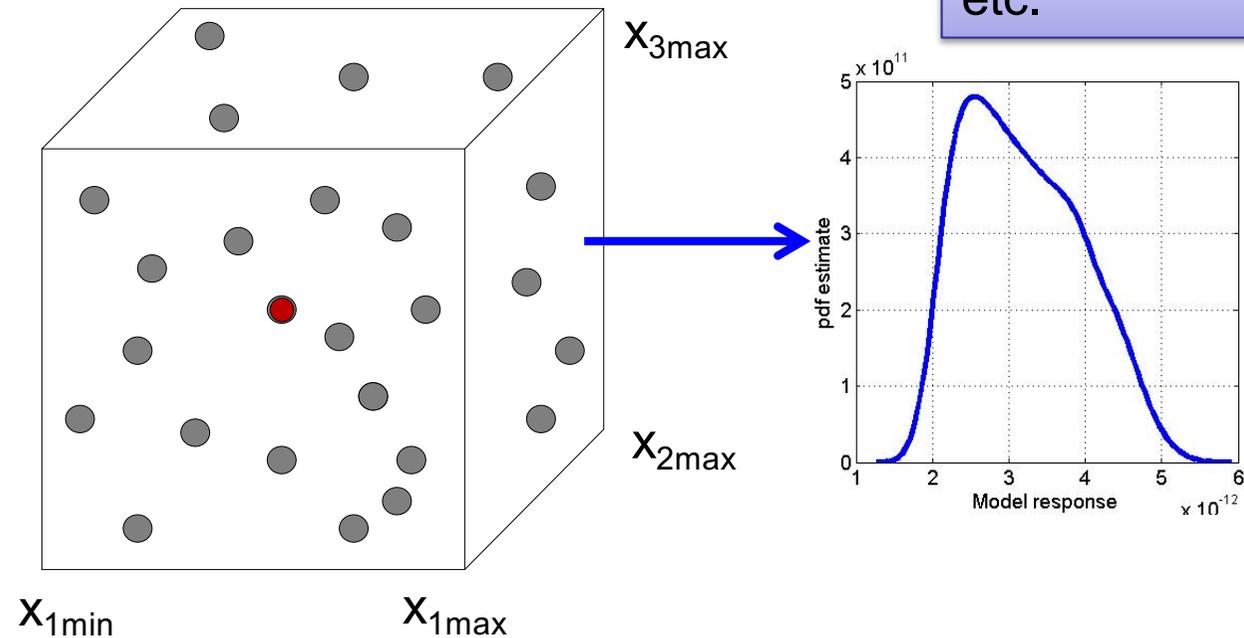


Probability distribution of predicted Y_i



Global sensitivity/uncertainty methods

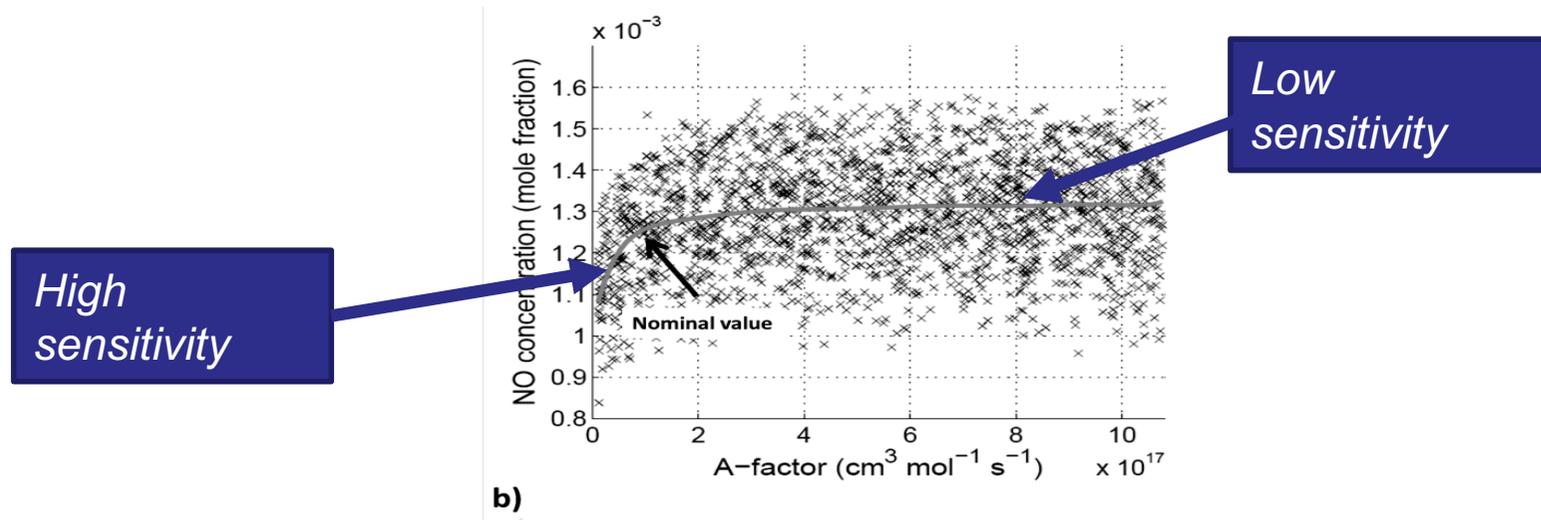
Global - attempts to cover whole input space using a sampling method.



Najm, Wang, Frenklach,
Sheen, Tomlin, Turányi
etc.

Why use global methods?

- Local sensitivity and uncertainty methods are usually based on a single (best estimate) value of the parameters.
- If the sensitivity of the output changes depending on the values of the parameters then local methods could be inaccurate.
- Particularly important for **non-linear models** and models with **large uncertainties**.



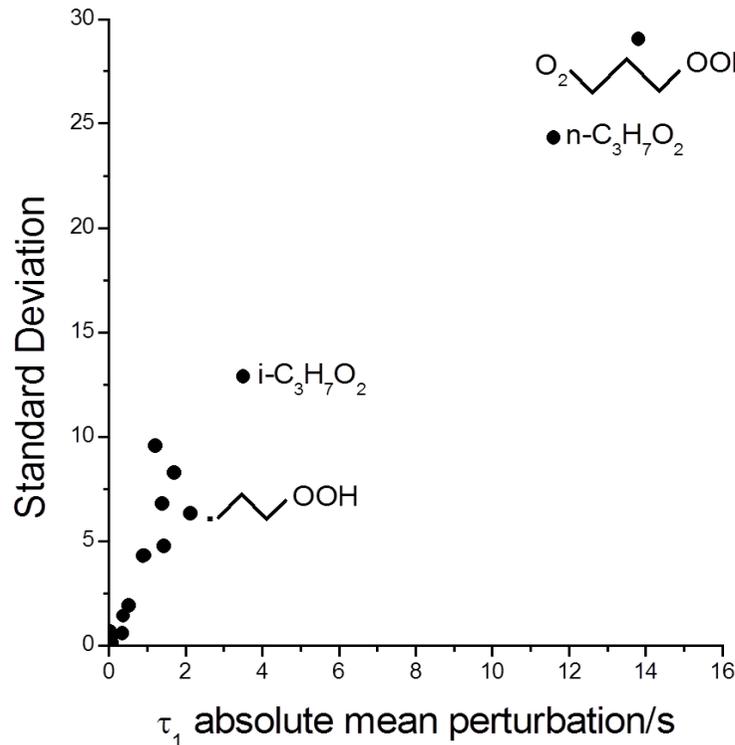
Disadvantages of global methods

- In order to cover the regions of parameter uncertainty, **sampling based methods** need to be used and therefore a **large number of model runs** is needed instead of the single run required for local sensitivity analysis using e.g. finite difference methods.
- The methods also require **prior knowledge of the input parameter distributions**.
- Methods are then required to interpret the data from a large number of samples to determine the **sensitivity indices**.
- For large parameter systems sample sparsity can be an issue.
- Screening methods are therefore often first applied to identify **unimportant** parameters which do not need to be varied in the full global approach.

Screening methods.

- Can be based on **local sensitivity coefficients**.
- Problematic unless it is applied at various values of the nominal parameters e.g. recommended value, rv , $rv \times 2$, $rv \times 0.5$.
- Can be automatically calculated using simple finite differences approaches in Chemkin/Cantera for simple outputs such as peak T , peak $[OH]$.
 - Adds to model run time but not significantly.
- Can be run as **Brute Force Method**, changing each parameter in scheme once and assessing sensitivity of target outputs.
 - Very expensive for large models.
- **Morris method** also used for screening and applies a one at a time method, changing one parameter by a fixed amount for each run of the model starting with a random seed.
- Several random seeds used at different points in parameter space.
 - Probably 10 times more expensive than even the Brute Force Method.

Examples of application of screening method



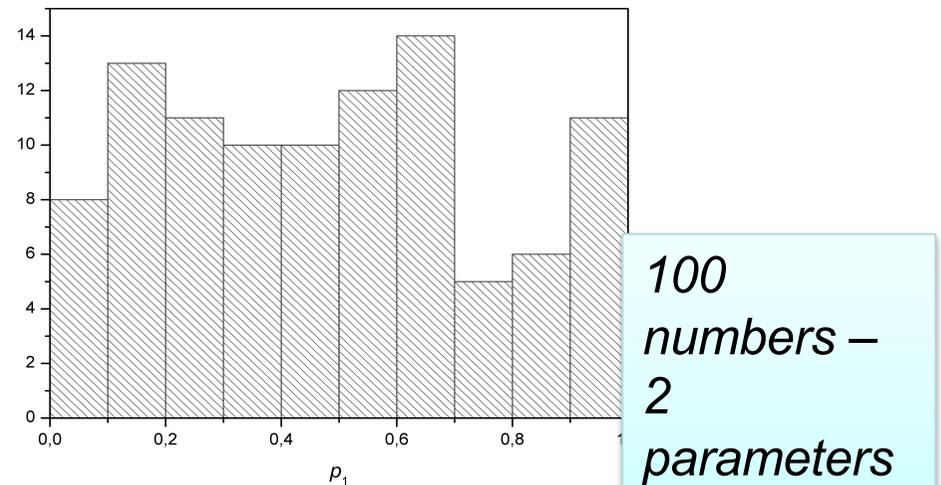
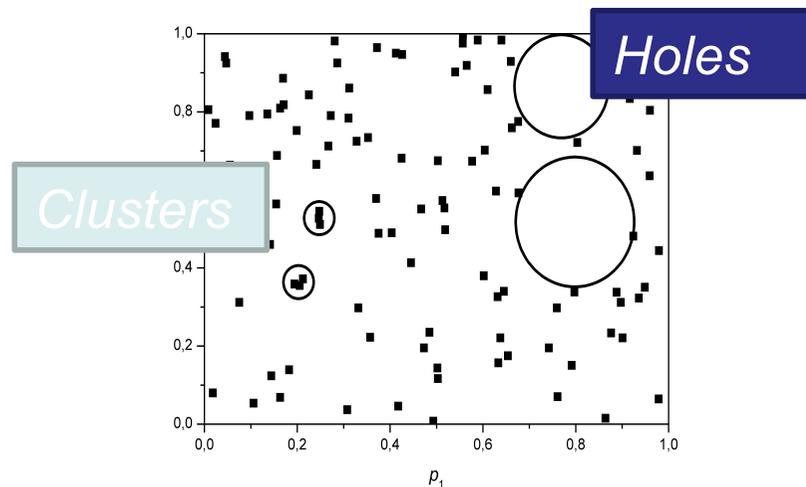
- Note the high standard deviation of the outputs compared to the mean.
- Very nonlinear responses requiring large sample size to converge.

*Morris analysis for species ΔH_f° with respect to **time to cool flame for propane oxidation**. $T = 593\text{ K}$, equimolar $\text{C}_3\text{H}_8 + \text{O}_2$ at 53.4 kPa , diluted by N_2 to 101.3 kPa (Hughes et al., 2006)*

4.3 Global sampling methods

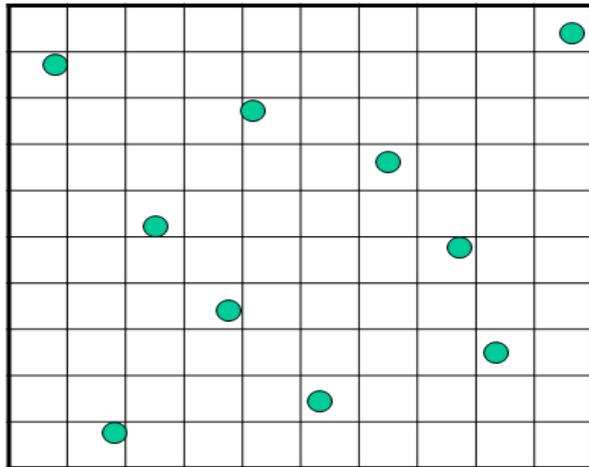
Monte Carlo

- For a global sampling method it is important to get good coverage of the input parameter space – which may be high dimensional.
- Typical random sampling methods can lead to clustering and holes.



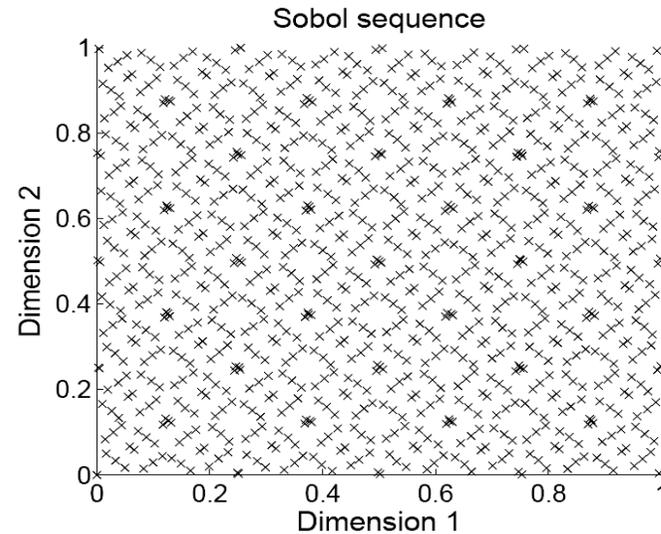
Structured sampling

Latin Hypercube



- Points generated by Latin hypercube sampling according to a uniform distribution.
- Each horizontal and vertical stratus contains a single point, while the location of the point is random in the corresponding small square.

Low discrepancy sequences



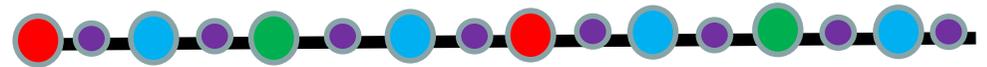
d)

Successive sample points are added to positions as far away as possible from existing sample points so that clustering can be avoided.

Sobol sequence

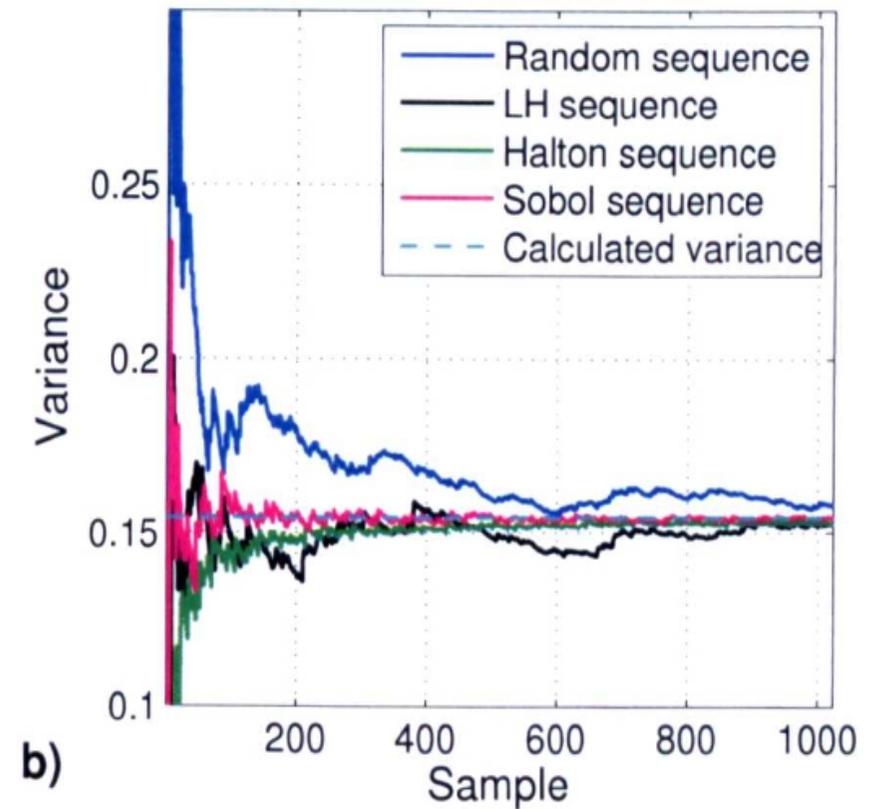
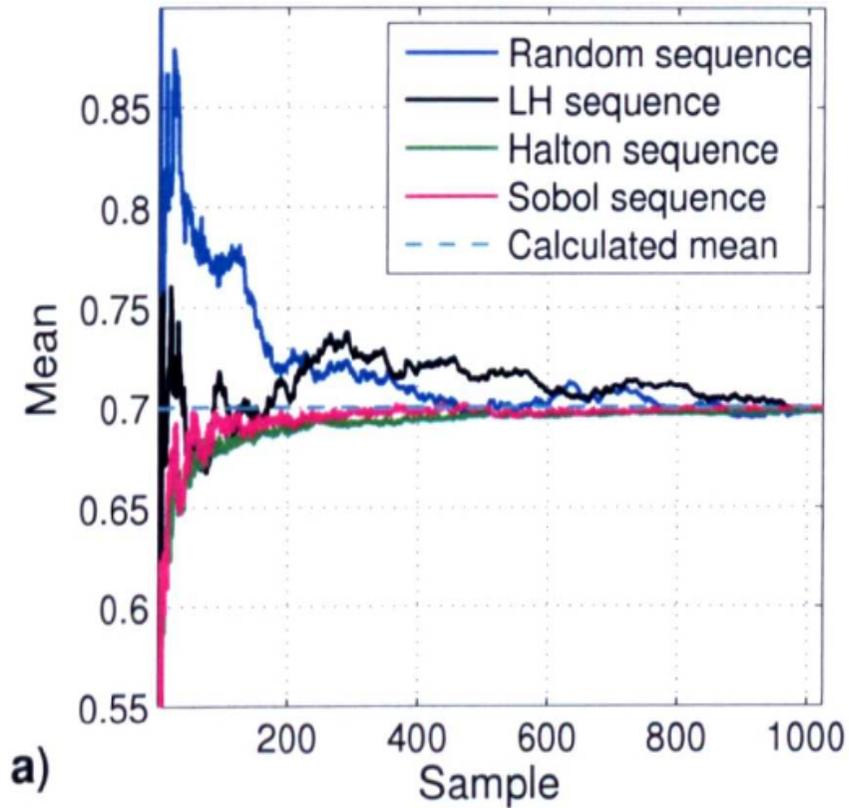
Sobol sequences use a base of two to form successively finer uniform partitions of the unit interval and then reorder the coordinates in each dimension.

0.000e+00	0.000e+00	0.000e+00
5.000e-01	5.000e-01	5.000e-01
7.500e-01	2.500e-01	7.500e-01
2.500e-01	7.500e-01	2.500e-01
3.750e-01	3.750e-01	6.250e-01
8.750e-01	8.750e-01	1.250e-01
6.250e-01	1.250e-01	3.750e-01
1.250e-01	6.250e-01	8.750e-01
1.875e-01	3.125e-01	3.125e-01
6.875e-01	8.125e-01	8.125e-01
9.375e-01	6.250e-02	5.625e-01
4.375e-01	5.625e-01	6.250e-02
3.125e-01	1.875e-01	9.375e-01
8.125e-01	6.875e-01	4.375e-01
5.625e-01	4.375e-01	1.875e-01
6.250e-02	9.375e-01	6.875e-01



The Sobol sequence is designed to have the best convergence properties and hence can lead to savings in sampling based sensitivity and uncertainty analysis because smaller sample sizes are needed to get equivalent accuracy in the results.

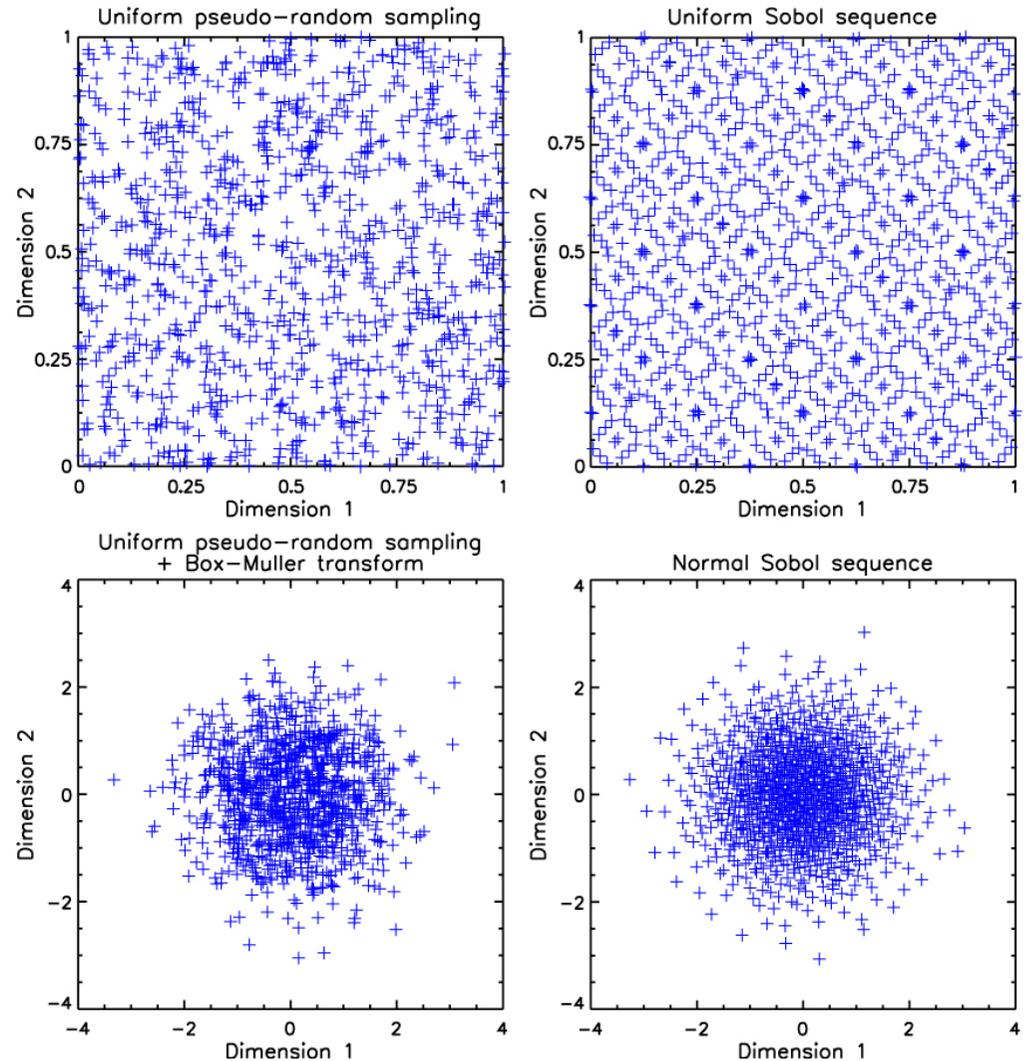
Comparison of convergence properties of different sampling strategies for a simple test model: $f(x) = x_1 + x_2^4$



Probabilistic sampling

If probabilistic information known then we may wish to sample from this distribution e.g. **a normal distribution** based on 2σ uncertainties (Hébrard et al., 2015)

- 2-parameter samples, $N = 1000$.
- Box-Muller transformation applied to an uniform pseudo-random sample (bottom left)
- Normal inverse cumulative function of a Sobol's quasi-random sequence sample (bottom right).



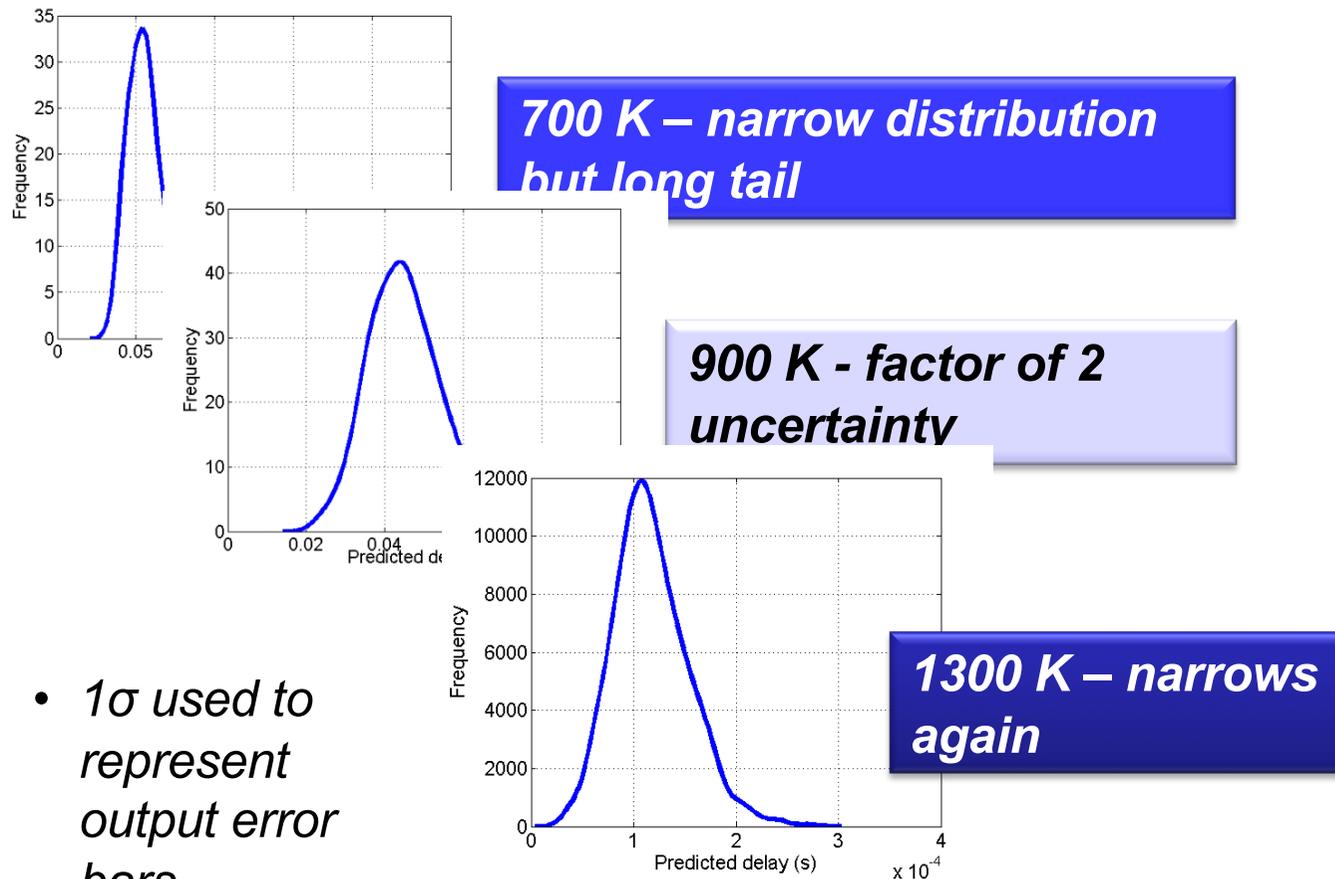
What parameters to include?

- *In an ideal world, just for fundamental devices:*
 - All Arrhenius parameters
 - Thermodynamic parameters - used to calculate reverse reaction rates
 - Species transport data
 - Other potential model errors
 - Temperature profile
 - Heat transfer coefficients
 - Residence times
 - Loss rates to the walls of the reactor vessel
- In reality many of these are often ignored and a most common approach is to simply look at the *A*-factors for each forward reaction.
 - Tells us something about the important reactions but does not give a full picture of uncertainties.

Examples of outputs

Ignition delays:

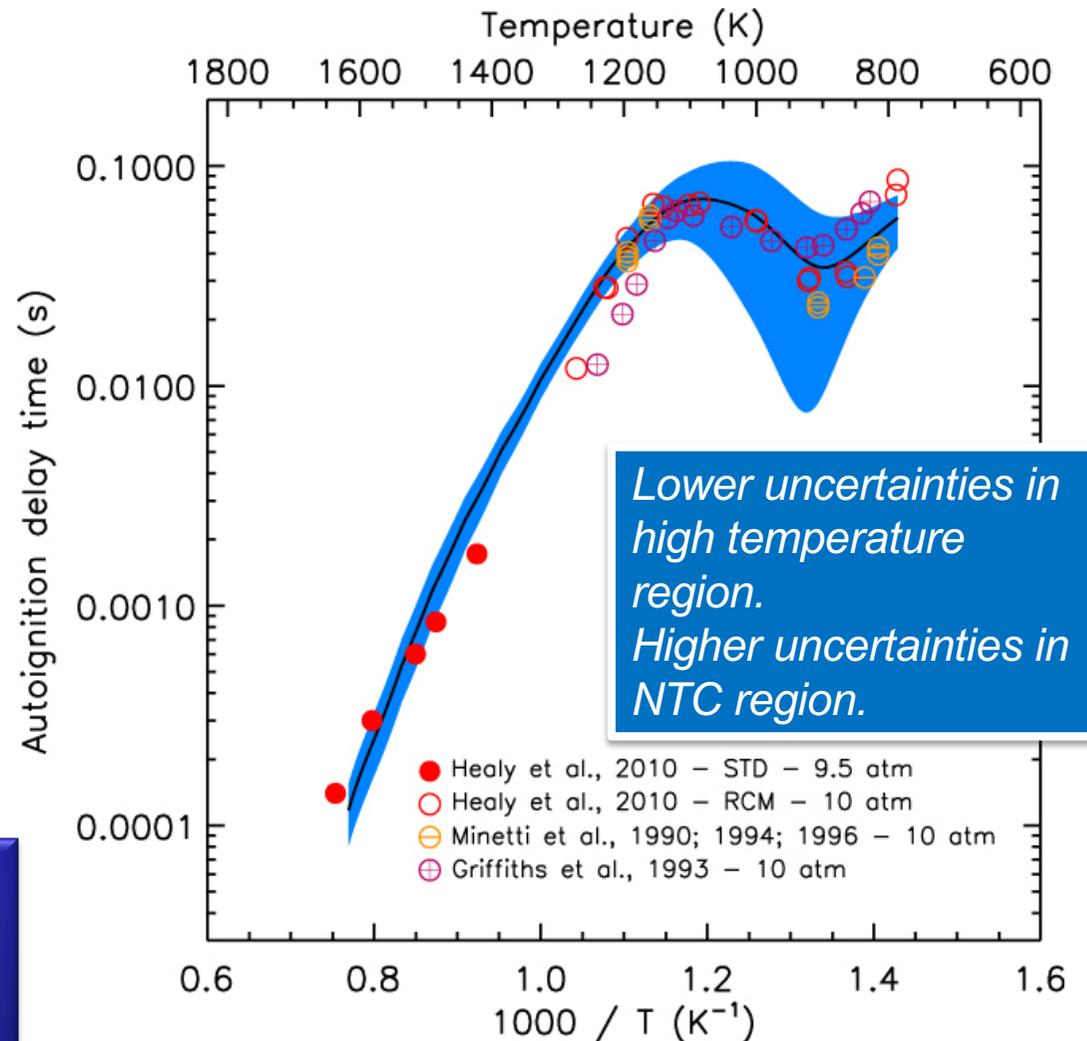
Predicted output distributions (butane model)



Interpreting output distributions

- Example from simulations of ignition delay time for a butane oxidation system.
- The blue shaded area represents 1σ of the outputs based on a sampled normal distribution of the input rate parameters.
- Hébrard et al. (2015)

Reasonable agreement between model and shock tube and RCM data if uncertainties are taken into account.

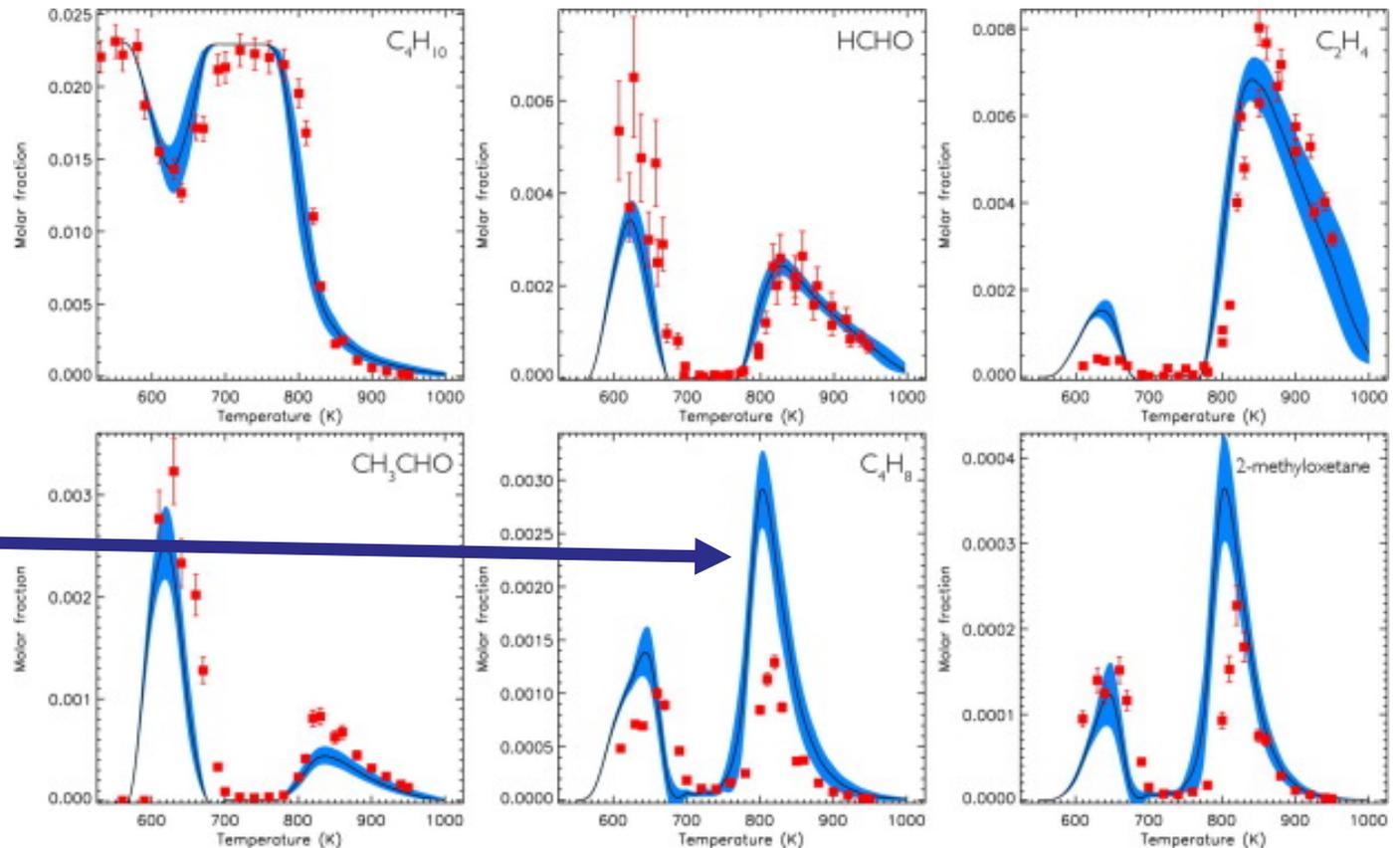


JSR data

Some discrepancies between model and experimental data even when accounting for estimated uncertainties.

Missing reaction steps?

Other uncertainties not identified?



(Hébrard et al., 2015)

4. 4 CALCULATING SENSITIVITY INDICES FROM SAMPLING METHODS

Sobol's method

- Is a sampling based method to calculate fraction of total variance that can be attributed to each parameter in a joint pdf distribution.
- If the model result $Y_i = f_i(x_1, x_2, \dots, x_N)$ is influenced by independent random parameters, then the joint pdf of the parameters $P(x_1, x_2, \dots, x_N) = \prod_{j=1}^N p_j(x_j)$.

- The mean or expected value $E(Y_i)$ of the calculated result Y_i is then given by:
$$E(Y_i) = \iiint \dots \int f_i(x_1, x_2, \dots, x_N) \prod_{j=1}^N p_j(x_j) dx_j$$

- while the variance $V(Y_i)$ of the calculated result Y_i is specified as:

$$\begin{aligned} V(Y_i) &= \iiint \dots \int (f_i(x_1, x_2, \dots, x_N) - E(Y_i))^2 \prod_{j=1}^N p_j(x_j) dx_j \\ &= \iiint \dots \int f_i^2(x_1, x_2, \dots, x_N) \prod_{j=1}^N p_j(x_j) dx_j - E^2(Y_i) \end{aligned}$$

- If integral calculated with **fixed value of a single parameter x_j** , then variance caused by all other parameters except for x_j , (Y_i/x_j) is obtained.
- If $V(Y_i/x_j)$ is calculated for many values of x_j , selected according to its pdf, then the expected value $E(V(Y_i/x_j))$ can be calculated.
- This requires integration of $V(Y_i/x_j)$ over pdf of x_j (Saltelli et al., 2002).
- The value $V(Y_i) - E(V(Y_i/x_j))$ is equal to the reduced variance of Y_i caused by fixing the value of x_j , and is equal to $V(E(Y_i/x_j))$.
- By dividing this conditional variance by the unconditional variance, the first-order sensitivity index for parameter x_j can be calculated:

$$S_{j(i)} = \frac{V(E(Y_i|x_j))}{V(Y_i)}$$

- This measure shows **the fraction of the total variance of Y_i which is reduced when the value of x_j is held at a fixed value** and is therefore a measure of the influence of uncertainty in x_j .

2nd order indices

- If the values of two parameters (e.g. x_j and x_k) are fixed, second-order sensitivity indices are obtained:

$$S_{kj(i)} = \frac{V(E(Y_i|x_k, x_j)) - V(E(Y_i|x_k)) - V(E(Y_i|x_j))}{V(Y_i)}$$

- The second-order sensitivity index characterizes the interaction of the corresponding parameters.
- Can be repeated up to higher and higher orders but the sample sizes required for the calculation of integrals using a Monte Carlo/sampling approach makes this prohibitive.

Cost – high!!

- The method provides sensitivity indices which are between 0 and 1, although sometimes this is multiplied by 100 yielding $S_{j(i)}\%$.
- The calculation of integrals is non-trivial and the use of a Monte Carlo sampling method is described in Saltelli et al., (2002) requiring **$N (2m+1)$ model runs for first-order indices** where N is the sample size chosen for the Monte Carlo estimates.
- *The computational time requirement increases exponentially with the order of indices required.*
- **This is not really feasible for large combustion mechanisms even if screening is used first.**

Response Surface Methods, RSM

- RSM based methods attempt to reduce computational cost of Variance based sensitivity methods by first developing a fitted *meta-model* accurately representing **relationship between model parameters and outputs**.
- If *meta-model* can be fitted with a lower number of model runs then it can be used to calculate variance based indices at lower cost.
- Some similarities with Monte Carlo approaches:
 - first input parameter ranges must be selected
 - then a suitable sampling approach taken so that full model runs are obtained across a design suitable for development of accurate meta-model.
- Cost of method driven by cost of providing accurate surrogate model.
- This is not always dependant on size of scheme but is driven by the complexity of the response surface.
 - Could be cheaper than Brute Force.

Polynomial chaos expansion, PCE methods (Najm et al., 2009)

- Here an uncertainty factor u_i is first assigned to each input variable.
 - Note that this uncertainty parameter u_i is related to uncertainty parameter f by $u_i = 10^f$.
- Taking the example of rate coefficients, they are then normalised into factorial variables \mathbf{x} as follows:

$$x_i = \frac{\ln k_i / k_{i,0}}{\ln u_i}$$


The diagram shows the equation $x_i = \frac{\ln k_i / k_{i,0}}{\ln u_i}$. A blue box labeled "Nominal value" has an arrow pointing to the term $k_{i,0}$ in the numerator of the fraction.

- Hence $x_i = 0$ gives the nominal value of the rate coefficient, and -1 and +1 represent the upper and lower bounds.
- A response surface of the predicted combustion properties is then generated with respect to \mathbf{x} .

- Often restricted to a 2nd order polynomial expansion which for the r 'th model response $\eta_r(\mathbf{x})$ can be written as:

$$\eta_r(\mathbf{x}) = \eta_{r,0} + \sum_{i=1}^m a_{r,i} x_i + \sum_{i=1}^m \sum_{j \geq i}^m b_{r,i,j} x_i x_j$$

- The uncertainty in \mathbf{x} may be expressed as a polynomial expansion of basis random variables ξ :

$$\mathbf{x} = \mathbf{x}^{(0)} + \sum_{i=1}^m \boldsymbol{\alpha}_i \xi_i + \sum_{i=1}^m \sum_{j \geq i}^m \boldsymbol{\beta}_{ij} \xi_i \xi_j + \dots,$$

where $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are column vectors of expansion coefficients, m is the number of rate coefficients under consideration and $\mathbf{x}^{(0)}$ is a column vector of normalised rate coefficients which is a zero vector for the nominal reaction model.

- If the \mathbf{x} 's are independent of each other and normally distributed, then the usual choice for the form of ξ would be a set of unit-normal random variables.
- If $\ln u_i$ represents 2 times the standard deviation of $\ln k_i$ then α is $\frac{1}{2} \mathbf{I}_m$, where \mathbf{I}_m is the m -dimensional identity matrix. β and all higher order terms are zero (Sheen et al. 2009).
- In the general case, combining the above two equations and truncating the higher order terms gives:

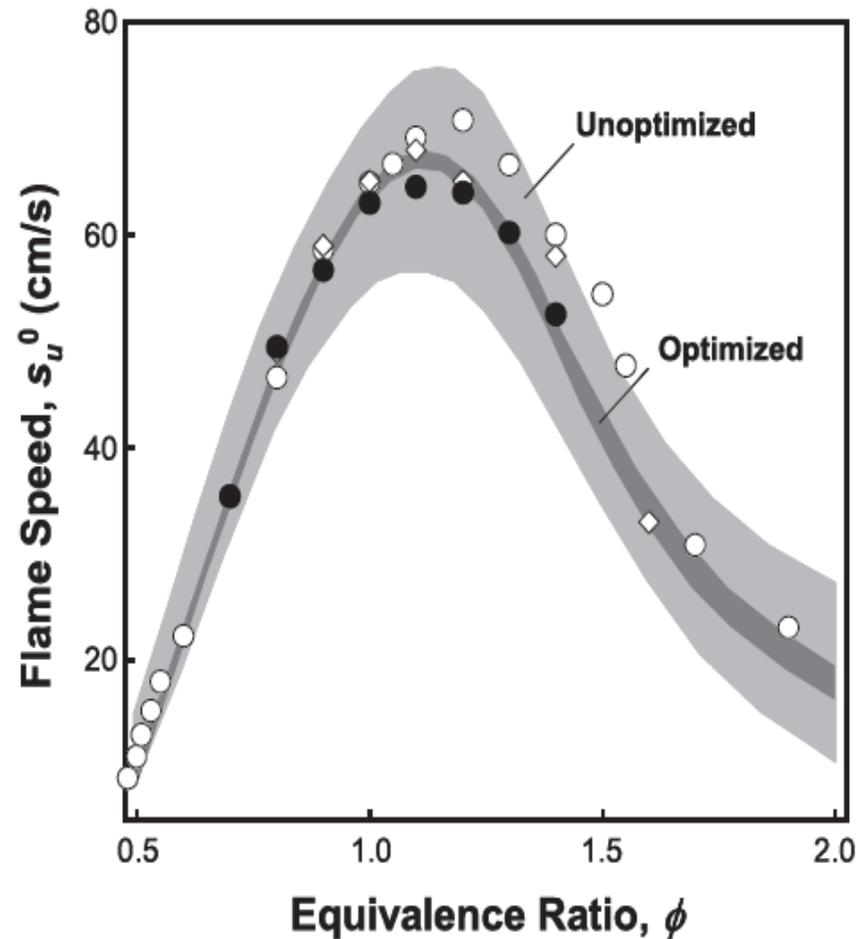
$$\eta_r(\xi) = \eta_r(\mathbf{x}^{(0)}) + \sum_{i=1}^m \hat{\alpha}_{r,i} \xi_i + \sum_{i=1}^m \sum_{j \geq i}^m \hat{\beta}_{r,ij} \xi_i \xi_j + \dots,$$

$$\hat{\alpha}_r = \frac{1}{2} \mathbf{I}_m \mathbf{a}_r \quad \hat{\beta}_r = \frac{1}{4} \mathbf{I}_m^T \mathbf{b}_r \mathbf{I}_m$$

- What this equation shows is that the overall model prediction is given by its nominal value plus uncertainty contributions from each rate coefficient.

$$\sigma_r(\xi)^2 = \sum_{i=1}^m \hat{\alpha}_{r,i}^2 + 2 \sum_{i=1}^m \hat{\beta}_{r,ij}^2 + \sum_{i=1}^m \sum_{j > i}^m \hat{\beta}_{r,ij}^2$$

Examples of application



- Experimental data and computed 2σ uncertainty bands for the laminar flame speed of ethylene-air mixtures at $p = 1$ atm. (Sheen et al., 2009).
- Note that following the application of an optimization procedure, the uncertainty bounds are much narrower.
- The polynomial chaos expansion is used within the optimisation procedure.

**ANOVA (ANALYSIS OF
VARIANCES)
DECOMPOSITION AND
HDMR METHODS**

Variance decomposition

- For independent inputs (i.e. no correlations exist between inputs), a unique decomposition of the unconditional variance $V(Y)$ can be obtained (Li et al., 2010):

$$V(Y) = \sum_{i=1}^n V_i + \sum_{1 \leq i < j \leq n} V_{ij} + \dots + V_{12\dots n} = \sum_{j=1}^{2^n-1} V_{x_j}$$

$$\sum_{j=1}^{2^n-1} \frac{V_{x_j}}{V(Y)} = \sum_{j=1}^{2^n-1} S_{x_j} = 1$$

- The approach is therefore analogous to the classical approaches described above but instead of directly calculating the conditional variances using e.g. Monte Carlo samples, now a meta-model is developed first and the sensitivity indices are calculated using the meta-model.

RSM approaches to ANOVA decomposition

- Polynomial chaos expansions were one method to achieve this ANOVA decomposition.
- Other methods are based on **High Dimensional Model Representations** (HDMR).
- HDMR originally developed to provide a straightforward approach to explore input-output mapping of models without requiring large numbers of runs (Sobol', 1990; Rabitz et al., 1999; Li et al., 2001).
- The use of truncated expansions is possible because usually only low-order correlations between inputs have a significant effect on the outputs.
- Because of the **hierarchical form** of HDMR component functions, sensitivity indices can be determined from them in an automatic way in order to rank the importance of input parameters and to explore the influence of parameter interactions.

Basic mapping

- The mapping between the inputs x_1, \dots, x_n and the output variable $Y(\mathbf{x}) = f(x_1, \dots, x_n)$ can be written in the following hierarchical form:

$$Y(\mathbf{x}) = f_0 + \sum_{i=1}^n f_i(x_i) + \sum_{1 \leq i < j \leq n} f_{ij}(x_i, x_j) + \dots + f_{12\dots n}(x_1, x_2, \dots, x_n)$$

- Here the zeroth-order component f_0 denotes the mean effect, which is the expected value of the model output $f_0 = E(Y)$.
- The first-order component functions $f_i(x_i)$ give the effect of variable x_i acting independently (although generally nonlinearly) upon the output $Y(\mathbf{x})$:

$$f_i(x_i) = E(Y|x_i) - f_0$$

- The function $f_{ij}(x_i, x_j)$ is a second-order term describing the cooperative effects of the variables x_i and x_j upon the output $Y(\mathbf{x})$:

$$f_{ij}(x_i, x_j) = E(Y|x_i, x_j) - f_i - f_j - f_0$$

If we find an **accurate meta-model** with which to represent the HDMR expansion, we can provide an accurate estimate of the partial variances and therefore the global sensitivity indices.

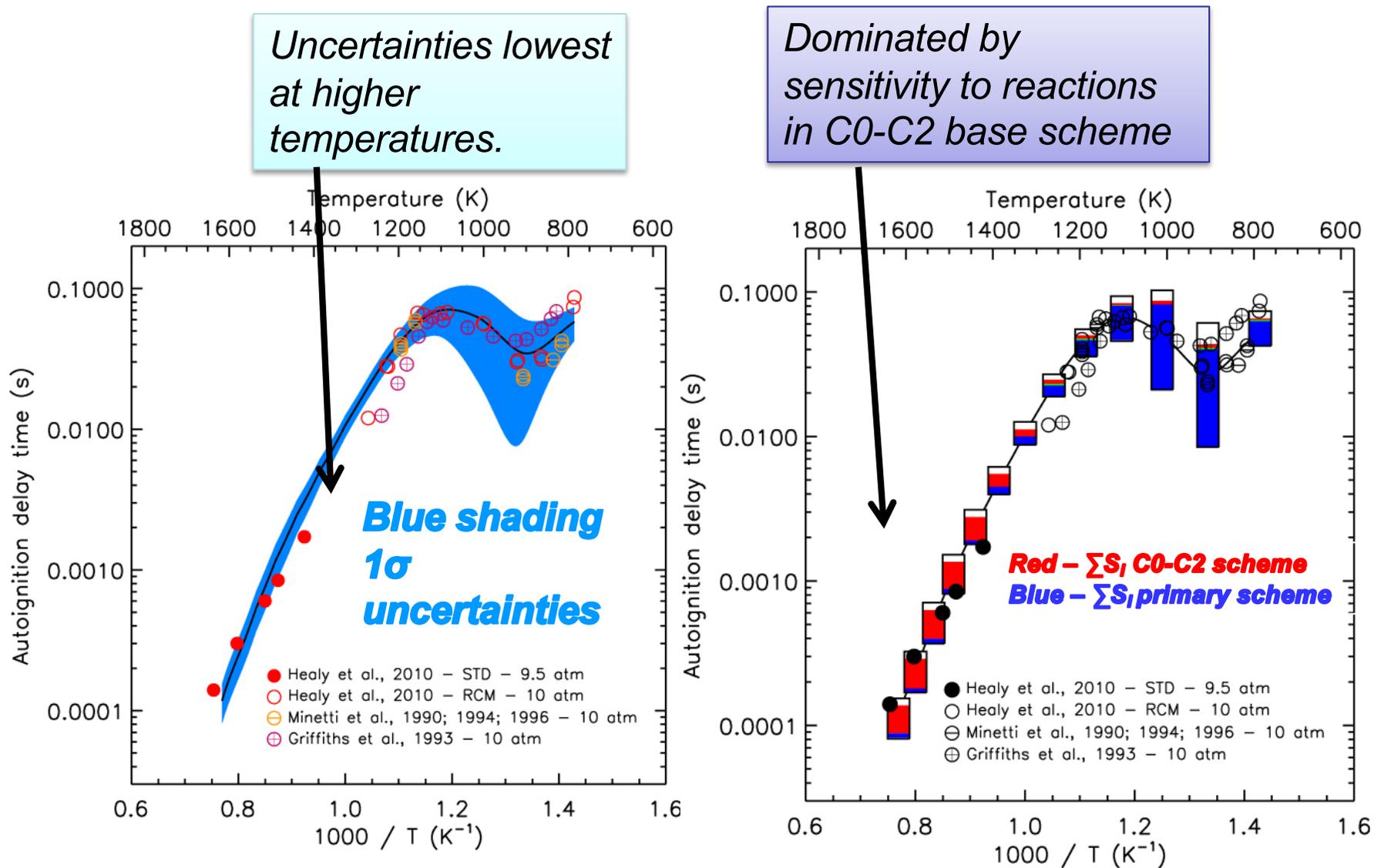
QRS-HDMR

- **Quasi-random sequences** such as a Sobol sequence have better convergence properties than other sampling approaches.
- Therefore we expect the Sobol' sequence to be a good choice of sampling strategy for fitting an HDMR meta model.
 1. A quasi-random sample is developed for chosen input parameter space.
 2. The full model would be run for each sample (e.g. 1024, 2048, etc) and target outputs stored.
 3. A meta-model would be fitted to the input-output relationships for each target output. **Orthonormal polynomials** are generally used.
 4. The fitted HDMR meta-model would be used to derive global sensitivity indices.
- The accuracy of the meta-model determines the accuracy of the calculated indices and needs to be checked carefully.

Sample size

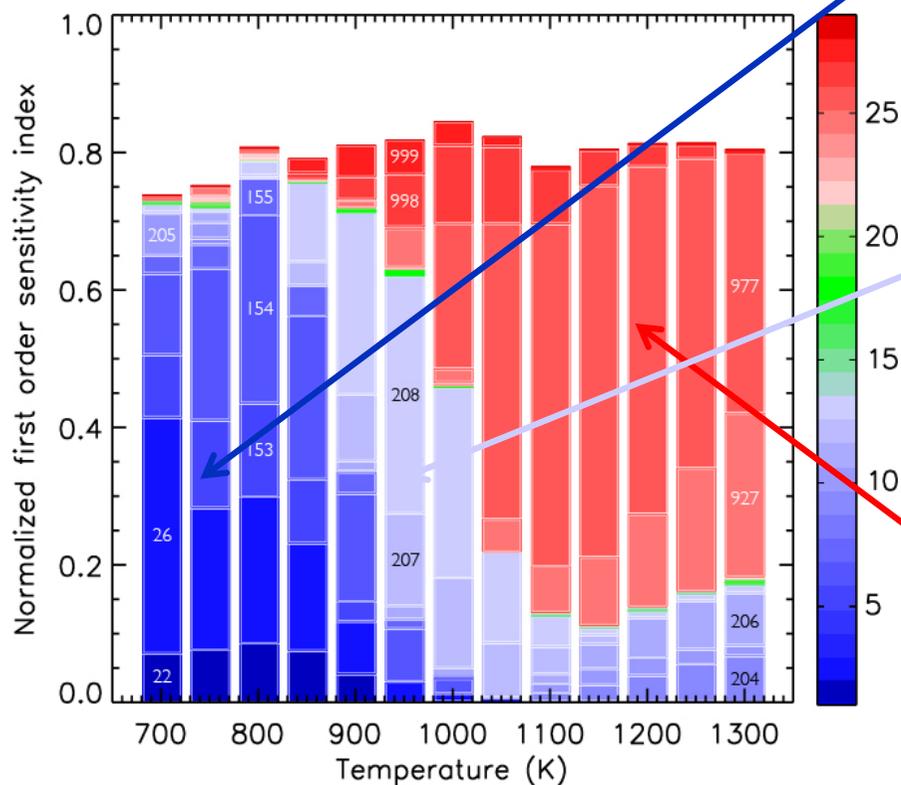
- The coefficients are determined using Monte Carlo integration over the chosen input sample (Li et al., 2002).
- The approximation of the component functions reduces the sampling effort dramatically so that only one set of quasi-random samples N is necessary in order to determine all RS-HDMR component functions and subsequently the sensitivity indices.
- For first-order indices this sample can usually be quite small (e.g. 1024).
- If significant second-order effects are present then the sample size will need to be bigger.
- **Remember – base 2 system so sample size increases as 2^{Ns}**
 - **2, 4, 8, 16, 32, 64, 128, 256, 512, 1024, 2048 etc!**

Example: Ignition delays of butane: sources of uncertainties

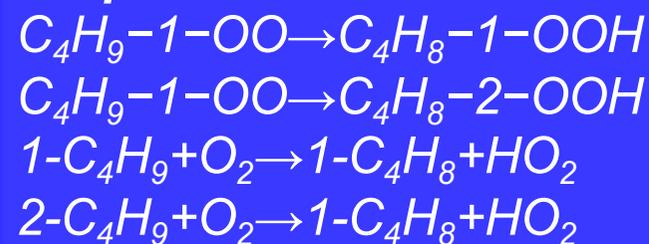


(Hébrard et al., 2015)

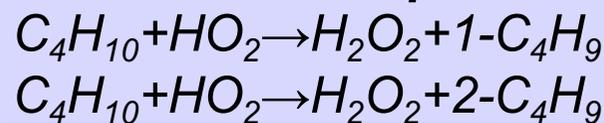
Ignition delays: 1st-order global sensitivities



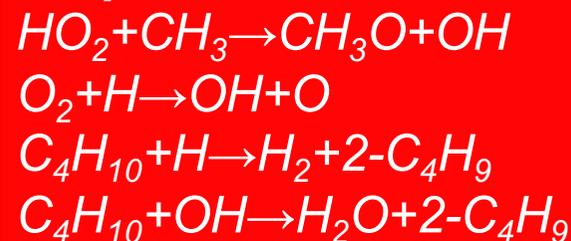
Key reactions at low temperatures



Key reactions at intermediate temperatures



Key reactions at high temperatures



SECTION 5
CHEMICAL MODEL
REDUCTION

Why is it necessary?

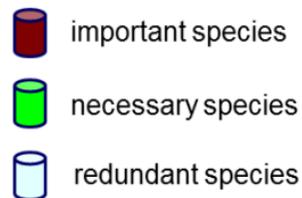
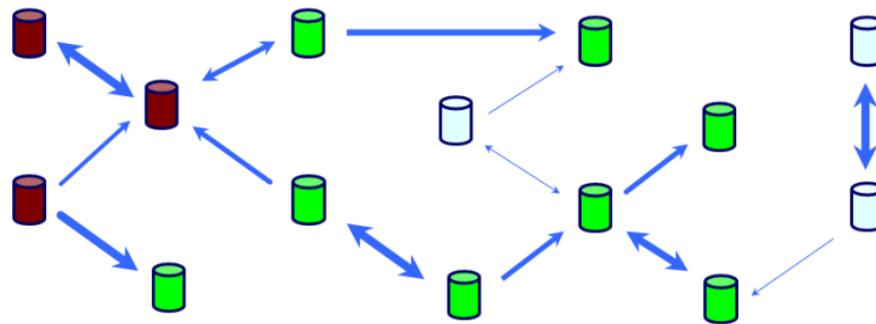
- Reactive flow models may involve resolving complex 3D turbulent flows within complex geometries.
- In order to achieve realistic computational times something has to be sacrificed:
 - **Spatial resolution**
 - **Highly averaged turbulence models**
 - **Use of simplified chemistry.**
- Detailed chemistry is often sacrificed but some phenomena require models that couple turbulent mixing and chemical processes in a resolved way.
- **Can we simplify detailed chemistry in such a way that we do not lose the important chemical information?**

Types of chemical model reduction

- **Skeletal model reduction – usually local i.e. specific C , P , T**
 - Methods for removing species and reactions that are not required to accurately simulate the desired target quantities or phenomena.
 - Sensitivity or graph theory based.
- **Time-scale based methods**
 - Rely on the fact that chemical processes take place on a wide range of time-scales and both SLOW and FAST processes can be simplified.
 - Usually processes faster than the mixing time-scales can be assumed to locally equilibrate, a kind of quasi-steady-state, QSS.
 - Simplified expressions can then be found for these QSS species so that their rate equations need not be solved.
- **Lumping**
 - Can be applied to reactions or species based on different principles.
 - Reaction lumping based on QSS arguments.
 - Species lumping based on reactive or structural similarities of species.
- **Tabulated or functional representations of chemistry.**
 - Pre-solve chemical problem in some way and store the results for use in CFD.

5. 1 Skeletal reduction

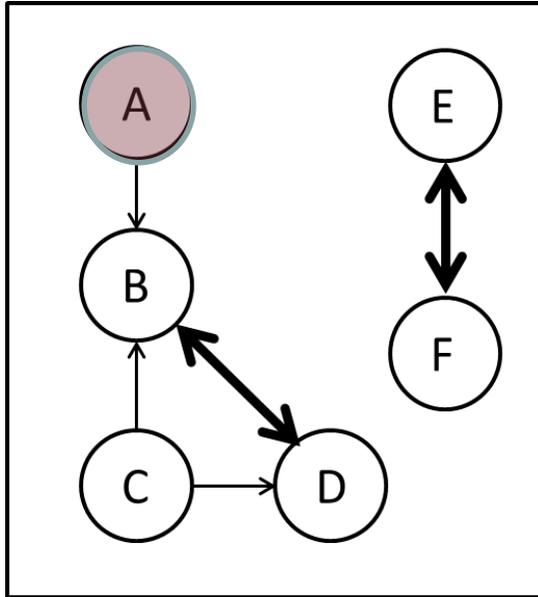
- Species and reactions that are redundant over wide ranges of conditions (T , P , composition) can be removed from the scheme.
- **IMPORTANT** to ensure that reduced model has been developed over conditions covering final application – wide C , P , T .



Important species identified by user. Methods find *Necessary* species and reactions required.

Redundant species removed.

Directed relation graph based methods



- Lu & Law (2005) suggested graph based methods for exploring couplings between species.
- Such methods applied to remove groups of species that can be internally coupled, through e.g. fast reactions, but are not strongly coupled to important processes: **species E, F**
- Each node in DRG represents a species and an edge from vertex A to B exists *if and only if* the removal of species B directly induces significant error to the production rate of species A.
- An edge from A -> B means B has to be kept to correctly evaluate the production rate of A.

$$R_{i \rightarrow j}^{(\text{Lu})} = \frac{\sum_{\alpha \in C(i,j)} |v_{i\alpha} r_{\alpha}|}{\sum_{\alpha \in R(i)} |v_{i\alpha} r_{\alpha}|}$$

$$I_i^{(\text{DRG})} = \begin{cases} 1 & \text{if species } i \text{ is a target species} \\ \max_{j \in S} (\min(R_{j \rightarrow i}, I_j^{(\text{DRG})})) & \text{otherwise} \end{cases} < \varepsilon$$

threshold

Connection weight: R_i - set of reactions related to species i ; $C_{i,j}$ set of reactions in which both species i and j participate, $v_{i\alpha}$ is the stoichiometric coefficient of species i in reaction α , and r_{α} is the net reaction rate

Examples of variants of DRG

$$R_{i \rightarrow j}^{(\text{Luo})} = \frac{\max_{\alpha \in C(i,j)} |v_{i\alpha} r_{\alpha}|}{\max_{\alpha \in R(i)} |v_{i\alpha} r_{\alpha}|}$$

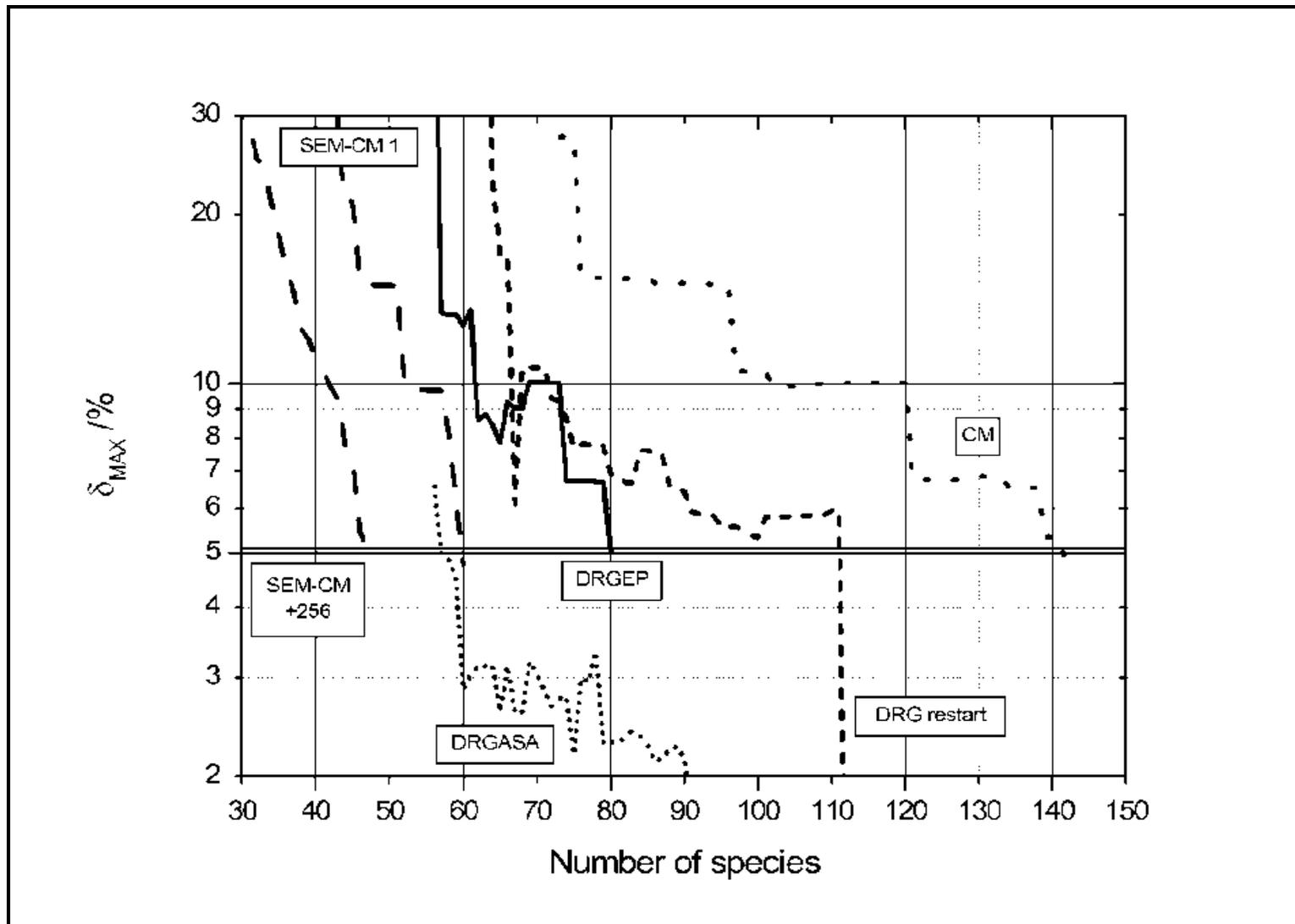
- Use of maximum norm (Luo et al., 2010).
- DRG with restart, two-stage reduction where the DRG procedure is repeated on the DRG-reduced mechanism (Lu & Law, 2006).
 - Graph structure likely will change on first reduction step.
- Flux-based DRG (Tosatto et al., 2011), considers effects of transport fluxes in flames.
- DRG-aided sensitivity analysis (DRGASA), (Nieymeyer et al., 2010)
 - Not as name suggests a sensitivity method, but a method that includes testing simulation error of proposed mechanisms with tighter and tighter thresholds.
- DRG with error propagation (DRGEP), (Pepiot & Pitsch, 2008)
 - Errors are damped as they propagate along the graph from the initially selected important species.
- **Factor of 3 reduction** in species and reactions is typical when starting with comprehensive mechanisms.

Simulation Error Minimization Connectivity Method (SEM-CM)

- Connectivity determined iteratively using: $B_i = \sum_j \left((y_i / f_j) (\partial f_j / \partial y_i) \right)^2$
- Shows the effect of a change in the concentration of each species on the concentrations of all **important + necessary** species, j .
- Gaps in B_j values show groups of un-connected species in a similar way to un-connected groups in the DRG.
- Several trial reduced mechanisms are created, and the simulation results obtained guide the further search for the nearly optimal reduced mechanism (Nagy & Turányi, 2009).
 - Adds to computational expense.
- **ALL THESE METHODS** should be applied over many pre-simulations to ensure all conditions covered in a reactive flow simulation will be included in reduction process.

Comparison of methods (Nagy & Turányi, 2009)

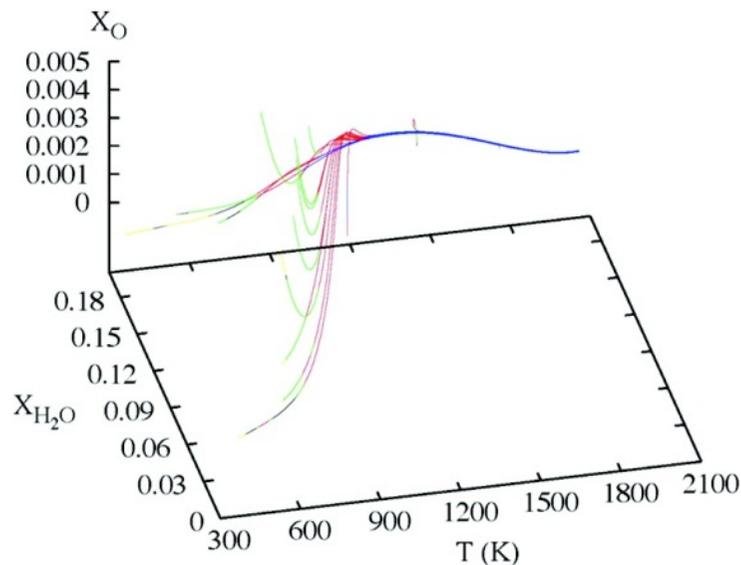
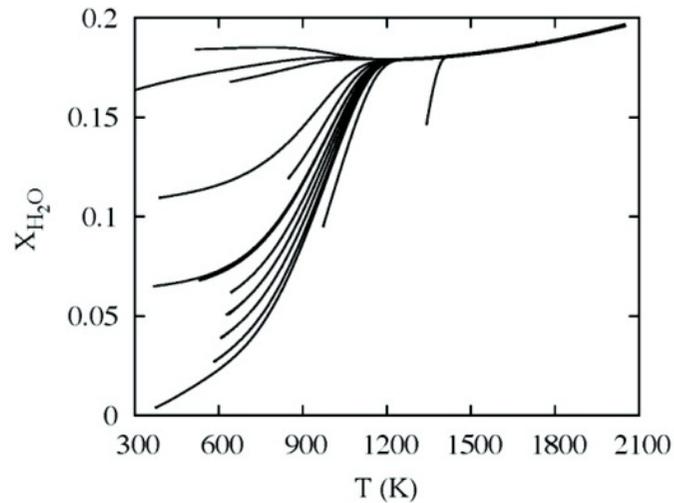
methane partial oxidation mechanism



5.2 Time-scale based methods

- Chemical systems contain a large range of time-scales due to the differing behaviour of highly reactive radicals, slower intermediates, initial reactants and products.
- Creates problems for numerical methods since the eigenvalues of the Jacobian can span many orders of magnitude creating *stiffness*.
- Very small time-steps are then required for standard methods hugely adding to the computational costs.
- **On the other hand....**
- This range of time-scales can be exploited within chemical model reduction by assuming that very fast time-scales are in local equilibrium with the slower variables.
- Allows a range of different methods to be used to limit the solution of chemical rate equations to only slower species.

Collapse of system dimension



- Example of premixed laminar hydrogen oxygen flame.
- In phase space trajectories converge from all boundary conditions to final equilibrium point.
- Colours show underlying system dimension as the time-scales collapse.
- $n = 1$ (blue), $n = 2$ (red), $n = 3$ (green), $n = 4$ (black), and $n = 5$ (yellow).
- Depending on temperature space the model is trying to predict, different reduced models could be developed.
- **HOW??**

Quasi-steady-state assumption QSSA

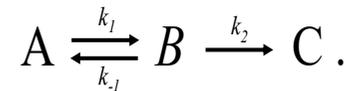
- Goes all the way back to Bodenstein (1913)
- Here **time-scales are associated with species directly.**
- Error induced by assuming QSSA for a species relates to its chemical lifetime within the system – 1/diagonal Jacobian element and its net production rate (Turányi et al., 1993).

$$\Delta Y_i = \left(-\frac{dY_i}{dt} \right) \left(-\frac{1}{J_{ii}} \right)$$

- Or for coupled groups of QSS species: $\frac{d\mathbf{Y}^{(QSS)}}{dt} = \mathbf{J}^{(QSS)} \Delta\mathbf{Y}^{(QSS)}$
- Consistent with ***small local error for species consumed in fast reactions*** and in such cases the local production rate of the QSS species can be large - counter intuitive.
- Term quasi-steady state means that concentrations do not change significantly ***with respect to the slow species*** which may exhibit steep concentration gradients in time.

How to apply QSSA

- Set right hand side of rate equation to zero and solve algebraically.
- Some times this can be done using symbolic algebra and a lumped reaction can be formed completely removing QSS species.



- If QSSA applied to B

$$\frac{d[B]}{dt} = 0, \quad [B] = \frac{k_1}{k_{-1} + k_2} [A]$$

$$\frac{d[C]}{dt} = k_2[B] = \frac{k_1 k_2 [A]}{k_{-1} + k_2} \text{ and}$$

B can be removed providing the global reaction step: $A \rightarrow C$

with
$$k' = \frac{k_1 k_2}{k_{-1} + k_2}$$

- In other cases numerical iteration methods are needed.

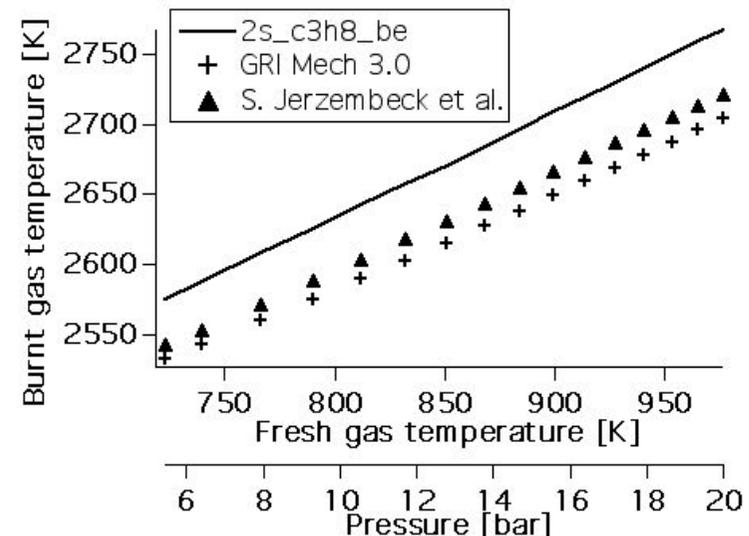
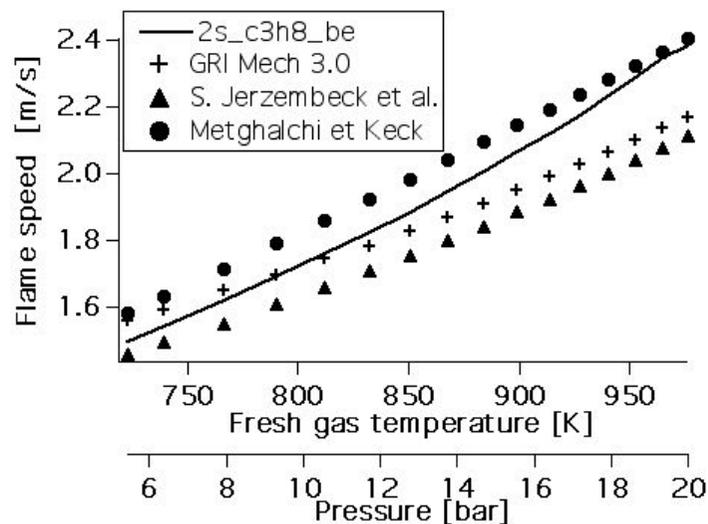
Global reaction schemes

- Global reaction schemes often used in complex reacting flows are usually generated using similar approaches to this e.g. (Peters & Rogg, 1993).
- Few species may be contained in the global schemes but the reaction rates contain complex expressions due to the lumping.
- Or they can be fitted as Arrhenius expressions to e.g. full model or experimental data.

Example from CERFACS – **note non-integer stoichiometries**:

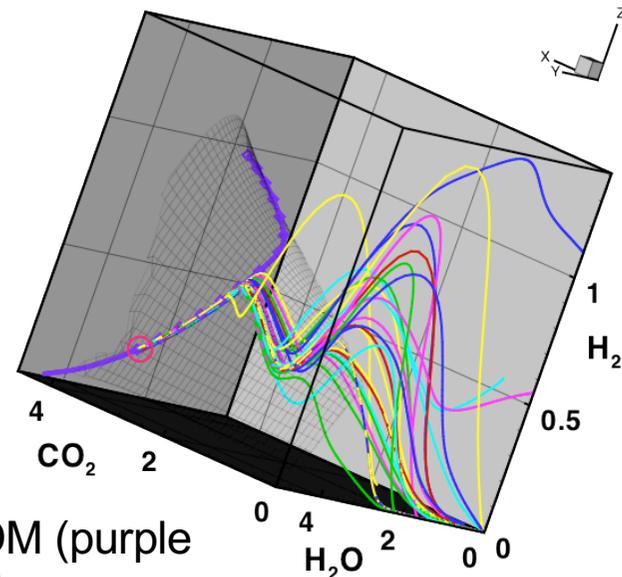
Reaction 1 reaction("C3H8 + 3.5 O2 => 3 CO + 4 H2O", [5.82320E+12, 0, 34000], order = " C3H8:0.8 O2:0.86 ")

Reaction 2 reaction("CO + 0.5 O2 <=> CO2", [2.00000E+09, 0, 12000])



Intrinsic low dimensional manifolds (ILDm)

- The QSSA is restrictive in the sense that it associates time-scales with specific species concentrations.
- More general formulations look for intrinsic low dimensional hypersurfaces with the phase space that exist when the fast time scales have collapsed – low dimensional or **slow manifolds**.
- By restricting the chemical changes to such ILDMs the dimensionality of the problem can be vastly reduced.
- **Hard part:** defining the dynamic chemical changes within the manifold.



ILDm (black mesh) for iso-octane-air system 1D ILDM (purple symbols), 0D ILDM (equilibrium, red circle). Lines - homogeneous reactor calculations for different fuels using different reaction mechanisms. (Blasenbrey & Maas, 2000)

Formulation of ILDM

General reaction diffusion system:

$$\frac{\partial \psi}{\partial t} = F(\psi) - \vec{v} \cdot \text{grad} \psi + \frac{1}{\rho} \text{div} D \text{ grad} \psi$$

where $\psi = (\psi_1, \psi_2, \dots, \psi_{S+2})^T$ is the thermokinetic state, $\psi = (h, \rho, w_1, \dots, w_S)^T$, F the chemical source term, \vec{v} the velocity, ρ the density and D the matrix of transport coefficients.

Using operator splitting the chemical source term can be separated: $\frac{\partial \psi}{\partial t} = F(\psi)$

System is then separated into three parts representing conserved, slow and fast subspaces:

$$\begin{pmatrix} Z_c & Z_s & Z_f \end{pmatrix} \cdot \begin{pmatrix} \tilde{Z}_c \\ \tilde{Z}_s \\ \tilde{Z}_f \end{pmatrix} = I$$

$$\begin{aligned} \tilde{Z}_c \frac{\partial \psi}{\partial t} &= \tilde{Z}_c F(\psi) && \text{Equilibrate fast time-scales} \\ \tilde{Z}_s \frac{\partial \psi}{\partial t} &= \tilde{Z}_s F(\psi) && \tilde{Z}_f F(\psi) = 0 \\ \tilde{Z}_f \frac{\partial \psi}{\partial t} &= \tilde{Z}_f F(\psi) && \text{Project onto slow subspace} \end{aligned}$$

$$\frac{\partial \psi}{\partial t} = (I - \tilde{Z}_f Z_f) F(\psi)$$

(Maas & Pope, 1992; Lam & Goussis, 1994)

Intrinsic dimensionality

- Two key aspects to using ILDMs/slow manifolds:
 - What is the **required dimension** of manifold to get desired accuracy?
 - How are the chemical changes along the **manifold defined**.

Z_c and Z_f are defined via invariant subspaces associated with the local Jacobian of the chemical source term according to:

$$F_\psi = \begin{pmatrix} Z_c & Z_s & Z_f \end{pmatrix} \cdot \begin{pmatrix} N_c & & \\ & N_s & \\ & & N_f \end{pmatrix} \cdot \begin{pmatrix} \tilde{Z}_c \\ \tilde{Z}_s \\ \tilde{Z}_f \end{pmatrix},$$
$$|\lambda_i(N_c)| < \tau_c, \quad \lambda_i^{\text{real}}(N_f) < \tau_s < \lambda_i^{\text{real}}(N_s)$$

τ_c is upper limit for the eigenvalues λ associated with very slow processes (“almost conserved scalars”), and τ_s is upper limit for eigenvalues associated with fast relaxing (negative) time-scales.

Hence, by an eigenvalue analysis gaps in the time-scale spectrum can be found and a dimension defined.

Computational Singular Perturbation (CSP) Theory uses a similar approach with slightly different formulation (Lam & Goussis, 1994):

5.3 Operator splitting

- For many models of reacting flows, the chemistry equations dominate the CPU usage.
- Stiffness adds further issues.
- Using operator splitting the chemical part can be separated from the solution of the flow terms, allowing reduction or special numerical strategies to be applied to chemical source term rather than having to apply them everywhere.
- Sportisse, 2000, suggests that the **stiff terms** should be **solved last** within each time-step.
 - Advection due to mean flow → diffusion, turbulent mixing → chemistry
 - Allows system to relax back onto slow manifold.
- Representation of chemical changes on the slow manifold e.g. using **tabulation** or **fitting** can overcome some of these problems (Pope, 1997). *See later for these methods.*

5.4 LUMPING

What does lumping mean?

- Combining information into “lumps” in such a way that we can still represent detailed kinetics but with fewer species or equations.

- Can take two forms:

– Reaction Lumping $A \rightarrow B \rightarrow C$

becomes: $A \rightarrow C$

Vertical

– Species Lumping $[Y] = [A] + [B] + [C]$

Horizontal

- **WHY?**

– Skeletal mechanism reduction methods are useful but sometimes not sufficient to make the mechanism small enough for use in e.g. CFD codes.

– By combining species or reactions we can compress the mechanism further and potentially reduce the number of equations we need to solve.

Advantages and Disadvantages

Advantages

- Reduction in number of variables and therefore equations to solve.
- When combined with time-scale analysis a reduction in system stiffness.
- Computational speed-up.
- Less species to “transport” in CFD code.

Disadvantages

- Lumped model cannot always be expressed as a kinetic scheme.
- Lumped scheme may “lose” information that was contained in full scheme.
- Cannot always recover original species concentrations.
- Need a method to define lumped reaction rates.

Crucial issues for successful species lumping

1. To determine which species are to be lumped;
2. To classify how the selected species should contribute to the lumped species, *i.e.* define the **lumping transformation**;
 - could also require defining the **inverse transformation** *i.e.* how to get back to the original species from the lump;
3. To estimate kinetic parameters for the reactions of the lumped species.

Two types of methodology are commonly used:

i) Chemical Lumping: based on chemical knowledge of species involved e.g. structural similarities.

ii) Mathematical Lumping: based on looking for similar mathematical quantities or applying mathematical rules.

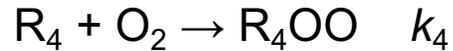
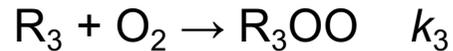
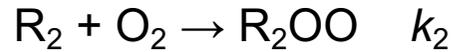
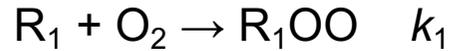
The two can often be equivalent since species with the same reaction steps and rate constants will lead to mathematical similarities within the equations.

Using mathematical approaches does not usually rely on chemical knowledge or intuition.

Chemical Lumping

- Has some commonality with topics on automatic mechanism generation since often based on **isomers** being involved in the same **reaction classes**.
- For *n*-heptane the classes of propagation routes are defined as:
 1. Decomposition and isomerization of alkyl radicals R.
 2. H-abstraction with O₂ to form HO₂ and conjugate olefins.
 3. Direct and reverse O₂ addition to R to form peroxy radicals ROO.
 4. Internal isomerisation between ROO and hydroperoxyalkyl radicals QOOH.
 5. Decomposition of QOOH radicals to form olefins.
 6. Decomposition of QOOH radicals to form HO₂ and conjugate olefins.etc.
- Reference rate parameters defined for each reaction class based on literature data or **similarity rules**.
- The **pathways for each isomer** and the resulting intermediate radicals can then potentially be **lumped** to give a simplified scheme with only a single pathway representing degradation to the average products of all the isomers (Ranzi et al., 1995).
 - Commonly used by Polimi in their mechanism generation.

n-heptane scheme - 4 alkyl radicals noted by R_1, R_2, R_3, R_4 giving rise to 4 reactions involving the addition of O_2 .



The lumped alkyl radical is then defined by:

$$[R] = [R_1] + [R_2] + [R_3] + [R_4],$$

with the corresponding lumped reaction given by:



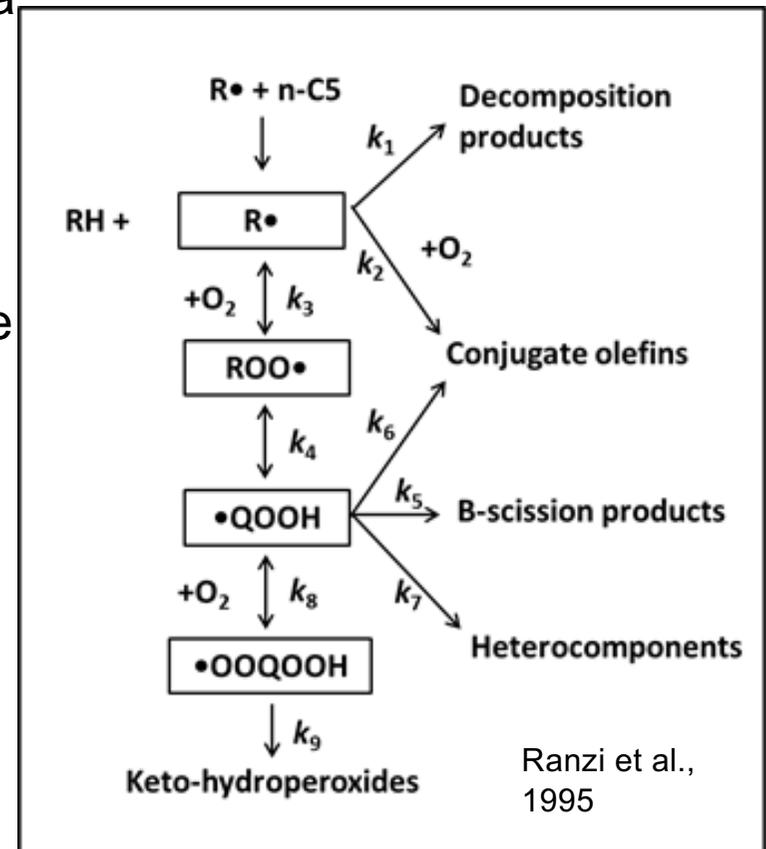
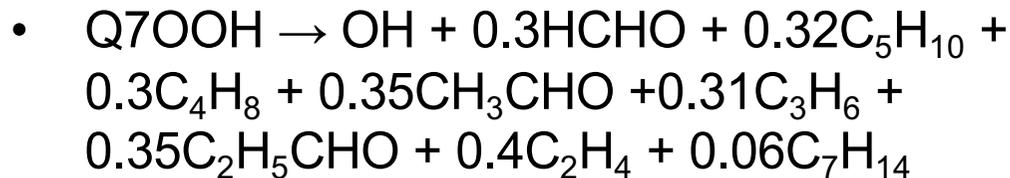
Lumped rates defined by **fitting** with respect to experimental data or with respect to the complex full model (MAMOX, Milan) or **weighted averages** for the different component isomers depending on the relative **weights** within the initial fuel or from the **weighted mean of the elementary rate coefficient** for the individual isomers (Fournet et al., 2000):

$$k_5 = \frac{k_1[R_1^\bullet] + k_2[R_2^\bullet] + k_3[R_3^\bullet] + k_4[R_4^\bullet]}{[R^\bullet]}$$

*Much easier if
all the rate
constants are
the same!*

Applications of Chemical Lumping

- Mechanisms developed in Milan tend to incorporate lumping and have now addressed a large number of parent fuel compounds.
- Key example is that for *n*-heptane which contains only 4 lumped radicals.
- High degree of lumping leads to reactions with non-integer stoichiometries which represent the relative weights of the different product channels.

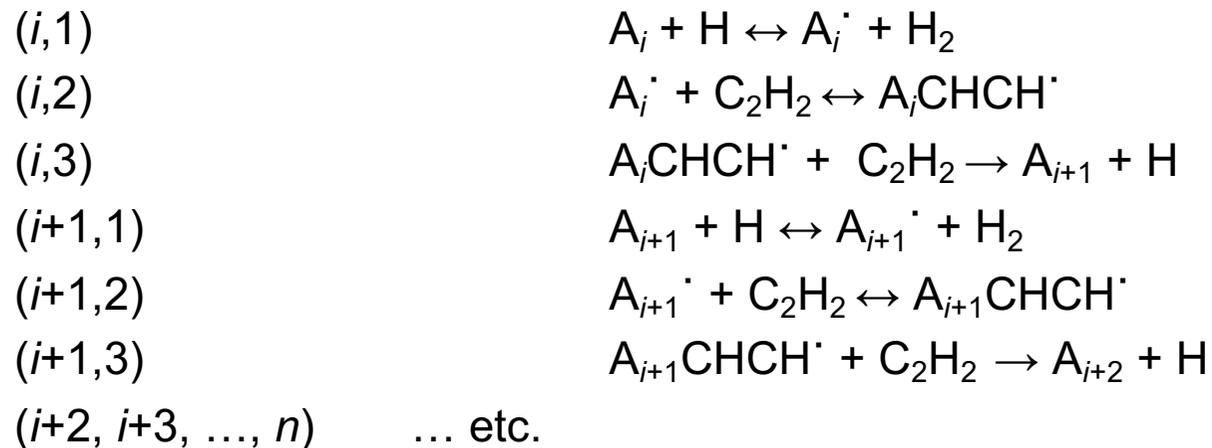


Applications of Chemical Lumping

- Battin Leclerc et al. (2000) reduced primary mechanism for *n*-heptane combustion from 410 free radicals and 70 molecules in 1654 reactions, to a lumped scheme with only 25 free radicals and 70 molecules in 189 reactions.
- The lumped mechanism was shown to give a good representation of the prediction of *n*-heptane conversion compared to the full scheme in the negative temperature coefficient regime.
- Lumping process included as an integral part of the automatic reaction generation software EXGAS in order to allow the user to limit the size and improve the computational efficiency of the generated schemes where required.

Soot modelling – the HACA Reaction Sequence

- Chemical reactions describing polymer growth are of the same type, rate parameters and thermodynamic data vary only slightly with polymer size.
- Reaction described by distribution function for degree of polymerization, and repeating reaction cycle for particle growth with structure and rate coefficients for each cycle treated as the same.
- Lumping guided by similarities in structure of hydrocarbon species (Frenklach, 1990).



where A_i is an aromatic molecule containing i fused aromatic rings, A_i^\cdot is an aromatic radical formed by H abstraction and A_iCHCH^\cdot is a radical formed by adding C_2H_2 to A_i^\cdot

In non-lumped form the reaction system is described by the following set of rate equations:

$$\frac{d[A_i]}{dt} = r_o - k_1[A_i][H] + k_{-1}[A_i][H_2]$$

$$\frac{d[A_i]}{dt} = k_1[A_i][H] - k_{-1}[A_i][H_2] - k_2[A_i][C_2H_2] + k_{-2}[A_iCHCH\cdot]$$

$$\frac{d[A_iCHCH\cdot]}{dt} = k_2[A_i][C_2H_2] - k_{-2}[A_iCHCH\cdot] - k_3[A_iCHCH\cdot][C_2H_2]$$

$$\frac{d[A_{i+1}]}{dt} = k_3[A_iCHCH\cdot][C_2H_2] - k_1[A_{i+1}][H] + k_{-1}[A_{i+1}][H_2]$$

$$\frac{d[A_{i+1}]}{dt} = k_1[A_{i+1}][H] - k_{-1}[A_{i+1}][H_2] - k_2[A_{i+1}][C_2H_2] + k_{-2}[A_{i+1}CHCH\cdot]$$

$$\frac{d[A_{i+1}CHCH\cdot]}{dt} = k_2[A_{i+1}][C_2H_2] - k_{-2}[A_{i+1}CHCH\cdot] - k_3[A_{i+1}CHCH\cdot][C_2H_2]$$

... etc.

- Rate coefficients k_j assumed to have same value for each cycle due to chemical similarities between the species.
- Allows chemical lumping to be applied in order to reduce the number of variables.
- Most severe lumping comes from summing together all species giving:

$$\frac{dM_o}{dt} = r_o$$

where $M_o = [A_i] + [A_i'] + [A_iCHCH'] + [A_{i+1}] + \dots$

- This one dimensional system describes the evolution of the total PAH concentration M_o . The details of the dynamics of the system are lost however if such a severe lumping is used.
- Another approach is to multiply each of the equations by an integer which roughly corresponds to the molecular mass of the species *i.e.* the number of carbon atoms, before summing the terms.

$$\begin{aligned} \frac{dM_1}{dt} &= \left(m_o \frac{d[A_i]}{dt} + m_o \frac{d[A_i]}{dt} + (m_o + 2) \frac{d[A_i\text{CHCH}\cdot]}{dt} + (m_o + 4) \frac{d[A_{i+1}]}{dt} + \dots \right) \\ &= m_o r_o + 2k_2[\text{C}_2\text{H}_2] \sum_i [A_i] - 2k_{-2} \sum_i [A_i\text{CHCH}\cdot] + 2k_3[\text{C}_2\text{H}_2] \sum_i [A_i\text{CHCH}\cdot] \end{aligned}$$

where $M_1 = m_o[A_i] + m_o[A_i] + (m_o + 2)[A_i\text{CHCH}\cdot] + (m_o + 4)[A_{i+1}] + (m_o + 4)[A_{i+1}] + \dots$,

is the total number of carbon atoms accumulated in the PAHs *i.e.* **the first moment of the PAH distribution.**

- In terms of species lumping we can now see that it is possible to define a new set of variables which define the lumped species:

$$\hat{c}_1 = \sum_i [A_i]$$

$$\hat{c}_2 = \sum_i [A_i\cdot]$$

$$\hat{c}_3 = \sum_i [A_i\text{CHCH}\cdot]$$

- The corresponding lumped equation system is then given by:

$$\begin{aligned}\frac{d\hat{c}_1}{dt} &= r_o - k_1[\text{H}]\hat{c}_1 + k_{-1}[\text{H}_2]\hat{c}_2 + k_3[\text{C}_2\text{H}_2]\hat{c}_3 \\ \frac{d\hat{c}_2}{dt} &= k_1[\text{H}]\hat{c}_1 - k_{-1}[\text{H}_2]\hat{c}_2 - k_{-2}\hat{c}_3 \\ \frac{d\hat{c}_3}{dt} &= k_2[\text{C}_2\text{H}_2]\hat{c}_2 - k_{-2}\hat{c}_3 - k_3[\text{C}_2\text{H}_2]\hat{c}_3\end{aligned}$$

- In this case lumping based on **chemical similarities** results in new variables which are simply linear sums of the original species concentrations.
- The lumped system has only 3 variables and in this case since it was assumed that the **rate constants were the same for each species of the same structure** the definition of the lumped rate constants is simple.

Mathematical Approaches: linear lumping

- The previous example showed that a simple linear transformation could be applied to define new lumped variables that were weighted sums of the original species.
- This type of lumping can be written in a more formal way.
- The formal definition of lumping is the transformation of the original vector of variables \mathbf{Y} to a new transformed variable vector $\hat{\mathbf{Y}}$ using the transformation function \mathbf{h} :

$$\hat{\mathbf{Y}} = \mathbf{h}(\mathbf{Y})$$

- The dimension \hat{n} of the new variable vector $\hat{\mathbf{Y}}$ is smaller than that of the original concentration vector. A new kinetic system of ODEs is formed:

$$\frac{d\hat{\mathbf{Y}}}{dt} = \hat{\mathbf{f}}(\hat{\mathbf{Y}}, \hat{\mathbf{k}}) \quad \hat{\mathbf{Y}}(t_0) = \hat{\mathbf{Y}}_0$$

Linear Lumping

In the linear case the transformation is simply a matrix multiplication operation:

$$\hat{\mathbf{Y}} = \mathbf{M}\mathbf{Y}$$

where \mathbf{M} is a matrix of size $\hat{n} \times N_S$. Consider for example:

$$\mathbf{M} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 1 \end{pmatrix}$$

Lumping matrix transforms original concentration vector (Y_1, Y_2, Y_3, Y_4) to the concentration vector *of lumped species*, (\hat{Y}_1, \hat{Y}_2)

where

$$\hat{Y}_1 = Y_1$$
$$\hat{Y}_2 = Y_2 + Y_3 + Y_4$$

5.5 Fitted models

- Sometimes e.g. in repeated design calculations, it is possible to solve the chemical source terms and store the information for use in more complex reactive flow simulations.
- Methods based on e.g.:
 1. Fitting a functional equation e.g. polynomial
 2. Look-up tables
 3. Flamelets
- If not specifically probing kinetics can be useful.
- **Caution:** if chemical scheme updated, stored data can easily go out of date unless in situ methods are used.

Use of difference equations for time dependent models – repro-modelling

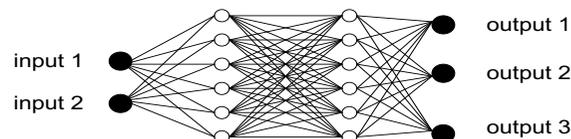
- For chemical kinetic systems we usually solve differential equations to determine the change in species concentrations over time.
- For large, complex, nonlinear systems requires sophisticated numerical integration techniques.
- For repeated calculations (e.g. in CFD codes) the same conditions of composition, temperature, pressure may be revisited many times.
- May be quicker to store the model results to reuse later.
- This can be achieved via the tabulation of model quantities (see later) or by the use of fitted difference equations.

1. Δt is selected to achieve good resolution of the characteristic system time-scale.
2. Several thousand, spatially homogeneous simulations carried out with series of initial concentrations and/or T , representative of circumstances of final applications.
3. $\mathbf{Y}(t)$, $\mathbf{Y}(t+\Delta t)$ concentration vector pairs are stored in a database.
4. Function \mathbf{G} is fitted to data and to predict change in concentration after time step
$$\Delta t : \mathbf{Y}(t+\Delta t) = \mathbf{G}(\mathbf{Y}(t)).$$

Operator splitting allows difference equation to be applied to only chemical time-step.

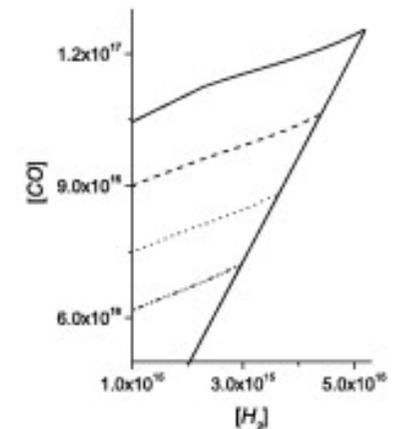
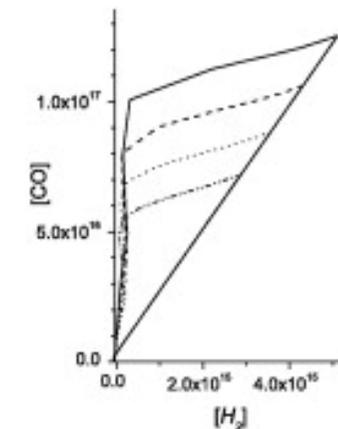
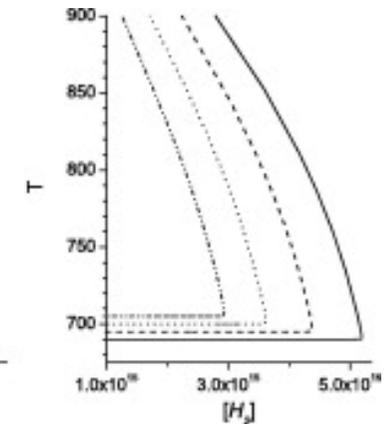
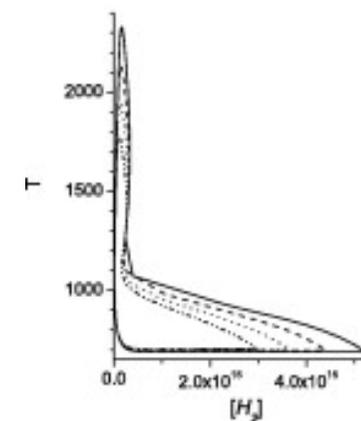
Different approaches

- The application of *orthonormal polynomials* (Turányi, 1994) can be advantageous for this task, since their *coefficients can be determined independently* from each other.
- Overall aim is to get a good fit using as few monomials as possible.
- For large complex systems, rapidly convergent hierarchical correlated function expansions in the input variables, or HDMR, can be used (as in global sensitivity analysis section).
 - Applied in Li et al. (2008) to the simulation of ignition within homogeneous H₂/air mixtures over wide ranges of temperatures and pressures ($1000 < T_0 < 1500$ K, $0.1 < P < 100$ atm)
- Artificial Neural Networks, ANNs, have also been used for this purpose (Christo et al., 1996; Blasco et al., 2000).
- Fitted models can be used to represent dynamics within the slow low dimensional manifold.
- Reduces dimension and stiffness and uses less memory than look-up tables.



Oscillatory ignition example

- Orthonormal polynomials used for the generation of a repro-model describing the **oscillatory ignition of CO-H₂ mixtures** in a continuously stirred tank reactor (CSTR) at very low pressures (Brad et al., 2007).
- **4-variable repro-model based on 6th order polynomials**, successful representation of the regions of steady state, cool flames and large temperature oscillations achieved based on fits to a 14-variable full model.
- [H₂], [O₂], [CO] and T used for fitted model.
- Dynamically complex system.
- Regions of high accuracy were required during oscillatory ignition.
- Whole composition space was partitioned to achieve accurate fits.



PRISM (Piecewise Reusable Maps)

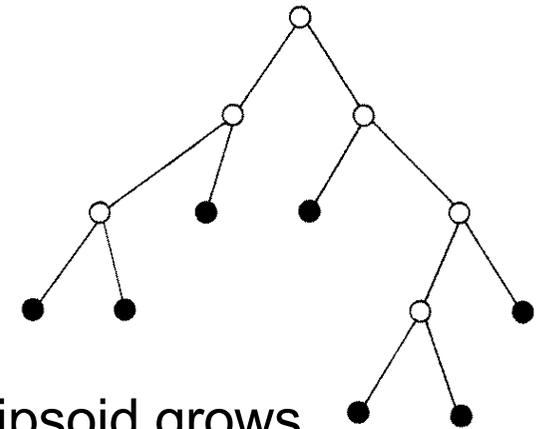
- Polynomial approach (Tonse et al., 1999) whereby fitted polynomial functions are **developed during the calculation**, and then **reused** when the region of composition space is revisited in subsequent time steps or different spatial regions (c.f. ISAT later).
- Uses **second-order polynomials** so that in order to cover the realisable region, multiple expressions are used, each valid over a different portion of composition space.
- Integration of full kinetic equations provides the solution at selected points throughout a hypercube, in order to determine the polynomial coefficients.
 - Increase in accuracy with reduced hypercube size.
- Trade-off between accuracy and the efficiency of polynomial generation as well as storage and retrieval.
 - **Polynomial construction only allowed for those hypercubes that are revisited enough times to make the construction worthwhile.**
- Successful application to hydrogen ignition, a 1D laminar hydrogen flame, a 2D axisymmetric turbulent jet (Tonse et al., 1999; Tonse et al., 2003) and a turbulent premixed hydrogen flame (Bell et al., 2000).

5.6 The use of look-up tables

- Key quantities of chemical changes e.g. species concentrations and rates of change calculated using simple models:
 - Perfectly stirred reactors, laminar flames
- Stored as a function of key quantities:
 - T , concentrations, reaction progress variable.
- Key aspect is coverage of appropriate phase space that will be encountered in CFD model.
- When CFD code receives input vector, it locates points within table close to input point. Output vector is composed using linear interpolation between output vector elements at the storage points.
- Critical aspects are **accuracy**, **storage** and **efficiency** of retrieval.
- Latter two can be vastly improved by tabulating on ILDMs which are much lower dimensional than the full composition space.
 - **Use of full mechanism and tabulation gives improvement compared to creating table from global mechanism.**

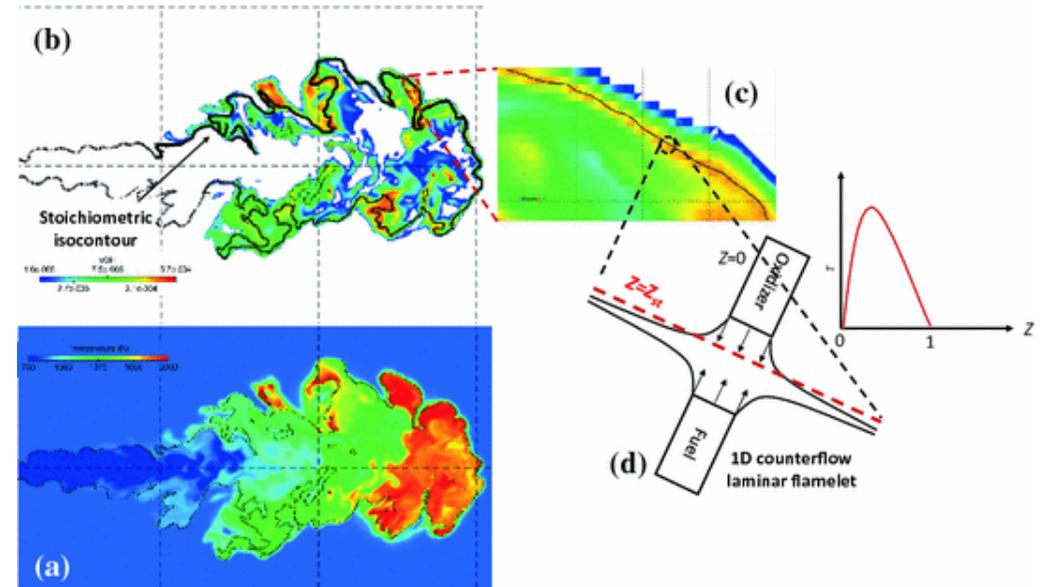
In situ adaptive tabulation (ISAT), (Pope, 1997)

- Exploits the fact that during reactive flow calculations, regions of composition space may be **revisited many times**.
- Calculate the first time and then **store and retrieve** in subsequent requests.
- Since systems naturally **relax to low dimensional manifolds** over time, creating tables on the fly automatically requires less variables and hence much smaller tables.
- Storage within a **binary tree structure**.
- Interpolation error controlled by adaptive refinement of mesh.
- Error controlled using ellipsoid of accuracy for stored points – as new points are tabulated ellipsoid grows.
- Many examples of use in turbulent reacting flows by incorporating operator splitting.



Flamelets (Bray, 2016)

- Used to approximate the edge of a turbulent flame by an **ensemble of discrete, steady laminar flames**, called flamelets.
- Individual flamelets assumed to have a similar structure to laminar flames for the same concentration, T conditions.
 - Detailed calculations of flamelet chemistry obtained from lower dimensional numerical calculations and potentially stored as look-up tables of species compositions and reaction rates in terms of suitably chosen reaction progress variable.
 - Coupling with assumed probability density function (PDF) for this variable then provides an estimate for mean properties.
 - Alternative is to provide a laminar flamelet expression for the PDF, $P(c;\mathbf{x})$.



Kundu et al,
2018

Flamelets (Bray, 2016)

Advantages:

- Rapid and usually low dimensional in terms of numbers of state variables.
- Commonly used in CFD packages using RANs and LES approaches.
- Detailed chemistry can be used in developing flamelet tables and hence problems with using global reactions can be avoided.

Disadvantages:

- Can fail in situations of significant flame stretch, intense small-scale turbulence, and flame-flame interactions.
- Difficult to estimate errors induced by assumption except by comparison with DNS.
- DNS data suggests that preheat zone structure differs from that of an unstretched laminar flame much more strongly than the high temperature side.

YOU NEED TO KNOW FROM WHAT CHEMISTRY THE FLAMELET WAS GENERATED...

Tabulation vs. Fitted Models?

Tabulation

- Highly accurate at tabulation points.
- Requires interpolation methods in between so accuracy depends on resolution.
- Trade off between resolution and storage and retrieval requirements.
- Can provide significant speed-ups over implicit integration methods.
- If in situ-then unlikely to lead to extrapolation but this leads to higher cost penalty.

Fitted Models

- Need to store far less information since not storing all input-output mapping – just fitted coefficients.
- Not necessarily 100% accurate anywhere. Depends on quality of fit and therefore sample size OR hypercube fitting region resolution.
- Unless calculated in-situ (e.g. PRISM) needs to be re-fitted each time model updated.
- Can provide significant speed-ups over implicit integration methods.
- Extrapolation dangerous.

Final Considerations

- The level of detail you decide to use to represent chemistry depends on your research goals.
- If you are probing kinetics, then a skeletal model may be ideal, so that elementary reactions can be retained and explored.
- To simulate turbulent combustion, tabulation/fitting may be only way to gain enough speed to incorporate detailed chemistry.
- Should always be aware of underlying chemistry:
 - If using a table/flamelet when was it created and using which detailed scheme? *Is it up to date?*
 - If using global reaction scheme, *are sufficient intermediates retained*, are underlying rate constants up to date?
- **Always be wary of over-extrapolation.**
- **Tracking uncertainties always useful** if affordable.
 - Tells us whether our model is likely to be robust or if process may be missing.
 - With SA tells us areas of model to focus on to improve the models predictive capabilities.

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