TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

2021 SUMMER SCHOOL ON COMBUSTION

Combustion Chemistry

Alison Tomlin

University of Leeds

July 11−17, 2021

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Reaction Kinetics and Modelling Chemical Processes in Combustion

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and Process Engineering

Acknowledgements

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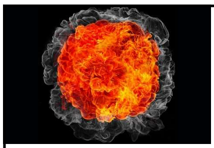
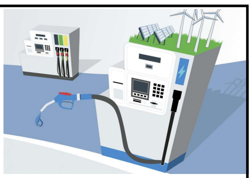
  - Professor Mike Pilling, Professor Bill Green, Scott Wisemann, Dr. Mike Burke, Dr. Brandon Rotavera, Professor Stephen Klippenstein, Dr. Christian Michelbach.
  - Cheers!



The Future World



- We live in a rapidly changing world.
- The energy status quo cannot/should not be maintained.
- In a low carbon future what role could/should combustion science and research play?
  - ➢ Development of strategies for utilising low carbon fuels.
    - ➢ Hydrogen, E-fuels, biofuels, ammonia, metals, biomass and use of CCS?
    - ➢ What are the potential broader environmental impacts of their use?
    - ➢ In what sectors does combustion have a role to play? Heat? Heavy duty trucks? Shipping? Aviation?
  - ➢ What are the fire and explosion risks of low carbon energy vectors and strategies.
    - ➢ Batteries, electrification, hydrogen storage and transport, biofuel storage.
    - ➢ Fire risk from energy efficiency measures.
    - ➢ Hydrogen safety in nuclear plant.
  - ➢ What additional risks will climate change pose?
    - ➢ Wild fires, air quality threats.

Future challenges

- Use of low carbon fuels requires re-designing many devices.
  - ➢ Additional challenges posed by blending or using pure hydrogen in gas turbines, domestic heat appliances.
  - ➢ Design of heavy duty engine and gas turbine operation on biofuels, E-fuels and blends.
  - ➢ Can we even design effective devices based on ammonia or metal combustion without impacting on air quality?
- Assessing fire risks involves understanding the combustion of complex materials.
  - ➢ Batteries, polymers used in insulation, complex biomass sources in fuel storage and wild fires, interactions with atmospheric flows.

Many questions which could be assisted by modelling combustion processes which requires the coupling of flow and chemical processes.

What is the purpose of a model?

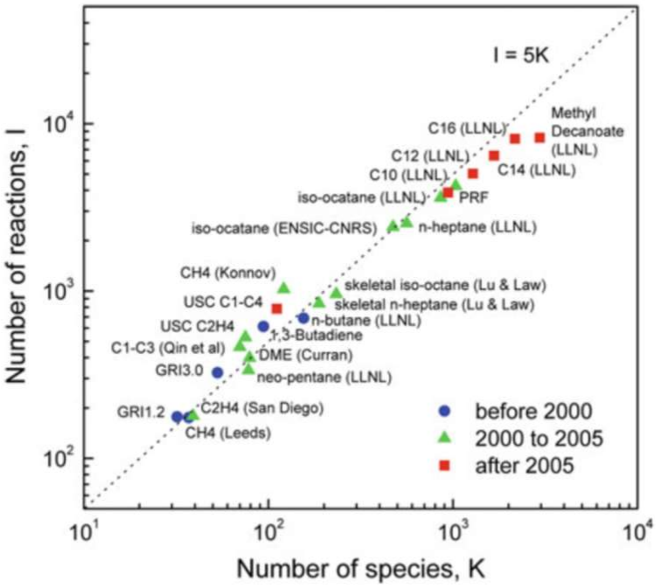
- A model is an ***interpretation*** and an ***approximation*** of physical reality.
- A construction which helps us to understand the governing principles behind physical/chemical phenomena we are trying to describe.
- We also need it to make predictions about physical behaviour.
    - means telling us ***things we do not yet know or have not yet measured* - *extrapolation.***
    - **potentially saving time and money performing experiments**.
    - **hopefully helping with the design of sustainable processes.**
- 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)

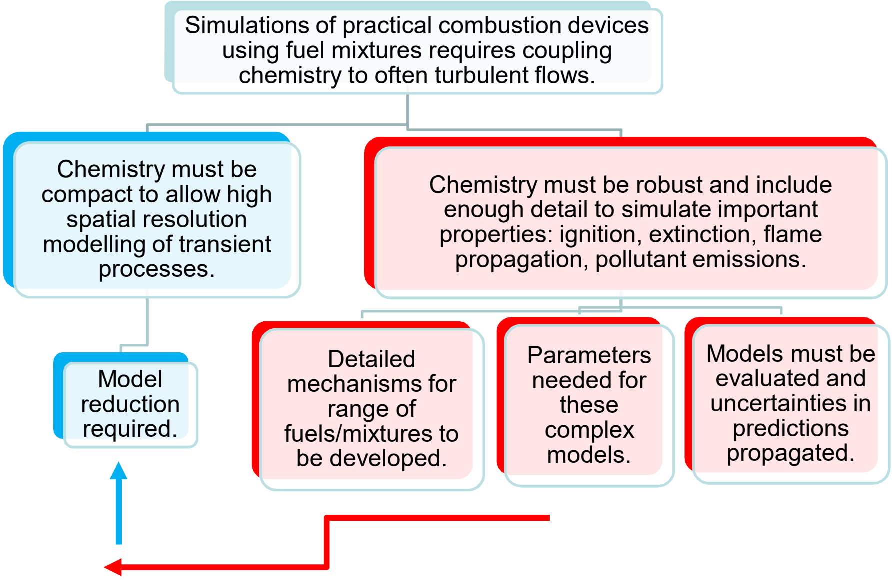


Many different models for same chemistry

- **Perfect Fidelity model:** Very large number of species & elementary step reactions, true thermo & rate coefficients. We think this would exactly predict the true chemistry in full detail. Humans never achieve this.
- **"Detailed Chemistry":** Human attempt at high fidelity: many (but not all) species & elementary step reactions, best known thermo & rate parameters.
- **"Reduced Model":** Often an approximation to "Detailed Chemistry" with fewer species and reactions. Often the rate expressions are not mass-action-law (e.g. maybe derived from steady state approximations).
- **"Empirical models"**: Small models focused on the (small number) of experimental observables. Try to keep number of parameters small so they can be determined from limited experimental data.

Often multiple models have been created for the same system, with different numbers of species and reactions, and different thermo & rate parameters.

Narrative of lectures…in reverse…



Simulations of practical combustion devices using fuel mixtures requires coupling chemistry to often turbulent flows.

Chemistry must be compact to allow high spatial resolution modelling of transient processes.

Chemistry must be robust and include enough detail to simulate important properties: ignition, extinction, flame propagation, pollutant emissions.

Model reduction required.

Detailed mechanisms for range of fuels/mixtures to be developed.

Parameters needed for these complex models.

Models must be evaluated and uncertainties in predictions propagated.

Overview

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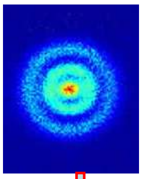
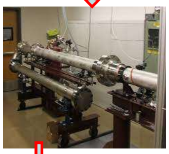
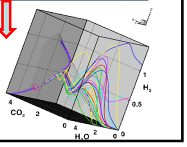
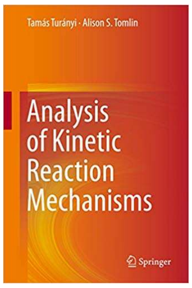






MODELLING FUNDAMENTALS



- ***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 lecture notes and some refs included in slides.*

SECTION 1
REACTION KINETICS BASICS

Pre-amble - Definition of a Chemical Species

- **Experimental view:** I think my detector response is proportional to concentration of X. Whatever my detector sees is “species X”.
  - **Chromatography:** whatever elutes at a certain time is X.
  - **Mass Spec:** whatever makes an ion of certain mass is X.
  - **Spectroscopy:** whatever absorbs or fluoresces at certain wavelength is X.
  - Sometimes deconvolute interferences (where 2 different species both give same signal on detector) by using two different detectors.
- **Theoreticians’ view:** Certain geometric arrangements of the atoms are called “species X”.
  - E.g. “OH” is when R(O-H) < 1.5 Angstrom, and all other atoms are more than 2 Angstroms away from this O and H.
  - Can define these boundaries more specifically as valleys in potential energy surface V(R).

All these species definitions are somewhat inconsistent…

Potential Energy Surface $V(\underline{R})$

- To a good approximation, the potential energy of a system containing atoms depends only on the positions $\underline{R}$ of all the atoms: $V(\underline{R})$.
- Can compute $V(\underline{R})$ using quantum mechanics.
- Usually V is insensitive to certain changes in $\underline{R}$ (e.g. a uniform translation). So we work in the subspace of $\underline{R}$ which significantly affects V, e.g. by change of variables to project out the uninteresting degrees of freedom. Called “internal coordinates” or “normal coordinates”.
- Using classical mechanics, for thermalized systems, the probability of the system being at $\underline{R}$ scales as **the Boltzmann factor** $\exp(-V(\underline{R})/k_BT)$.
- So most of the time the system is down in the “valleys” of small $V(\underline{R})$, near the **minima of $V(\underline{R})$.**
- If valleys with small $V(\underline{R})$ separated by regions with high $V(\underline{R})$, system gets stuck in valley for a long time: **natural definition of “Species”.**
  - We call the $\underline{R}$ at minimum of $V(\underline{R})$ in a valley the “equilibrium structure” or “the geometry” of that species. But really the atoms are always wiggling around, a species includes all atomic arrangements $\underline{R}$ down near the bottom of the valley.

Definition of “Species” Sets Definition of “Reaction”

- Definition of species as being a valley in V(R) implies “**dividing surface**” between species along the mountain ridge separating valleys A and B.
- Rate of reaction A → B is number of trajectories moving atoms from geometries in valley A to geometries in valley B, minus the reverse trajectories from valley B to valley A.
- All these trajectories cross the dividing surface, so count them there, no need to look at what is happening inside the valleys. Basis of transition state theory (TST).
  - **Analogy: To get change of number of cars in Manhattan, we can count cars crossing bridges and tunnels into and out of Manhattan. We don’t need to watch what cars are doing inside the city.**

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.

$$2\ H_2 + O_2 = 2\ H_2O$$

- 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.

For: $2\ H_2 + O_2 = 2\ H_2O$

- 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:

$$0 = -2\ H_2 - 1\ O_2 + 2\ H_2O$$

- Any multiple of this equation is also true.
- If we denote the formulae of the chemical species by the vector **A** = (A_1, A_2, A_3), and the corresponding multiplication factors by vector $\nu=(\nu_1, \nu_2, \nu_3)$. In this case A_1 = „H_2”, A_2 = „O_2”, A_3 = „H_2O”, and $\nu_1 = -2$, $\nu_2 = -1$, $\nu_3 = +2$. The corresponding general stoichiometric equation is:

$$0 = \sum_{j=1}^{N_s} \nu_j \mathrm{A}_j$$

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 CO_2 and H_2O.
- E.g. for methane and propane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \text{and} \quad C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

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

$$\mathrm{AFR} = \frac{m_{air}}{m_{fuel}}, \qquad \mathrm{FAR} = \frac{1}{\mathrm{AFR}}$$

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

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

- ϕ = 1 stoich; ϕ < 1 lean; ϕ > 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:

$$r = \frac{1}{\nu_j}\frac{\mathrm{d}Y_j}{\mathrm{d}t}.$$

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 Π 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 $2\ H_2 + O_2 = 2\ H_2O$, the order is not usually equal to the stoichiometric coefficient v_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:

R1	$H_2 + O_2 = H + HO_2$	k_1
R2	$O_2 + H = OH + O$	k_2
R3	$H_2 + OH = H + H_2O$	k_3
R4	$H_2 + O = H + OH$	k_4
R5	$O_2 + H + M = HO_2 + M$	k_5
R6	$HO_2 + OH = H_2O + OH$	k_6

Stoichiometry

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

$$\sum_j \nu_{ij}^L \mathrm{A}_j = \sum_j \nu_{ij}^R \mathrm{A}_j$$

- The **stoichiometric coefficients** on the left hand side (ν^L_{ij}) and the right hand side (ν^R_{ij}) 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: $$\nu_{ij} = \nu_{ij}^R - \nu_{ij}^L$$
- ν^L_{ij} should be positive integers, while ν^R_{ij} 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).

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:

$$\frac{\mathrm{d}\,Y_j}{\mathrm{d}\,t} = \sum_{i}^{N_R} \nu_{ij}\, r_i; \quad j = 1,\ 2,\ \ldots, N_S$$

or in vector form

$$\frac{\mathrm{d}\,\mathbf{Y}}{\mathrm{d}\,t} = \boldsymbol{\nu}\mathbf{r}$$

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:

$$C_p \frac{\mathrm{d}\,T}{\mathrm{d}\,t} = \sum_{i=1}^{N_R} \Delta_r H_i^{\ominus}\, r_i - \frac{\chi\, S}{V}\left(T - T_0\right)$$

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:

$$\frac{\mathrm{d}\,\mathbf{Y}}{\mathrm{d}\,t} = \mathbf{f}(\mathbf{Y},\mathbf{k}) \qquad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

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

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

- 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

R1	$H_2 + O_2 \rightarrow H + HO_2$	$r_1 = k_1\,[H_2]\,[O_2]$	
R2	$O_2 + H \rightarrow OH + O$	$r_2 = k_2\,[O_2]\,[H]$	
R3	$H_2 + OH \rightarrow H + H_2O$	$r_3 = k_3\,[H_2]\,[OH]$	
R4	$H_2 + O \rightarrow H + OH$	$r_4 = k_4\,[H_2]\,[O]$	
R5	$O_2 + H + M \rightarrow HO_2 + M$	$r_5 = k_5\,[O_2]\,[H]\,[M]$	*3rd order but not termolecular*
R6	$HO_2 + OH \rightarrow H_2O + OH$	$r_6 = k_6\,[HO_2]\,[OH]$	

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

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

$$\frac{\mathrm{d[H_2O]}}{\mathrm{d}t} = k_3\,[\mathrm{H_2}][\mathrm{OH}] + k_6\,[\mathrm{HO_2}][\mathrm{OH}]$$

Etc.

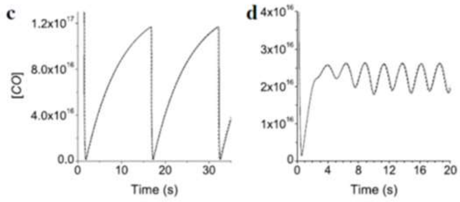
Try forming the Jacobian for this simple system.

Closed vs. open systems

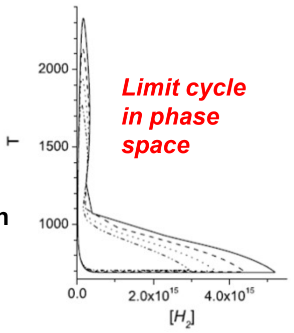
- In a **closed vessel**, system would tend towards a **final equilibrium point.**
- In an **open vessel** e.g. a continuously stirred tank reactor, CSTR, fresh reactants can be flowed into the vessel and products flow out. The system has a residence time t_{res} and can tend towards a **non-equilibrium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

$$\frac{\mathrm{d}\,Y_j}{\mathrm{d}\,t} = \left(\frac{Y_i^0 - Y_i}{t_{res}}\right) + \sum_i^{N_R} \nu_{ij}\, r_i; \quad j = 1,\ 2,\ \ldots,\ N_S$$

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



Oscillations in wet CO CSTR system
(Brad et al., 2007)



Limit cycle in phase space

PARAMETERISATION OF RATE COEFFICIENTS FOR USE IN COMBUSTION MODELS

Temperature dependence of rate coefficients

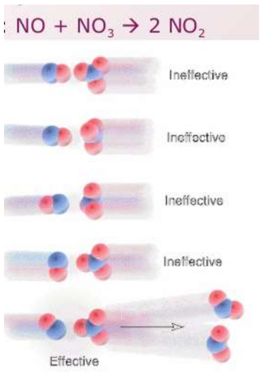
- Arrhenius argued that for reactants to transform into products, they must first acquire a minimum amount of energy, called the **activation energy E_a**.
- Consider the chemical reaction between two molecules, A and B, and the associated **potential energy changes** during the reaction.
- Reaction 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_a.**
- 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

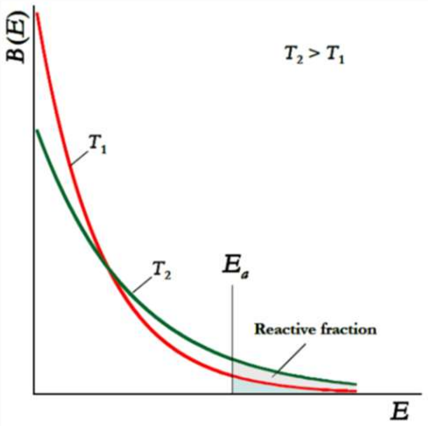
- The calculations for reaction rate coefficients involve an energy averaging over an MB distribution with E_a as lower bound.
- By assuming a Boltzmann distribution, we know that the fraction of collisions which will have a kinetic energy high enough to pass over this potential barrier is given by: $e^{-E_a/RT}$.

- ***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_a.
- **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:

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



- Only molecules / collisions with energy above the reaction barrier can react.
  Small change in T can dramatically increase rate!



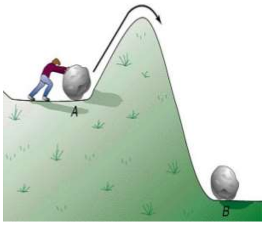
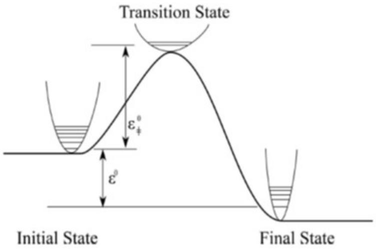


Figure 3.4 Boltzmann distribution of kinetic energy and reactive fractions of molecules.

Temperature dependence of rate coefficients

- If reaction between two molecules is an elementary one, occurring in a single step, *A* is related to frequency of collisions between 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*).

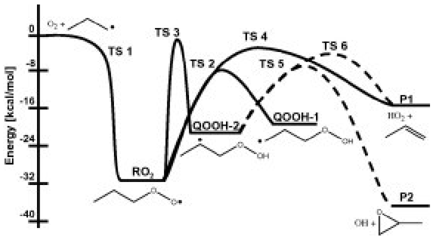


Transition State Theory

- The rate at which the final state is attained is determined by the **number of activated complexes formed** and the **frequency** with which they go over to the final state. These quantities may be calculated for simple systems by using statistical-mechanical principles.
- TST is now commonly used for calculating rate constants but requires knowledge of the **potential energy surface (PES)**.

We'll come back to this later but for excellent reviews on this topic see:

1. Zador et al., *Kinetics of elementary reactions in low-temperature autoignition chemistry, 2011.*
2. Klippenstein, *From theoretical reaction dynamics to chemical modeling of combustion, 2017.*



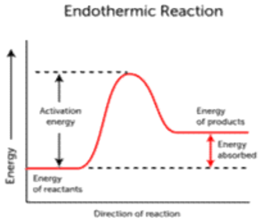
Example PES for n-propyl + O_2 (Goldsmith et al., 2017)

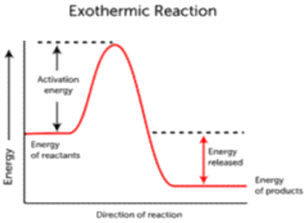
Temperature dependence of rate coefficients

- 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.

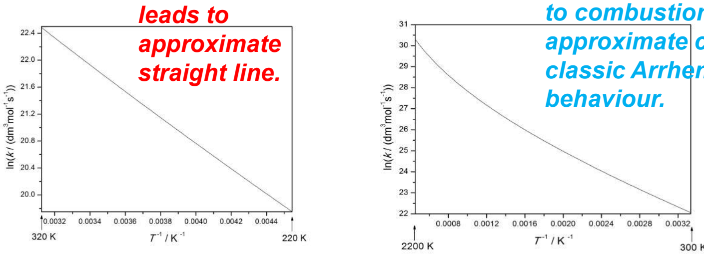




If the temperature dependence of the rate coefficient can be described by the original Arrhenius equation, then plotting *ln(k)* as a function of 1/*T* (Arrhenius plot) gives a straight line. The slope of this line is –*E/R*, and the intercept is *ln(A)*.

Narrow T range leads to approximate straight line.

Wider T range of relevance to combustion leads to approximate curve – non-classic Arrhenius behaviour.



Arrhenius plot of the temperature dependence of the rate coefficient of reaction CH_4+OH → CH_3+H_2O. (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:

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

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 can be calculated from the slope of the curve, i.e. the derivative of the temperature function with respect to $1/T$.

Worth remembering that the Arrhenius equation is basically a fit to data.

- 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 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. HO_2+OH=H_2O+O_2 (Burke et al., 2013) with expressions:

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

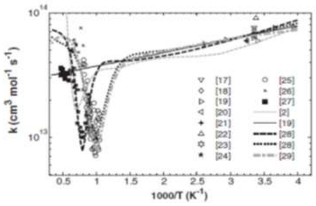
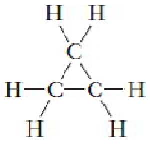


Fig. 1. Rate constants for $OH + HO_2 = H_2O + O_2$ (R4). Symbols represent experimental determinations [17–27], and lines represent proposed rate constant expressions [2,19,28,29] as indicated in the legend.

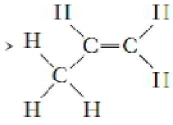
Declared as duplicate reaction

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 ⇄ C* + M and C* → P.

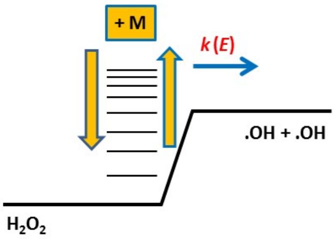


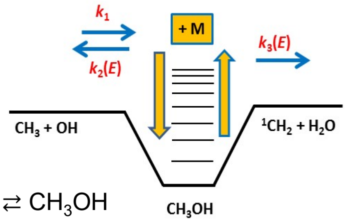
cyclopropane



propene

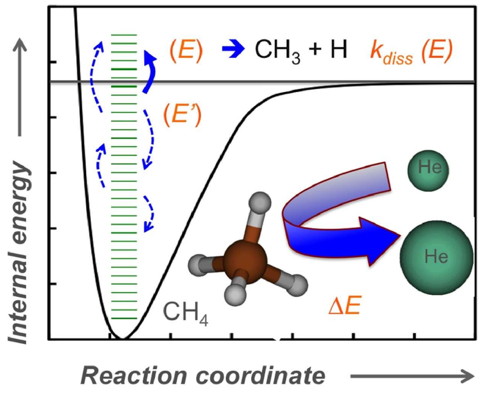
- Later shown that collisions create excited reactant species having a wide range of rovibrational energies. Cyclopropane molecules can **move up and down an energy ladder** and rate coefficient depends on energy of excited reactant.
- This example not of high practical significance but there are many other similar *unimolecular reactions* of importance in combustion.
- Decomposition of H_2O_2 is important in combustion of hydrogen, wet CO and hydrocarbons. See examples later….
- 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.





$CH_3 + OH \rightleftarrows CH_3OH$
$CH_3 + OH \rightleftarrows {}^1CH_2 + H_2O$

Example of dissociation reaction



- Collisions with He atoms induce transitions up and down energy levels for CH_4 molecules.
- Occasionally, molecule excited to internal energy state exceeding dissociation threshold forming CH_3 and H - in competition with further collisions with bath gas, which may further excite or de-excite the molecule, perhaps back below dissociation threshold.
- **Competition** between **dissociation** and **collisional excitation/de-excitation** ultimately determines pressure dependence.

(Klippenstein, PROCI, 2017)

Example of dissociation reaction

- In low-pressure limit, every molecule excited above dissociation threshold dissociates.
  - Rate of dissociation determined by rate of exciting molecules above threshold.
  - Rate linearly dependent on number of collisions and thus pressure.
  - Rate roughly proportional to density of states at the dissociation threshold, $\rho(D_e)$, times a Boltzmann factor in the dissociation energy, $\exp(-D_e/k_BT)$.
- In high-pressure limit, molecules undergo numerous collisions even after they are excited above the dissociation threshold.
- Distribution of excited molecules maintains form of a Boltzmann distribution even above dissociation threshold and rate coefficient now independent of pressure.
  - Reduces to a Boltzmann average of the microcanonical dissociation rates.
- At intermediate pressures, the rate is a complicated function of the competition between dissociation and collisional energy transfer.
  - **See later on how to deal with this.**

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, 1996).
- 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:

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

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:

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

- Metcalfe et al. (2013): [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.
- NB: Recent work from Mike Burke’s group has question the use of these simple linear mixture rules, suggesting sums should be on the basis of reduced pressure not pressure. **Watch his Webinar.**

- In H_2O_2 (+M) ⇄ 2 OH (+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 M = He, Ne, Ar, Kr, H_2, N_2, 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

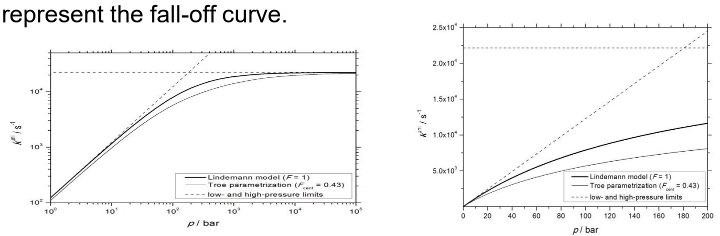
Lindeman equation can be improved by the application of the pressure and temperature dependent parameter *F*. In the Troe formulation (Gilbert et al., 1983), *F* is represented by a more complex expression:

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

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

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

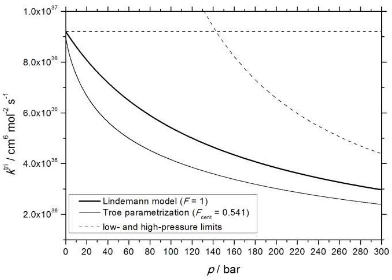
so that four extra parameters *α, T***, T*, T*** must be defined in order to represent the fall-off curve.



The change of the apparent first-order rate coefficient k_{uni} with pressure for reaction H_2O_2 ⇄ 2OH at temperature T=1000 K using bath gas N_2 (Troe, 2011).

Pressure dependence of bimolecular reactions

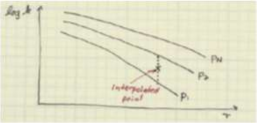
- ***Complex-forming bimolecular reactions*** may also be pressure dependent due to the complex losing extra energy in collisions leading to thermal equilibration.
- An example is the reaction of CH_3 + OH forming the CH_3OH complex. With the main products the stabilization product CH_3OH and decomposition products CH_2+H_2O.
- The Troe formulation accurately represents the fall-off region for single-well PE surfaces (Venkatesh 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*.

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



- 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 Venkatesh et al. (1997).

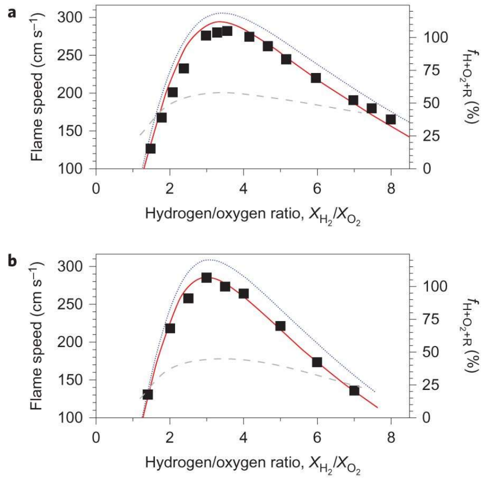
$$\log k(\tilde{T},\tilde{P}) \approx \sum_{i=1}^{N}\sum_{j=1}^{M} a_{ij}\varphi_i(\tilde{T})\varphi_j(\tilde{P}).$$

$$\varphi_i(x) = \cos[(i-1)\,\mathrm{acos}(x)]; \quad i = 1,2,\ldots,$$

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

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 = 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.**



a Hydrogen–air mixtures at atmospheric temperature and pressure

b Hydrogen–oxygen flames diluted with helium at atmospheric temperature for a pressure of 5 atm
and $X_{O2}/(X_{O2} + X_{He}) = 0.08$

Symbols experimental;
blue dotted lines indicate results from simulations where H + O_2 + R reactions were not included;
red solid lines indicate results from simulations where H + O_2 + R reactions were included.
The peak fraction of total HO_2 + R reaction flux through H + O_2 + R, $f_{H+O2+R} = \omega_{H+O2+R}/(\omega_{H+O2+R} + \omega_{HO2+R})$, is also indicated with a thin grey dashed line.

Burke & Klippenstein, 2017

Thermodynamics/Thermochemistry

- All Kinetics is leading toward equilibrium. So good to start by figuring out where we are going (later we can worry about how fast we will get there…).
- We need thermodynamic data to:
  - Compute equilibrium compositions
  - Determine the heat release in a combustion process
  - Calculate the equilibrium constant for a reaction – this allows us to relate the rate coefficients for forward and reverse reactions

- Other part, “Thermochemistry”, is about reactions.

  - 1st Law gives energy density, final temperature.

  - 2nd Law related to detailed balance (and so reverse rate coefficients), final composition at equilibrium.

Basic thermodynamic quantities

Enthalpy

- Enthalpy *H* comprises a system's internal energy: the energy required to create the system (internal energy, *U*), 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. $\frac{H^{\Theta}}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$ *a’s NASA polynomials*
- The enthalpy of reaction can be calculated by summing the enthalpies of the reactants and products of the reaction at a given temperature:

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

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

Tabulated thermodynamic quantities. Standard enthalpy of formation

Standard enthalpy change of formation, $\Delta_f H^\ominus$

The standard enthalpy change when 1 mole of a substance is formed from its elements in their reference states, at a stated temperature (usually 298 K). The reference state is the most stable state at that temperature, and at a pressure of 1 bar.

e.g. $C(s) + 2H_2(g) \rightarrow CH_4(g)$

$\Delta_f H^\ominus = -74.8 \text{ kJ mol}^{-1}$

The standard enthalpies of formation of C(s) and H_2(g) are both zero.

LHV of a fuel is computed easily from enthalpies

- Usually people define lower heating value (LHV) for a fuel as standard heat of reaction of combustion, where the final products are CO_2 and steam (at room temperature).

$$LHV(CxHy) = x\, H_{f,298}(CO_2) \; + y\, H_{f,298}(H_2O, gas) \; - H_{f,298}(fuel)$$

- This gives a “lower” heating value than that obtained from a real bomb calorimetry experiment, where the final product is liquid water not steam.

Definitions of HV

- The LHV (also known as net calorific value or NCV) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25°C) and returning the temperature of the combustion products to 150°C, which **assumes the latent heat of vapourisation of water in the reaction products is not recovered**.

- The higher heating value (HHV, also known gross calorific value, GCV or gross energy) of a fuel is defined as the amount of heat released by a specified quantity (initially at 25°C) once it is combusted and the products have returned to a temperature of 25°C, which **takes into account the latent heat of vapourisation of water** in the combustion products.

1 Kg/scf Natural gas:	**1 Kg/scf H_2**
LHV: 47.13/983.0 MJ	LHV: 119.96/290.0 MJ
HHV: 52.21/1089.0 MJ	HHV: 141.88/343.0 MJ

Hydrogen will need to be compressed for storage….

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

$$\Delta G^\ominus = \sum n\Delta G^\ominus_f(products) - \sum m\Delta G^\ominus_f(reactants)$$

- 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 $\Delta G^\ominus$ 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.**

Equilibrium composition minimizes Free Energy

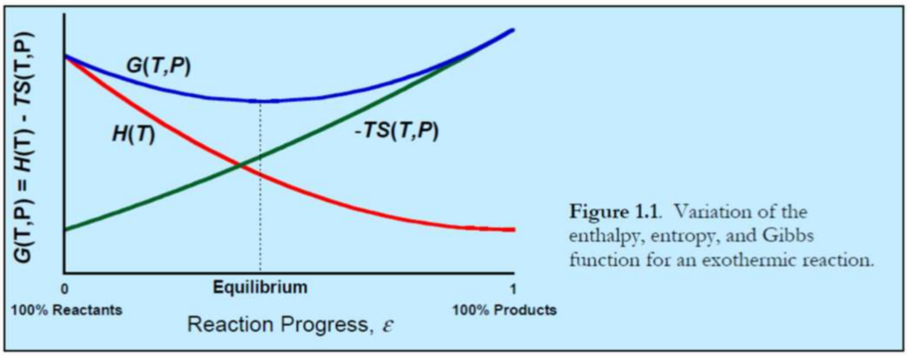


Figure 1.1. Variation of the enthalpy, entropy, and Gibbs function for an exothermic reaction.

Constrained minimization: conservation of C,H,O atoms; adiabatic

Free Energy Constrained Minimizer Software is Available. See e.g. EQUIL in CHEMKIN package.

How do programs like EQUIL work to compute equilibrium concentrations?

- Take as input the **initial composition** and **temperature**.
- Take as input a database of molecules with thermochemical data (usually in form of **NASA polynomials**).
- Assume ideal gas, ideal mixture, adiabatic so: $G = \sum_{i=1}^{Ns} \bar{g}_i N_i$

where $\bar{g}_i$ is the partial molal Gibb's function and N_i is the number of moles of each species *i* in the system. N_s is the total number of species.

For ideal-gas mixtures, the partial molal Gibb's functions are given by:

$$\bar{g}_i = g_i(T,P) + RTln(X_i)$$

where $g_i(T,P)$ is the Gibb's function for the pure species *i*, evaluated at the system temperature and pressure; *R* is the universal gas constant; and X_i is the mole fraction of the ith species.

- **Equilibrium solution at given *T* and *P* is distribution of N_i that minimizes the system *G***, subject to atomic population **constraints** (and non-negative N_s).
- Atomic population constraints are: $\sum_{i=1}^{Ns} n_{ji} N_i = p_j$ where n_{ji} is number of *j*th atoms that appear in *i*th molecule, p_j is the total population in moles of the *j*th atom in the system, and *M* is the total number of elements present in system.

When might Chemical Equilibrium Calculations be Useful?

- For **final product prediction** in closed reactors.
- In cases where the chemical time-scales are much faster than other processes such as transport, crank angle rotation etc.
- For calculating properties such as **adiabatic flame temperatures**.
- In general for complex flows and stirred continuous reactors the behaviour is far from equilibrium and we must solve for chemical kinetics.
- However, most systems at least partially equilibrate and model reduction methods such as the ***rate-controlled constrained-equilibrium method*** (RCCE) make use of free energy minimisation (**see later**).

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 $C_P = \frac{\Delta H}{\Delta T}$ (amount of energy applied to one unit of mass of substance for increase of one unit in temperature).

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

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

$$H_{Tf} = H_{Ti} + C_P\left(T_f - T_i\right)$$

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 “⇄”.
- The use of irreversible reactions denoted by a single arrow “→” 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 calculated from thermodynamic properties through 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^{Θ}), enthalpy (H^{Θ}) and entropy (S^{Θ}). The standard molar reaction enthalpy $(\Delta_r H^{\Theta}_j)$ and entropy $(\Delta_r S^{\Theta}_j)$ can be calculated from the following equations:

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

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

$$\Delta_{\mathrm{r}} G^{\Theta} = -RT \ln K \qquad K = \exp\left(\frac{\Delta S^{\Theta}}{R} - \frac{\Delta H^{\Theta}}{RT}\right)$$

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

$$K_c = K\left(\frac{p^{\Theta}}{RT}\right)^{\Delta\nu}$$

where p^{Θ} is the standard pressure and $\Delta\nu = \sum_i \nu_i$ is the sum of stoichiometric coefficients.

Knowing thermodynamic properties of species allows the reverse rate constant to be calculated. NB An error of 5 kcal/mol in Gibbs free energy will result in an equilibrium constant that is off by a factor of 12 at 1000 K (Goldsmith 2012).

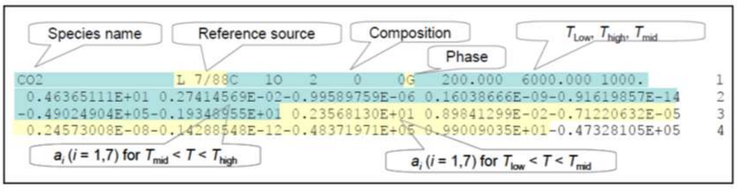
Representation in typical combustion models

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

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

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

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



```
CO2                     L 7/88C   1O   2    0    0G   200.000  6000.000 1000.        1
 0.46365111E+01 0.27414569E-02-0.99589759E-06 0.16038666E-09-0.91619857E-14    2
-0.49024904E+05-0.19348955E+01 0.23568130E+01 0.89841299E-02-0.71220632E-05    3
 0.24573008E-08-0.14288548E-12-0.48371971E+05 0.99009035E+01-0.47328105E+05    4
```

2nd Law and 3rd Law ways of computing entropy

3rd Law method:

integrate C_p/T from T=0 K, using fact that S=0 at 0 K.

$$S^0(T) = S^0(T^o) + \int_{T^o}^{T} (C_p(T')/T')dT'$$

2nd Law method: Set up an experiment where a reaction is equilibrated. Measure that reaction's equilibrium constant K by measuring the concentrations of all the species involved.

- Use $\Delta_r G^\ominus = -RT \ln K$
- If is $\Delta_r H$ known, use $\Delta_r G = \Delta_r H - T\,\Delta_r S$ to determine $\Delta_r S$
- Else, measure K as a function of T: $\Delta_r S = d\,\Delta_r G/dT$.

Computing thermodynamic quantities: Statistical mechanics basics

- Based on quantity Q called the "partition function" for ensemble

$$Q = \sum_i g_i \exp(\frac{-E_i}{k_B T})$$

where E_i are the possible energies of the system (quantum mechanics only allows certain quantized energy levels), and g_i is the number of quantum states with energy E_i (energy level is g_i fold degenerate).

- Q contains enough information to compute all the normal thermochemical quantities. For example:

Internal energy $U(T,V) = \sum g_i E_i \exp(\frac{-E_i}{k_B T})\frac{1}{Q} = {}^{-\partial(lnQ)}\!\Big/_{\partial(\frac{1}{k_B T})}$

Helmholtz Free Energy: $F = U - TS = G - PV = -k_B T lnQ$

$$S = -k_B \ln Q + \frac{1}{T}\frac{\partial(\ln Q)}{\partial({}^1\!/_{k_B}\,T)}$$

All we need to know is the set of possible energies $\{E_i\}$

HOW DO WE COMPUTE THE ALLOWED ENERGIES {E_i} FOR A SINGLE MOLECULE?

First we need the potential field V(<u>R</u>) for our molecule

- Can’t measure V(<u>R</u>), need to compute it using
  - **Wave function based methods** - Schrödinger equation.
  - Solve for the electron density using **density-functional** (DFT) based methods.
- These are the fields of “quantum chemistry”.
- Forces between atoms are electrostatic, but electrons are so light that quantum mechanics effects dominate, so we solve Schrödinger equation. This is an eigenvalue equation; the lowest eigenvalue is the value of V(<u>R</u>).
- Unfortunately, the Schrödinger equation is a Partial Differential Equation (PDE) in **$3N_{electrons}$ dimensions**, with tricky constraints: too hard to solve exactly.
- We can **solve it approximately** by:
  - Expanding the solution wave-function in a finite basis set, and making many other approximations.

Overall summary of approaches

Vereecken et al, 2015

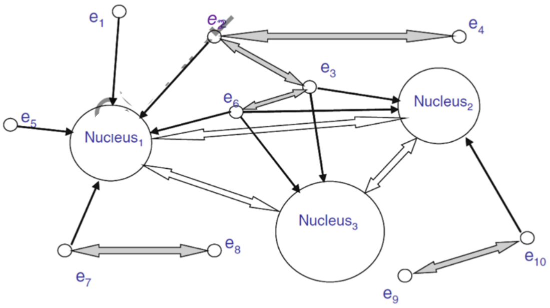
- Quantum chemical calculations can typically be divided into three categories:
  - **Ab initio calculations** based on a wavefunction description of the molecules,
  - **Density functional theory (DFT)** based on a description of the electron density in a molecule, and
  - Semi-empirical calculations that involve using parametrised integral approximations.
- Ab initio wavefunction calculations utilising sophisticated treatments of electronic correlation provide most accurate results **BUT** carry a high computational cost.
  - Mainly suitable for small molecules (4-6 atoms)
- DFT methods are less costly to execute, but rely on functionals, the exact form of which is unknown.
  - Accuracy is improving and commonly used for larger molecules.

Ab Initio Methods

- ***Ab initio quantum chemistry methods*** attempt to solve electronic Schrödinger equation given the positions of the nuclei and the number of electrons in order to yield useful information such as electron densities, energies and other properties of the system.
- Many electron function generally a linear combination of many simpler electron functions with the dominant function being the Hartree-Fock function (**see later**).
- Each of these simple functions then approximated using only one-electron functions.
- The one-electron functions are then expanded as a linear combination of a finite set of **basis functions**.
- Approach has advantage that it can be made to converge to exact solution, when basis set tends toward limit of complete set and where all possible configurations are included (called "Full CI – full configuration interaction").

Wave Function Methods – the Hamiltonian

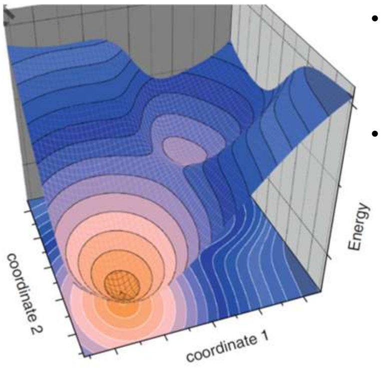
- The Hamiltonian operator *H*, consists of kinetic energy operators of electrons and nuclei and ensemble of attractive potential energy terms describing nucleus-electron interaction, and electron–electron as well as nucleus–nucleus repulsions.
- Energy terms in Hamilton operator for a polyatomic molecule (water in this example: $\text{Nucleus}_1 = \text{Nucleus}_2 = \text{H}$; $\text{Nucleus}_3 = \text{O}$).
- Only a few examples of each kind of interaction are shown.



Black arrows denote attractive interactions, gray and white arrows the electron–electron and nucleus–nucleus repulsions.

$$H = T_{nucl} + T_{el} - V_{nucl\text{-}el} + V_{el\text{-}el} + V_{nucl\text{-}nucl}$$

Born Openheimer and PESs



- Separation of nuclear and electronic motion due to differences in mass.
- Electrons have high kinetic energies, so move very fast compared to nuclei.
  - expect nuclei to feel time-averaged force exerted by swarm of electrons.
- Electrons quantum mechanical (wave-like), described by Schrödinger Eq.
  - Split into two parts. Solve the electron-motion problem first, assuming nuclei are stationary at different geometries R, yielding potential field V(R) that the nuclei are moving in.
  - Energy eigenvalues correspond to different electronic states.
  - Potential energy function corresponding to each electronic state of the system (PES).
- Having determined V(R), quantify motion of nuclei - forces acting on the atoms, represented by the nuclei are derived from the PES.

Hartree-Fock (HF) theory

- Fundamental to much of electronic structure theory.
- Basis of molecular orbital (MO) theory, which posits that each electron's motion can be described by a single-particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons.
- Only for the hydrogen atom (or other one-electron systems, like He+) are orbitals exact eigenfunctions of the full electronic Hamiltonian.
- **Generally missing electron correlations.**
- As long as we are content to consider molecules near their equilibrium geometry, Hartree-Fock theory often provides a good starting point for more elaborate theoretical methods which are better approximations to the Schrödinger equation.
- Many types of calculations begin with a Hartree–Fock calculation and subsequently correct for electron-electron repulsion.
- Scales nominally as N^4 – N number of electrons.

Basis set expansion: the concept

The electronic Schrödinger equation, for fixed positions of the atomic nuclei $\underline{R}$, and ignoring complexities due to electron spin, is

$$H\Psi(\underline{r}) = V(\underline{R})\,\Psi(\underline{r})$$

where H is a linear operator that includes partial derivatives w.r.t to the electron positions $\underline{r}$.

- **Basis set expansion:** approximate $\Psi(\underline{r}) = \Sigma\, c_n\Phi_n(\underline{r})$, then multiply both sides with any desired test function $\chi_m(\underline{r})$ and integrate to convert the partial differential equation into an algebraic equation in the unknowns $\{c_n\}$ and $V(\underline{R})$:

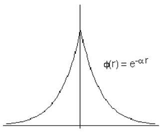
$$\int \chi_m H\Psi d\underline{r} = \sum c_n \int \chi_m H\Phi_n \, d\underline{r} = V(\underline{R}) \sum c_n \int \chi_m \Phi_n d\underline{r}$$

i.e. Generalized eigenvalue problem $A*c = V(\underline{R})\, B*c$

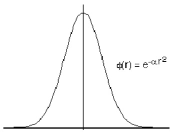
We want to know the lowest eigenvalue, that is the physically important one that corresponds to $V(\underline{R})$.

Basis set expansion: the concept

- The use of basis sets essentially turns a PDE into a set of coupled algebraic equations that can be efficiently solved computationally (**cf finite element methods in fluid flow – except here basis sets mimic molecular orbitals**).
- Single-particle states (molecular orbitals, MOs) expressed as linear combinations of basis functions giving approximate but not exact resolution.

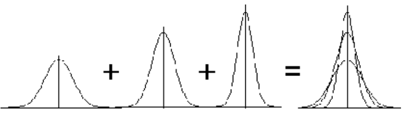


Slater-type 1s orbital



Gaussian-type 1s orbital

STO-3G 1s Basis function



- Examples:
  - Slater-type orbitals (STOs), which are solutions to the Schrödinger equation of hydrogen-like atoms.
  - Gaussian functions – **less physically realistic computationally quicker.** Often use sums to approximate STOs.
- The higher the number of basis functions in a basis set, the more flexibly the electron positions can be described (e.g. anharmonicity, polarisation) - **at of course increasing cost.**

Configuration Interaction

- **Configuration interaction (CI)** allows for a complete description of the correlation energy, within the limits of the BO approximation and size of basis set.
- Expands wavefunction into a linear combination of configuration state functions, i.e., electronic states where a number of electrons are promoted from ground-state orbital to a virtual orbital.
- If a single electron is promoted - so-called single-excitation determinants, changes of two electrons describe double excitations, and so on.
- Coefficients in CI linear combination then optimized, such that additional flexibility in describing wavefunction allows for electron correlation.
- If all possible excitations included, obtain the full-CI result (FCI).
  - computationally prohibitively expensive for all but smallest of molecules and basis sets.
- CI expansion typically truncated e.g., **CISD includes only single and double excitations.**

Specialized approximations

- Need many test functions $\{\chi_m\}$ to get enough equations to determine the unknowns. If practical we would like to use a very large basis set to accurately approximate Ψ.
- Clever choices of $\{\Phi_n\}$ and $\{\chi_m\}$, or adding constraints on the c's, can make the approximations more accurate, the integrals easier to compute, and the equations easier to solve numerically.

Some approaches:

- $\chi_n(\underline{r}) = \Phi_n(\underline{r}) = \Pi\, \phi_{n,k}(x_k,y_k,z_k)$ $\phi = \Sigma$ Polynomials*Gaussians

"CI", gives guaranteed upper bound on true value of V($\underline{R}$).

- $\Phi_n(\underline{r}) = \{\Pi\, \Pi\, (1 - \exp(-\,||\underline{r}_n - \underline{r}_m||))\ \} * \Pi\ \phi_k(x_k,y_k,z_k)$

called "F12" forces the physically correct behaviour when electrons m and n are close to each other (e.g. zero probability they will be exactly on top of each other).

Coupled Cluster Approach is a little different

- Instead of explicitly constructing linear combinations of the basis functions in the process of finding the eigenvalues, instead do a **similarity transform of the Hamiltonian** operator *H*:

  $H \rightarrow \ \exp(-T(\underline{c}))\, H \exp(+T(\underline{c})) = H'(\underline{c})$
- The Coupled Cluster equations are different, too:

$$\int \chi_m H'(\underline{c}) \Phi_0 d\underline{r} = V(\underline{R}) \int \chi_m \Phi_0 d\underline{r}$$

- Because the adjustable coefficients $\underline{c}$ are inside the exponentials, this is a large system of nonlinear algebraic equations.
- Coupled-cluster approach does not guarantee an upper bound on V(R), but it does guarantee "size-extensivity", i.e. doubling the system doubles its energy as it should.
- Empirically, Coupled Cluster approximation using F12 basis for the zero-order guess Φ_0(r) gives high-accuracy V($\underline{R}$) values.
- **CCSD(T)-F12 is a high-accuracy method for computing V($\underline{R}$) but expensive, CPU ~ N^7.**

Other methods

- **Møller–Plesset perturbation theory**
  - Missing electron correlation in the HF wavefunction is added as a series of perturbations to this wavefunction.
  - Uses Rayleigh–Schrödinger perturbation theory (RS-PT), usually to second (MP2), third (MP3) or fourth (MP4) order.
- CC and MP methods can be applied simultaneously;
  - CCSD(T), calculating coupled cluster configurations with single and double excitations, with perturbative inclusion of triples.
- Still need a Hartree-Fock wavefunction to provide a valid starting point.
- **Complete active space perturbation theory** (CASPTn) is a multireference electron correlation method for computational investigation of molecular systems.

Available Software

- Quantum chemists have developed efficient software for many of these approximate ways of computing $V(\underline{R})$, and tested most of them so you can get an idea of their accuracy.
- Software is not perfect, but more packaged and easy to use than most CFD software.
- If you ask for the same basis set and level of approximation with the same geometry $\underline{R}$ in different software packages, you will usually get computed $V(\underline{R})$ values which agree to many significant figures, i.e. the error is in the approximation & basis set, not in the implementation inside each software package.
- Some of the famous commercial software packages are **GAUSSIAN** and **MOLPRO** + many other commercial and free quantum chemistry packages.
- **All of them can compute $V(\underline{R})$ to various degrees of accuracy with some differences in required CPU time and RAM.**
  - **Know what you are using – rather than treating as a black box!**

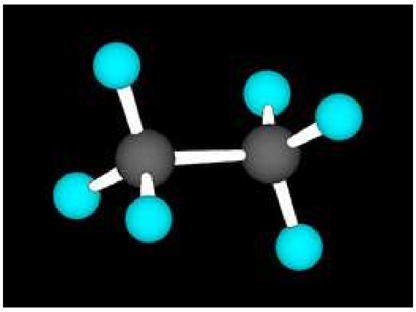
Suppose we have a quantum chemistry package, and so can compute V(<u>R</u>). How do we compute the molecular energy levels $\{E_i\}$ needed to compute the thermochemistry/microcanonical rate coefficients?

Nuclear motion

- The absolute energy at a certain nuclear arrangement does not characterize a real molecule.
- Molecules are semi-rigid structures oscillating around some equilibrium geometry, rotating, and flying in space.
- Amplitude of vibrations, speed of rotations, i.e., the internal energy corresponding to the given quantum state, as well as the velocity of flight is generally different for each molecule in the ensemble.
- Macroscopically observable properties are **averages over ensembles of molecules in thermal equilibrium**, characterized by T.
  - The **population of various quantum states follows the Boltzmann distribution**.
- Hence, when thermodynamic properties are calculated, the effects of intra- and intermolecular nuclear motion, the thermal contributions need also be taken into account:
  - solve the Schrödinger equation for nuclear motion.
  - determined by shape of PES near the equilibrium molecular structure.

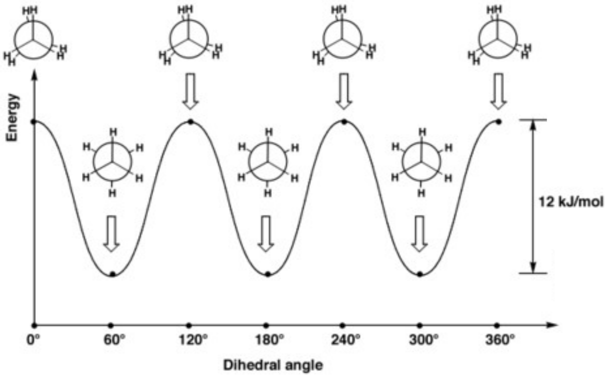
Computing Partition Functions: RRHO approximation

- We assume the molecule translates without interacting with the other molecules in the gas, as a particle of mass *m*.
- For rigid molecules (i.e. all vibrations are “small-amplitude”, no floppy degrees of freedom) it is a good approximation to assume that **vibrational motions of atoms are tiny compared to bond lengths**. Then we can approximate molecule as rotating as a rigid body with the moments of inertia defined by the equilibrium geometry $R_{\text{equilibrium}}$.
- Because we are assuming the vibrational motions are tiny, it is reasonable to keep only the lowest order nonzero terms in a Taylor expansion of V(R) about $R_{\text{equilibrium}}$.
- These terms are quadratic. Changing coordinates to normal modes removes the cross terms leaving a set of **harmonic oscillators**.
- **Beware: RRHO is often used when it is not valid, e.g. when the molecule has a floppy vibration such as a torsion (internal rotor).**
  - the torsional motion, a hindered internal rotation has a lower barrier than the second (or sometimes even the first) harmonic vibrational energy level, causing the obvious failure of the approximation.



Internal rotation; hindered internal rotation and torsional vibrations; e.g. ethane

- Energy levels in torsional wells and effect of temperature on freedom of motion.
- Potential energy of the geometry depends on the angle of rotation



Quantized energies & partition functions: vibrations

Partition function characterizes statistical properties of system at thermochemical equilibrium. For single molecule, **partition function defined as sum of all available quantum states.**

$$Q = \sum_i g_i \exp\left(\frac{-\epsilon_i}{kT}\right)$$

g_j is the degeneracy factor

We usually approximate each of the vibrations in a molecule as a harmonic oscillator. (This is not always an accurate approximation, but it simplifies the maths!) The quantized energy of a harmonic oscillator with characteristic frequency ν are:

$$E_{vib,n} = \left(n + \frac{1}{2}\right)h\nu \qquad n = 0, 1, \ldots ,$$

Recommended to choose the zero of energy to be the lowest state (all the vibrations have $n_i=0$), and handle the zero-point-energy (ZPE) = $\frac{1}{2} h \Sigma \nu_i$ separately. Then $E_{vib} = h \Sigma n_i \nu_i$ and

$$q_{vib} = \Pi \left(1 - \exp(-h\nu_i/k_B T)\right)^{-1}$$

Where do we get the vibrational frequencies $\{\nu_i\}$?

- For some small molecules: experiment (from IR spectroscopy).
- More commonly, only a few or zero of the vibrational frequencies have been measured. Need to calculate:
  - Functional groups have some characteristic frequencies, but not all frequencies can be predicted.
  - For stable closed-shell organic molecules, there are pretty good force fields which can be used.
  - For small molecules, you can use high-level quantum chemistry, e.g. CCSD. Very accurate & very CPU-intensive…
  - **Most common approach for larger molecules in combustion chemistry is to do a DFT calculation.** Quantum chemistry programs are set up to do this calculation automatically for you, and DFT is not CPU-intensive.

Density Functional Theory (DFT)

- Different approach to ***ab initio*** methods – using electron density functional and not directly solving for wave function.
- Need to find correct electron density, from which one can get the electronic energy at the selected molecular geometry. General mathematical form of energy functional not known.
- Kohn & Sham showed a good way to proceed, based on varying orbitals $\psi(x,y,z)$, one for each electron. $\rho = \Sigma\ |\psi_n(x,y,z)|^2$
- **Easier to expand functions of 3 variables** in a basis set. Cf. handling functions of large no. of variables all coupled (as in Schrödinger Eq.)!
- 1980's: first accurate approximate functionals $E[\rho]$, actually $E[\{\psi\}]$, were discovered. Since then many more. Names like "B3LYP", "PBE" and "M06-2X". Convenient, fairly accurate way to compute $E=V(R)$ for not much CPU. Can reach ~1 kcal mol^{-1} accuracy.
- Functional should match that obtained for selected systems from ab initio calculations considered to be exact (Similar to fitting model to exp. Data).

DFT for geometry ($R_{\text{equilibrium}}$)

- Programs such as GAUSSIAN, Q-Chem, MOLPRO compute $E[\rho]=V(\underline{R})$ and its derivatives w.r.t. $\underline{R}$.
- With the gradient $\partial V/\partial \underline{R}$ it is relatively easy to move downhill on the PES to compute the minimum energy geometry $R_{\text{equilibrium}}$.
- Usually minima are found using the BFGS optimization algorithm, based on an initial guess geometry provided by the user.
- Beware that there are multiple local minima on V(R)! You need to provide a guess geometry starting near the valley that corresponds to the species you are interested in.
- Often your "valley" is connected to several other local minima by very low ridges. Instead of calling these distinct "species" we call the set of minima the "conformers" of species A.
- You definitely want to find the lowest-energy conformer, that is $R_{\text{equilibrium}}$, and it is helpful to find the other conformers if you can.

DFT for Vibrational Frequencies (ν)

To compute the Vibrational Frequencies:

- First, Taylor expansion of V(R) about R_{equil} (where $\partial V/\partial \underline{R} = 0$)

$$V(R) = V(R_{equil}) + \tfrac{1}{2} \Sigma \Sigma \, (\partial^2 V/\partial R_i \, \partial R_j) \, (R_i - R_{equil,i})(R_j - R_{equil,j}) + \ldots$$

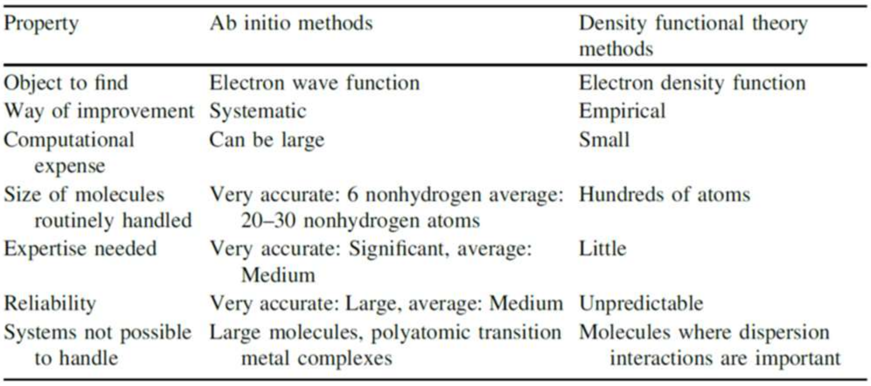
- We call $(\partial^2 V/\partial \underline{R} \, \partial \underline{R})$ the force constant matrix **F.** Many quantum chemistry packages compute this analytically for a wide choice of density functionals.
- The eigenvalues of the mass-weighted force constant matrix

$$M^{-1/2} \, F \, M^{-1/2}$$

are the squares of the normal mode frequencies.

- This whole calculation is done for you automatically by GAUSSIAN and other quantum chemistry packages. All you need to do is supply a guess at the equilibrium geometry, specify which functional to use, and which basis set.

Comparison between *ab-initio* and DFT



Property	Ab initio methods	Density functional theory methods
Object to find	Electron wave function	Electron density function
Way of improvement	Systematic	Empirical
Computational expense	Can be large	Small
Size of molecules routinely handled	Very accurate: 6 nonhydrogen average: 20–30 nonhydrogen atoms	Hundreds of atoms
Expertise needed	Very accurate: Significant, average: Medium	Little
Reliability	Very accurate: Large, average: Medium	Unpredictable
Systems not possible to handle	Large molecules, polyatomic transition metal complexes	Molecules where dispersion interactions are important

Total partition function of a system versus a single molecule

For N identical non-interacting molecules in a volume *V* (e.g. an ideal gas):

$$Q = \frac{(q_{vib}\ qtrans\ qrot\ qelec)^{N}}{N!}$$

$\ln Q \sim N\ ln(q_{vib}\ qtrans\ qrot\ qelec)\ -N \ln(\frac{N}{e})$ last term is Stirling’s approximation

$$= N \ln\left[\left(e q_{vib}\ qrot\ qelec\right)\left(\frac{q_{trans}}{V}\right)\left(\frac{V}{N}\right)\right]$$

Note *V/N* = *$k_B T/P$* for an ideal gas. If you are computing normal standard-state thermo, use P= 1 atm . If you are computing properties for an arbitrary gas mixture, use P = the partial pressure of the species.

Comments about system Q versus molecule q

The quantity (q_{trans} /V) appears often, sometimes people call that “q_{trans}” and define

q = (e q_{vib} q_{rot} q_{elec})(q_{trans} /V)

So they can just write ln Q = N ln {q k_BT/P }

Note for most stable molecules there is only one accessible electronic state, so q_{elec} ~ 1. For most radicals q_{elec} ~2. For molecules with low-lying non-degenerate electronic states one should evaluate the partition function q_{elec} exactly.

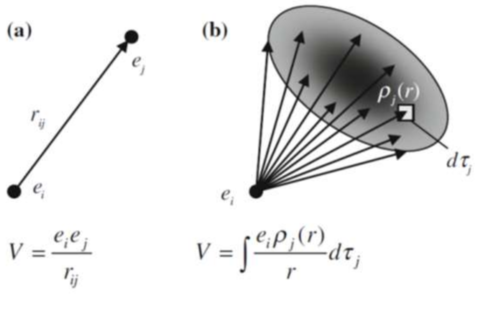
If the molecules are interacting weakly (e.g. non-ideal gas), one can correct the expression above for Q using the Equation of State. For liquids q_{rot} and q_{trans} are significantly different, but usually q_{vib} stays about the same as in gas phase.

You can calculate “ideal gas phase” S without knowing anything about the condensed phase behavior:

$$S = -k_B \ln Q + \frac{1}{T}\frac{\partial(\ln Q)}{\partial\left(1/_{k_B}\, T\right)}$$

Assumptions - electron correlation

- Single MO methods (e.g. HF) ignore correlations between electrons (b not a in diagram below).
- In Complete Active Space (CAS) methods, the coefficients and the atomic orbitals in the MOs and the coefficients in the CI expansion are simultaneously optimized to overcome this.
- Coupled cluster methods essentially takes the basic HF MO method and construct multi-electron wave-functions using the exponential cluster operator to account for electron correlation.

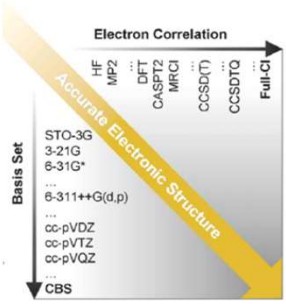


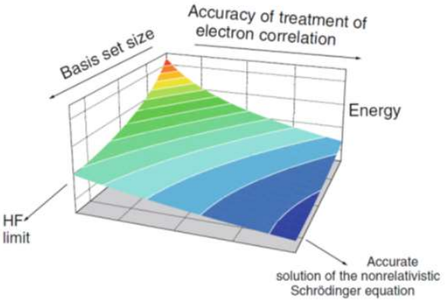
Beware Internal Rotors & Floppy Motions!

- The normal vibrational partition function formulas are for harmonic oscillators.
- Some types of vibrational motions (torsions/internal rotations, umbrella vibrations, pseudo-rotations) are NOT harmonic.
  - E.g. rotations about C-C bonds
  - Puckering of 5-membered rings like cyclopentane.
- Many of the entropy values in standard tables are derived using ***approximate formulas*** to account for internal rotation. Often not clear what formulas used to estimate other floppy motions. They can be significantly in error!
- If you care about the numbers, **read the footnotes in the tables** to see how the numbers were computed. Just because it is in a table does not mean it is **Truth**.
- **Always look at the uncertainties/error bars!**
- **Check convergence of calculations with respect to basis sets and assumptions.**

Approximation	Main feature not covered	Occurrence of failure
Born-Oppenheimer separation of electronic and nuclear motion	Nonadiabatic effects	Mostly away from equilibrium geometries
Nonrelativistic electronic Schrödinger equation	Inner shell relativistic effects; spin-orbit coupling	Mostly in compounds of atoms with large atomic number
One-electron (mean field) approximation	Dynamical and chemical electron correlation	Everywhere
Expansion of molecular orbitals in terms of atomic orbital basis sets	Accuracy because of incompleteness of basis set	Everywhere

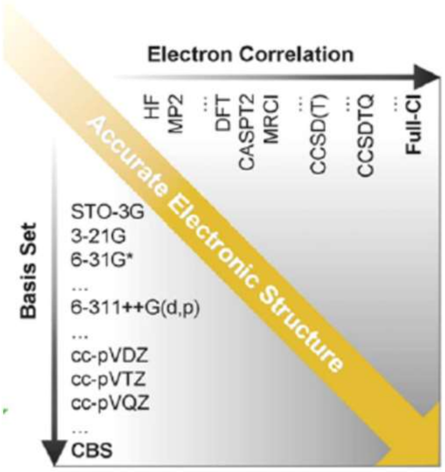
The combination of the method and the basis set used for MOs is referred to as “level of theory”.





Approaches to accurate electronic structure calculations 1.

- A basis set is composed of atomic orbitals, yielding linear combination of atomic orbitals approach (LCAO). The CBS limit is an extrapolated estimate of a result obtained using an infinitely large (complete) basis set
- Electron correlation is the interaction between electrons. Correlation energy is a measure of how much the movement of one electron is influenced by the presence of all other electrons.
- The Hartree Fock method has minimal electron correlation. **Full configuration interaction** (or **full CI**) is a linear variational approach which provides numerically exact solutions (within the infinitely flexible complete basis set) to the electronic Schroedinger equation.

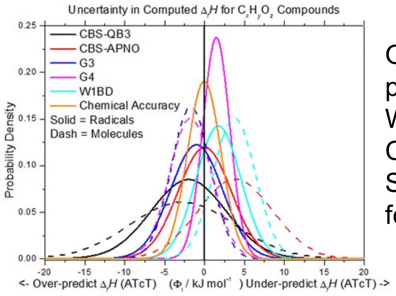


Zador et al Prog Energy Comb Sci 2011, 37, 371

Composite Methods

- Combine methods with high level of theory and small basis sets with methods that employ lower levels of theory with larger basis sets.
- Examples are G2, G3, CBS-QB3, CBS-APNO.
- Somers and Simmie (2015) benchmarked composite methods against the Active Thermochemical Tables for the formation enthalpies of radicals with molecular formula $C_xH_yO_z$

If errors are random – average them.
If bias
- Methods like bond additivity correction



Order of accuracies and precisions: G3 > G4 > W1BD > CBS-APNO > CBS-QB3.
Systematic biases found.

- Later we will look at the impact of uncertainties which result from choice of different methods for computing the PES in terms of the calculation of **phenomenological rate coefficients.**

Importance of thermochemistry

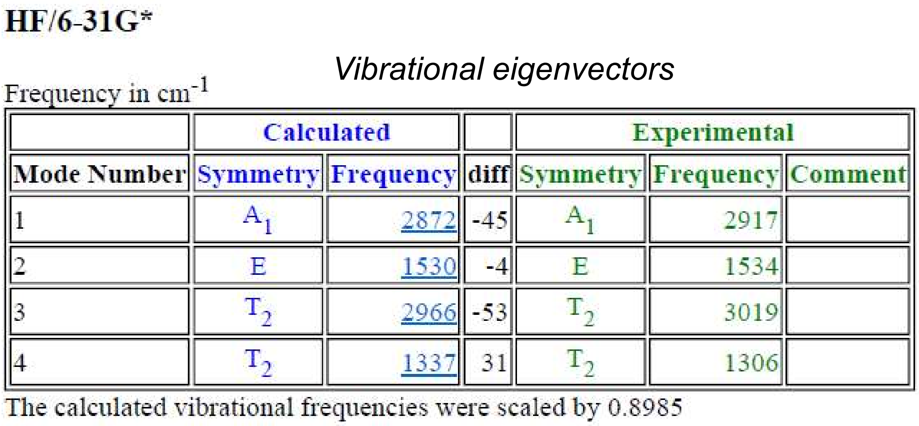
- We will see later that may target outputs from combustion systems depend on accurate thermochemistry e.g:
  - Calculation of reverse rates.
  - Low temperature oxidation routes for hydrocarbon fuels involving RO_2 and QOOH species.
  - The prediction of heat release rates.
  - Prediction of adiabatic flame temperatures.
- Large molecules are challenging.
- Goldsmith et al. (2012) presented a method and data for 200 molecular species of interest in combustion chemistry.
- **A bond additivity correction (BAC)** was developed to account for shortcomings in the treatment of multiple bonds and to remove systematic errors that appeared for different bond types compared to Active Tables (see later): C—H, C—C, C═C, C≡C, O—H, C—O, C═O, and O—O.
  - **2σ uncertainties of 0.58 kcal/mol**
- A high level of theory can produce <0.2 kcal/mol uncertainty but at large CPU cost.

Computational Chemistry Comparison and Benchmark DataBase - http://cccbdb.nist.gov/

- The CCCBDB contains links to experimental and computational thermochemical data for a selected set of 1272 **gas-phase** atoms and molecules. Tools for comparing experimental and computational ideal-gas thermo-chemical properties.
- **Species in the CCCBDB**
  - Mostly atoms with atomic number less than 18 (Argon). A few have Se or Br.
  - Six or fewer heavy atoms and twenty or fewer total atoms. *Exception:* Versions 8 and higher have a few substituted benzenes with more than six heavy atoms. Versions 12 and higher have bromine-containing molecules.
- Specific experimental properties 1. Atomization energies 2. Vibrational frequencies 3. Bond lengths 4. Bond angles 5. Rotational constants 6. Experimental barriers to internal rotation

Methane

Vibrational eigenvectors



HF/6-31G*

Frequency in cm^{-1}

	Calculated			Experimental		
Mode Number	Symmetry	Frequency	diff	Symmetry	Frequency	Comment
1	A_1	2872	-45	A_1	2917	
2	E	1530	-4	E	1534	
3	T_2	2966	-53	T_2	3019	
4	T_2	1337	31	T_2	1306	

The calculated vibrational frequencies were scaled by 0.8985

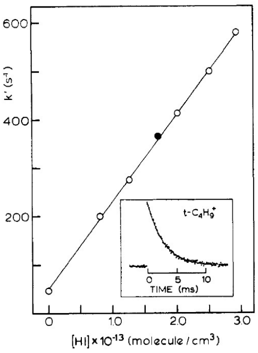
Enthalpies of formation of radicals

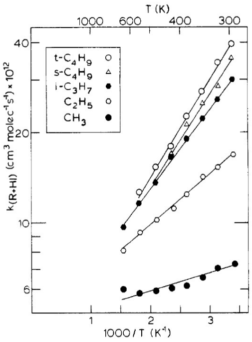
- Enthalpies of formation of stable compounds, such as hydrocarbons, are determined from measurements of enthalpies of combustion, using Hess's Law.
  - The enthalpy change accompanying a chemical change is independent of the route by which the chemical change occurs.
- This approach is not feasible for radicals. An IUPAC evaluation of thermodynamic data for radicals can be found in *Ruscic et al. J Phys Chem Ref Data, 2005, 34, 573.*
- Example: CH_3. Determined by:
  - Kinetics, e.g. J Am Chem Soc, 1990, 112, 1347
  - Photoionization spectroscopy, e.g. J Chem Phys, 1997, 107, 9852
  - Electronic structure calculations, e.g. J Chem Phys, 2001, 114, 6014.
- Recommended value by IUPAC: $\Delta_f H^\ominus(298.15\ K) = 146.7 \pm 0.3\ kJ\ mol^{-1}$.

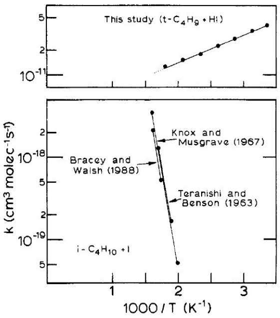
Kinetics and thermodynamics of alkyl radicals

Seetula et al. J Am Chem Soc, 1990, 112, 1347

- Measured *k*(*T*) for R + HI, using laser flash photolysis / photoionization mass spectrometry, and combined with existing data for reverse reaction (I + RH) to determine equilibrium constant. Enthalpy of reaction determined by second and third law methods.







Photoionization spectrum of CH_3

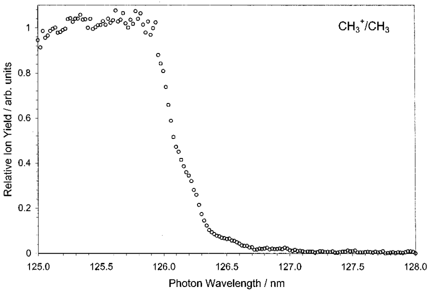
Litorja and Ruscic, J Chem Phys, 1997, 107, 9852

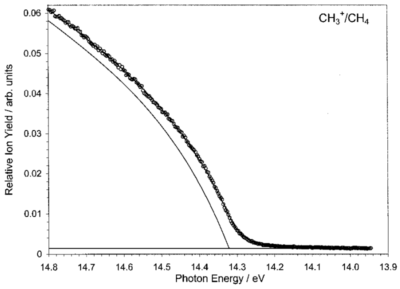
- Measure the photionization threshold for CH_3 and the appearance potential of CH_{3+} from CH_4 photexcitation. Obtain the dissociation energy of CH_3-H:

$CH_3 \rightarrow CH_3^+ + e$ R1

$CH_4 \rightarrow CH_3^+ + H + e$ R2

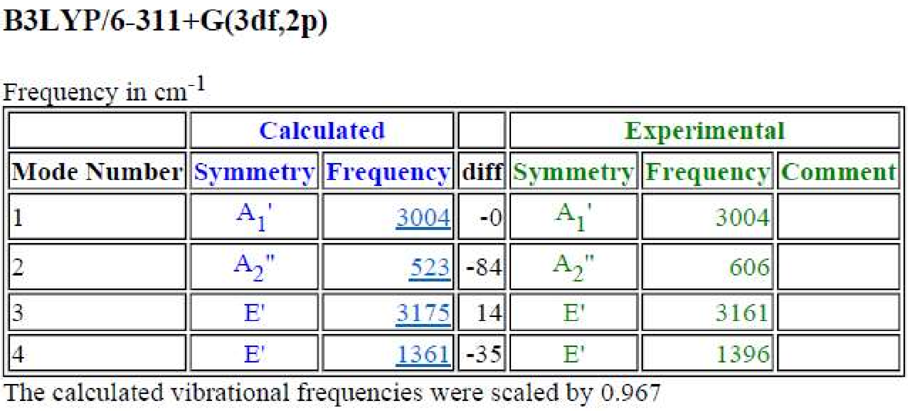
R2-R1: $CH_4 \rightarrow CH_3 + H$





Computed data (Quantum Chemistry)

- Geometries, vibrational frequencies, entropies, energies, means for comparing data CH_3



B3LYP/6-311+G(3df,2p)

Frequency in cm^{-1}

	Calculated			Experimental		
Mode Number	**Symmetry**	**Frequency**	**diff**	**Symmetry**	**Frequency**	**Comment**
1	A_1'	3004	-0	A_1'	3004	
2	A_2''	523	-84	A_2''	606	
3	E'	3175	14	E'	3161	
4	E'	1361	-35	E'	1396	

The calculated vibrational frequencies were scaled by 0.967

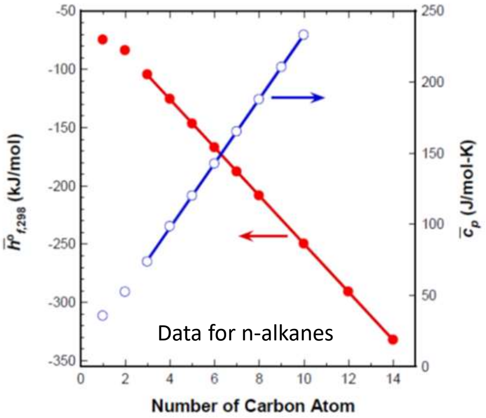
Active Tables (more later on this topic)

- New paradigm to develop accurate, reliable, and internally consistent thermochemical values 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 (**see earlier**) to reduce uncertainties in data (Burcat & Ruscic, 2005).
- Network of Computed Reaction Enthalpies to Atom-Based thermochemistry **(NEAT)** *Csaszar and Furtenbacher (2010)*
- **Results in highly correlated parameters – be careful of the effects of neglecting such correlations!**

Species Name	**Formula**	**$\Delta_f H°(0\ K)$**	**$\Delta_f H°(298.15\ K)$**	**Uncertainty**	**Units**	**Relative Molecular Mass**	**ATcT ID**
Dihydrogen	H2 (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	C7H16 (l)	-201.46	-223.91	± 0.74	kJ/mol	100.2019 ± 0.0057	142-82-5*500
Octane	C8H18 (l)	-226.61	-249.73	± 0.79	kJ/mol	114.2285 ± 0.0065	111-65-9*500
2,2,4-Trimethylpentane	(CH3)2CHCH2C(CH3)3 (l)	-224.4	-258.9	± 1.5	kJ/mol	114.2285 ± 0.0065	540-84-1*500

Group Additivity

- Experimentally, for alkanes it is observed that *H*, *S*, and C_p all vary linearly with the number of Carbons.
- One can assign a value to the increments caused by inserting one more CH_2 group into the alkane chain.
- This approach works for many different chemical functional groups: adding the group to the molecule adds a set amount to *H, S,* C_p called a GAV.
- For *S*, need to add a symmetry correction to the sum of the GAV.



S.W. Benson constructed tables of these Group Addivity Values (GAV). Several researchers, especially Bozzelli and Green, have added to these tables using quantum chemistry to fill in gaps in experimental data.

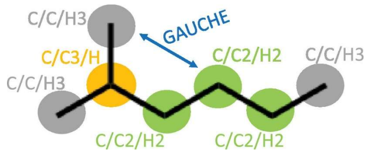
Programs to estimate thermo with Group Additivity

- http://webbook.nist.gov/chemistry/grp-add/
- THERGAS (Nancy group, Blurock)
- THERM (Bozzelli)
- RMG (Green group, MIT)
- Several others...

➢ All of these programs are based on Benson's methods described in his textbook "Thermochemical Kinetics" and in several papers by Benson. See also several improvements to Benson's method by Bozzelli.

➢ Group additivity is related to the "functional group" concept of organic chemistry, and to "Linear Structure-Activity Relationships" (LSAR).

Basic concepts



- $\phi_i(\psi) = \sum_j^m a_{i,j}\psi_j$
- where $a_{i,j}$ is the number of groups j in species i and ($\psi_j = \Delta h_{f,j}$(298 K), s^0_j(298 K), $c_{p,j}$ (T)).
- For the standard entropy, mixing effects due to symmetry and optical isomerism need to be taken into account additionally, so that it can be computed from the intrinsic standard entropy as:
- $s^0_j(298\ \mathrm{K}) = s^0_{\mathrm{int},j}(298\ \mathrm{K}) - R \ln(\sigma_i / n_{\mathrm{OI},i})$
- where σ_i is the symmetry number and $n_{\mathrm{OI},i}$ the number of optical isomers of the species.
- Optical isomer contribution is accounted for by means of adding one "OI" group with an entropy group value of $R\ln(2)$ for every chiral centre in the species.
- OI groups also added for OO and OOH groups in peroxy and hydroperoxide species, which are commonly regarded as pseudochiral centres.

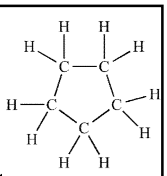
(Vom Lehn, 2020)

Treatment of Radicals

- Typically the **hydrogen bond increment (HBI)** approach used, as implemented in THERM.
- Radical thermochemistry based on thermochemistry of **corresponding parent molecule** by adding a so-called **bond dissociation (BD) group**, that accounts for difference in thermochemistry between radical and its parent due to broken hydrogen bond.
- $\Delta h_{f,j,}^{radical}(298\ \mathrm{K})$

  $= \Delta h_{f,j,}^{parent}(298\ \mathrm{K}) + \Delta h_{f,j,}^{BD}(298\ \mathrm{K}) - \Delta h_{f,j,}^{H}(298\ \mathrm{K})$
- $\Delta h_{f,j,}^{H}(298\ \mathrm{K}) = 217.998\ \mathrm{kJmol^{-1}}$, enthalpy of formation of the abstracted hydrogen atom.
- Optical isomers may be different for a radical and its parent molecule.

Problems with Group Additivity



- While the group additivity method is intuitively simple, it has its drawbacks stemming from the need to consider **higher-order correction terms** for a large number of molecules.
- Take e.g. cyclopentane, the addition of group contributions yields H^o = –103 kJ/mol, yet the experimental value is –76 kJ/mol. Difference is caused by ring strain, not accounted for in the group value of C–(C2,H2) obtained from unstrained, straight-chain alkane molecules.
- Cyclics are biggest problem for group additivity, but some other species also do not work well, e.g. halogenated compounds, and some highly branched compounds.
- Very small molecules are often unique (e.g. CO, OH), so group additivity does not help with those.
- Species with different resonance forms can also cause problems, e.g. propargyl CH2CCH can be written with a triple bond or two double bonds, not clear which should be used when determining groups.
- ***Many methods have been developed using straight chain alkanes but future fuels might not look like this….***

Summary

- Species concentrations in the Hot Exhaust Zone of a combustor are nearly in equilibrium due to the high temperature & high radical concentrations.
  - Whatever system you are studying, it is good to know what the equilibrium is, that is where the kinetics are heading!
- Can compute equilibrium composition using EQUIL and similar programs, but need **thermochemical parameters** for each species.
- Thermochemical parameters also allow us to **infer reverse rate coefficients** from forward rate coefficients.
- These parameters are obtained in a variety of ways, many of them not quite accurate enough for quantitative modeling.
  - Most convenient are **group contribution methods** - very fast.
- **High level quantum chemistry** methods and **Active Thermochemical Tables** can achieve excellent accuracy, **BUT** so far mostly for smaller molecules.
  - Still large uncertainties in important species for fuel combustion affecting ability to model heat release etc. (see later).

Section 2a

Measurement of rate coefficients for elementary reactions

With thanks to Prof Mike Pilling for many of these slides

What does a measurement system look like?

- Ideally, isolate the individual reaction and study it at the appropriate combustion conditions.
  - i.e. no sensitivity to other possible secondary reactions occurring in the system.
  - Experiment can be conducted at *T*, *P* required for application of rate constant.
- Not always possible:
  - May have to model the system to extract rate coefficients of interest.
    - **Rate then subject to uncertainties in the model.**
  - May need to extrapolate to appropriate *T, P*. Ideally achieve this with the help of theory (**see next section**).

Techniques covered

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

Pulsed laser photolysis

Principles (Pilling and Seakins, 1996)

- Reactant and precursor species are premixed and flow into **photolysis cell**.
- **Pulse of light** used to produce a transient species e.g. a radical or excited state atom using photolysis.
  - E.g. H_2O_2 or t-butyl hydroperoxide photolysed to produce OH radicals.
- The concentration of this species is then monitored as a function of time.
- If photolysis beam of uniform intensity and reactant well mixed – uniform reactant concentration obtained.
- Pulsed laser photolysis allows to study short reaction times.
- Key is to **minimise secondary reactions** e.g. transient with precursor.
  - Measurement distant from reactor walls.
  - Low precursor concentrations – use of high pulse energy lasers e.g. excimer laser.

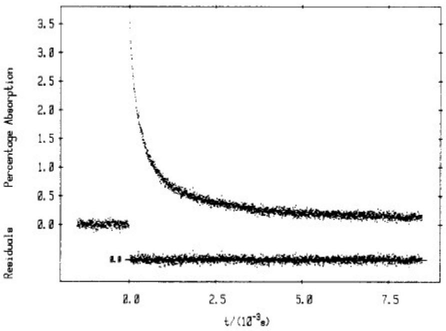
Detection methods

1. Absorption spectroscopy

  - Light of a frequency corresponding to a vibrational or electronic absorption of radical is passed through cell and detected by suitable detector.
  - Decay of absorption signal represents change in concentration of transient via Beer-Lambert Law.
  - $I = I_0 \exp(-\varepsilon c l)$, ε absorption coefficient, *c* concentration, *l* path length.
  - Example: voltage change ΔV from photomultiplier ∝ to change in light intensity and hence related to *c*.
    - if path length, ε known.
- Differences in light intensities difficult to detect with accuracy.

C_3H_5 + C_3H_5 :Absorption spectroscopy

- Reaction is second order in C_3H_5
- Need to know absolute concentration of radical – absorption spectroscopy provides a good route to this (see Macpherson, 1985 for discussion for CH_3).
- $I/I_0 = \exp(-s[C_3H_5]L)$ where I_0 is the incident and I the transmitted light intensity, s is the absorption cross section and L is the path length.
- Similar method applied to CH_3 + CH_3.

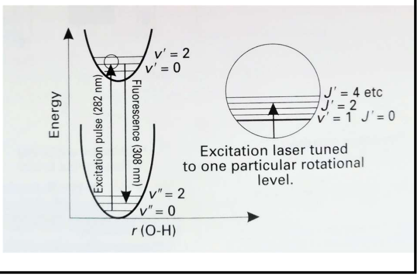


Detection methods

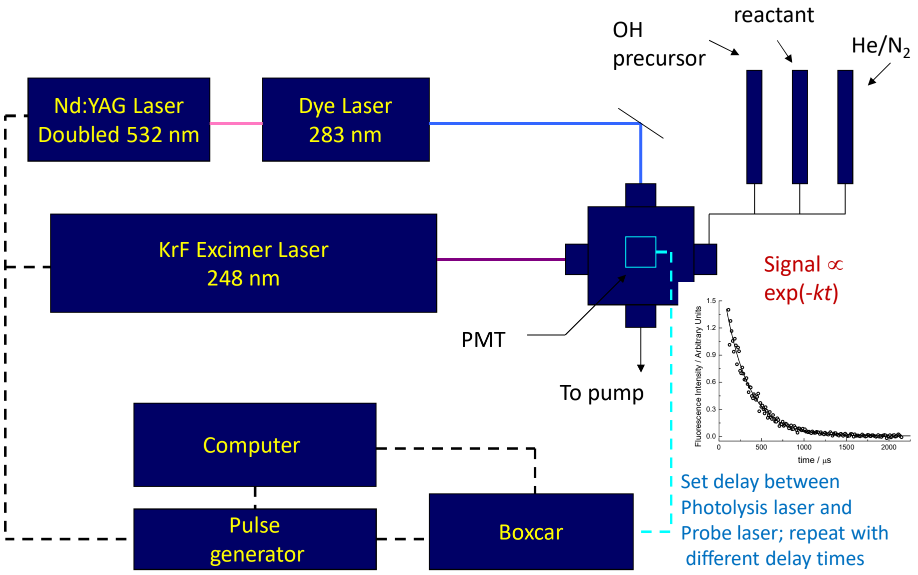
2. Laser Induced Fluorescence (LIF)

- Signal detected relative to zero background.
- Increases linearly with excitation intensity.
- Can detect much lower concentrations ~10^8 molecules.
- Dye laser used to excite radical to upper electronic state (matched to rovibronic transition).

- Relaxation leads to fluorescence.
- Provides relative measure of concentration.
- Experiment designed to minimise scattered light.



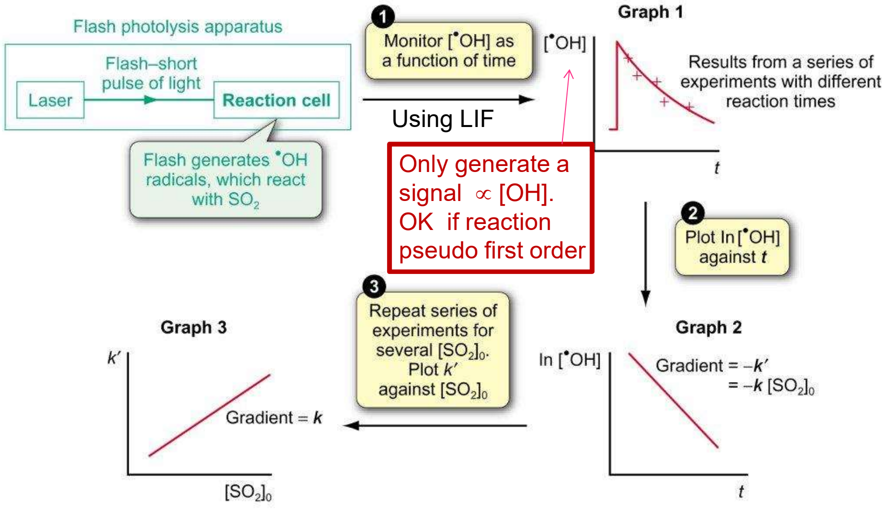
Laser flash photolysis (LFP) / laser induced fluorescence (LIF) for the study of OH + reactant



Signal ∝ exp(-kt)

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

Procedure for determining rate coefficients for pseudo first order reactions using LFP for OH + SO_2



① Monitor [$^{\bullet}$OH] as a function of time

Using LIF

Only generate a signal ∝ [OH]. OK if reaction pseudo first order

Results from a series of experiments with different reaction times

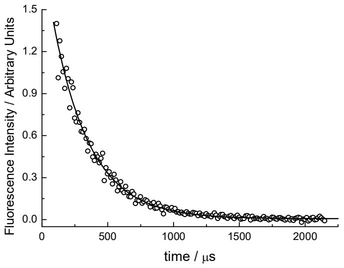
② Plot ln [$^{\bullet}$OH] against t

Gradient = $-k'$ = $-k$ [SO_2]$_0$

③ Repeat series of experiments for several [SO_2]$_0$. Plot k' against [SO_2]$_0$

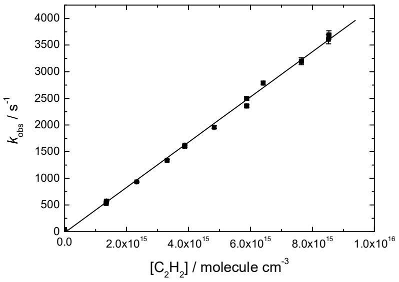
Gradient = k

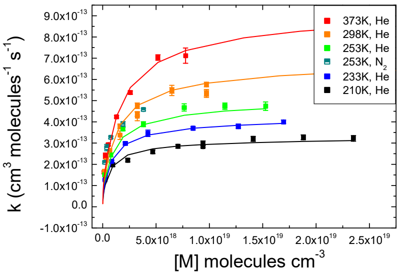
OH + C_2H_2 + M → C_2H_2OH + M



- Pressure dependent (association) reaction.
- Study as a function of temperature and pressure.
- Results fitted to Troe expression

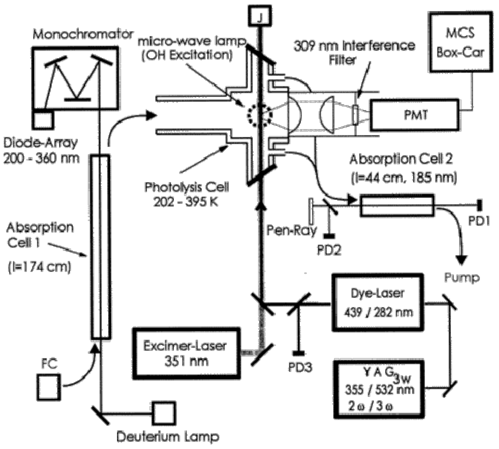
(McKee, 2007)

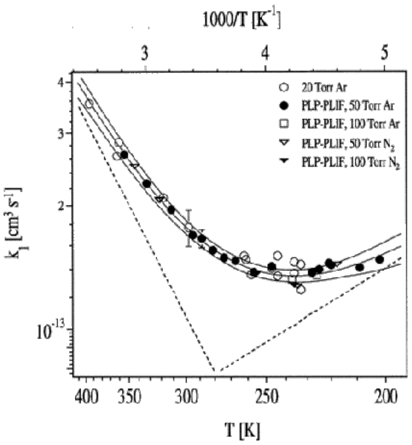




OH + acetone, (Wollenhaupt, 2000)

Laser flash photolysis, resonance fluorescence/laser induced fluorescence to measure [OH] (relative). Optical measurement of [acetone] before and after reactor.





k_1 (202−395 K) = 8.8 $\times$ 10^{-12} exp(−1320/T) + 1.7 $\times$ 10^{-14} exp(423/T) cm^3 s^{-1}, indicating that simple H atom abstraction may not be only mechanism

Minimising secondary reactions

- In order to be able to use a simple pseudo first order approach to the analysis of the data, secondary reactions must play a negligible role.
- This involves keeping the initial radical concentration low.
- See Vaghjiani and Ravishankara (1991) for a classic experimental analysis of this problem for $OH + CH_4 \rightarrow CH_3 + H_2O$.
- Typical radical decay timescales in pulsed photolysis reactions are ~ 0.1 – 1 ms.
- k($OH + CH_3$) is ~ 10^{-10} cm^3 molecule^{-1} s^{-1}. The timescale for removal of OH by this reaction is ~ 0.1 s for $[CH_3] = 10^{11}$ cm^{-3} and 1 ms for $[CH_3] = 10^{13}$ cm^{-3} .
- So essential to keep amount of OH generated in photolysis pulse low if this secondary reaction is to make a negligible contribution to the observed decay of OH.
- Need a sensitive detection technique – LIF is ideal.

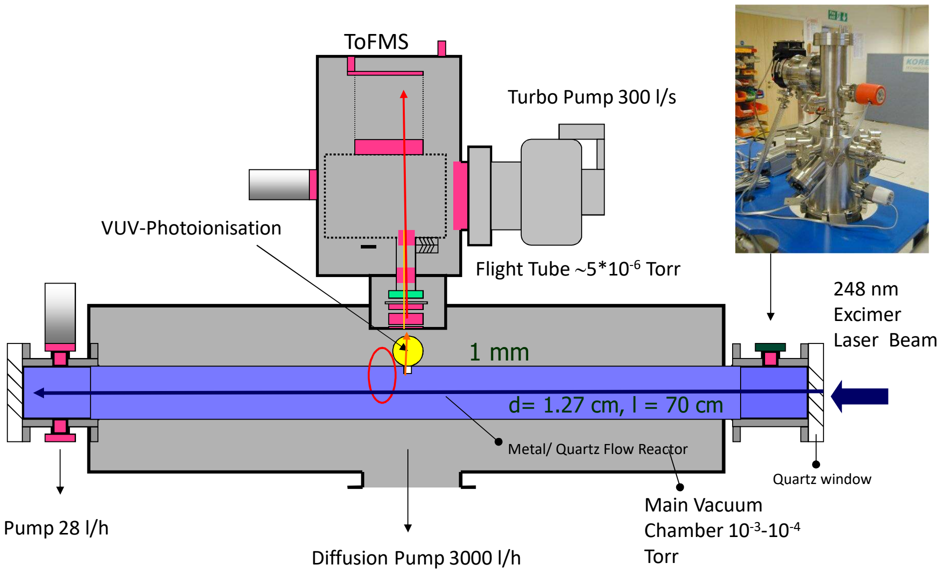
Detection methods

3. Mass spectrometry

  - Measures the mass-to-charge ratio (*m/z*) of ions typically presented as plot of intensity as a function of the mass-to-charge ratio - the mass spectrum.
  - Ionisation achieved e.g. by bombardment with electrons or photo-ionisation e.g. using pulsed laser.
  - **Time-of-flight (TOF) analysers** use electric field to accelerate ions through the same potential measuring time taken to reach detector.
  - If particles have same charge, velocities will depend only on their masses. Initial velocities vary and time-lag techniques used.
- Not *in-situ* method – requires sampling.
- Can measure several species simultaneously.

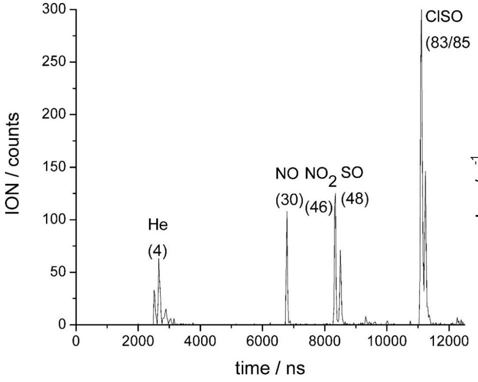
Detection using time of flight mass spectrometry

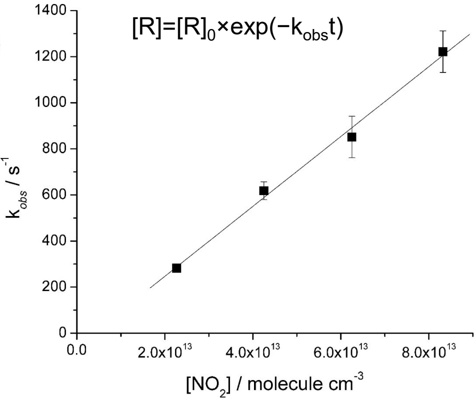
Blitz et al. 2007



Detection of NO, NO_2, SO allows determination of rate constant for SO+NO_2

Individual mass kinetic traces fitted to exponential growths/decays. NO_2 in excess, pseudo 1st order.





$[R]=[R]_0 \times \exp(-k_{obs}t)$

TOF-MS from 248nm photolysis of Cl_2SO/NO_2, 500 shot averaging. The two masses at ~8300ns are fully resolved and correspond to NO_2 (46amu) and SO (48amu).

Application of synchrotron radiation to distinguish enols from aldehydes in flames (ALS, Lawrence Berkley)

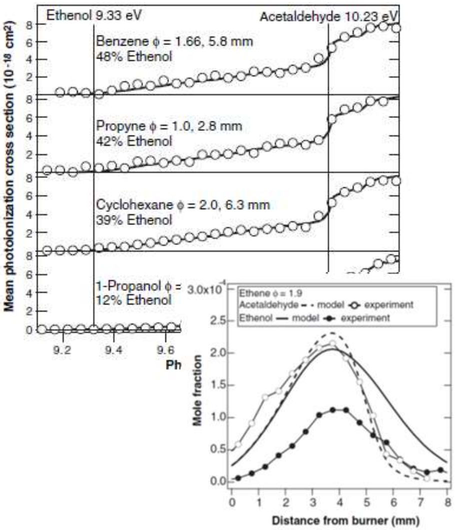
Taatjes et al. *Science* 2005, **308**, 1887

- Synchrotron tuneable vacuum ultraviolet (SVUV) light - pulsed-extraction TOFMS.
- **ALS is tuneable** (different photon energies used) making it feasible to **distinguish isomers, with same mass**, through their differing photoionization efficiency curves.
- Mole fractions for acetaldehyde and ethenol are derived by scaling the observed ion signals from species in the flame by their relative photoionization cross sections.

  acetaldehyde: CH_3CHO

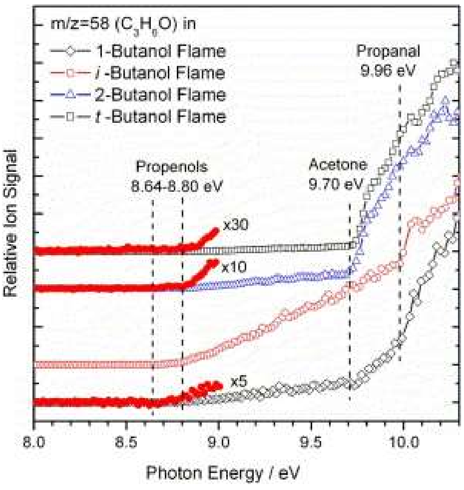
  ethenol: $CH_2{=}CHOH$

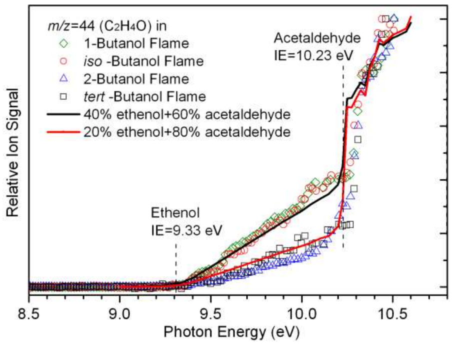
Photoionization efficiency curves taken for m/z 0 44 ions



Yang et al. (2007)

NSRL China
Various butanol flames,





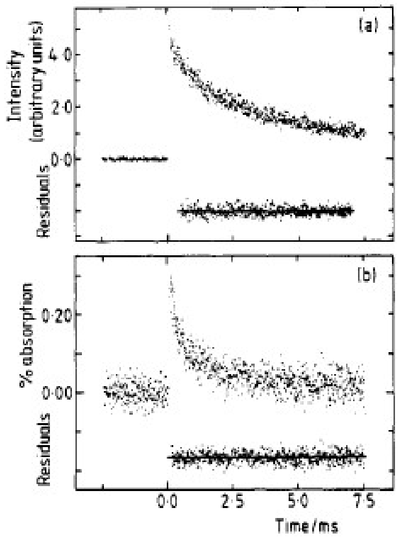
Cavity Ring Down Spectroscopy

- Used to study gas samples which absorb light at specific wavelengths, and to determine mole fractions down to the parts per trillion level.
- Setup consists of a laser which illuminates a high-finesse optical cavity, in its simplest form two highly reflective mirrors.
- Resonance with a cavity mode, builds up intensity in the cavity due to constructive interference.
- When laser turned off - **measurement of exponentially decaying light intensity leaking from the cavity**.
- Reflection back and forth between mirrors gives effective path length for extinction on the order of a few kilometres.
- If light-absorbing material placed in cavity, mean lifetime decreases.
- A CRDS setup measures time for light to decay to 1/e of its initial intensity.
- This "ringdown time" can be used to calculate the concentration of the absorbing substance in gas mixture in the cavity.

Examples

Radical-radical reactions
Experimental determination of *k* (CH_3 + H))

- This reaction presents an additional problem – the need to detect two radicals
- Laser flash photolysis of acetone producing H and CH_3 with $[H] << [CH_3]$
- H by resonance fluorescence, CH_3 by absorption. Need absolute $[CH_3]$, since $k'(H) = k[CH_3]$
- Brouard et al. J. Phys. Chem. 1989, 93, 4047-4059



From $1/[CH_3] = 1/[CH_3]_0 + 2k_2t$

Experimental results for CH_3 + H

$\boxed{\Delta_0 = \sigma[CH_3]_0L}$

CH_3 absorption analysed via

$$D(t) = 1 - \exp\{-(\Delta_0^{-1} - \frac{2k_2t}{\sigma L})^{-1}$$

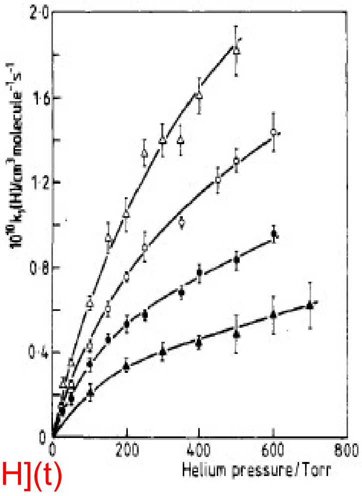
Where $D(t) = \Delta I/I_0$, Δ_0 is the peak optical density, σ is the absorption cross section and *L* is the path length.

H fluorescence analysed via

$$[H] = [H]_0\left\{1 + \frac{2k_2\Delta_0 t}{\sigma L}\right\}^{-\frac{k_1}{2k_2}} \exp(-k_3t)$$

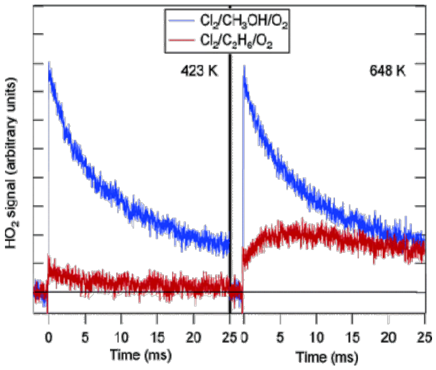
- Where k_2 refers to CH_3 + CH_3 and k_3 to other 1st order loss processes for H.
- Plot shows rate coefficients vs *p* at 300, 400, 500, 600 K.

From $d[H]/dt = - k_1[H](t)[CH_3](t) – k_3[H](t)$



Determination of product yields by Laser Flash Photolysis: $C_2H_5 + O_2$

- Taatjes et al. (J. Phys. Chem. A 104 (2000) 11549 – 11560) observed the formation of OH and HO_2, determining the fractional yields. Used 100% yield of HO_2 from $CH_2OH + O_2$ to calibrate the system.
- HO_2 yield↑ as T↑ and P↓
- Two timescales at higher T
- OH yield is small.



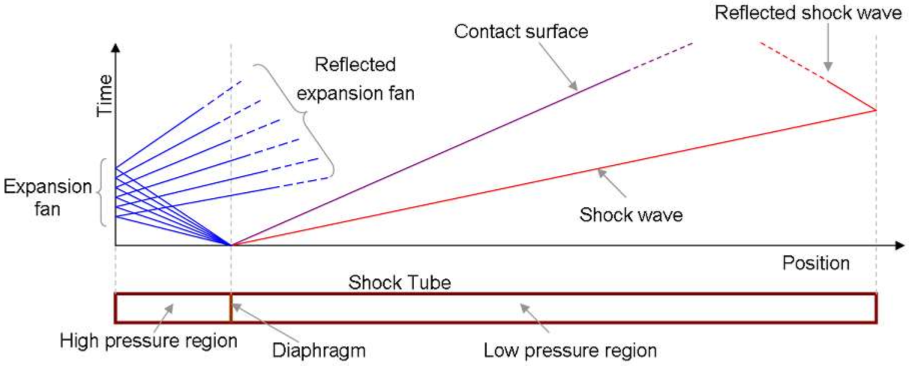
$$C_2H_5 + O_2 \rightarrow C_2H_5O_2^*$$
$$C_2H_5O_2^* + M \rightarrow C_2H_5O_2 + M$$
$$C_2H_5O_2^* \rightarrow C_2H_4 + HO_2$$
$$C_2H_5O_2 + M \rightarrow C_2H_4 + HO_2$$

Shock tubes

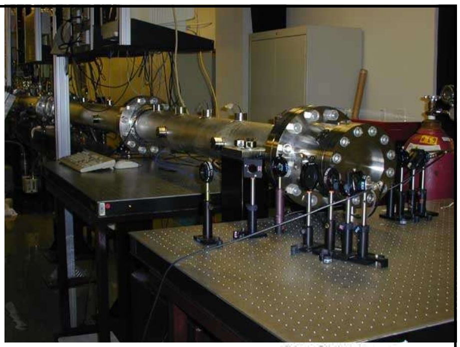
Shock tube - basics

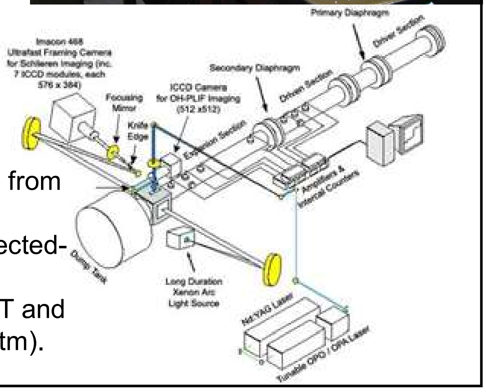
Basic concept:

- High-pressure driver gas expands upon diaphragm opening, creating shock wave.
- Test gas is instantaneously compressed and heated to combustion temperatures by incident and reflected shocks.
- High-temperature experiments monitored near end wall.



Shock tube:
Hanson lab at Stanford

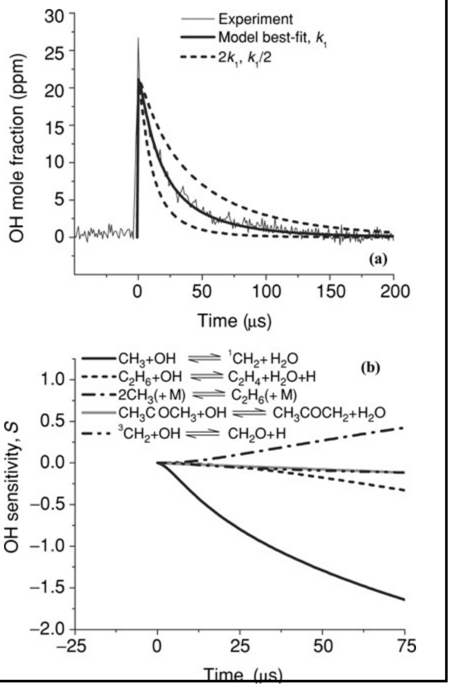




- Instantaneous heating/compression from shock waves.
- Accurately known incident- and reflected-shock conditions.
- Wide range of post-reflected shock T and P possible (600-4000 K, 0.1-1000 atm).

Shock tubes

- Radicals generally formed from thermal dissociation of precursor.
- Test times 1-10 ms.
- Single shot, so no signal averaging, but impressive optimisation of signal.
- Generally need to assess secondary reactions and use numerical chemical model with sensitivity analysis to show viability of measurements.
- Example: Measurement of CH_3 + OH by Hanson group.



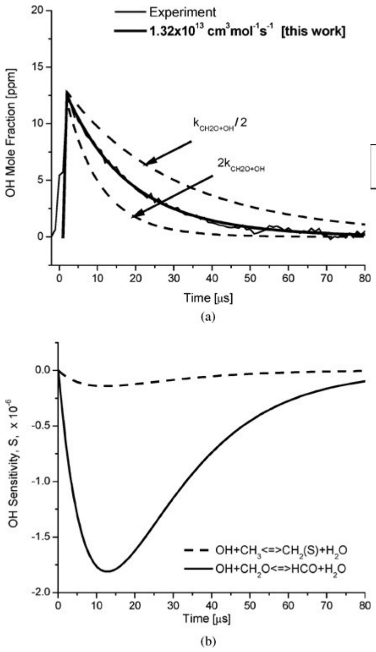
Vasudevan et al, (2008)

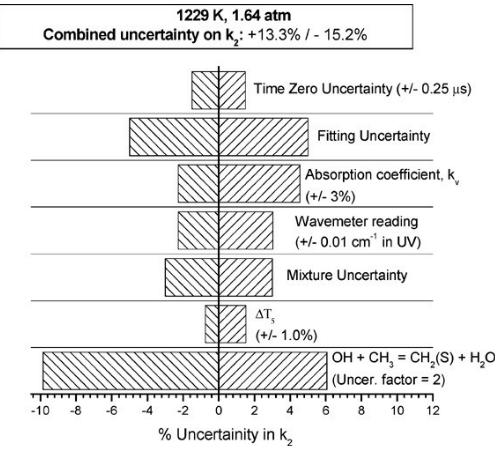
OH + HCHO, 934 K to 1670 K, 1.6 atm

- OH radicals - shock-heating tert-butyl hydroperoxide.
- 1,3,5-trioxane [$(CH_2O)_3$] was used in the pre-shock mixtures to generate reproducible levels of CH_2O
- OH concentration time-histories were inferred from laser absorption using the R1(5) line of the OH A-X (0, 0) band near 306.7 nm.
- Other reactions contribute to the OH time profile, especially CH_3 + OH.
- Rate coefficient determined by fitting to detailed model (GRI-Mech), with addition of acetone chemistry, deriving from dissociation of OH precursor (t-butylhydroperoxide).
- Detailed uncertainty analysis.

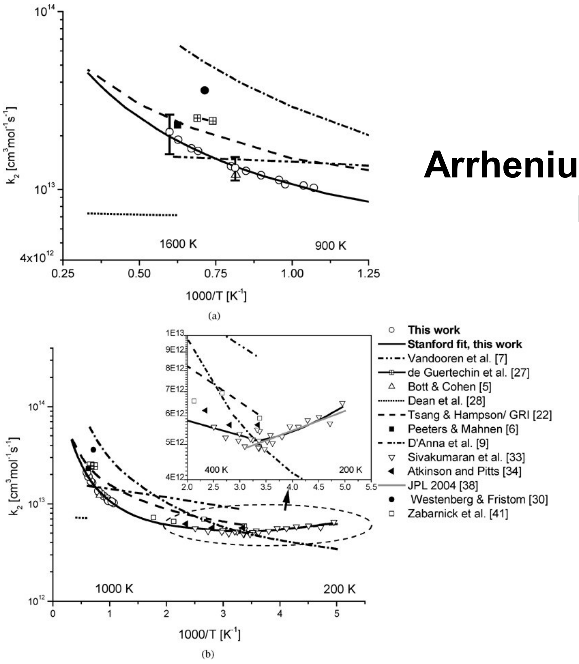
Vasudevan et al, (2005)

Determination of *k* and uncertainty analysis





Arrhenius plot for OH + HCHO

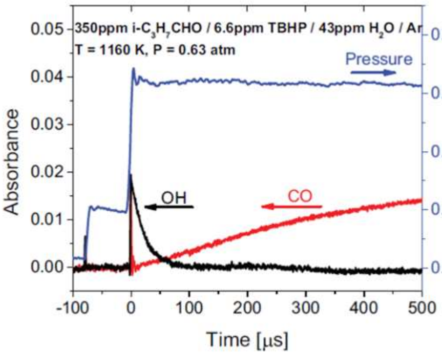


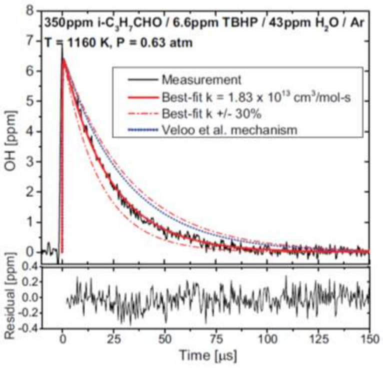
$k_2 = 7.82 \times 10^7 T^{1.63} \exp(531/T)$ / cm^3 mol^{-1} s^{-1}

OH + Aldehydes

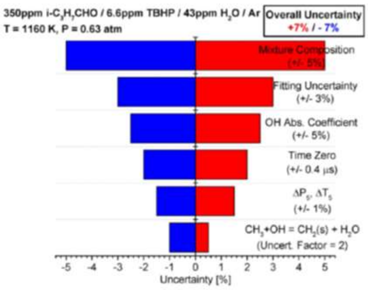
(Wang et al., 2017)

- Absorption technique; 976 – 1346 K, 0.6 atm.
- Some dissociation of aldehyde at higher T.
- Monitor by CO absorption.





OH + aldehydes contd.



$k_{iC_3H_7CHO+OH} = 7.70 \times 10^{13} \exp(-1700\ K/T) \pm 7\%;$

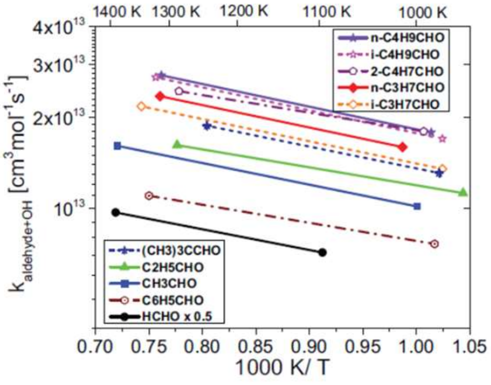
$k_{nC_4H_9CHO+OH} = 1.03 \times 10^{14} \exp(-1730\ K/T) \pm 7\%;$

$k_{iC_4H_9CHO+OH} = 1.02 \times 10^{14} \exp(-1750\ K/T) \pm 10\%;$

$k_{(CH_3)_3CCHO+OH} = 7.20 \times 10^{13} \exp(-1670\ K/T) \pm 8\%;$

$k_{C_2H_5CHCHCHO+OH} = 6.93 \times 10^{13} \exp(-1340\ K/T) \pm 8\%;$

$k_{C_6H_5CHO+OH} = 3.10 \times 10^{13} \exp(-1380\ K/T) \pm 8\%.$

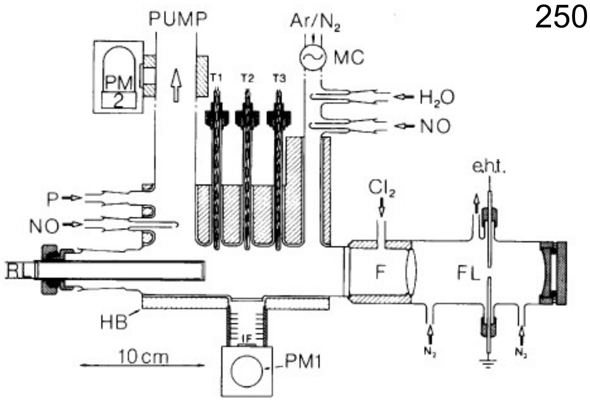


Flow tubes for elementary reactions and whole systems

Combined flow tube and pulsed photolysis: O + OH

Howard and Smith, 1981

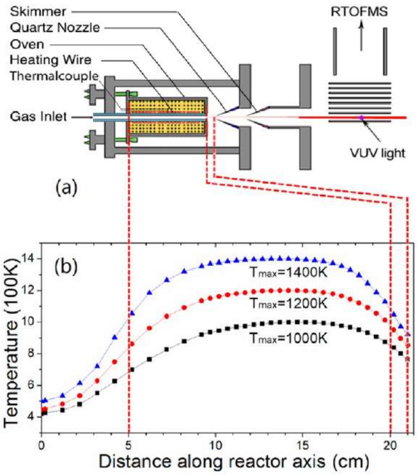
250 to 515 K



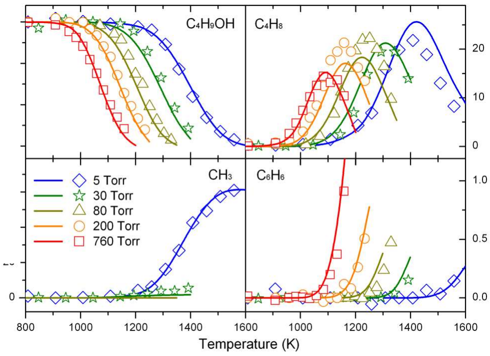
- O generated in discharge, OH by pulsed photolysis of H_2O, with [O]>> [OH]. [O] generated from N + NO and concentration determined by titration.

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

Cai et al. (2012)

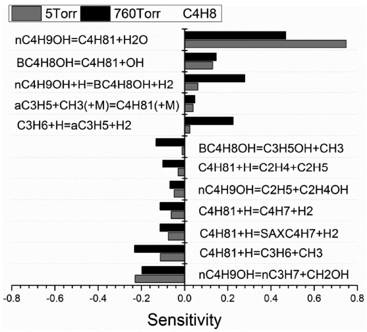


Synchrotron vacuum ultraviolet photoionization mass spectrometry used for identification and quantification of pyrolysis species mole fractions.

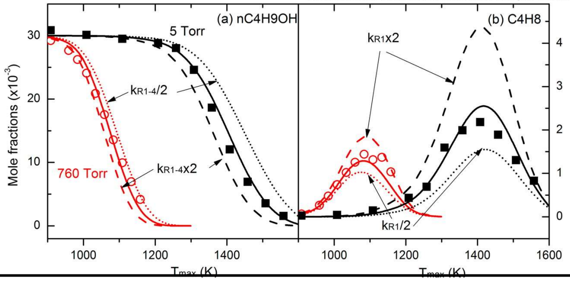


Use of species concentrations in flow reactor to determine rate coefficients: butanol dissociation

Cai et al. (2012)



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

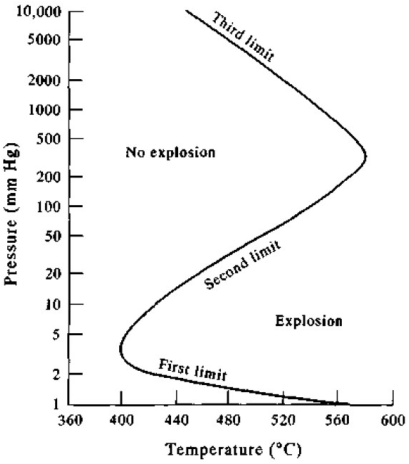


Experimental mole fraction profiles (symbols) and modelling results (lines) of nC_4H_9OH pyrolysis at 5 and 760 Torr.

Examples from the $H_2 + O_2$ system

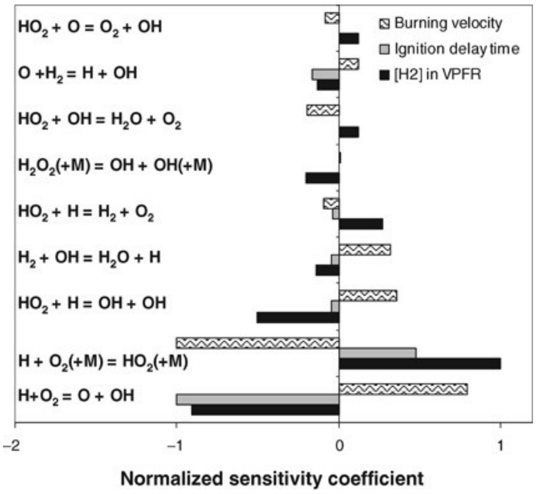
Reminder Interaction of elementary reactions in $H_2 + O_2$

- **Three ignition (explosion) limits.**
- **Competition** between **termination** (removing radicals, decelerating rate) and **branching** (accelerating rate).
- **First limit** – competition between wall termination e.g. $H \rightarrow$ wall (rate ↑as pressure ↓) and $H + O_2 \rightarrow OH + O$.
- **Second limit** – competition between $H + O_2 + M \rightarrow HO_2 + M$ (rate ↑as pressure ↑) and $H + O_2 \rightarrow OH + O$.
- HO_2 is low reactivity radical and reacts mainly by $HO_2 + HO_2 + M \rightarrow H_2O_2 + M$.
- **Third limit –** H_2O_2 dissociates generating OH radicals ($H_2O_2 + M \rightarrow 2OH$) and propagation and branching recommence.

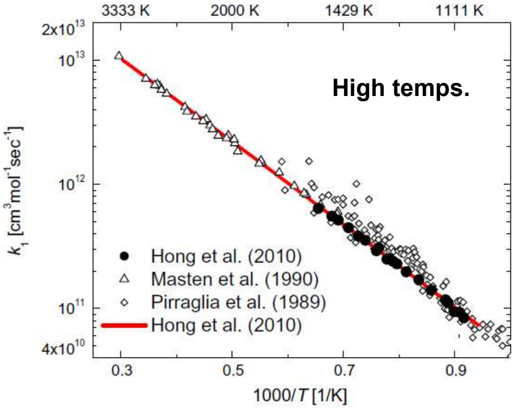


Hydrogen oxygen system

- Burke (2012) presented full evaluation of system showing sensitivities of target outputs to each reaction.
- Note the significance of
  - ➢ $H + O_2$ branching step,
  - ➢ termination step $H + O_2 + M$
  - ➢ and $H + HO_2$ steps for both ignition and burning velocities.



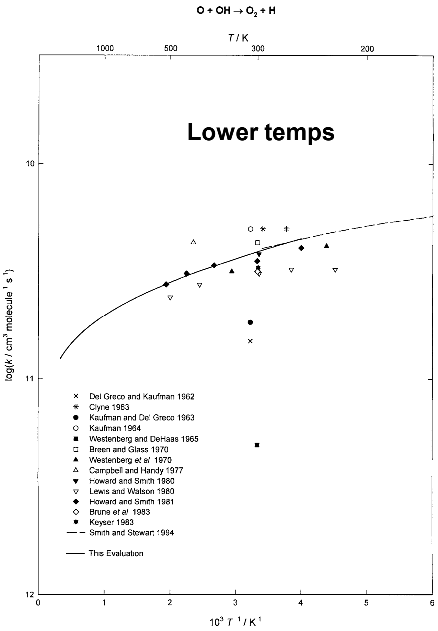
$H + O_2 \rightarrow OH + O$



- From Hong et al. (2011) shock tube measurements.
- $k = 1.7\times 10^{-10} \exp(-7670/T)$ (1100 – 3370 K). Uncertainty ± 10%.
- See Burke et al. (2012), who support the rate coefficient.

Reverse reaction: O + OH → H + O_2

- Studied 150 – 500 K, mainly by discharge flow / laser flash photolysis.
- Not of great importance in combustion, but provides additional information on reverse reaction through thermodynamics.
- k = $2.00 \times 10^{-10}\ T^{-0.352}$ exp(113/T) cm^3 $molecule^{-1}$ s^{-1} over the range 250–3000 K.
- Δlog k = ± 0.2 over the range 250–3000 K.



Second branching step O + H_2 → OH + H

- Sutherland et al. used
  - – flash photolysis, monitoring O by resonance fluorescence, and
  - – shock tube, generating O by flash photolysis of NO and monitoring by Atomic Resonance Absorption Spectroscopy (ARAS).
- Davidson and Hanson (1990) used a shock tube, generating O by laser flash photolysis of NO and by pyrolysis of N_2O. O monitored by ARAS: 2120 – 2750 K.
- Javoy et al. (2000). ARAS: 2021 – 3356 K.

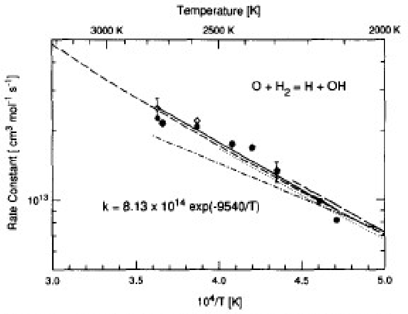


Fig. 2. Arrhenius diagram: O + H_2 → OH + H. Filled circles—data derived from photolysis method. Open diamonds—data derived from pyrolysis method. Error bars represent ±10%. Solid line—best fit to present data. Dotted line—Sutherland et al. [8]. Dashed line—Natarajan and Roth [9]. Dot-dashed line—Pamidimukkala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

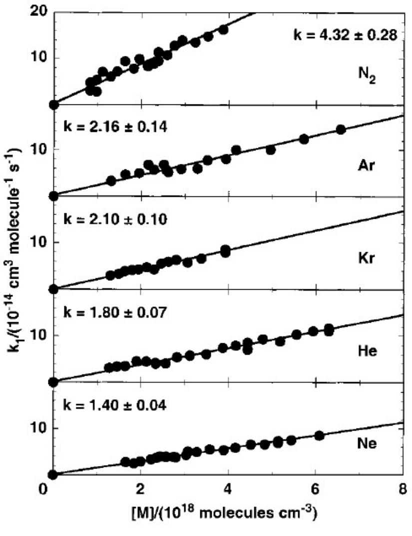
Sutherland et al. (21st Symp(Int) Comb, 1986, 929).

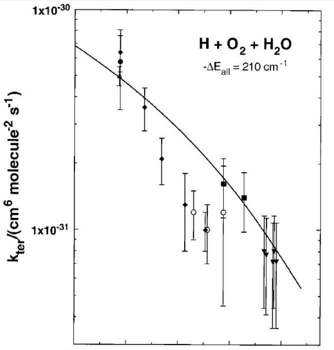
$H + O_2 + M \rightarrow HO_2 + M$

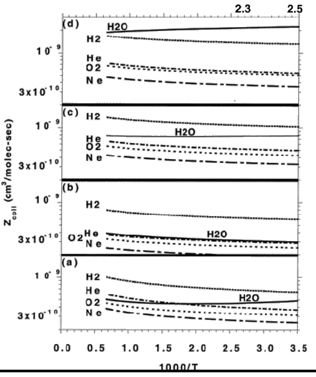
- Termination step at lower *T*, converting reactive H into less reactive HO_2.
- At higher *T* acts as a route to branching through formation of H_2O_2 through HO_2 + HO_2 (and HO_2 + RH in hydrocarbon combustion).
- Reaction is at the third order limit except at higher pressures.
- Michael et al. (2002) used flash photolysis at room *T* for a wide range of third bodies, and a shock tube at higher *T* for Ar,. O_2 and N_2. Showed that H_2O is an unusually effective third body.
- Detailed analysis of collision frequencies and energy transfer parameters. $A + B \rightleftharpoons AB^* \rightarrow AB$

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

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





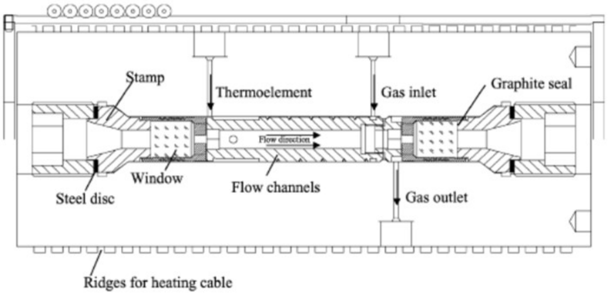


T dependence of Z_{coll}

Units of k: 10^{-32} cm^6 $molecule^{-2}$ s^{-1}

High pressure pulsed photolysis / flow reactor

(Fernandes et al., 2008)



- H + O_2 + M → HO_2 + M, 300 – 900 K, 1.5 – 950 bar
- H from photolysis NH_3 at 193 nm.
- HO_2 detected by absorption spectroscopy at 230 nm.
- At these higher pressures, the reaction moves into the fall-off region.

H + O_2 + M → HO_2 + M

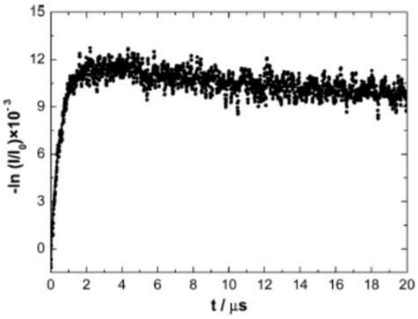


Fig. 2 Absorption–time profile of HO_2 (λ = 230 nm, T = 600 K, p = 300 bar, M = N_2).

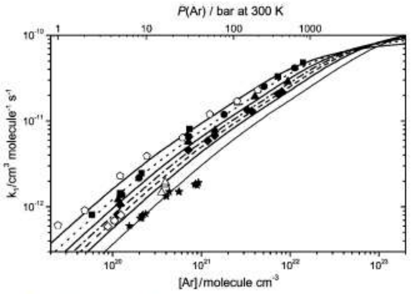


Fig. 5 Falloff curves for the recombination H + O_2 (+Ar) → HO_2 (+Ar) (representative upper pressure scale for 300 K; T/K = 300 (■), 400 (●), 500 (▲), and 600 (♦) from this work; 300 (⬠, ref. 19), 820 (◇, ref. 20), 1200 (★, ref. 22), and 1325 (△, ref. 21); the fitted curves at left from top to bottom are for T/K = 300, 400, 500, 600, 700, 820, and 1200, resp.).

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

- Data for different third bodies and temperatures can be rationalised and placed on the same plot using reduced falloff curves.
- Requires calculation of high pressure limiting rate coefficient (that isn't accessible to experiment for this reaction).

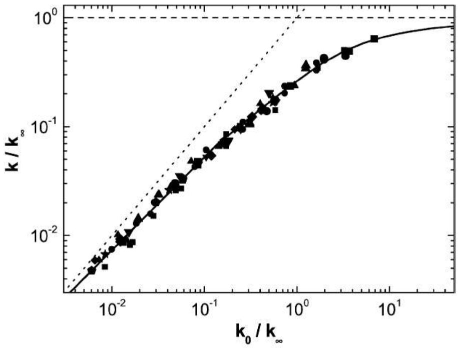
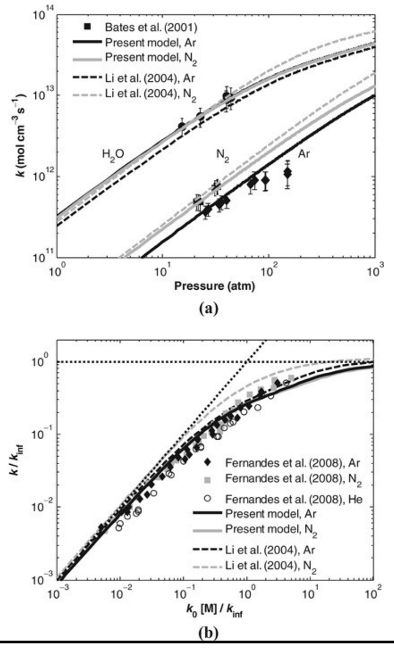


Fig. 7 Doubly reduced falloff curves for the recombination $H + O_2$ $(+M) \rightarrow HO_2$ $(+M)$ in the bath gases M = He, Ar, and N_2 (experimental points from this work from Tables 1–3; T/K = 300 (■), 400 (●), 500 (▲), 600 (▼), 700 (♦), 800 (★), and 900 (⬟), see text).

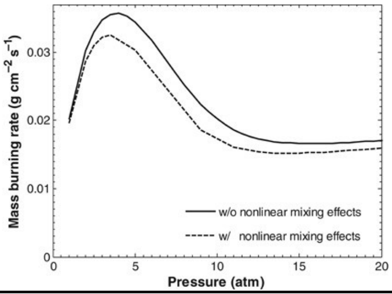
Evaluation: Burke et al., 2012



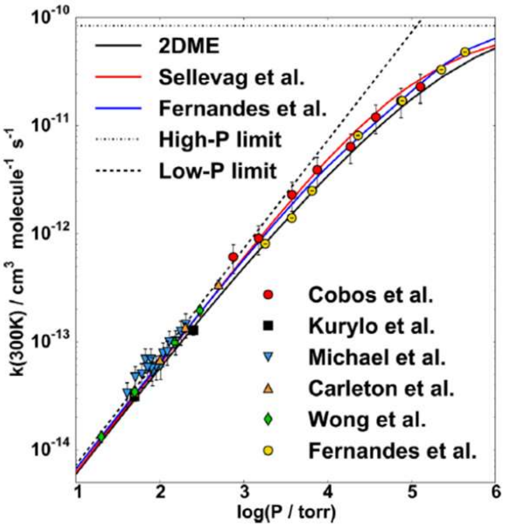
(a)

(b)

- Full model evaluation for high pressure combustion.
- Fall-off updated using high pressure limit values from ab initio studies of Harding and Troe.
- Mostly consistent for different bath gases bar fall off region for Ar.
- Bath gas mixture rules add additional uncertainty.



Latest comparison of purely *a priori* theory and experiment, M=Ar (Klippenstein, 2017)



1. **solid black line**: *a priori* energy transfer based 2D-ME predictions, coupled with dynamically corrected variable reaction coordinate TST based on a high accuracy well-validated MRCI PES

2: **solid red line**: fitted master equation results of Sellevag et al. J Phys Chem A 2008, 112, 5085.

3. **solid blue line**: analytic fit of Fernandes et al. Phys Chem Chem Phys 2008, 10, 4313

A priori theory values within error bars of experiments.

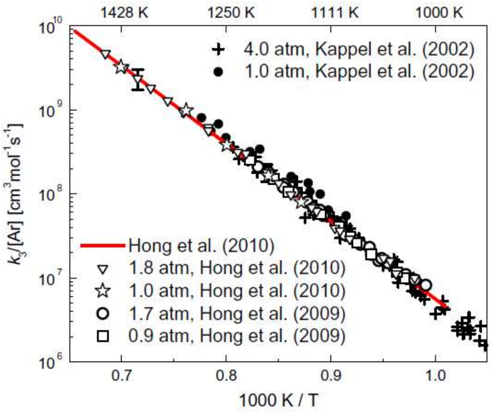
$H_2O_2 + M \rightarrow 2OH + M$

(Troe, Combustion and Flame 2011, 158, 594–601)

- The thermal dissociation/recombination reaction of hydrogen peroxide $H_2O_2 \rightleftharpoons$ 2OH. Analysis and representation of the temperature and pressure dependence over wide ranges.
- Reaction is far from the high pressure limit. To obtain a representation of *k(T,P)*, Troe used the statistical adiabatic channel model to calculate k_∞, using an ab initio surface (Phys. Chem. Chem. Phys. 10 (2008) 3915; J. Chem. Phys. 111 (1999) 2565.
- An important aspect of this work was the use of thermodynamics to relate forward and reverse reactions, using the revised enthalpy of formation of OH.

H_2O_2 dissociation

(Hong et al. Comb Flame 2011, 158, 633)



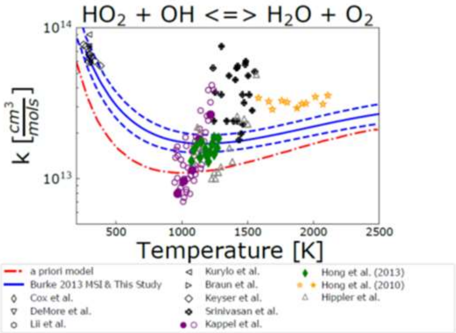
- Data refer to low pressure limit. Used shock tube with laser absorption detection of H_2O and OH.

MULTI-SCALE INFORMATICS (MSI)

$OH + HO_2 = H_2O + O_2$
An example of multi-scale modelling

- Focusses on H_2O_2 decomposition system where large uncertainties persist in *T/P/*M dependence.
- *T* dependence of rate for $HO_2 + OH = H_2O + O_2$ subject of debate.
  - Radical-radical reactions are difficult to study experimentally.

- Experimental data mostly low *T*.
- Non-Arrhenius behaviour at between 900 -1300 K.
- Deep, narrow “well” with a minimum ~ order of magnitude lower than atmospheric and high-temperature values.
- Later data from Srinivasan et al. and Hong et al. suggest weaker *T* dependence.
- **HOW TO RESOLVE?**

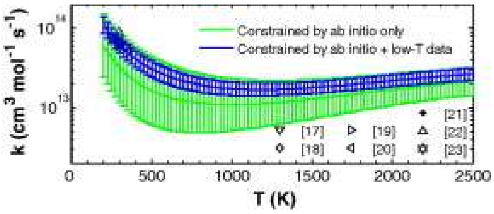


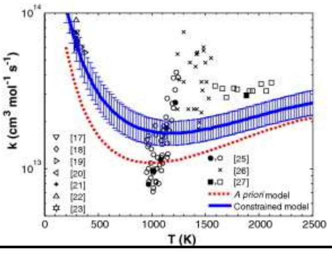
Burke et al., 2013, 2021

$OH + HO_2 = H_2O + O_2$
An example of multi-scale modelling

- Multi-scale modelling approach uses combination of **exp. data** (at limited conditions), **coupled with theory** within an **optimisation approach** to find a functional form consistent with all sources.

- *ab initio* transition-state theory within their associated uncertainties.
- Uncertainties in barrier heights, frequencies, exp. *T*, *P*, third body efficiencies included in optimisation.
- Finds rate minimum near 1200 K, although *T* dependence is substantially less pronounced than previously suggested.





$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

- < 800 K: flash photolysis, absorption spectroscopy.
- Open circles: shock tube, absorption spectroscopy *(Kappel et al, Phys Chem Chem Phys, 2002, 4, 4392)*.
- Reference 5: Hippler et al. J Chem Phys 1990, 93, 1755
- Significant disagreement > 1000 K
- Burke et al. (2012) 'Difficult to discern which, if any, (of the high T) determinations is reliable.' More measurements needed under combustion conditions.

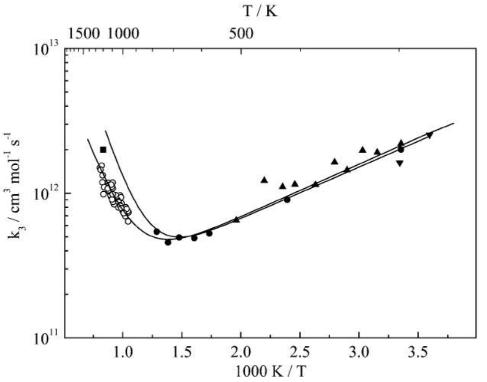


Fig. 10 Rate constants k_3 (■: ref. 2, ▲: ref. 35, ▼: ref. 36, ●: ref. 37, ○ and lower line: this work, upper line: ref. 5).

$HO_2 + HO_2$ new channel proposed, MSI approach

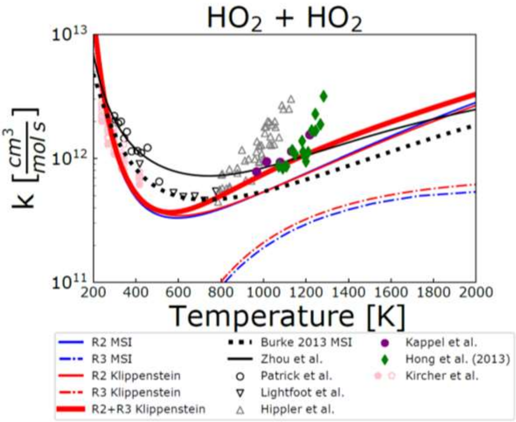
- Again, scatter, leading to discrepancies between experimental data. Most recent data – shock tube study of Hong et al.
- Two channels now proposed:

  $HO_2+HO_2=H_2O_2+O_2$ (R2)

  $HO_2+HO_2=OH+OH+O_2$ (R3)

based on theory calcs of Klippenstein.

- MSI resolves data and supports new channel.
- Both reactions of importance for high T flame speeds in various flames – not just H_2.



Section 2b
Theoretical basis of Chemical Kinetics

WHY THEORY?

- Model help us to **extrapolate** thermo-kinetic data to pressures/temperatures where experiments don't exist or are not possible.
- A single highly accurate source of data would help is to establish **consistency between mechanisms**.
- At least for small molecules theory can now achieve **comparable levels of accuracy** to experiments.
- Can perhaps be more easily **automated** for large number of reactions than developing laboratory robots…
- To design and improve rate rules in a hierarchical framework.
- To support **fundamental understanding** of kinetic systems.

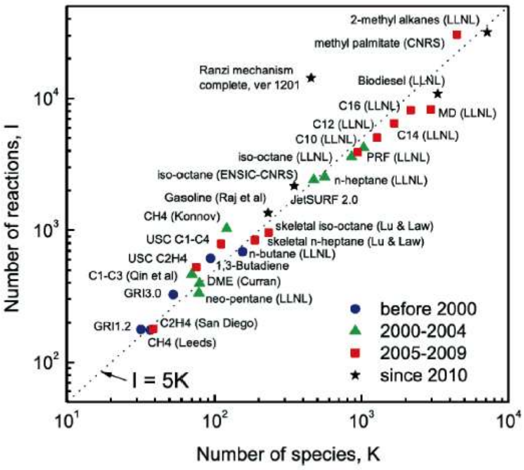
Klippenstein webinar (2021)

Klippenstein: From theoretical reaction dynamics to chemical modeling of combustion

Proc Comb Inst 2017, 36, 77

- "The accurate prediction of the temperature and pressure dependence of gas phase reactions requires state-of-the- art implementations of a variety of theoretical methods: ab initio electronic structure theory, transition state theory, classical trajectory simulations, and the master equation."
- "Future progress in the fidelity of the chemical modeling of combustion will benefit from more widespread applications of theoretical chemical kinetics and from **increasingly intimate couplings of theory, experiment, and modeling**."
- New paper from Miller et al. reviews these links.
  - Combustion chemistry in the twenty-first century: Developing theory-informed chemical kinetics models, Miller et al. 2021.

Numbers of species and reactions in mechanisms for combustion of hydrocarbon fuels **(Lu and Law, 2017)**



- Larger mechanisms require thousands of rate constants.
- Can't measure them all – calculation essential.

Synopsis

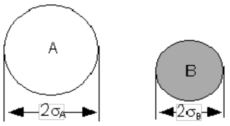
- Examine the basis of collision theory and transition state theory (TST).
- Treatment of reactions with no (or small) energy barrier – variational transition state theory (VTST).
- Pressure dependent reactions and reactions involving multiple wells – Lindemann, RRK, RRKM, Master Equation.
- Master Equation Methods.
  - Influence of uncertainties in electronic structure calculations.

Basis of Theory

- Theory of chemical kinetics should ideally predict rates at which reactants with a given **energy distributed about specific excitation modes** pass over to products of equally well defined energy within a **multi-dimensional PE hypersurface**.
- Requires:
  - Complete description of PES.
  - Energy distributions of reactants and products.
- Even with developments of CPU resource difficult for all but smaller molecules.
  - Simplifications made e.g. Collision theory, Transition State Theory.

Simple Collision Theory (Wayne, 1969)

- Assumes hard spheres.
- Rate of reaction relates to collision frequency for collisions with relative kinetic energy greater than critical value E_c along lines of centre.
- Derived by applying Boltzmann distribution to the relative velocity of two colliding species (A, B say).
- Gas collision rate:



$$Z\ (\varepsilon > \varepsilon_c) = n_A n_B \sigma^2 \left(\frac{8\pi kT}{\mu}\right)^2 e^{-\varepsilon_{c}/kT}$$

where ε_c is the critical energy per molecule, $\sigma = ½ (\sigma_A + \sigma_B)$, $\mu = m_A m_B/(m_A+m_B)$

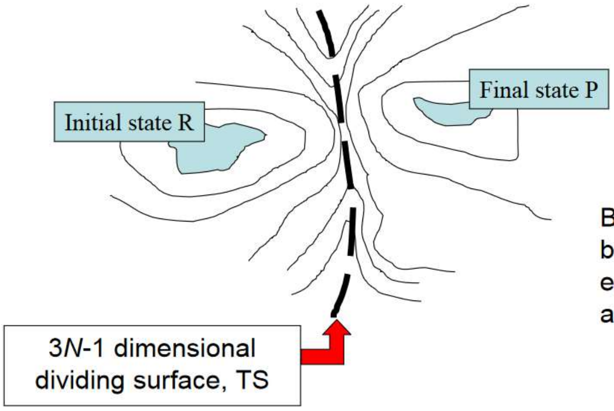
- When using per mole *k* is replaced with *R* in equation.
- Limited by lack of consideration of:
  - Steric factors/Longer range interactions.
  - Activation through internal degrees of freedom such as vibration (important for uni-molecular reactions).
- Use of Lennard-Jones potentials allow improve on hard sphere assumption.

Transition State Theory (TST)

- Simple collision theory takes no account of nature of colliding species except to consider if they carry enough energy to get over an energy barrier to reaction.
- TST focuses on configuration of reactants at highest point on PES – the ***transition state*** or ***activated complex***.
  - Activated complexes studied near the saddle point of a PES.
- Assumes quasi equilibrium between reactants and activated complexes.
- They are converted into products and kinetic theory used to calculate rate of conversion.
- TST assumes that all trajectories originating from reactant region cross a reactant/product dividing surface in phase space only once
  - all forward-crossing trajectories lead directly to products
  - dividing surface assumed to be dynamical bottleneck.
- Conventional TST - dividing surface passes through saddle point on PES.

Main idea of TST

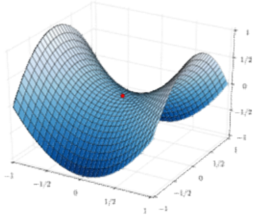
Identify a 3*N*-1 dimensional dividing surface, a Transition State (TS), that represents a **bottle neck** for going from an initial to a final state:



Initial state R

Final state P

3*N*-1 dimensional dividing surface, TS



Bottle neck can be due to an energy barrier and/or entropy

k^{TST} = (probability of being in TS) • (flux out of TS)

TST formulations

- Both **classical** and **statistical** versions of TST can be formulated.
- Statistical thermodynamic formulation allows calculation of equilibrium constant between reactants and complex from partition functions.
  - Of course accurate knowledge of partition functions requires accurate methods for calculating PES.
- Collision theory requires that only the height of the energy barrier is known.
- TST requires information about shape of PES around the saddle point.

Statistical mechanics – a reminder

- The equilibrium constant for a generalised reaction

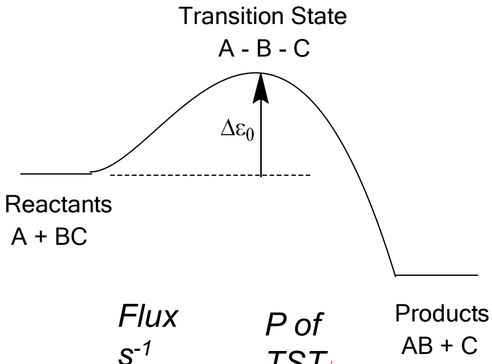
$$\sum_i \nu_i X_i = 0$$

where X_i is a chemical species and ν_i is the stoichiometric coefficient (positive products, negative reactants) is given by:

$$K_c = \prod \left(q_{X_i}/V\right)^{\nu_i} \exp\left(-\frac{\Delta\varepsilon_0}{kT}\right)$$

- Dividing the total partition function by V removes the volume term from the translational partition function. q/V is given the symbol Q
- $\Delta\varepsilon_0$ is the difference in zero point energies of the products and reactants.
- This equation is used in the formulation of the Transition State Theory expression for the rate constant.

Transition State Theory



Flux *s^{-1}*

P of TST

$$k(T) = \alpha \frac{k_B T}{h} \frac{Q^{\ddagger}_{TS}}{Q_A Q_{BC}} \exp\left(\frac{-\Delta\varepsilon_0}{k_B T}\right)$$

Contributions from translation, rotation and all internal degrees of freedom

- Transition State Theory provides a method for calculating the rate constant, *k*(*T*), using statistical mechanics.
- *Q* is the molecular partition function, *q*, divided by the volume, *V*.
- The ‡ sign indicates that one vibrational mode (along reaction coordinate) has been removed from the partition function for TS – constraint along reaction coordinate.
- Need barrier height and good description of partition functions.

α is a correction factor: most common source from incorporation of tunnelling through the barrier in H atom transfer reactions and symmetry factors.

Thermodynamic formulation of TST

$$K(T) = \prod_i Q_i^{\nu_i} \exp\left(-\frac{\Delta\varepsilon_0}{kT}\right) = \exp\left(-\frac{\Delta G^\ominus}{RT}\right)$$

where K is the equilibrium constant and $\Delta\varepsilon_0$ is the difference in zero point energies of the reactants and products. ΔG is the (molar) Gibbs energy change for the reaction.

- Note the change from molecular to molar units in classical formulation and that $R = kN_A$, where N_A is the Avogadro number. Applying this equation to TST:

$$k(T) = \alpha \frac{kT}{h} \frac{Q_{TS}^{\ddagger}}{Q_A Q_{BC}} \exp\left(\frac{-\Delta\varepsilon_0}{kT}\right) = \alpha \frac{kT}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$\Delta G^{\ddagger}$ is the Gibbs energy of activation.

Molecular degrees of freedom

- A molecule composed of N atoms has 3N nuclear degrees of freedom:
  - 3 translation
  - 2 rotation (linear molecule), 3 rotation (non-linear)
  - 3N-5 vibration (linear), 3N-6 vibration (non-linear).
- The interaction between the electrons and the nuclei provides a potential energy surface that defines the equilibrium geometry of the molecule and the response to the relative motion of the atoms – the **vibrations and internal rotations**.
- The molecule is described by an overall wavefunction, ψ; remember the Born-Oppenheimer principle states that this can be separated into nuclear and electronic components, because of the difference in masses.

$$\psi = \psi_{\text{electronic}}\, \psi_{\text{nuclear}}$$

Molecular degrees of freedom

- **Translation**
  - Change in position - linear momentum.
- **Rotation**
  - Molecules have rotational energy owing to rotational motion of the nuclei about their centre of mass (angular momentum).
  - Due to quantization, energies take only certain discrete values.
  - Rotational transition thus corresponds to transition of the molecule from one rotational energy level to the other through gain or loss of a photon.

Molecular degrees of freedom

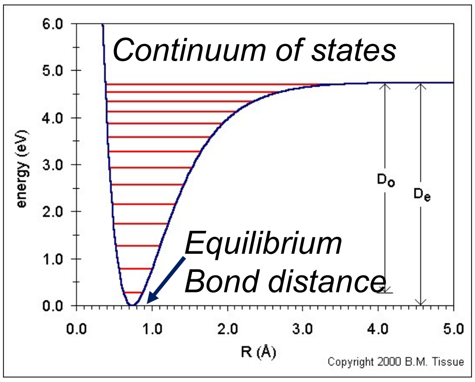
- **Vibration**
  - A periodic motion of the atoms of a molecule relative to each other, such that the centre of mass of the molecule remains unchanged.
  - A **diatomic molecule** has **one normal mode** of vibration - it can only stretch or compress the single bond.
  - Vibrations of polyatomic molecules are described in terms of independent normal modes.
  - Molecular vibration is excited when molecule absorbs energy, ΔE, corresponding to the vibration's frequency, v: $\Delta E = hv$.
  - Motion in normal vibration approximated using **harmonic oscillator**. Vibrational energy is a quadratic function (parabola) with respect to the atomic displacements.
  - In reality motion is anharmonic and first overtone has frequency that is slightly lower than twice that of the fundamental.
  - Excitation of higher overtones involves progressively less and less additional energy and **eventually leads to dissociation**.

Partition Functions and Reaction Coordinate

- To evaluate rate constants using the statistical thermodynamic formation of TST we need the partition functions for reactants and activate complex.
- Needed for various degrees of freedom.
  - $Q = Q_{trans}Q_{vib}Q_{rot}Q_{elec}$

- Calculation of these requires accurate knowledge of the form of the PES at the transition state.
- Special cases exist.
- Use of **reaction coordinate** assumes reaction system treated as motion along just one path.
  - Allows determination of vibrational term to be omitted from partition function for activated complex.
  - Generally insensitive to choice but can be problematic for e.g. cis-trans isomerisations.
  - Obtained via normal mode analysis of vibrations.

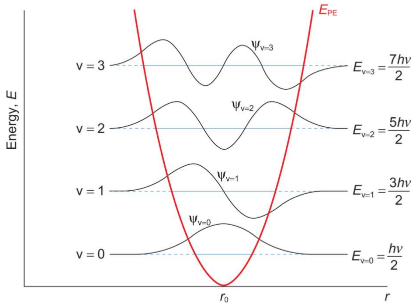
Potential energy surfaces. 1. Diatomic molecule



- The potential energy surface in a diatomic depends on one variable – the internuclear distance: V(R).
- Reaction coordinate is vibration along lines of centres.
- Vibration is anharmonic and energy levels are not evenly spaced, but converge.

- Note the zero point energy (zpe) = hν/2. The dissociation energy from this state is D_0. Electronic structure calculations of the potential energy return an energy without zpe, which must be added once the frequencies have been determined.
- The dissociation energy from the minimum in V(R) is D_e.
- Note that many calculations use a RRHO model for the rotations and vibrations.

Vibrational energy levels and wavefunctions



- Model for vibrational motion in a molecule – harmonic oscillator

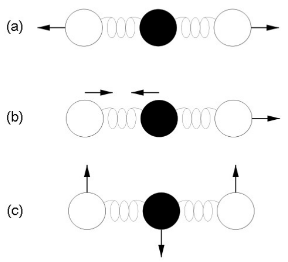
$$V = \frac{1}{2}k(r - r_0)^2$$

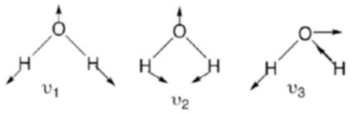
- Wavefunctions are Gaussian functions – they are not simple sine functions because (*E*-V) depends on *r.*
- Note the penetration of the wavefunction into the *non-classical* region where *V* > *E :* the kinetic energy is negative – *quantum mechanical tunnelling*
- In this region, the wavefunction is no longer oscillatory but decreases to zero at $(r - r_0) = \infty$

Rotation - rotational motion is slower than vibrational. The energy levels depend on the moment of inertia and hence on the average bond distance. Translation - just depends on the mass. Treat classically.

Normal modes of vibration – triatomic molecule

3N-6 vibrations (non-linear)
3N-5 vibrations (linear)





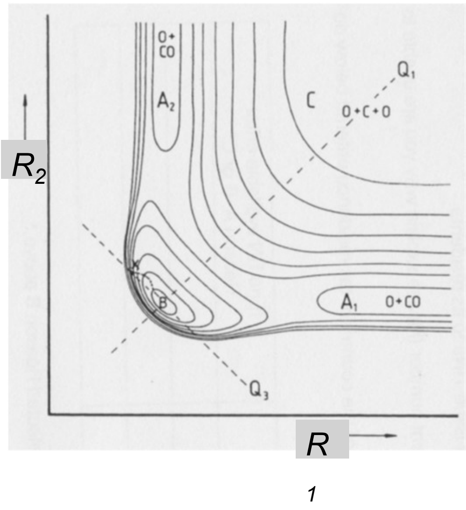
- **Carbon dioxide** (4 vibrations)

- Symmetric stretch
- Asymmetric stretch
- Bend (doubly degenerate)

- **Water** (3 vibrations)

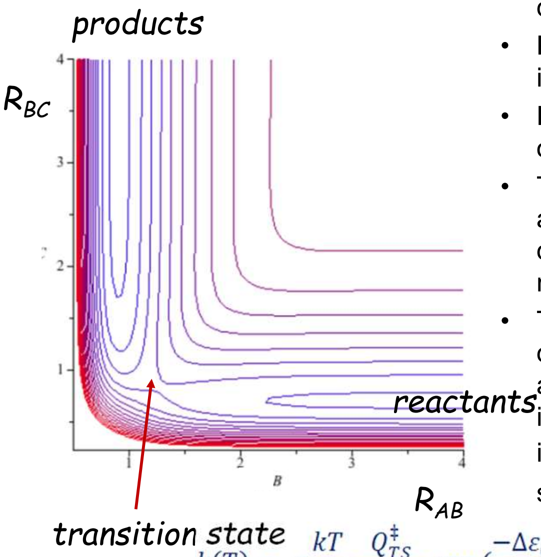
- Symmetric stretch
- Bend (non- degenerate)
- Asymmetric stretch

Potential energy surface. 2. Triatomic molecule



- There are 3 internal coordinates for a triatomic – the bond distances, R_1 and R_2 and the bond angle θ. This 2D figure is for constant θ.
- Two <u>normal modes </u>of vibration are shown – the <u>symmetric </u>stretch – both R_1 and R_2 increase (and decrease) together and the asymmetric stretch where R_1 decreases as R_2 increases
- The other vibration(s) – bending – involve changes in θ.

Potential energy surface 3. Reaction: A + BC →AB + C

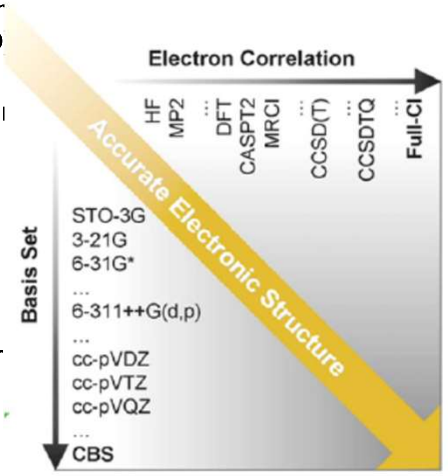


- Reactants approach as R_{AB} decreases.
- Products separate as R_{BC} increases.
- Figure relates to a fixed angle of approach.
- The symmetric stretch (R_{AB} and R_{BC} both increase or decrease) is at a potential minimum –a true vibration.
- The asymmetric stretch (R_{BC} decreases as R_{AB} increases is at a potential maximum – this is the reaction coordinate and is not included in $Q^{\ddagger}_{TS}$. It is the source of the $\frac{kT}{h}$ term

$$k(T) = \alpha \frac{kT}{h} \frac{Q^{\ddagger}_{TS}}{Q_A Q_{BC}} \exp\left(\frac{-\Delta\varepsilon_0}{kT}\right)$$

Reminder - approaches to accurate electronic structure calculations

- A basis set is composed of atomic orbitals, yielding linear combinatior of atomic orbitals approach (LCAO
- The CBS limit is extrapolated estimate of result obtained using aı infinitely large (**complete**) **basis set**.
- Electron correlation is interaction between individual electrons.
- Hartree Fock method has minimal electron correlation.
- **Full configuration interaction** (or **full CI**) is a linear variational approach which provides numerically exact solutions (within infinitely flexible complete basis se.., to electronic Schrodinger equation.

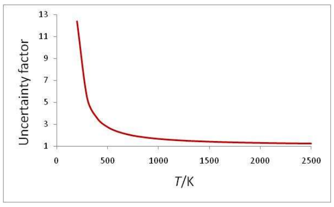


Zador et al Prog Energy Comb Sci 2011, 37, 371

Approach to calculating rate coefficients using TST

- The approach is most simple for a constrained transition state – one where there is a significant maximum on the reaction coordinate.
- The potential energy surface (PES) is calculated using electronic structure methods and the TS located.
- The energy of the TS relative to the reactants is determined along with the structure of the TS (which allows the moments of inertia to be calculated) and the vibrational frequencies.
- *k* (T) can then be calculated using Transition State Theory, and assuming rigid rotor – harmonic oscillator (RRHO) behaviour.
- Problems arise with hindered internal rotors and more complex calculations are needed.
- Classical mechanics assumes that probability of particle overcoming an energy barrier is 0 if it has less energy that barrier height.
- **However**, quantum mechanical **tunnelling** through the energy barrier can be important for particles of small mass and H transfer reactions.

Accuracy of TST calculations

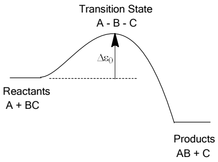


- **Kinetic accuracy**
  - Uncertainty of barrier height is typically ~ 4 kJ mol^{-1} (1 kcal mol^{-1}). Graph shows a plot of exp(E/RT) vs T with E = 4 kJ mol-1, which represents the uncertainty factor in *k* deriving from the uncertainty in the activation energy.
- **Deficiencies** in the TS model
  - Rigid rotor harmonic oscillator model
  - Tunnelling model – generally use Eckart.
- **Improvements via** – higher level ab initio calculations, variational effects, anharmonicities, multidimensional tunnelling …
- Often tune the barrier height obtained from lower level calculations to experimental data, allowing improved extrapolation of the latter.
  - **See later examples from Shannon, Burke etc.**

Microcanonical rate theory

- Microcanonical rate theory examines the rate at a specific energy; it gives:

$$k(E) = \frac{hW^{\ddagger}(E)}{N(E)}$$



- where $W^{\ddagger}(E)$ is the sum of states at the transition state, from energy zero at the TS to *E* and *N*(*E*) is the density of states at energy *E* for the reactant(s).
- We will use this approach when dealing with **master equation** calculations.
- Integrating this expression over a Boltzmann distribution of reactants gives the TST result for *k*(*T*).

Variational TST (VTST)

- Some reactions have only a small or no energy barrier.
  - exact location of the TS is problematic
  - e.g. radical-radical reactions.
- In **variational transition state theory (VTST)** location of dividing surface is variationally optimized either to:
  - maximize Gibbs free energy of activation in a canonical ensemble.
  - minimize number of states of generalized transition state in a microcanonical ensemble.
- Microcanonical VTST achieved by optimizing the TS for each internal energy E, and even for each J quantum number for molecular rotation.
- Once energy-specific optimal TS is known, temperature-dependent rate coefficient recovered for each *T* by averaging over appropriate Boltzmann distribution.
- Every additional dimension that is optimized increases the computational cost, but also improves the quality of description.

Further limitations of Transition State Theory (TST)

- Valid in gas phase bimolecular reactions - inelastic collisions of reactants efficient enough to repopulate rovibrational states maintaining local equilibrium.
- Problems in gas-phase **unimolecular reactions** unless pressure is extremely high, since **rovibrationally excited states not in local equilibrium**, and rate constants **fall off** as pressure is lowered and reactive states are depleted faster than they can be repopulated.
- Need a different set of methods for **pressure dependent reactions.**

Lindemann theory for Unimolecular Reactions

- The schematic reaction A+M→P is assumed to consist of two elementary steps:
  - STEP 1: Bimolecular activation of A

    $A + M \rightleftharpoons A^{*} + M$ **2^{nd} *order, forward k_1, reverse k_{-1}***
  - STEP 2: Unimolecular reaction of A^{*}

    $A^{*} \rightarrow P$ **1^{st} order, k_2**
- A is a reactant molecule which can be excited on collision with M to form energised A* which may be collisionally deactivated or react to form products.
- Quasi-steady state approximation applied to A* gives

$$\frac{d[P]}{dt} = \frac{k_1 k_2\,[A][M]}{(k_{-1}[M] + k_2)}, k_{uni} = \frac{k_1 k_2 [M]}{(k_{-1}[M] + k_2)}$$

- k_{uni} is a function of pressure.
- At high pressures $k_{-1}[M] \gg k_2$ i.e. collisional deactivation much faster than unimolecular reaction of A* and k_{uni} becomes pressure independent. Overall kinetics 1st order.
- At low pressures $k_{-1} \ll k_2$ and $k_{uni} = k_1[M]$. Bimolecular step rate determining.

Problems with Lindemann Theory

- Assumptions that $k_1$can be approximated by simple collision theory $k_1 = \zeta \exp(-E/RT)$ do not hold.
  - Bimolecular step takes no account of energy dependence of activation; the **internal degrees of freedom** of the molecule are completely **neglected**, the theory consequently underestimates the rate of activation.
- Plots of $1/k_{uni}$ vs $1/[M]$ are not generally linear.
  - Unimolecular step fails to take into account that a unimolecular reaction specifically involves one **particular form of molecular motion**.

Hinshelwood extension

- Hinshelwood modelled internal modes of A by a hypothetical molecule having *s* equivalent simple harmonic oscillators of frequency *v,* using statistical methods to determine the probability of the molecule being collisionally activated to a reactive state.
- The number of ways of distributing a given number of quanta, v, among the *s* oscillators (i.e. the number of degenerate states of the system at an energy (v +½)h*v*) is g_v = (v+s-1)! / v!(s-1)!.
- The fraction of molecules in state v is given by the Boltzmann distribution: $\frac{n_\mathrm{v}}{N} = \frac{g_\mathrm{v}\exp(-\frac{\mathrm{v}h\nu}{k_BT})}{q}$ where q is the partition function.
- Strong collision assumptions made. Probability of deactivation on collision is 1. Hence k_{-1} = ζ (collision frequency) and because the collisions promote equilibrium, the probability of forming a state v in a collision is given by the Boltzmann distribution. The rate constant for activation to state v is therefore given by:

$$k_1^\mathrm{v} = \zeta\frac{g_\mathrm{v}\exp(-\frac{\mathrm{v}h\nu}{k_BT})}{q}$$

- The overall rate of activation (i.e. rate of formation of collisionally excited A* with enough energy to react) obtained by summing over levels which can dissociate i.e. all levels with an energy greater than the critical energy E_0 which the molecule needs to react. If the vibrational quantum number of the state with energy E_0 is *m*, we have:

$$k_1 = \sum_m^\infty \zeta\frac{g_\mathrm{v}\exp(-\frac{\mathrm{v}h\nu}{k_BT})}{q}$$

- In integral form if energy levels assumed to be continuous:

$$\mathrm{d}k_1 = \zeta\frac{N(E)\exp(-\frac{E}{k_BT})dE}{q}$$

- *N(E) dE* is number of energy levels in range *E-E+dE. N(E)* is the density of states and $\mathrm{d}k_1$ the rate of activation into the energy range. Integrating over all energies > E_0 gives:

$$k_1 = \frac{\zeta}{(s-1)!}(\frac{E_0}{k_BT})^{s-1}\exp(-\frac{E_0}{k_BT})$$

- Differs from Lindemann approach by $\frac{1}{(s-1)!}(\frac{E_0}{k_BT})^{s-1}$which is >1 particularly for large molecules with more oscillators, improving agreement with experiment.

RRK Theory

- Recognises that a minimum amount of energy must be localised in specific modes of molecular motion in order for the unimolecular step to take place.
  - activation is by collision, the molecules have many internal degrees of freedom, and reaction occurs when some special degree of freedom acquires at least a critical amount of energy.
- A new step is added to the Lindemann mechanism, in which the generally excited molecule A* is converted into the specifically excited 'activated complex' A‡ .

$$A^* \xrightarrow{k_{2a}} A‡ \xrightarrow{k_‡} P$$

- $k_‡$ is of the order of a vibrational frequency, and k_{2a} is generally much smaller. This means that conversion of A* to A‡ is rate determining, and k_{2a} is the overall rate coefficient for conversion of A* to products.
- Because $k_{2a} << k_‡$, [A‡] is very small and we can use the steady state approximation to find k_{2a}, giving:

$$k_{2a} = k_‡ \frac{[A‡]}{[A*]]}$$

- RRK theory assumes that energy can flow freely from one vibrational mode to another within the molecule.

RRK Theory

- As before in the discussion of the Hinshelwood theory, for a molecule with s equivalent oscillators, the degeneracy of the vth vibrational level is (v+s-1)! / v!(s-1)!.
- If we have to locate at least m quanta in one particular mode for dissociation to occur, this simply reduces our choice of quanta to (v-m), and the total number of ways of arranging these is (v-m+s-1)! /(v-m)!(s-1)!.
- The probability of locating at least m quanta out of v in the dissociation mode is the ratio of these two quantities

$$P_m^v = \frac{(v-m+s-1)!}{(v-m)!\,(s-1)!}\,\frac{v!\,(s-1)!}{(v+s-1)!} = \frac{(v-m+s-1)!\,v!}{(v-m)!\,(v+s-1)!}$$

- Assuming v,m >> s and writing this in terms of $P_{E_0}^E$ the probability of locating a minimum amount of energy E_0 out of the total energy E in the dissociation mode, we get:

$$P_{E_0}^E = (1-\frac{E_0}{E})^{s-1}$$

RRK Theory

- If energy randomisation takes place rapidly enough for the vibrational energy to be distributed statistically, then

  $\frac{[A^{\ddagger}]^E}{[A*]^E} = P^E_{E_0}$, and the rate constant is:

  $k_2(E) = k^{\ddagger}(1 - E_0/E)^{s-1}$.
- k_2 increases with energy, since the probability of localising a given amount of energy E_0 in one particular mode increases as E increases.
- The localisation probability decreases as the number of oscillators s increases since there are more modes to spread the energy across.
- Consequently, k_2 becomes smaller as the molecule becomes more complex, in contrast to the behaviour of the rate constant for activation k_1 .
- Quantum RRK theory (QRRK) is an extension to RRK, where energy dependence is partially considered through estimating a geometric mean frequency for the complex, rather than considering each specific frequency (as with RRKM).

RRKM

- For unimolecular reactions with a well-defined transition state, the common way of obtaining energy resolved microcanonical rate coefficients utilizes RRKM theory: a microcanonical formulation of TST.
- RRKM theory depends on assumption that the total phase space of a molecule at a particular energy is uniformly populated as the molecule passes from reactant to product through the TS, and the time scale for energy randomization is << that of reaction
  - thermal Boltzmann distribution is maintained at all energies, which is true at sufficiently high pressures.
- Applicable for TS dividing surfaces within constrained geometry with a well-defined energetic barrier.

RRKM

- Based on Hinshelwood and RRK theory, reaction mechanism can be rewritten to take account of fact that rates of collisional activation and unimolecular dissociation are energy dependent:

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{dk_1(E)}{\rightleftharpoons}} \mathrm{A}^*(\mathrm{E}) + \mathrm{M}$$

$$\mathrm{A}^*(\mathrm{E}) \xrightarrow{k_{2(E)}} P$$

Applying the QSSA to [A*(E)] gives the rate expression:

$$\frac{\mathrm{d}[\mathrm{P(E)}]}{\mathrm{dt}} = \frac{k_2(\mathrm{E})\mathrm{d}k_1(\mathrm{E})[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2(\mathrm{E})}$$

From which we can identify the unimolecular rate coefficient for energy range E-E+dE as:

$$k(\mathrm{E}) = \frac{k_2(\mathrm{E})\mathrm{d}k_1(\mathrm{E})[\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2(\mathrm{E})}$$

Thermal rate coefficient obtained by integrating from E_0 to ∞:

$$k = \int_{E_0}^{\infty} \frac{k_2(\mathrm{E})\mathrm{d}k_1(\mathrm{E})[\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2(\mathrm{E})} = \int_{E_0}^{\infty} \frac{k_2(\mathrm{E})\mathrm{d}k_1(\mathrm{E})}{k_{-1}(1 + \frac{k_2(\mathrm{E})}{k_{-1}[\mathrm{M}]})}$$

RRKM

- Energy of molecule partitioned into fixed and non-fixed components.
- Only non-fixed component E*, which can flow freely around various modes of motion can contribute to reaction.
- Various terms of rate expression evaluated using statistical mechanics:
  - $\frac{\mathrm{d}k_1(\mathrm{E}*)}{k_{-1}}$ is equilibrium constant for energisation of A in energy range E* to E*+dE* and can be calculated from partition function ratio $\frac{Q_{\mathrm{A}*(\mathrm{E}*)}}{Q_A}$.
  - k_2(E*) obtained by applying QSSA to activated complex A‡ as in RKK theory with modification that overall reaction is broken down into energy contributions from translation and from rotation/vibration.
  - Rate constant k‡ and ratio [A‡]/[A*] evaluated using partition functions (translation along reaction coordinate).
- In the general case, RRKM theory admits equilibrium between A* and A‡ , but not between A* and A.
- At high pressures A* and A are also in equilibrium.
- At high pressures the RRKM model becomes the same as the transition state theory model, and results of the two theories coincide.

Barrierless reactions

- RRKM theory is applicable for TS dividing surfaces located at a constrained geometry with a well-defined energetic barrier.
- When reaction in question is barrierless, a first principles determination of *k(E)* requires a variational approach – i.e. is calculated by minimizing rovibrational sum of states, *W*(*E*), on the PES in question.
- Alternative approach is using inverse Laplace transformation (ILT).
- Unimolecular microcanonical *k*(E) is determined from either experimental measurements or theoretical determinations of the canonical high pressure limiting rate coefficient, $k_\infty(T)$.
- Well suited for radical-radical reactions.

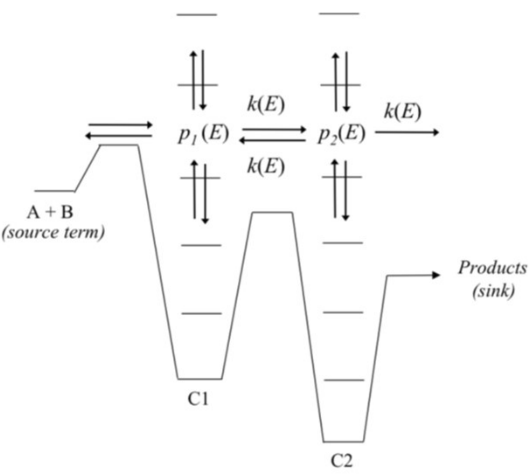
Limits of Commonly Used Methods

- The most commonly used theoretical models for describing chemical kinetics are accurate in two limits.
- When relaxation is fast with respect to reaction timescales, **thermal transition state theory (TST)** is the right tool.
- In the limit of slow relaxation, an energy resolved description like **RRKM theory** is more appropriate.
- More recently, Master equation approaches have been successfully used to analyse and predict non-equilibrium chemical kinetics for a range of intermediate relaxation regimes.
- MEs facilitate kinetic simulations over multi-well molecular energy topologies where energy transfer with an external bath impacts phenomenological kinetics.
  - i.e. the timescales for thermalisation are competitive with kinetic timescales.

Master equation model for pressure dependent reactions

Energy Grained Master Equation (EGME)

- EGME typically involves the calculation of energy resolved rate coefficients using microcanonical transition state theory (μTST) and collisional energy transfer models.
- Combined to construct a model describing phenomenological rate coefficients that arise from competition between reaction and thermalisation of non-equilibrium ensembles.
- Typical application is via a one-dimensional ME, wherein the total **rovibrational energy of the system, *E*,** is the independent variable, where angular momentum, *J* is averaged. E.g. in MESMER.
- **Assumption** - errors in molecular properties (e.g., energies and frequencies) and experimental measurements (e.g., of rate coefficients or product yields) tend to have more impact on ME results than errors introduced by neglecting *J.*



- Energy barrier to inter-conversion of species, and TS corresponds to first-order saddle point on the molecular PES.
- Thus, the reactant must be activated and energy supplied to overcome barrier.
- Typically, supplied through collisions with bath gas molecules.
- Some collisions are activating and some deactivating.
- Since collision events and amount of energy transferred are random quantities, energy transfer process can be regarded as random walk, and treated using techniques from stochastic process theory.

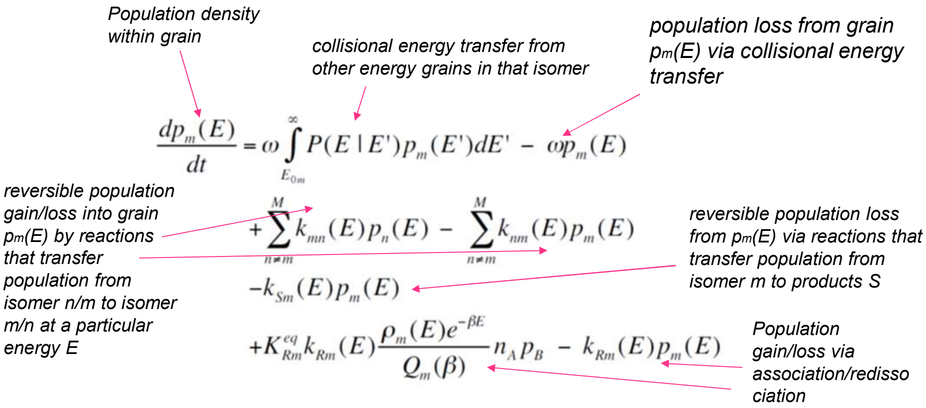
EGME Method

- Provides macroscopic kinetic description of reaction system in terms of the behaviour of isomers at energy resolved (or microcanonical) level.
  - Need microcanonical rate constants.
- Overcomes number of states by bundling together rovibrational states of similar energies into ‘grains’, and then describing the time evolution between these energy grains, which generally span no more than a few kJ mol^{-1}.

EGME method

Mesmer manual, Glowacki et al.

- *ω* is Lennard-Jones collision frequency, and *P*(*E*|*E'*) is the probability that collision with bath gas will result in a transition from a grain with energy *E'* to a grain with energy *E*.
- Q_m is the rovibrational partition function for the molecular species corresponding to isomer *m*, n_A is the number density of reactant A, and p_B is the population in reactant B.



Population density within grain

collisional energy transfer from other energy grains in that isomer

population loss from grain $p_m(E)$ via collisional energy transfer

$$\frac{dp_m(E)}{dt} = \omega\int_{E_{0m}}^{\infty} P(E\,|\,E')p_m(E')dE' - \omega p_m(E)$$
$$+\sum_{n\neq m}^{M} k_{mn}(E)p_n(E) - \sum_{n\neq m}^{M} k_{nm}(E)p_m(E)$$
$$-k_{Sm}(E)p_m(E)$$
$$+K_{Rm}^{eq}k_{Rm}(E)\frac{\rho_m(E)e^{-\beta E}}{Q_m(\beta)}n_A p_B - k_{Rm}(E)p_m(E)$$

reversible population gain/loss into grain $p_m(E)$ by reactions that transfer population from isomer n/m to isomer m/n at a particular energy E

reversible population loss from $p_m(E)$ via reactions that transfer population from isomer m to products S

Population gain/loss via association/redissociation

ME methods

- Also needed for closure:

$$\frac{dp_B}{dt} = \sum_{m=1}^{M}\int_{E_{0i}}^{\infty} k_{Rm}(E)p_m(E)dE$$
$$-n_A p_B \sum_{m=1}^{M} K_{Rm}^{eq}\int_{E_{0i}}^{\infty} k_{Rm}(E)\frac{\rho_m(E)e^{-\beta E}}{Q_m(\beta)}dE$$

- Whole system then solved by matrix diagonalization techniques using discrete form:

$$\frac{d}{dt}\mathbf{p} = \mathbf{Mp}$$

- **M,** the transition matrix, determines population evolution due to the collisional energy transfer and reaction processes.
- The total number of eigenvalues is equal to the number of grains.
- Grain size is a balance between cost and microscopic non-equilibrium detail.
- Eigenvalue of smallest magnitude gives rate coefficient.

Requirements for ME calculation

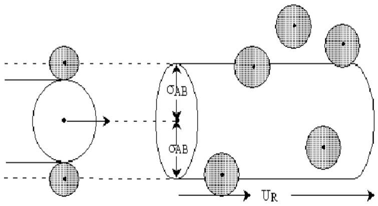
- Microcanonical rate constants ($k(E)$). Use electronic structure + TST, RRKM, ILT.
  - For TST essentially need barrier heights, well depths, frequencies.
- Collision frequency, $\omega = k_c[\mathrm{M}]$, where k_c is the rate constant for collisions and $[\mathrm{M}]$ is the concentration of the collider (the "third body") – see next slide.

- Energy transfer model: $P(E|E')$. Generally use exponential down model calculating upward transitions using detailed balance.

Rate constants for collisions

Hard Sphere

$$k_c^{HS} = \sqrt{\frac{8k_BT}{\pi\mu}}\,\pi d^2$$



Lennard-Jones

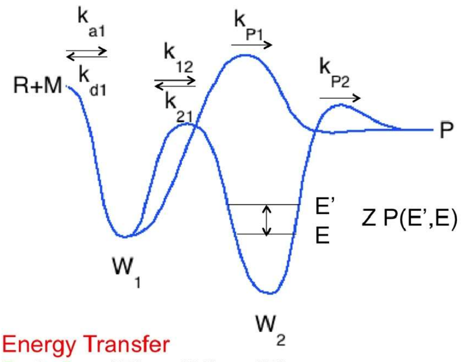
$$k_c^{LJ} = k_c^{HS}\Omega_{2,2}^*$$

$$\Omega_{2,2}^* = \frac{1.16145}{\left(T^*\right)^{0.14874}} + \frac{0.52487}{\exp\left(0.7732T^*\right)} + \frac{2.16178}{\exp\left(2.437887T^*\right)} \qquad T^* = k_BT/\varepsilon$$

- d is the collision diameter ($2\sigma^{AB}$). μ is the reduced mass $m_Am_B/(m_A+m_B)$.
- ε is the depth of the van der Waals well between the collider and the dissociating molecule. Ω is termed a collision integral and defined as a function of reduced temperature T^*.
- Basically a fitted approximation.

Example of isomerization and dissociation system

The Kinetic Model



Microcanonical
RRKM Theory
k_{a1} (E)
k_{d1} (E)
k_{12} (E)
k_{21} (E)
k_{P1} (E)
k_{P2} (E)

Phenomenological
Master Equation
$k_{R+M \rightleftarrows P}$ (T,P)
$k_{R+M \rightleftarrows W1}$ (T,P)
$k_{R+M \rightleftarrows W2}$ (T,P)
$k_{W1 \rightleftarrows W2}$ (T,P)
$k_{W1 \rightleftarrows P}$ (T,P)
$k_{W2 \rightleftarrows P}$ (T,P)

Energy Transfer
Bath Gas; [B] >> [M] >> [R]
Z; Lennard Jones Collision Rate
P(E',E); Exponential Down

(Klippenstein, 2017)

Ab intio calculations of energy transfer parameters

- See Jasper and Miller, J. Phys. Chem. A 2011, 115, 6438–6455
- Use dynamical calculations with high level ab initio potential energy surfaces for the interaction of the excited molecule and the collision partner, M. Also develop more efficient approximate methods.
- Assume that the exponential down model applies: that the energy transfer function depends on the amount of energy transferred but is independent of the initial and final energies individually.
- Determine the size of α ($=\langle\Delta E\rangle_{down}$) and its T dependence.

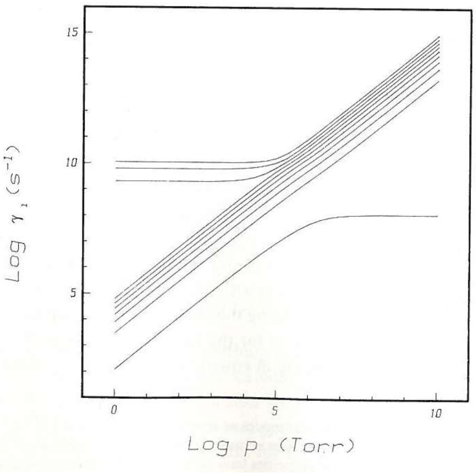
- Lennard Jones parameters are widely used to calculate the collision frequency, ω. These parameters have been calculated and tabulated for a wide range of species by Jasper and Miller, Combustion and Flame 161 (2014) 101–110.

Chemically Significant Eigenvalues

- The eigenvalues of **M** exhibit a separation in magnitude:
  - all are negative
  - majority are large in magnitude and govern the time evolution of the energy transfer process (IERE).
  - a smaller group of eigenvalues (CSE) govern the chemical evolution of the system.
- At low temperatures the number of CSE corresponds to the number of distinct chemical species being modelled and is usually the sum of the number of wells and source terms in the model.
- Separation in time scales allows a matrix rate equation to be set up relating purely to the CSEs that is identical to the rate equation for the chemical system.
- Rate constants determined from an eigen-pair analysis of the ME.
- This is only possible provided the IEREs and CSEs are well separated in time
- References: J. Chem. Phys., 1974, 60, 3474; J. Phys. Chem. A, 2002, 106, 9267; J. Phys. Chem. A, 2006, 110, 10528; Phys. Chem. Chem. Phys., 2007, 9, 4085–4097.

Example of eigenvalue distribution for dissociation reaction

H.O. Pritchard, The quantum theory of unimolecular reactions (CUP 1982)

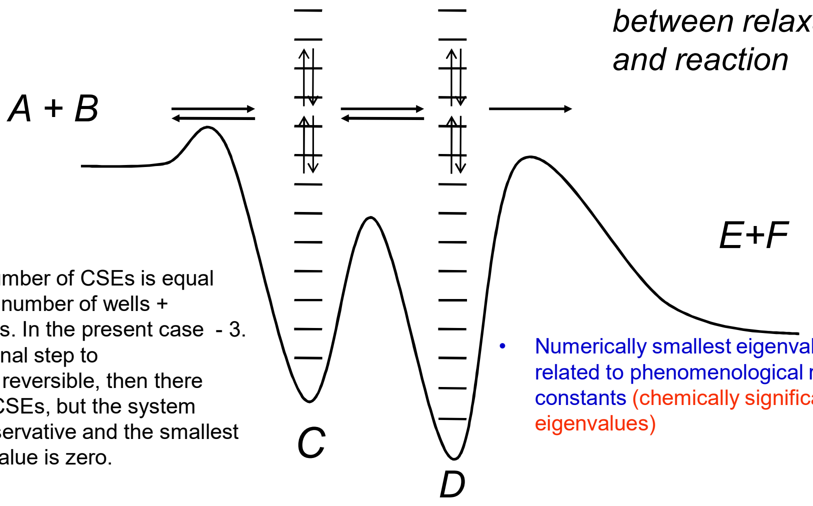


- Log($-\lambda_i$) for dissociation vs *P* at fixed *T*.
- Numerically smallest λ_i gives rate coefficient – fig shows limits k_∞ at high *p* and k_0[M] at low p.
- Relaxation λ_is are well separated from single chemically significant λ (CSE) and system is well behaved
  - a rate coefficient can be assigned.
- Collisional relaxation occurs on shorter timescale than reaction. Steady state distribution of reactant established and determines rate constant.
- SS distribution depends on *P* and approaches Boltzmann distribution at high *P* – high pressure limit.

Complex reactions.

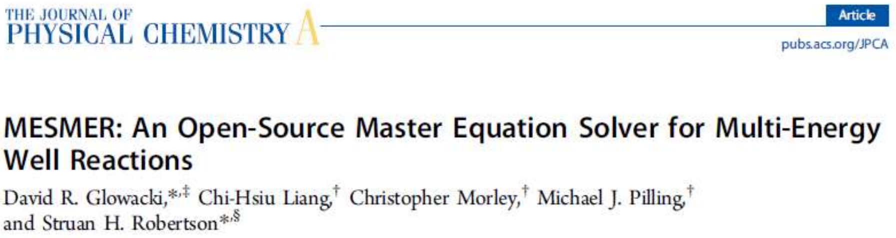
$A+B \rightleftarrows C \rightleftarrows D \rightarrow E+F$

Competition between relaxation and reaction



The number of CSEs is equal to the number of wells + sources. In the present case - 3. If the final step to E+F is reversible, then there are 4 CSEs, but the system is conservative and the smallest eigenvalue is zero.

- Numerically smallest eigenvalues related to phenomenological rate constants (chemically significant eigenvalues)



THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

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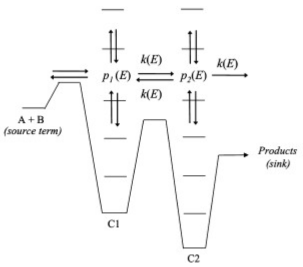
MESMER: An Open-Source Master Equation Solver for Multi-Energy Well Reactions

David R. Glowacki,[*,‡] Chi-Hsiu Liang,[†] Christopher Morley,[†] Michael J. Pilling,[†] and Struan H. Robertson[*,§]

J. Phys. Chem. A 2012, 116, 9545−9560

Abstract

.......Master Equation Solver for Multi-Energy Well Reactions (MESMER), a user-friendly, object-oriented, open-source code designed to facilitate kinetic simulations over multi-well molecular energy topologies where energy transfer with an external bath impacts phenomenological kinetics. MESMER offers users a range of user options specified via keywords …….



Master Equation Solver for Multi-Energy well Reactions (MESMER)

- Open source, object oriented code (C++).
- http://sourceforge.net/projects/mesmer/
- Facilitates kinetic simulations of multi-well systems where energy transfer with a bath gas impacts phenomenological kinetics.
- Provides interface with results of electronic structure calculations to allow set up of multi-well system.
- Output choices include chemically significant (and other) eigenvalues, species concentrations vs time, phenomenological rate constants.
- Allows fitting to experimental data using χ^2 minimisation.
- Includes MPI parallelization.
- Allows fitting to experimental decay traces.

Other master equation approaches

1. Multiwell. Uses a stochastic approach rather than the matrix methodology used in MESMER. Developed by John Barker. See:

   http://clasp-research.engin.umich.edu/multiwell/. and Int J Chem Kinet. 33, 232-45 (2001), 41, 748-763 (2009)

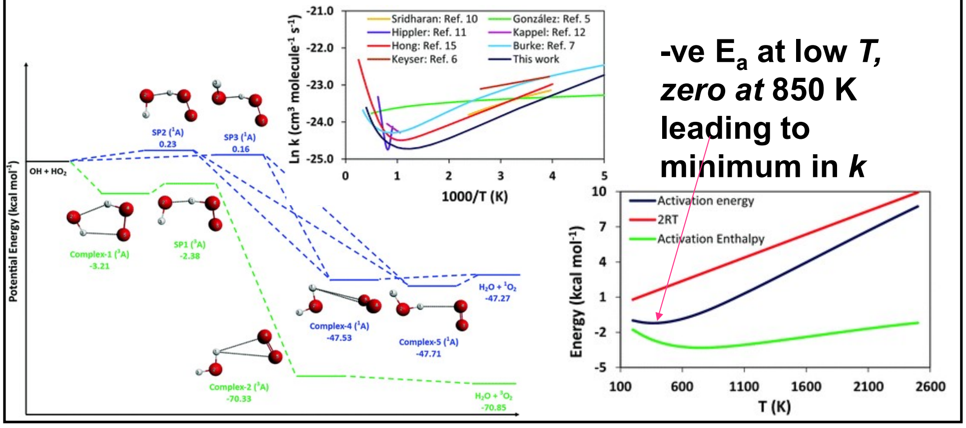
2. MESS. A matrix method, developed at Argonne National Labs by Georgevskii et al. See: http://tcg.cse.anl.gov/papr/codes/mess.html

   J. Phys. Chem. A 2013, 117, 12146−12154

Master equation
Some examples and Discussion of Uncertainties

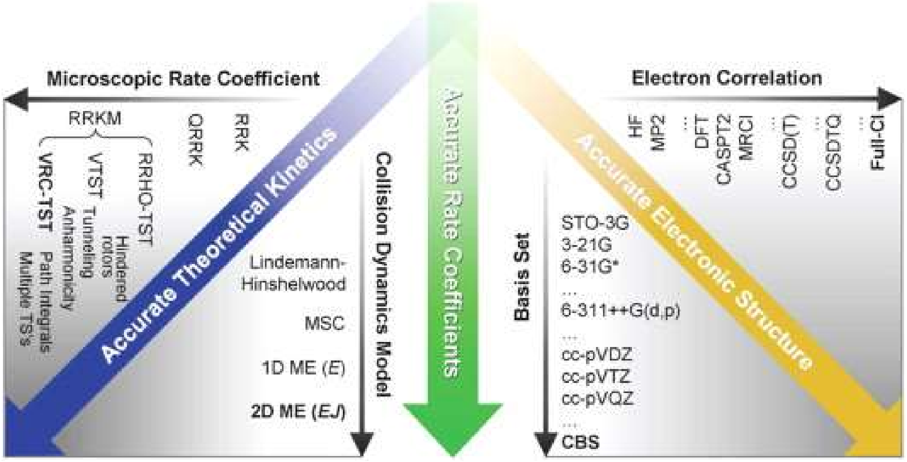
Returning to OH + HO_2

- Theory helps to explain unusual T dependence (Monge-Palacios and Sarathy, 2018).
- PES contains weak Van der Waals complex (CP1).
- Non-Arrhenius temperature dependence observed due to barrier-less reactions with an intermediate complex in the entry channel.



-ve E_a at low *T*, *zero at* 850 K leading to minimum in *k*

Level of detail in rate constant calculations



Uncertainties in derivation of phenomenological rate coefficients from theory: n-propyl radical oxidation

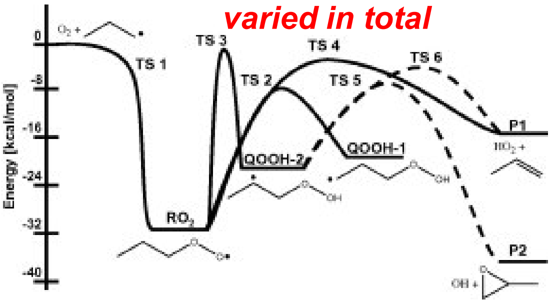
- Like other models Master Equations require a variety of **input parameters** which are **not known exactly**.
  - barrier heights, well depths, vibrational frequencies, collision frequency, and energy transfer parameters.
- Often determined from ab-initio calculations which have differing uncertainties depending on level of theory.
- Few studies emerging that propagate such uncertainties.
  - MESMER also has option to do this.
- Will take Goldsmith et al. (2013) **n-propyl oxidation** as example.
  - Theory used for PES described in Goldsmith (2012).

Inputs to ME

- Variations of ±0.5 and ±1.0 kcal/mol considered for electronic energy relative to O_2 + *n*-propyl for stable species and the transition states respectively.
- For each stationary point 3-5 lowest-frequency vibrations considered uncertain, except for O_2.
- $\langle \Delta E_{down} \rangle = (200 \pm 50\%)(T/298)^{(0.85\pm0.15)}\ \mathrm{cm}^{-1}$.
- Lennard Jones parameters varied by 20%.

67 parameters varied in total

- *Frequencies varied by:*
  - *±20% for hindered-rotors, and transition-state imaginary frequencies (for Eckart tunneling estimates)*
  - *±10% for harmonic vibrations*



Resulting reaction rate distributions

$O_2 + n-C_3H_7 \rightleftharpoons RO_2$ (R1)

$\rightleftharpoons$ QOOH − 1 (R2)

$\rightleftharpoons HO_2$ + propene (R3)

$\rightleftharpoons$ OH + propene-oxide (R4)

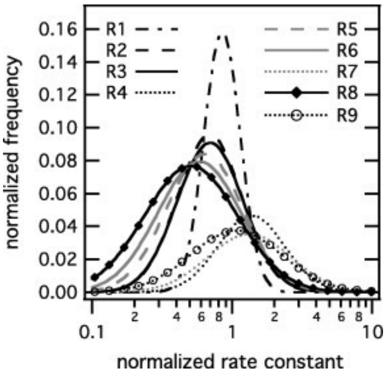
$RO_2 \rightleftharpoons$ QOOH − 1 (R5)

$\rightleftharpoons HO_2$ + propene (R6)

$\rightleftharpoons$ OH + propene-oxide (R7)

QOOH − 1 $\rightleftharpoons HO_2$ + propene (R8)

$\rightleftharpoons$ OH + propene − oxide (R9)



Rates at 3σ variances typically differ from most frequent values by factors of 4–6, decreasing with increasing temperature.

Sensitivity Analysis – which are most influential parameters?

1 atm			100 atm	
Reaction R5 $RO_2 \leftrightarrow$ QOOH-1				
Parameter	S_i, 600 K	S_i, 800 K	S_i, 600 K	S_i, 800 K
TS2 energy	0.667 (–)	0.621 (–)	0.697 (–)	0.701 (–)
RO_2 energy	0.198 (–)	0.169 (–)	0.184 (–)	0.182 (–)
Reaction R6 $RO_2 \leftrightarrow HO_2$ + propene				
TS4 energy	0.665 (–)	0.584 (–)	0.643 (–)	0.627 (–)
RO_2 energy	0.143 (–)	0.074 (–)	0.166 (–)	0.156 (–)
RO_2 $\langle \Delta E_{down} \rangle$ prefactor		0.080 (+)		

$CH_3CH(OH)CH_3$ + OH study (Prager, 2013)

- Importance to low temperature alcohol combustion.
- Branching fractions require extensive isotopic substitution that is difficult for larger alcohols.
  - **See example later for why these are important.**
- Theory therefore necessary and comparisons can be made against total fuel+OH rates from measurement.
- A range of theory calculations were compared for the calculation of optimized geometries and harmonic frequencies of the reactants and the transition state (TS) for the reaction channel:

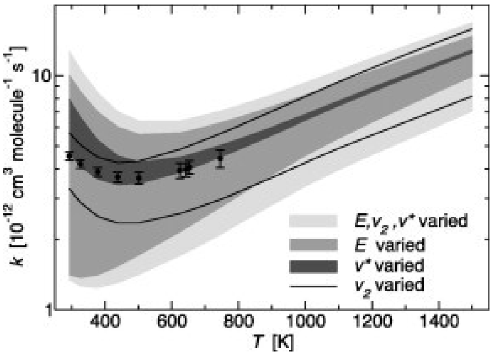
$$CH_3CH(OH)CH_3 + OH \rightarrow CH_3C{\cdot}(OH)CH_3 + H_2O$$

- Methods included DFT, Møller–Plesset perturbation, CASPT2, CBS-QB3, G3B3 and G3MP2 using Gaussian and Molpro.

Results of use of theory only

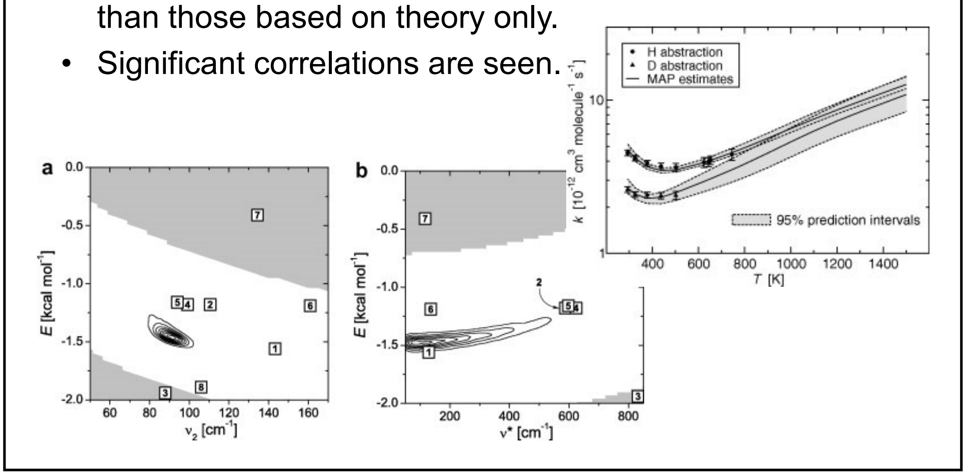
- Considerable scatter in calculated barrier height *E*, ranging from -1.94 kcal mol^{-1} (MP2) to -0.41 kcal mol^{-1} (G3B3).
- Less scatter in calculated frequencies although second lowest frequency v_2, and the imaginary frequency v^* show differences of up to a factor of 1.8.
- These parameters feed into uncertainties in predicted rate constants for the reaction.
- Energy transfer not included in UQ analysis.

Total uncertainty assuming uncorrelated parameters is factor of ~10 at 300 K, decreasing to ~2.5 at 800 K.



Combining theory with experiment

- Bayesian inference used to constrain input parameter distributions using available experimental data.
- Posterior distributions much more tightly constrained than those based on theory only.
- Significant correlations are seen.



Which theory is best?

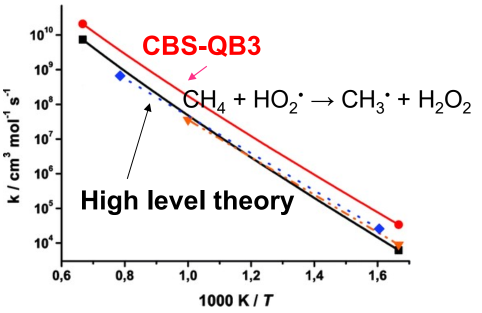
- Can we even answer this question?
- CASPT2 (multi-reference second-order perturbation theory), M062x, B3LYP (the two DFT methods), and CBS-QB3 (composite method) give energies close to the posterior estimates of *E.*
- However, B3LYP and CBS-QB3 yield values of v_2 larger by ~50% compared to the posterior estimates.
- CASPT2 and M062x predict imaginary frequencies v^* much higher than the posterior estimate.
- The TST calculations are however found to be consistent with the experimental data within their suggested uncertainties.

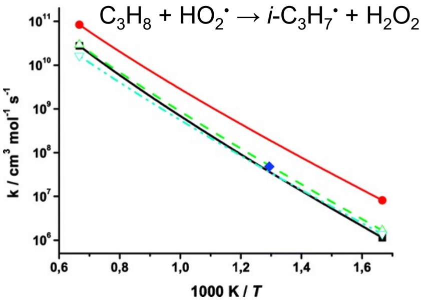
Use of benchmark calculations (Aguilera-Iparraguirre et al., 2008)

- Study of: $CH_4 + HO_2^\bullet \rightarrow TS^\ddagger \rightarrow CH_3^\bullet + H_2O_2$

using level of ROHF-CCSD-R12 theory. Extrapolated to give rate coefficients for higher alkanes + HO_2. Compared with CBS-QB3.

- Electronic wave functions depend explicitly on all of the electron−electron distances
  - capable of yielding results close to those that would be obtained in a complete basis set of atomic orbitals.





Use of MESMER to fit experimental data

- MESMER has a fitting facility that uses the Marquardt algorithm to fit to extensive sets of experimental data by minimising χ^2.
- The method is often **linked to electronic structure calculations of the PES**, with sensitive parameters (e.g. a transition state energy) allowed to float in the fitting process.
- Other parameters that are often fitted include those for energy transfer.
- MESMER can cope with different experiments using different bath gases.
- It is difficult to calculate association rate constants accurately (see earlier), but MESMER allows them to be fitted to experimental data using inverse Laplace transformation (ILT).

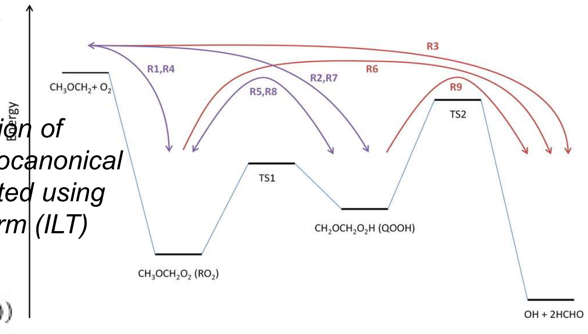
Can theory be used to optimise experimental design?

- PES parameters may be constrained further using experimental data.
- By using sensitivity analysis of the ME can we determine which experimental conditions will best constrain inputs such as barrier heights, frequencies etc. ??
- Shannon et al. (2015) applied this approach to the DME oxidation system. CBS-QB3 theory used within Master Equation.
- Energy transfer:

$$\langle \Delta E \rangle_{\mathrm{down}} = \langle \Delta E \rangle_{\mathrm{down,ref}} \left(\frac{T}{T_{\mathrm{ref}}} \right)^{d}$$

- *For barrierless association of CH_3OCH_2 with O_2, microcanonical rate coefficients calculated using inverse Laplace transform (ILT) method.*

$$k_a(T) = A \left(\frac{T}{T_0} \right)^{n} \exp(-E_a/(k_B T))$$

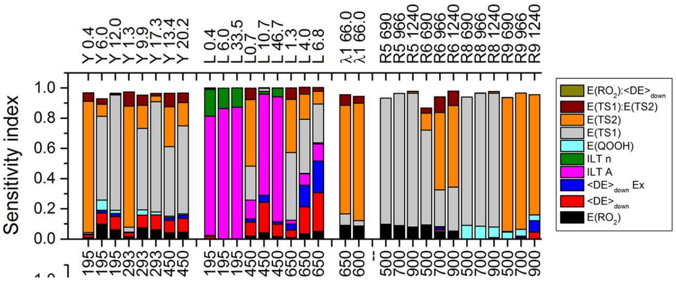


Uncertain parameters

	lower	upper
$E(RO_2)$/kJ mol^{-1}	−149.8	−141.4
$\langle \Delta E \rangle_{down}$/cm^{-1}	100.0	250.0
d	0	1
ILT *A*	0.8	2
ILT *n*	−1.0	−0.2
E(QOOH)/kJ mol^{-1}	−108.8	−100.4
E(TS1)/kJ mol^{-1}	−62.7	−35.1
E(TS2)/kJ mol^{-1}	−29.26	8.3

- *Prior uncertainties are effectively estimates.*
- *Previous theory work by Eskola et al. indicated the possible presence of multireference effects for TS2.*
- *Uncertainty bounds may end up being conservative.*

Sensitivity Analysis

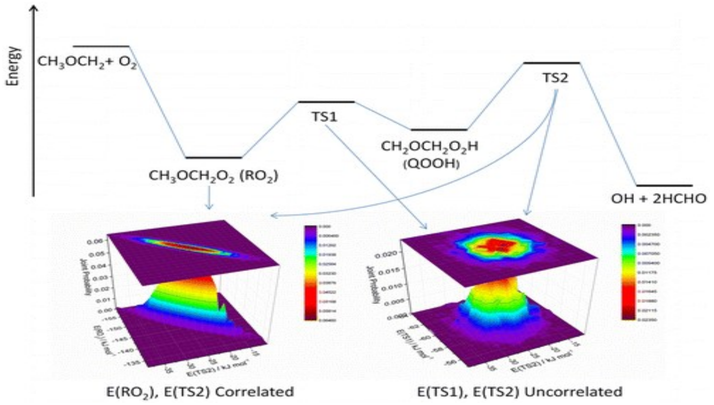


Y - OH yield
L - rate coefficient for CH_2OCH_3 loss,
λ1 - time constant corresponding to longer time formation of OH
R - particular elementary rate coefficient.
Pressure kPa

- A **global sensitivity analysis** was carried out to simulate possible experimental targets.
- Helps determine **which experiments constrain which parameters**.
- Rate coefficients at combustion conditions most sensitive to barrier heights TS1,TS2.
- OH yields best constrain TS1,TS2 and even do this at low pressures where experiments are performed.

Adding experimental constraints

- All eight parameters were defined through Marquardt fitting procedure based on experimental data of OH yields and decay rates at low pressures obtained using LIF.
- Uncertainties for rate coefficients under typical combustion conditions now constrained to within a factor of 2.
- Constrained parameters reveal some strong correlations.

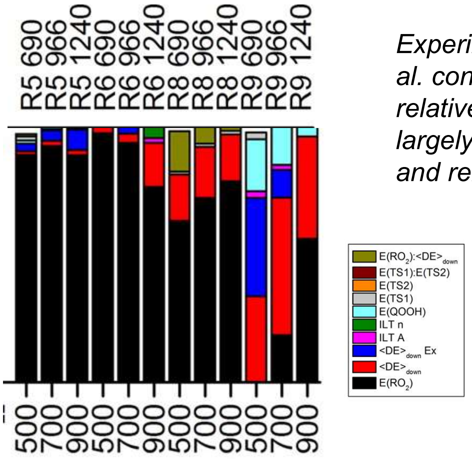


E(RO_2), E(TS2) Correlated

E(TS1), E(TS2) Uncorrelated

Remaining Uncertainties

- Remaining uncertainties dominated by E(RO_2) which is less well constrained by experiments – but highly correlated with E(TS2).



Experimental results of Eskola et al. constrain E(RO_2) and E(QOOH) relatively poorly, because they are largely confined to low temperatures and relatively low pressures.

Examples show that combining theory and experiment is crucial. See later too.

Extrapolation

- We said at the beginning that models are only useful if we can use them to **extrapolate** to conditions where we have no experimental data.
- Constraining a model across wide ranges of P,T,X_i can often not be afforded in terms of time or cost.
- **BUT** ME model inputs (e.g. barrier heights, frequencies, energy transfer parameters) are not dependent on thermodynamic conditions.
- Hence we can constrain these using combined theory/experiment and use the ME model to extrapolate to new conditions.
  - **Multi-Scale Informatics.**
  - **See earlier examples from Burke et al. and Shannon et al.**
- Watch Mike Burke's Combustion Webinar on this topic.

Final Remarks

- High level theory can increasingly play an important predictive role in determining phenomenological rate coefficients.
- Uncertainties are reducing as the level of theory possible increases with increasing CPU power. But they still remain.
- Theory allows us to understand and interpret experimental studies.
  - This interaction is key to understanding the validity of the more accessible theoretical methods.
- Theory provides a more flexible approach than experiment to determining rate data over a wide range of conditions – it is essential we understand both its strengths and its weaknesses and uncertainties involved.
- **Combined theory/experiment may help us to extrapolate**.

SECTION 3
CONSTRUCTION OF REACTION MECHANISMS

Constructing Chemical Mechanisms - Manual

- Historically mechanisms result from careful development work by experts.
- Begins with the selection of important species:
  - **reactants and products**
  - important **intermediates** necessary to predict production rates of key products or key quantities such as ignition delays, flame speeds or dynamic features such as extinction and oscillations.
- Types of reactions that can occur between these coupled groups of species then need to be specified along with appropriate thermochemical data.
- Over time, growing expertise led to **protocols** for different types of application.
  - Indicate ***reaction classes*** for each category of important species.
- Typically, certain reaction classes ignored if
  - rates very slow compared to overall time-scales of interest,
  - they are too endothermic or 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).

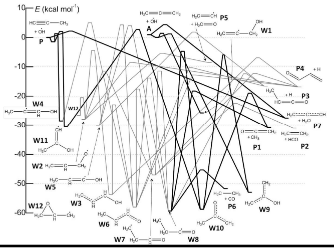
The concept of reaction classes

(Blurock, Battin-LeClerc, 2013)

- Developing detailed combustion mechanisms for oxidation of fuels with a large number of C atoms presents challenges in mechanism production philosophy.
  - Not possible to source parameters exclusively from experiments/detailed theory.
  - Estimates of reaction rate constants/thermo must come from physical/chemical principles based on fundamental kinetic studies for a smaller number of fuels.
- One way of encompassing 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 molecules 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 coefficients** 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, Curran et al., 1998)

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 $C_2H_5O_2$
8. Alkenyl radical decomposition
9. Alkene decomposition
10. Retroene decomposition reactions

Fuel molecule breaks apart

Something pulls off a H atom leaving alkyl radical

Alkyl radical either breaks apart or internally reorganises to new structure etc. etc.

Examples of Low Temperature Reaction Classes

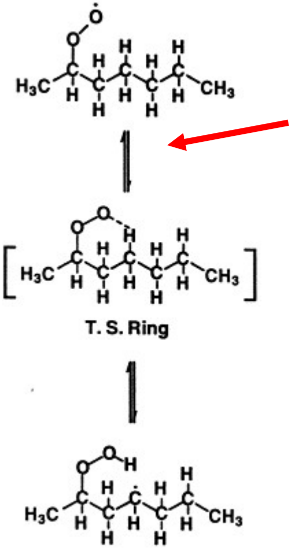
(e.g. RH any general alkane, Sarathy et al. 2011)

LOOK OUT FOR THESE IN EXAMPLES LATER

11. **Addition of O_2 to alkyl radicals ($R + O_2 = ROO$)**
12. R + ROO = RO + RO
13. $R + HO_2 = RO + OH$
14. $R + CH_3OO = RO + CH_3O$
15. **Alkyl peroxy radical isomerization (ROO = QOOH)**
16. Concerted eliminations (ROO = alkene + HO_2)
17. $ROO + HO_2 = ROOH + O_2$
18. $ROO + H_2O_2 = ROOH + HO_2$
19. $ROO + CH_3O_2 = RO + CH_3O + O_2$
20. $ROO + ROO = RO + RO + O_2$
21. ROOH = RO + OH
22. RO decomposition.
23. QOOH = cyclic ether + OH (cyclic ether formation)
24. QOOH = alkene + HO_2 (radical site beta to OOH group)
25. QOOH = alkene + carbonyl + OH (radical site gamma to OOH group)
26. **Addition of O_2 to QOOH ($QOOH + O_2 = OOQOOH$)**
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 HO_2
30. Decomposition of large carbonyl species and carbonyl radicals

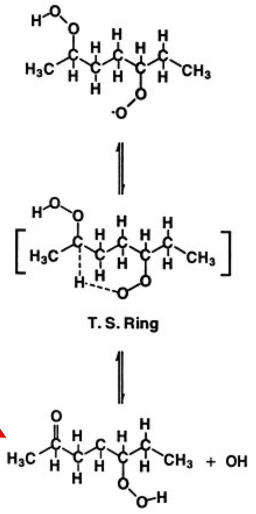
Typical low temperature chain branching route for alkanes

Example of RO_2 and QOOH isomerisation (Curran et al., 1998)



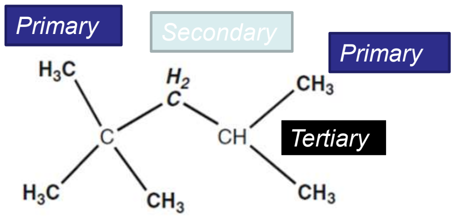
RO_2 to QOOH

O_2QOOH to ketohydroperoxide + ȮH



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

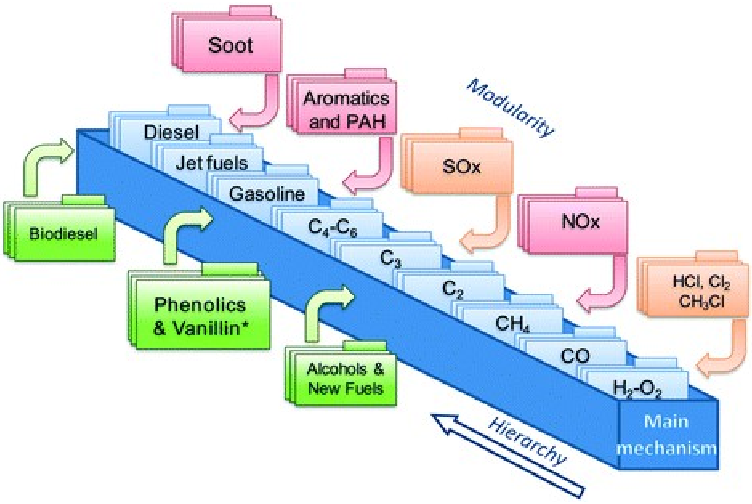
Table 2.1 Rate constants for alkylic hydrogen atom abstractions, expressed in the form $k = A T^b \exp(-E/RT)$, with the units cm^3, mol, s, kcal, by hydrogen atoms which can be abstracted (Buda et al. 2005)

H-abstraction	Primary H			Secondary H			Tertiary H		
by	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
·H	6.98	2	7700	6.65	2	5000	6.62	2	2400
·OH	5.95	2	450	6.11	2	−770	6.06	2	−1870
$\cdot CH_3$	−1	4	8200	11.0	0	9600	11.00	0	7900
$HO_2\cdot$	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



Pelucchi , 2019

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 H_2/O_2 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.

Automatic Reaction Generation Methods

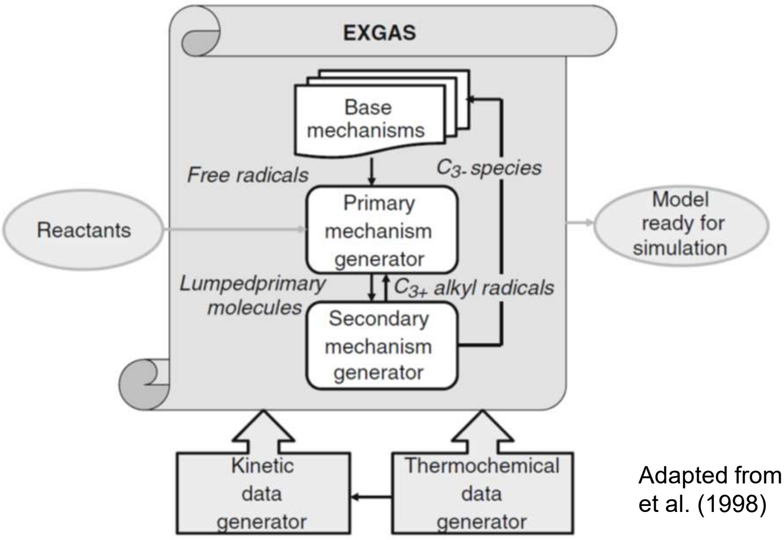
- Several reasons why this is important for mechanisms describing the oxidation of larger and more complex fuels:
  - simply too large a task for a single human
  - humans make mistakes
  - the production of larger mechanisms has to be careful and systematic to generate what could be mechanisms with 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 **expert system** based on **similar rules and reaction classes** discussed earlier but these are now encoded rather than applied by hand.
- Reduces 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., 1996).
  - 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


EXGAS
Base mechanisms
Free radicals
C_{3-} species
Reactants
Primary mechanism generator
Model ready for simulation
Lumpedprimary molecules
C_{3+} alkyl radicals
Secondary mechanism generator
Kinetic data generator
Thermochemical data generator

Adapted from Warth et al. (1998)

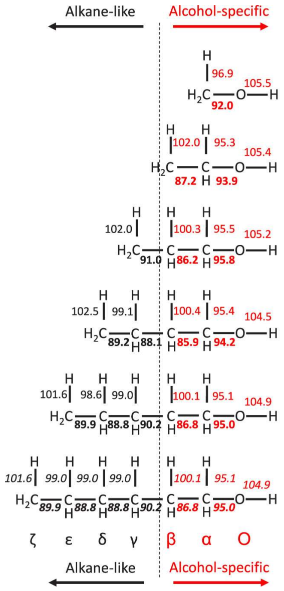
Different AMG codes and specificities

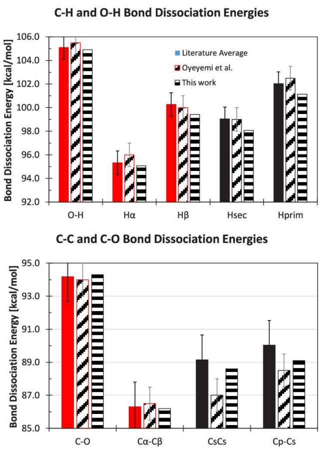
- **MAMOX ++**
  - Produces hierarchy of (highly) **lumped mechan**isms derived numerically from automatically generated detailed mechanisms.
- **EXGAS**
  - Has comprehensive reaction class database and large choice given to user for **mechanism tailoring**: e.g. low *T* vs high *T*, degree of lumping 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 and bond energies** 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, groups included for group additivity calculations.
- The existence of measured data for the reactions of such compounds is pretty SCARSE!

Bond energies for alcohols (Pelucchi, 2020)

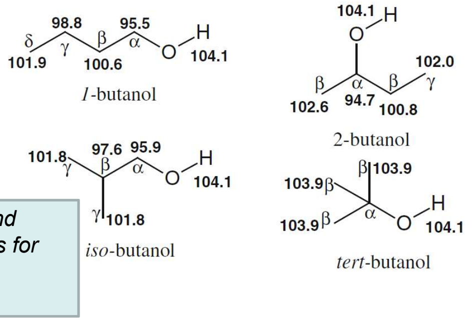




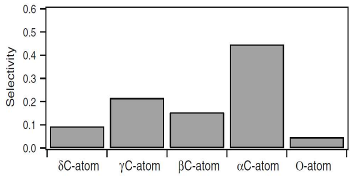
- Derived from theory and ATChTs.
- Will affect H abstraction rates at different *T*s, and therefore low *T* pathways.

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)

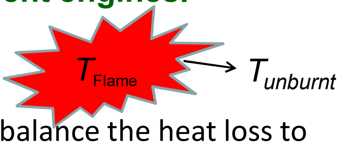
SECTION 4a
Low temperature chemistry and ignition

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.**



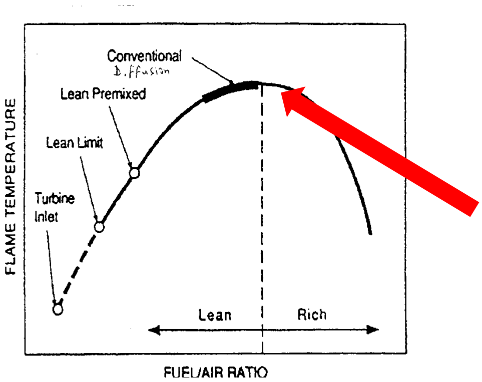
Ignition Condition:

(1) Start reaction – gas, liquid, solid

(2) The heat liberated by ignition must balance the heat loss to the surroundings.

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.



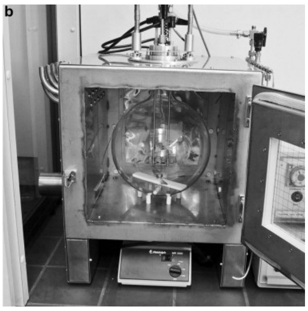
Every concentration has its minimum ignition energy.

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

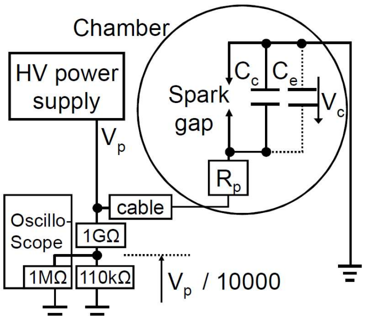
Heat generation rate is the key factor

Measuring minimum ignition energy

MIE is usually measured using high voltage capacitive sparks.



A stainless steel vessel is typically used

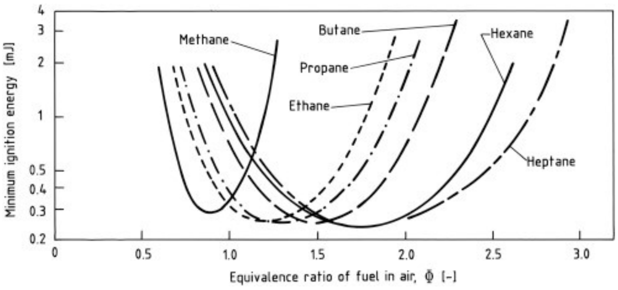


Electrical circuit

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.

Kumamoto et al., 2011

MIE for gases and vapours: hydrocarbons

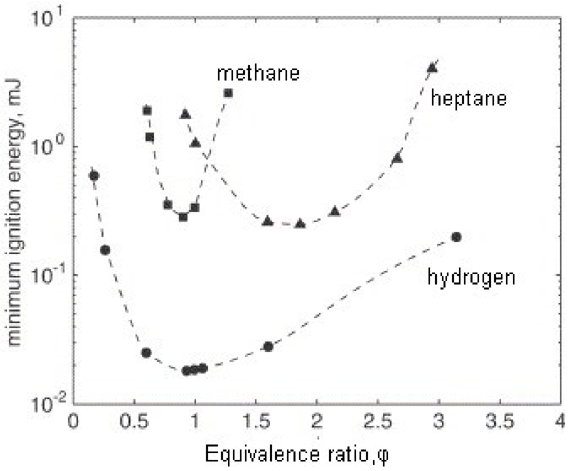


MIE increases near the lean and rich limits, but it is the minimum that is relevant to ignition safety.

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

Note that the **Ø for MIE is rich for higher carbon number HCs.**

MIE for gases and vapours: hydrogen



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

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 H_2/O_2 mixtures

Initiation reactions (generation of first radicals)

	ΔH_J (kcal)	
$H_2 + M \rightarrow H + H + M$	106	*Require lots of heat*
$H_2 + O_2 \rightarrow HO_2 + H$	109	

Chain branching (1 radical makes 2 radicals)

$H + O_2 \rightarrow OH + O$	16	*Require small heat*
$O + H_2 \rightarrow OH + H$	2	

Chain propagation (conversion between radicals)

$OH + H_2 \rightarrow H_2O + H$	-15	*Produce heat*
$H + O_2\ (+ M) \rightarrow HO_2\ (+ M)$	-24	

Termination (radicals are lost to form stable species)

$O + O + M \rightarrow O_2 + M$	-59	*Produce heat*
$OH + H + M \rightarrow H_2O + M$	-58	
$H, HO_2, O, OH \rightarrow$ *wall*		

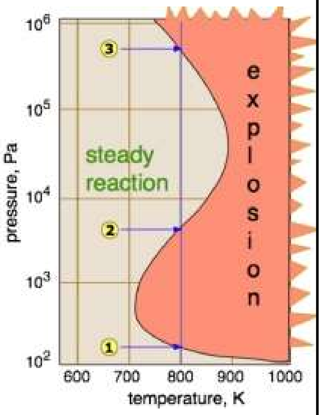
Hydrogen oxidation is controlled by the competition between chain-branching and pressure-dependent chain-propagation reactions:

$H + O_2 = O + OH$

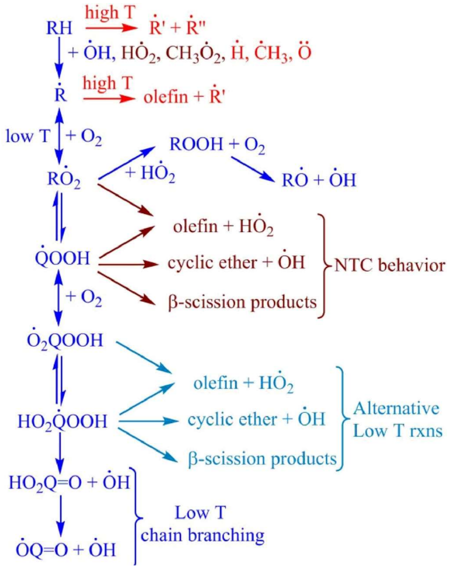
$H + O_2\ (+ M) = HO_2\ (+ M)$

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* ~160–5000 Pa chain branching dominates leading to explosion.
- Above ~5000 Pa (~0.05 bar) $H + O_2\ (+ M) = HO_2\ (+ M)$ 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



General scheme for fuel oxidation (Curran, 2019)

Competition between pathways depends on stoichiometry, T, P

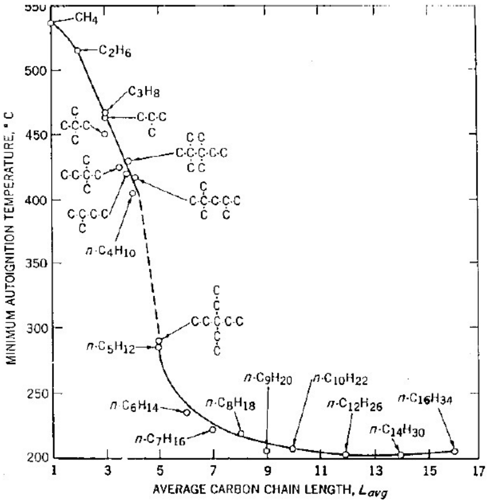
The Auto-ignition Temperature (AIT)

- 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/gasoline	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.

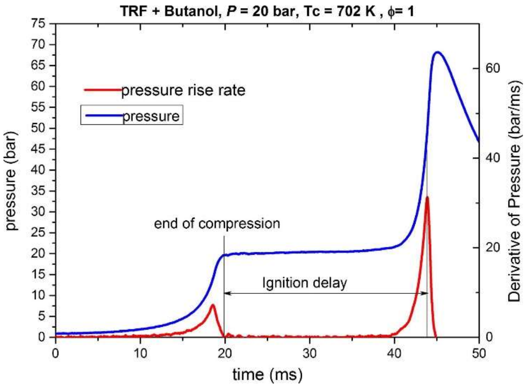
For many of the heavier liquid hydrocarbons the auto-ignition temperature is close to 200°C

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.

Ignition delay times

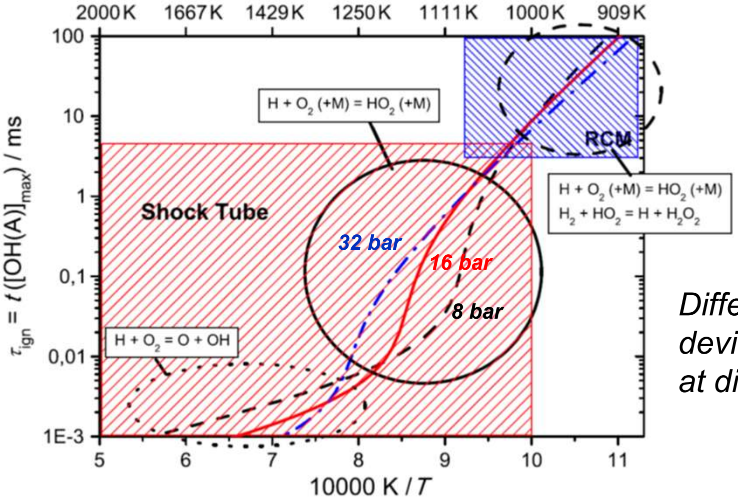
- As well as explosion characteristics we may also study the ignition delay of fuel/air/O_2 mixtures at different *T*,*P*.
- Tells us about reactivity and the ability of a fuel to auto-ignite e.g. under compression within a piston.



TRF + Butanol, *P* = 20 bar, Tc = 702 K , ϕ= 1

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 H_2 + O_2 + 3.76 Ar

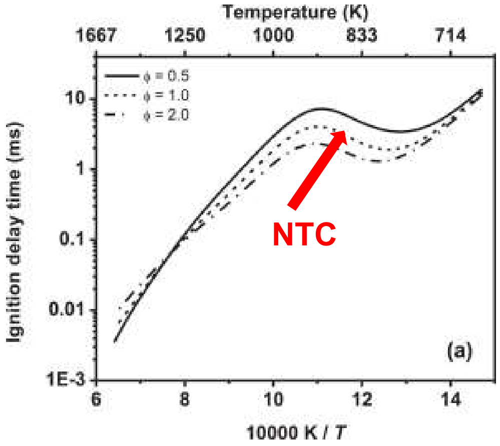


Different devices used at different T.

Kéromnès et al., 2013

Ignition regimes for hydrocarbons

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



Bugler et al., 2016

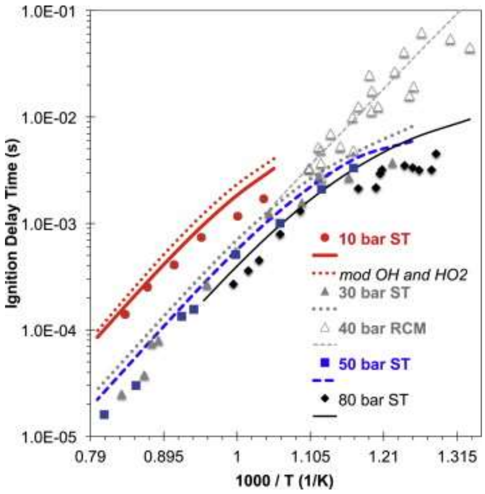
Data shows three distinct temperature ranges of reactivity:

- 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.*

Non- Arrhenius behaviour.

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(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

Initiation

- Alkyl radical decomposition
- Alkyl radical isomerisation

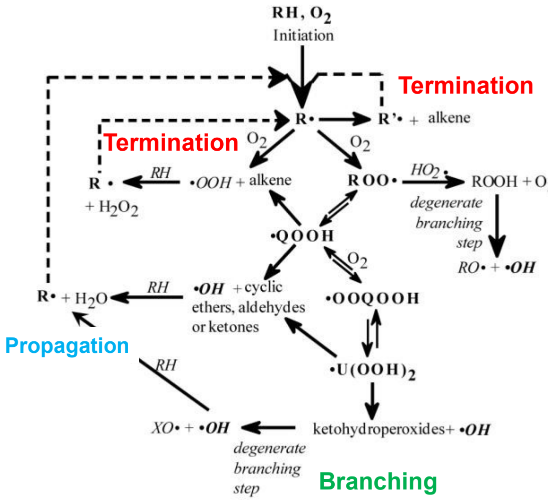
Low temperature reaction classes

- 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

See review by Curran, 2019; Cleaner Combustion, Battin LeClerc et al, 2013

Competition between branching and termination for generic alkane RH



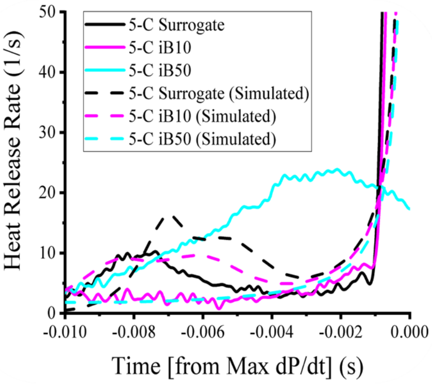
(Battin LeClerc et al., 2011)

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 (RO_2) radicals** which undergo a number of reactions depending on *T* and *P*.
- Most relevant for chain branching is isomerisation of $\mathrm{RO_2}$ via internal hydrogen abstraction onto the oxygen radical site through a transition state ring resulting in formation of **hydroperoxyalkyl radical** (QOOH, where $\mathrm{Q} = \mathrm{R_{H-1}}$).
- QOOH can undergo second O_2 addition with subsequent formation of OH + ketohydroperoxide, which again can form an additional OH. **Branching**
- At lower temperatures $\mathrm{RO_2}$ can reform original alkyl R + O_2 or can dissociate to produce an alkene + $\mathrm{HO_2}$.
- Formation of HO_2 and its fate is key to NTC. It is lower in reactivity than OH and at intermediate temperatures can go on to form H_2O_2.
- H_2O_2 is stable up to higher temperatures and hence its formation reduces overall radical pool, lowering reactivity increasing IDTs.
- At higher temperatures H_2O_2 can decompose to form two OH radicals, thus increasing reactivity again.

Three stage heat release occurring at low *T*

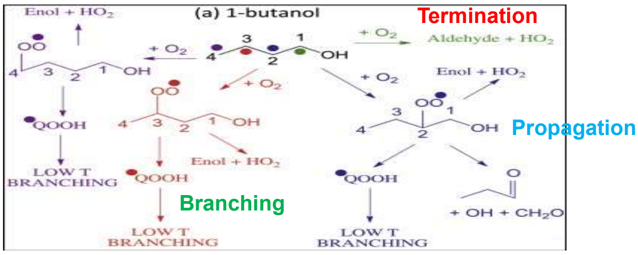


- Michelbach (2021) showed at 710 K that a gasoline surrogate displayed three stage heat release in both experimental and simulated data from RCM.
- Sarathy et al. (2019) reported similar for n-heptane.
- **1st stage** dominated by low T chemistry $RO_2 \rightarrow QOOH$, O_2+ QOOH and, $O_2QOOH \rightarrow$ 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. $OH + HO_2 \rightarrow H_2O + O_2$, $CO + OH \leftrightarrow CO_2 + H$.

Differences between alkanes and short chain alcohols (Sarathy at al., 2014)

- Addition of **iso-butanol supressed low *T* heat release**.
- This is generally true for short chain alcohols, especially ethanol.
- **H abstraction from α-site tends to dominate** due to lower energy barrier, leading to carbonyl + HO_2 pathways being favoured over those leading to QOOH + O_2 which occur for iso-butanol.
- Relative rates for these two abstractions is crucial for predicting ignition for alcohol fuels.
- Same is true for n-butanol – see diagram below.

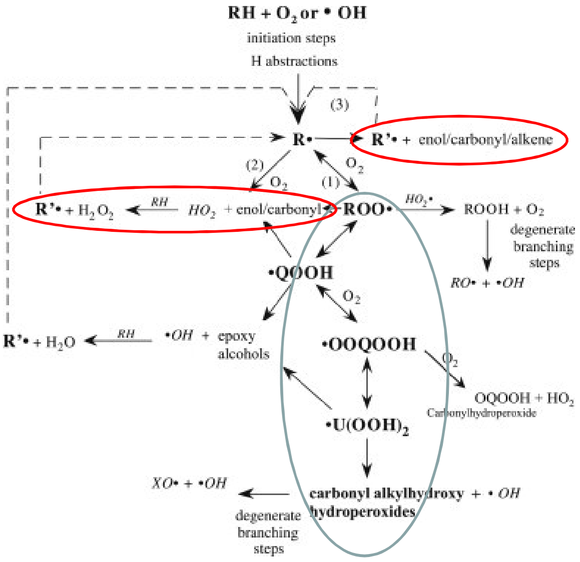


Termination

Propagation

Branching

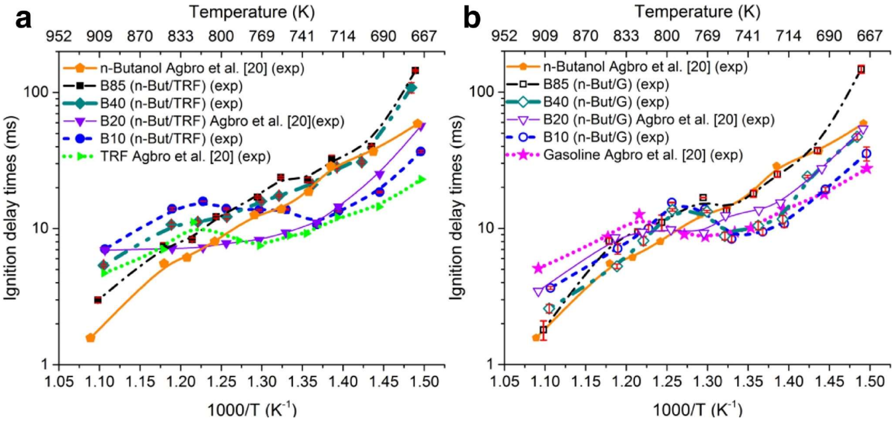
Pathways for linear alcohols (Sarathy, 2014)



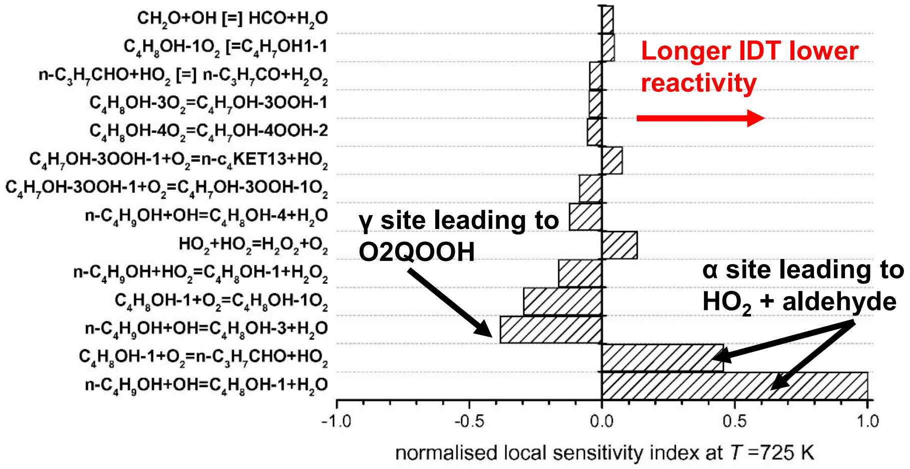
- Site of initial abstraction determines whether branching or termination routes dominate.

Differences between alcohols and gasoline/surrogate – n-butanol

- N-butanol shows Arrhenius response.
- Gasoline and surrogates show NTC which is gradually reduced by addition of n-butanol.



Sensitivity analysis for IDTs – stoichiometric n-butanol in air, 725 K

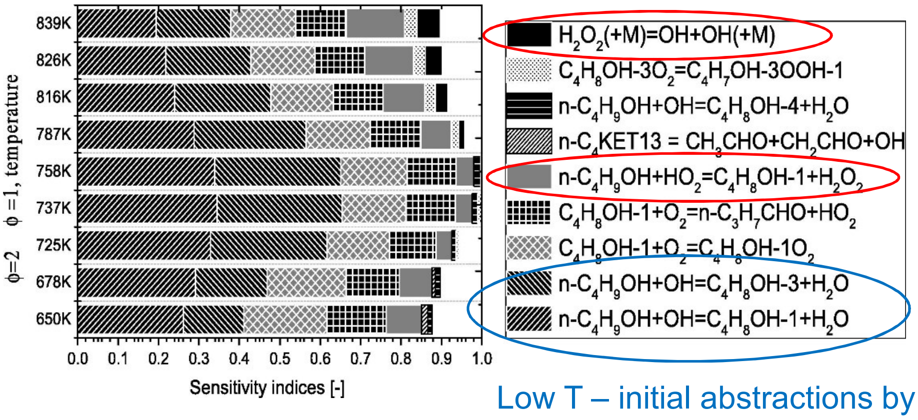


Longer IDT lower reactivity

γ site leading to O2QOOH

α site leading to HO_2 + aldehyde

Global sensitivity analysis – contributions of reaction uncertainties to variance in predicted IDTs (see later)

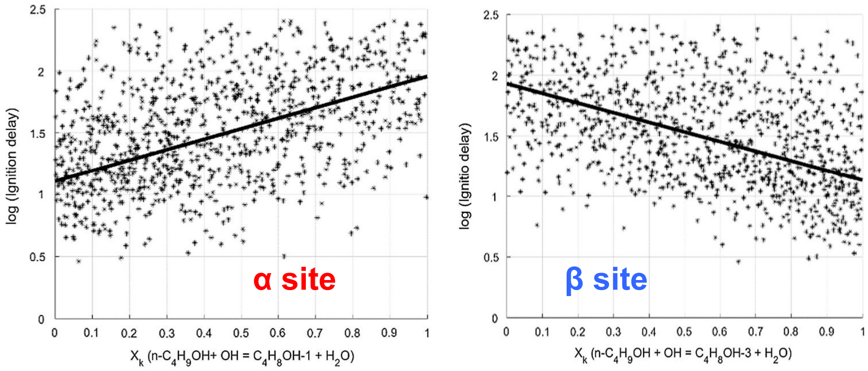


Low T – initial abstractions by OH dominate.

High T – HO_2, H_2O_2 chemistry increases in importance.

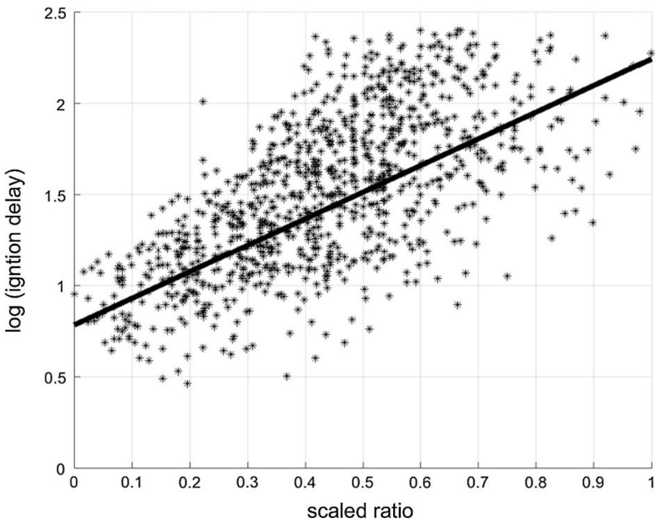
Global sensitivity analysis

Component functions of simulated log IDT on-top of the scatter
a) $n\text{-}C_4H_9OH + OH = C_4H_8OH\text{-}1 + H_2O$ **α site**
b) for $n\text{-}C_4H_9OH + OH = C_4H_8OH\text{-}3 + H_2O$ **β site**
15 bar, ϕ = 1, 725 K.



(a) (b)

Sensitivity to scaled branching ratio for α and γ H abstraction reactions



S index for ratio = 0.7.

S index for total rate of n-butanol + OH < 0.1.

It is the relative and not total rates that matter!

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 ºC).

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.**

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.

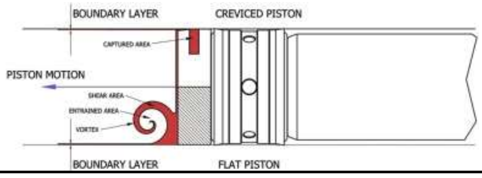
The Leeds RCM

Optimal RCM design features

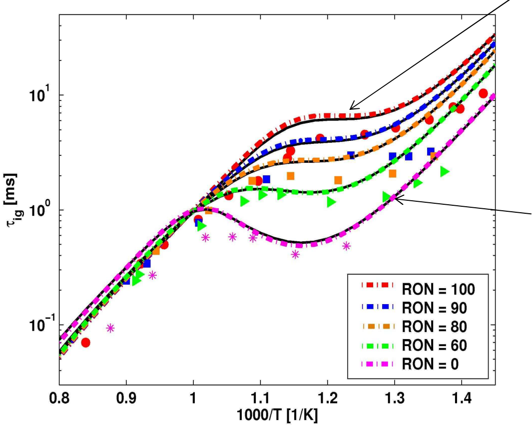
- Fast as possible compression time (10-70 ms) - adiabatic process.
- Constant as possible piston location at the end of compression - breaking and damping.

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



Unreactive fuel – iso-octane
RON = 100

Highly reactive fuel e.g. *n*-heptane – RON = 0

RON = Research Octane Number

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. **Adding octane boosters e.g. alcohols potentially useful.**
- 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.

Cetane number, CN

- Inverse function of a fuel's ignition delay used to define fuels for use in **compression ignition engines**.
- Higher cetane fuels have shorter IDTs than lower ones.
- Comes from cetane n-$C_{16}H_{34}$, which has a defined CN of 100 i.e. very readily ignites under compression.
- Typical range for diesel engine operating well is 48-50.
- Lower CNs mean longer IDTs needing longer for the fuel to combust.
  - Higher speed engines require higher CN fuels.
- Minimum CN in Europe = 51, US = 40.
- **Alternative fuels and their blends must meet standards**
  - See later.

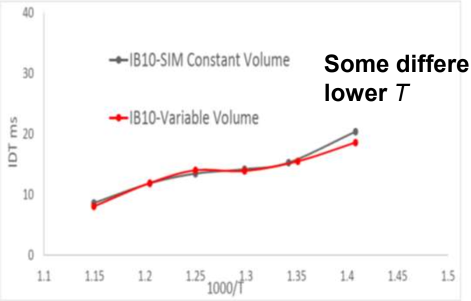
Modelling chemistry within the RCM

- 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.

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

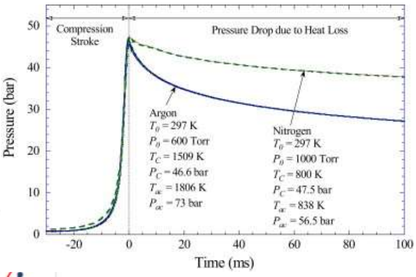
  - γ is temperature dependent ratio of specific heats for the mixture
- Simplest modelling approach closed, constant volume, well mixed reactor - in reality heat losses occur during compression.
- Thus "***non-reactive***" data also obtained using mixture with thermodynamic properties as reactive condition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

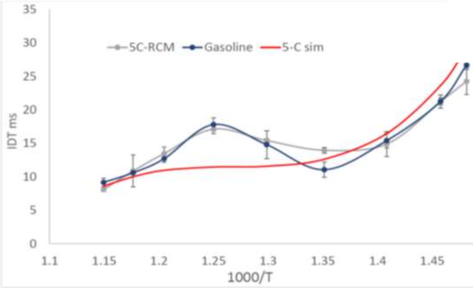
Constant vs. variable volume simulations



Some differences at lower *T*

Sung & Curran, 2014





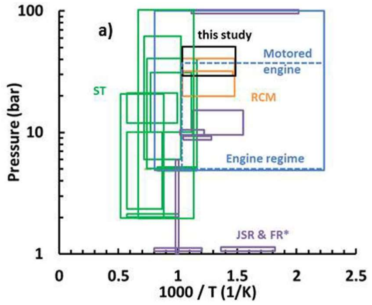
IDT data shows where chemical models are working and are not…e.g. this 5 component gasoline surrogate.

Michelbach, thesis, 2020

New experimental targets from ICM?

Speciation

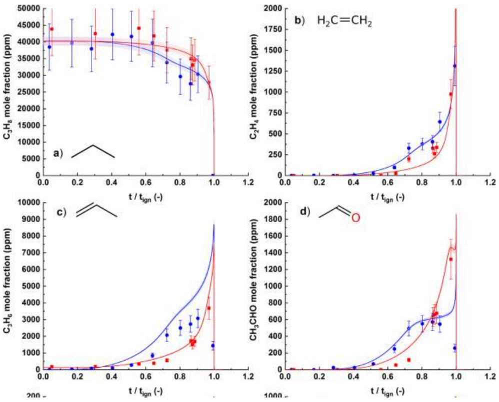
- IDTs can reach high pressures but only provide sensitivities to certain reactions that influence **branching vs termination** reactions.
- Jet Stirred Reactors etc. tend to be at low pressures.
- Need high pressure, low temperature species measurements to extend model validation regime.

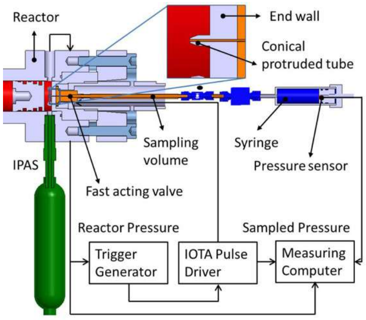


- Sampling method required that provides representative sample i.e. no change in composition due to sampling.
  - quenching entire reactive mixture into a large volume by puncturing diaphragm.
  - fast-acting sampling valve mounted on reactor end-wall which samples from reaction core and quenches into a sampling volume
- Subsequent GCMS and FID.
- See review by Goldsborough et al. 2017.

Example for propane oxidation (Ramalingham, 2020)

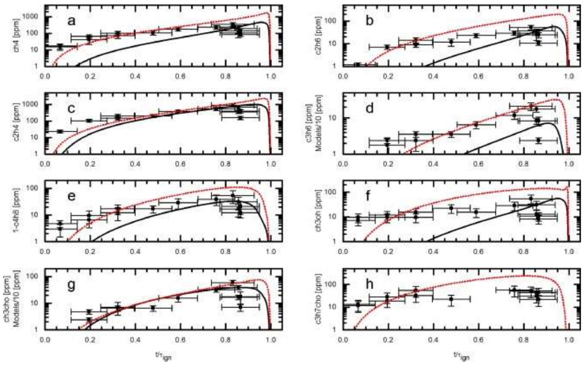
- New targets for species concentrations as function of time.





Example for Methyl *trans*-3-Hexenoate Autoignition (Wagnon et al., 2014)

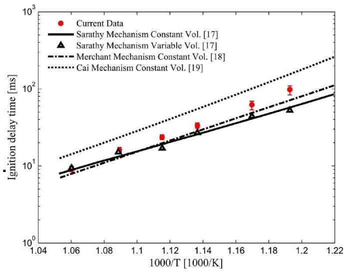
- While ignition delay time predictions were in agreement with experimental data, speciation highlighted uncertainties in the reaction chemistry of unsaturated esters and small hydrocarbon intermediates.

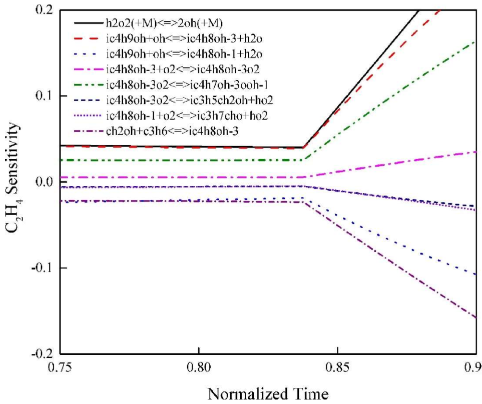


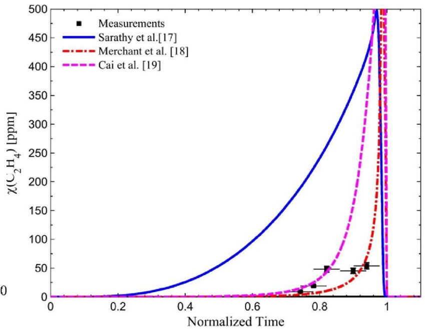
The black solid, and red dotted lines indicate the original and updated model results, respectively. Average conditions for the experiments were T_c = 934 K, p_c = 10.4 bar, φ = 0.30, diluent:O_2 = 3.76.

Iso-butanol example (Ji et al, 2015)

- Species sampling showed that best available mechanism well predicted IDT but:
  - overpredicted ethene by a factor of 6–10
  - underpredicted iso-butene by a factor of 2
  - overpredicted iso-butyraldehyde by a factor of 2.







Heat Release Analysis

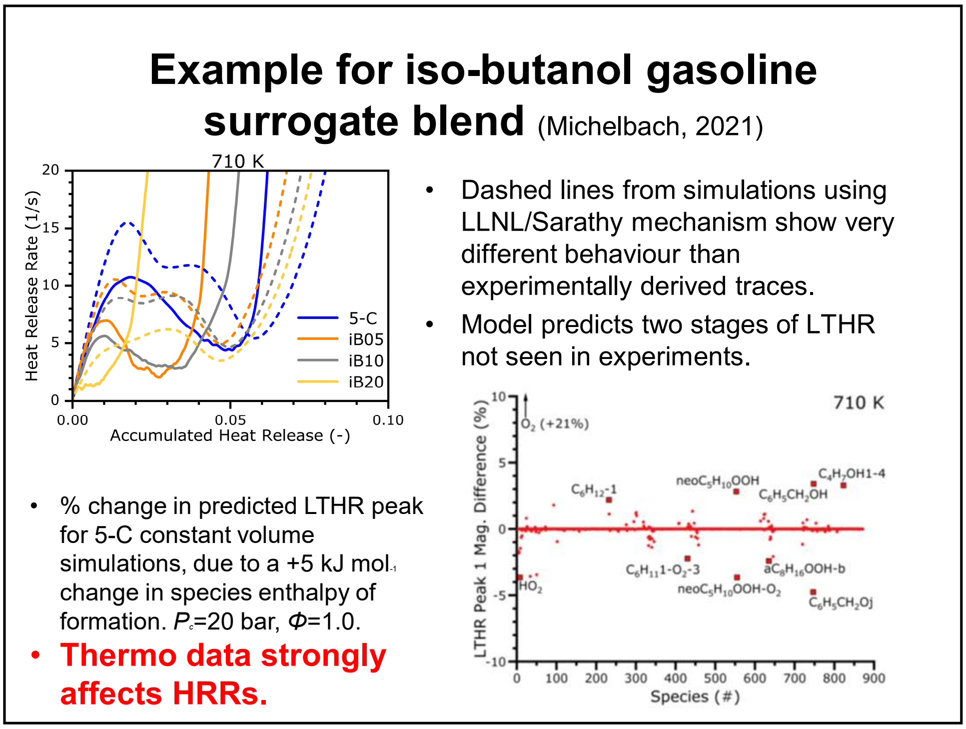
- Goldsborough (2019) developed a method to perform **heat release analysis (HRA)** from pressure traces for RCM experiments.

$$\frac{dU_s}{dt} = \dot{Q}_{chem} - \dot{Q}_{wall} - \dot{W}_{piston} - \dot{H}_{out} + \dot{H}_{in}$$

- U_s - total sensible internal energy, $\dot{Q}_{chem}$ - rate of heat released, $\dot{Q}_{wall}$ - rate of heat exchange with the chamber walls, $\dot{W}_{piston}$ - rate of work done by piston on gas and $\dot{H}_{out}$ and $\dot{H}_{in}$ are the rates of enthalpy flow out and in of the reaction chamber.
- Adiabatic core assumed. Non-reactive experiments used to account for heat losses from chamber.

$$HRR = \frac{\gamma}{\gamma - 1}\frac{dV}{dt}(P - P_{nr}) + \frac{1}{\gamma - 1}V\left(\frac{dP}{dt} - \left.\frac{dP}{dt}\right|_{nr}\right) - \frac{PV}{(\gamma - 1)^2}\left(\frac{d\gamma}{dt} - \left.\frac{d\gamma}{dt}\right|_{nr}\right)$$

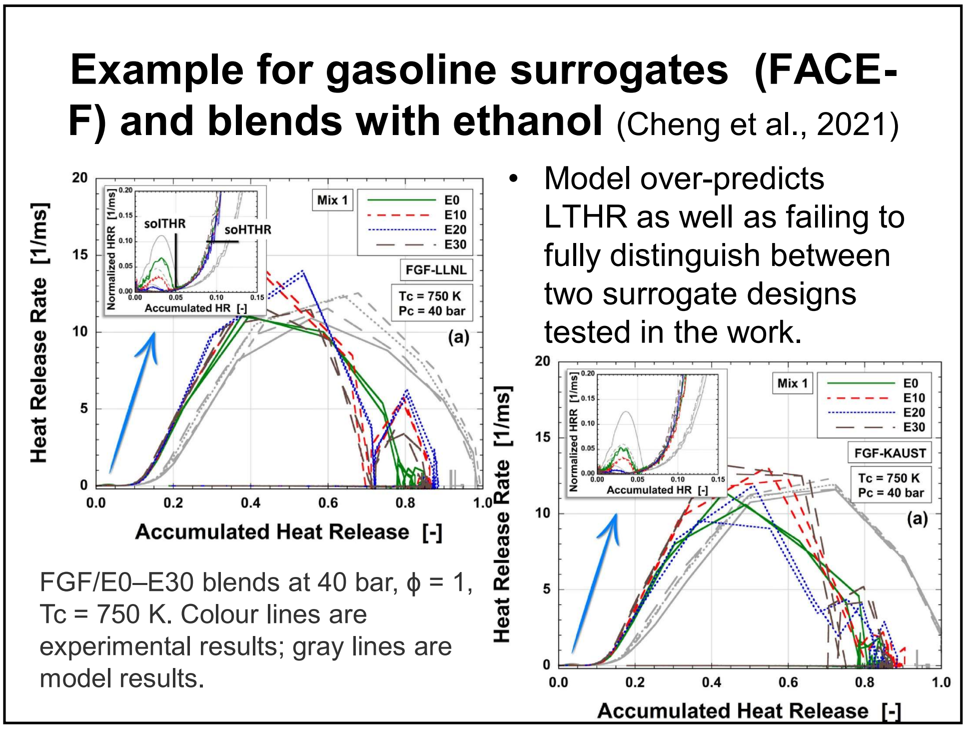
- γ - ratio of specific heats, V - reaction chamber volume (as calculated from the non-reactive pressure history.



Example for iso-butanol gasoline surrogate blend (Michelbach, 2021)

- Dashed lines from simulations using LLNL/Sarathy mechanism show very different behaviour than experimentally derived traces.
- Model predicts two stages of LTHR not seen in experiments.

- % change in predicted LTHR peak for 5-C constant volume simulations, due to a +5 kJ mol^{-1} change in species enthalpy of formation. P_c=20 bar, Φ=1.0.
- **Thermo data strongly affects HRRs.**



Example for gasoline surrogates (FACE-F) and blends with ethanol (Cheng et al., 2021)

- Model over-predicts LTHR as well as failing to fully distinguish between two surrogate designs tested in the work.

FGF/E0–E30 blends at 40 bar, ϕ = 1, Tc = 750 K. Colour lines are experimental results; gray lines are model results.

Categorising fuels

- Some controversy in using simple values of RON and MON within modern engines.
  - Can they be extrapolated to new *T, P* regimes?
- Octane sensitivity *S* (RON-MON) was developed to partially overcome this.
- Kalghatgi (2001) pioneered a practical method to correlate RON and MON to knock-limited spark advance (KLSA) using parameter *K*.
- Octane index OI = RON – *KS.*
- Where *K* is positive, higher OI → better anti-knock quality of fuel.
- In some cases *K* is negative; i.e. for a given RON, a fuel of *lower* MON has better anti-knock quality and will lead to better performance. Depends on engine conditions.

Measuring CN, ON

- Most accurate way to measure CN and RON/MON is in a Cooperative Fuel Research (CFR) engine, under standard test conditions.
- Compression ratio (and therefore peak cylinder pressure) is increased until the time between fuel injection and ignition is 2.407ms.
- Resulting CN calculated by determining the mixture of cetane (hexadecane) and isocetane (2,2,4,4,6,8,8-heptamethylnonane) resulting in same IDT.
- ON, by comparing results with those for mixtures of iso-octane and n-heptane.

Ignition Quality Tester (IQT)

- Fuel injected into constant volume combustion chamber at approximately 575 °C and 310 psi.
- Experimental parameters such as initial charge-air pressure, *T*, chamber wall temperature, oxygen concentration, and mass of fuel injected are well controlled.
- Time between start of injection and recovery of combustion chamber pressure to 310 psi is defined as the IDT.
- Measured IDT used to calculate the derived cetane number (DCN) of the fuel.
- Small sample size and short test time.

Categorising fuels

- ON and OI are simple measures.
- If we knew or could predict the auto-ignition behaviour of fuels across all possible *T*, *P*s we could do better.
- Hence the interest in developing detailed and accurate chemical models that could be used in engine design.
  - **How accurate and reliable are the models???**
- **Which way to go?**
  - Develop accurate models?
  - Perform ignition quality tests for specific conditions, blends and try to extrapolate to engine relevant blends and conditions?
  - Gets more complicated when we add alternative fuels to be blends such as alcohols, biodiesel, furans etc.
    - **Larger molecules, less detailed data, more reliant on estimates for parameters**.
    - Wide range of fuel properties to match (see later).

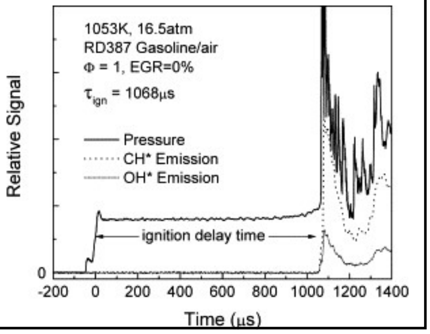
SECTION 4 CONT… MECHANISM VALIDATION VIA FUNDAMENTAL EXPERIMENTS

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

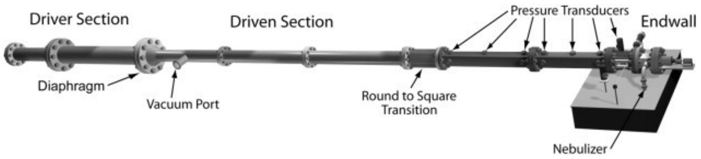
- IDT - time interval between arrival of reflected shock wave and onset of ignition at test location determined by *P* measurements or CH* and OH* emission. (Gauthier et al., 2004)
- Low T measurements limited by available test time
  - interval between the arrival of the reflected shock at the observation 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.



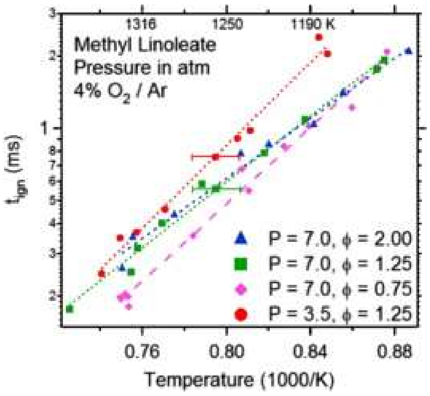
Aerosol Shock Tube

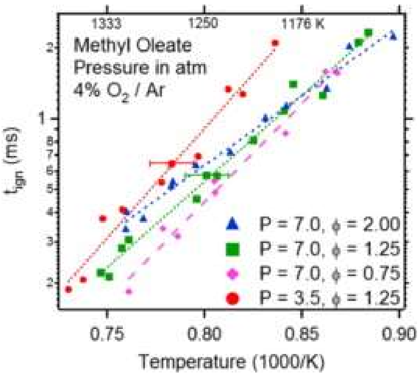
(Davidson, 2008)

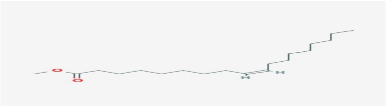
- Developed to enable studies of shock wave interactions with **liquid aerosols**, including droplet evaporation kinetics and subsequent chemical reaction of the vapour.
- Useful for studies of low vapour pressure fuels e.g. long chain hydrocarbons.
- Uniform spatial distribution of aerosol important for well behaved shocks.
- Also need narrow micrometer-sized aerosol size distribution that rapidly evaporates.
- Used for IDT measurements of high carbon number fuels e.g. n-dodecane/O_2/argon and JP-7/O_2/argon mixtures.



Example from aerosol shock tube study - fatty acid methyl esters







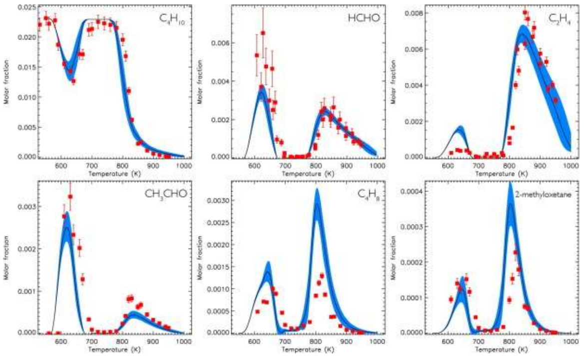
Validation data: Species profiles from Jet Stirred Reactors (JSRs)

- 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

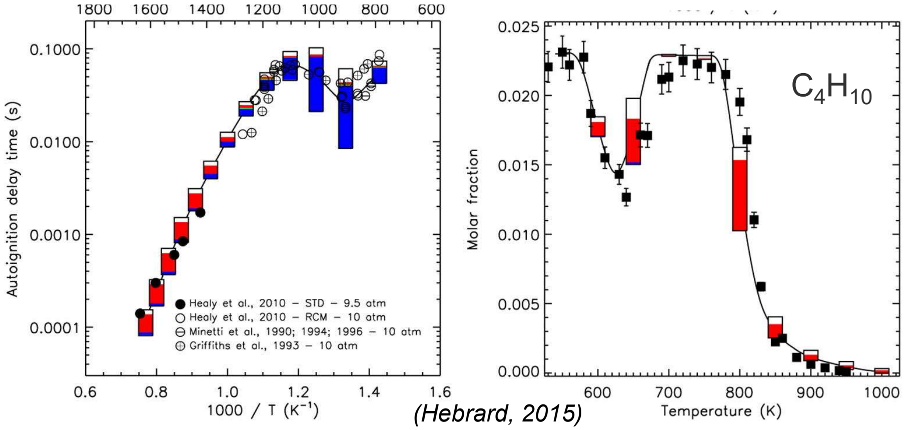


Differences in sensitivities for different targets: IDT vs C_4H_{10} mole fraction in JSR

- **BLUE:** Fuel specific reactions. **RED:** Base C2 chemistry.

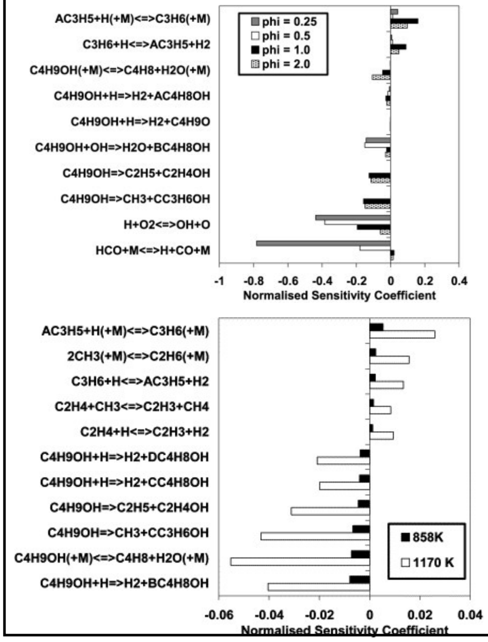
At low *T*, JSR sensitivities dominated by radicals generated from ketohydroperoxides decomposition e.g. $C_2H_5O \rightarrow HCHO + CH_3$

At high *T*, only reactions of HO_2, CH_3, HCHO, less so CH_3CHO



(Hebrard, 2015)

N-butanol study (Sarathy, 2009)



Sensitivity of *n*-butanol to select reactions in

TOP

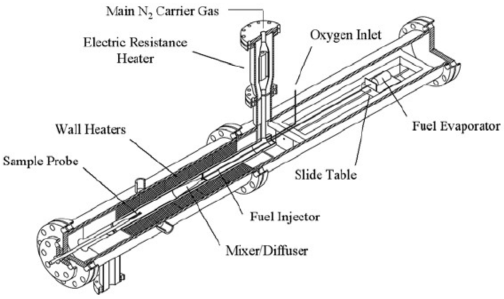
JSR at $\phi = 1$, $P = 1$ atm, $\tau = 0.07$ s, $T = 1160$ K

BOTTOM

Opposed flow diffusion flame.

Fuel decomposition highlighted along with small molecule chemistry.

Variable and atmospheric pressure flow reactors (Dryer etc.)

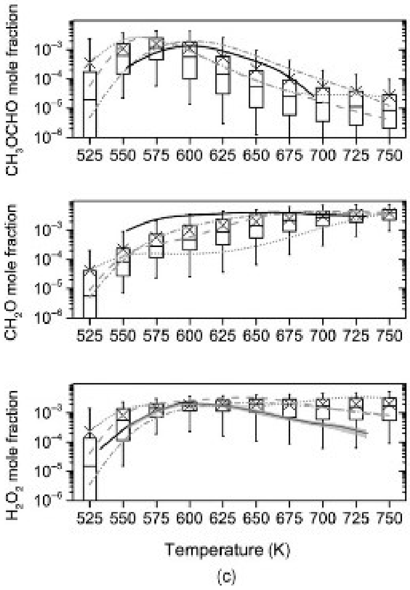


Reaction time varied by moving point of fuel injection

- APFR high temperature facility at atmospheric pressure.
- VPFR can access a wide range of conditions: T (550–1200 K), P (0.3–20 atm), and φ (pure pyrolysis to oxy-gen-rich conditions).
- Carrier gas is a turbulent flow of preheated nitrogen into which oxygen and water vapour are injected and premised to dilute amounts.

- Rapid mixing within quartz diffuser section, gives quasi-steady reaction along the length of a constant-diameter quartz test section.
- Dilute system used to limit heat release and establish quasi-isothermal conditions.

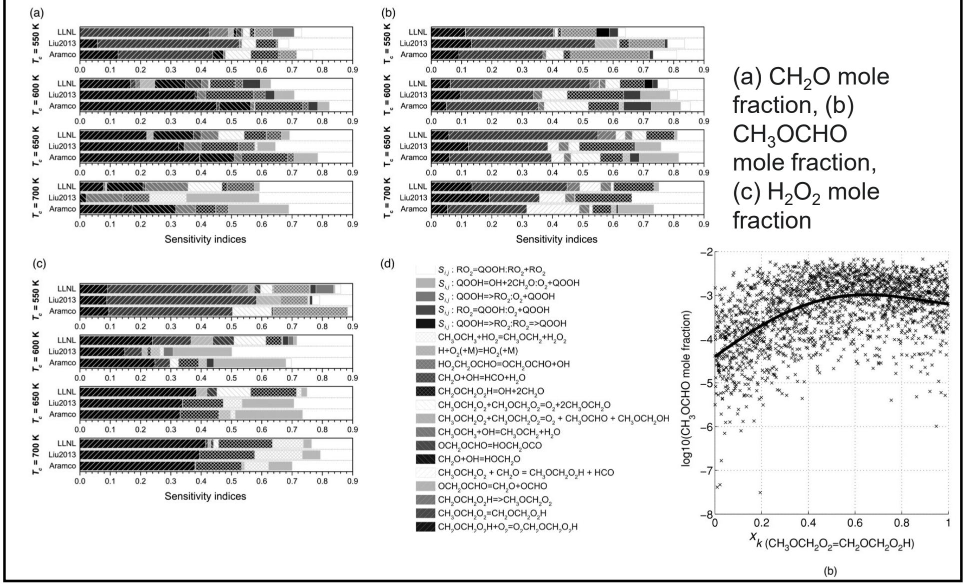
DME oxidation



- Data from Princeton flow reactor (solid line, Guo 2013) is compared against uncertainty profiles from simulations using Aramco Mech1.3 (2013).
- Dashed line original model.
- Boxes and whiskers represent uncertainty percentiles (*25th and 75th*).
- Overlap exists but uncertainty ranges are large
  - ➢ Further model constraints are needed.

Tomlin et al., 2014

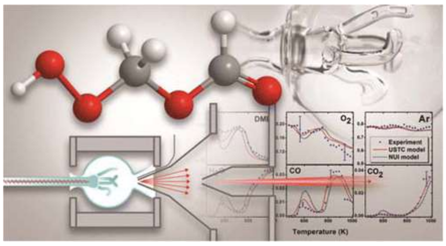
Comparison of sensitivities, DME flow reactor, note mechanism dependencies

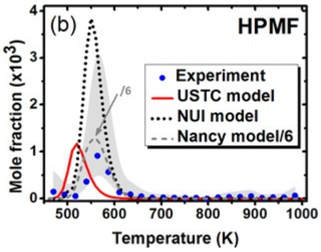


(a) CH_2O mole fraction, (b) CH_3OCHO mole fraction, (c) H_2O_2 mole fraction

Example – quantification of ketohydroperoxides during DME combustion

- Molecular beam mass spectrometry with single-photon ionization via tunable synchrotron-generated vacuum-ultraviolet radiation.
- Quantified profiles for 17 components including hydroperoxymethyl formate ($HOOCH_2OCH_2O$), a key intermediate in low-temperature oxidation of DME.
- Allows stringent model validation.





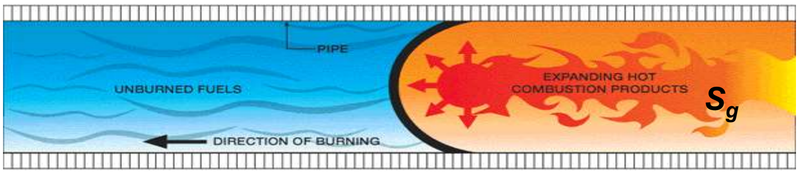
Moshammer et al. 2016

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.

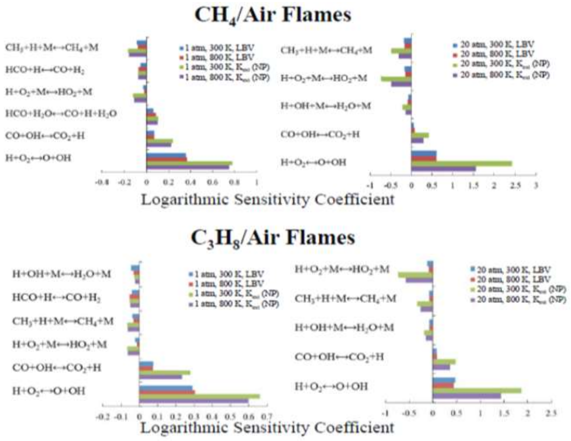


$$\boxed{S_s = S_L + S_g}$$

- 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.

Why does LBV matter?

- Sensitivities for LBV both pre-mixed and non-premixed flames similar to those for extinction so good test of model’s ability to **predict extinction for practical devices**, Egolfopoulos, 2014.
- Useful measure for estimating turbulent burning velocities.



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: $S_L = U_\perp = U_R \times \sin\theta$

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

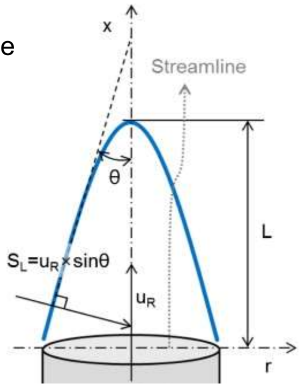
Typically $\theta \sim 30^o$:

For a stable flame: $U_R >= 2 \times S_L$

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

Difficulties in measuring angle/area.

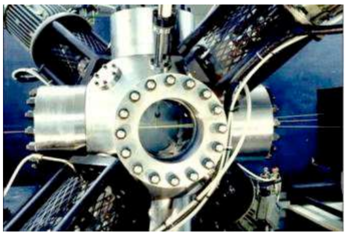
Possible influences of stretch for differential diffusion of reactant species.



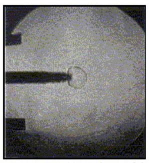
Bunsen burner

Measuring burning velocity - spherical bomb

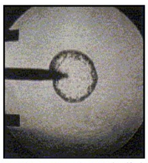
- S_L can also be measured in a constant volume spherical vessel.
- Pressure measurements or Schlieren photography can be used to evaluate burning velocities but requires interpolation.
- Instabilities, curvature and stretch cause measurement difficulties, particularly for pressure method. Need to extrapolate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



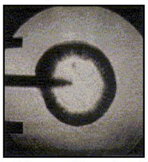
The bomb!



t = 5ms r_f= 9 mm (smooth)



t = 11ms r_f= 22 mm (cellular)

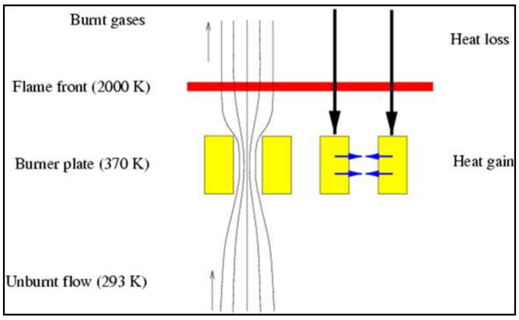


t = 21ms r_f = 35 mm (smooth)

t = 38 ms r_f= 53 mm (cellular)

Measuring burning velocity, flat flame burner

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

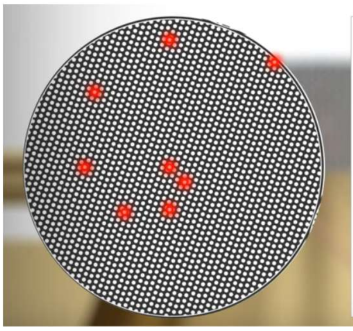


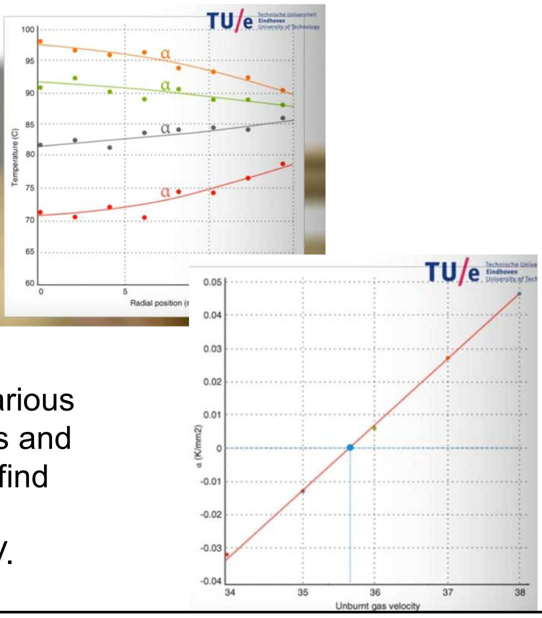
http://cms.heatfluxburner.org/home/

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.

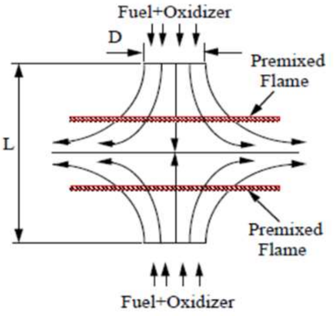
Interpolation method

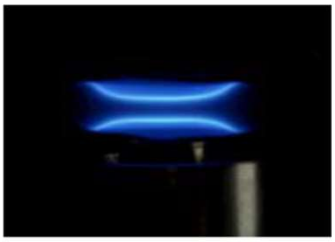




T profiles taken at various unburnt gas velocities and interpolation used to find zero gradient profile corresponding to LBV.

Counterflow flames



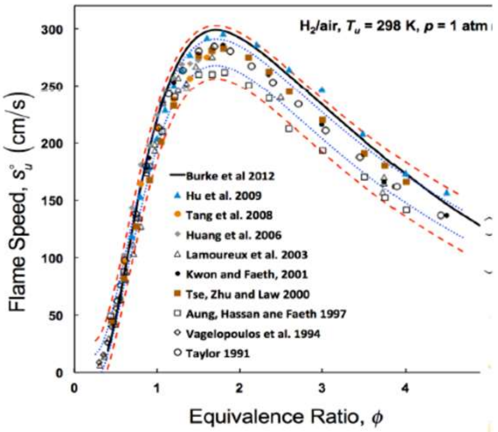


- Wu and Law, 1985 first used for LBV measurements demonstrating the influence of stretch.
- Stagnation flames achieved by:
  - impinging separate fuel and oxidizer streams
  - impinging two premixed streams
  - from a premixed stream impinging on a solid surface.
- Attractive as leads to flat flame 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



Measured flame speed – CH_4 and H_2

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

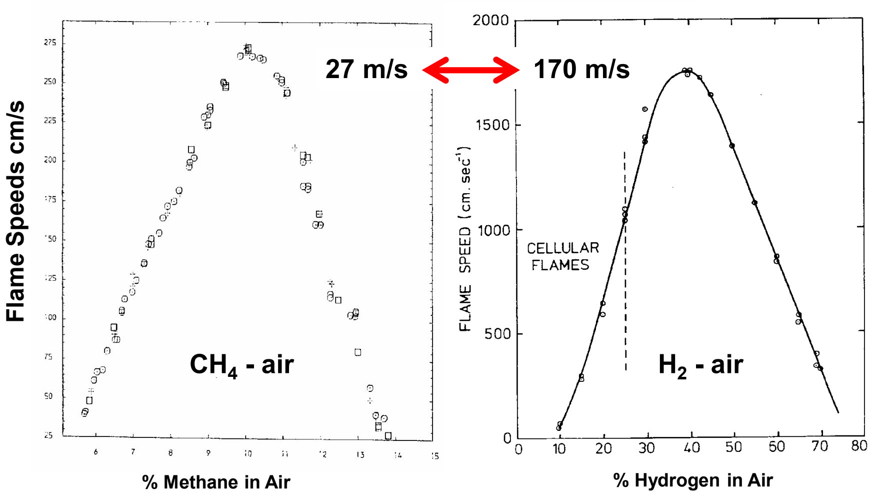
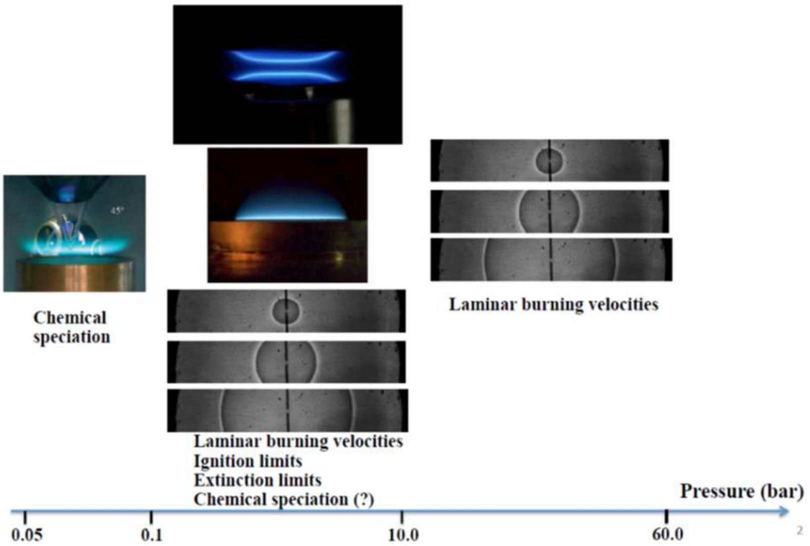


Fig. 8. Flame speeds for hydrogen-air at one atmosphere.

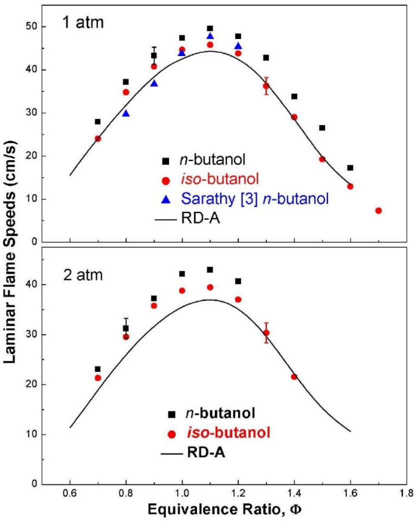
measured in a 0.5 m diameter by 0.5 m long closed vessel

Overall measurables in laminar flames,

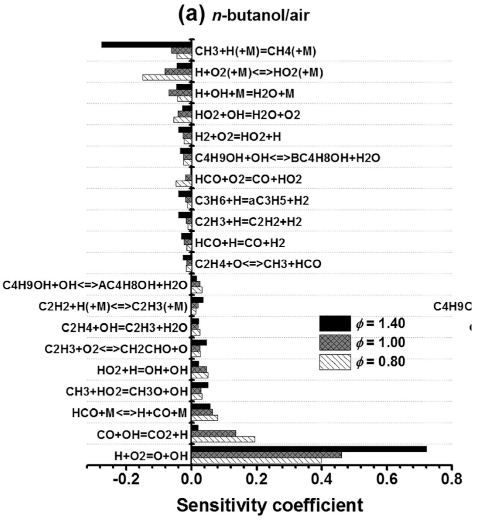
Egolfopoulos, 2014



Examples of flame speed studies - butanols

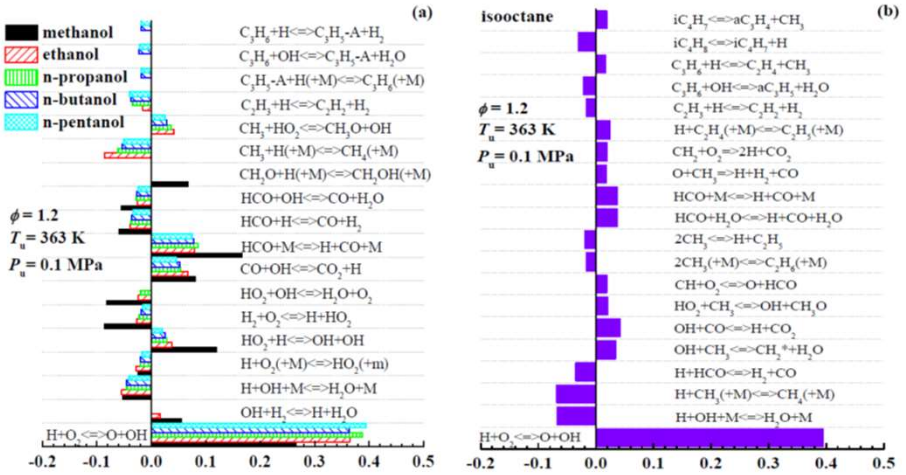


Liu et al. 2011



Sensitivity coefficients of LBVs for (a) n-butanol/air T = 423 K, Pu= 10 atm and ϕ = 0.80–1.40 (Wang et al., 2018).

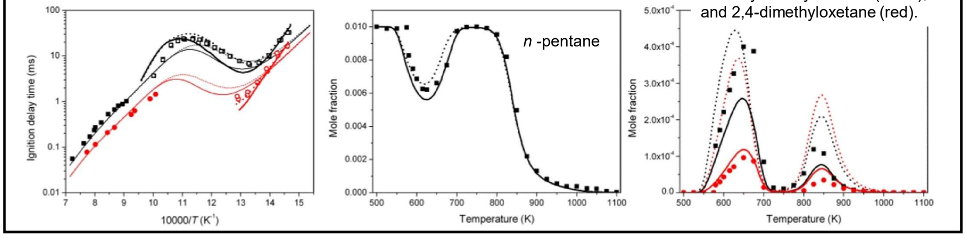
- **Flame speed sensitivities dominated by small molecule chemistry (Li, Energies 2016, 9, 511).**



Normalized rate constant sensitivity coefficients on laminar flame speed for (**a**) pure C1–C5 primary alcohols and (**b**) pure isooctane at 363 K, 0.1 MPa and the equivalence ratio of 1.2.

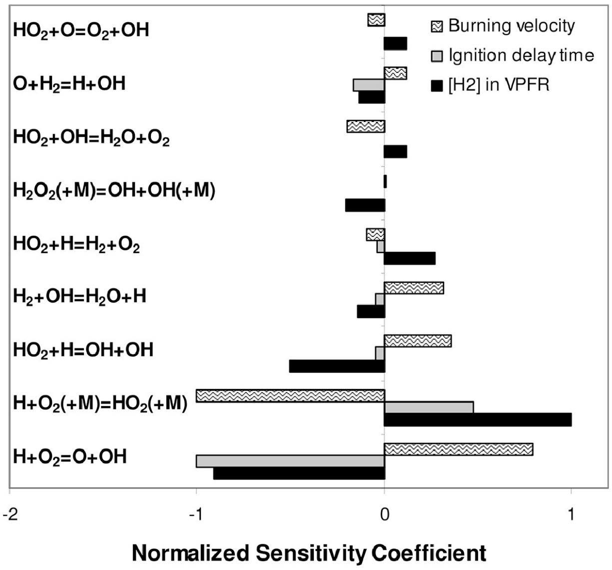
Advantages of using multiple target types- n-pentane ignition and cyclic ether formation

- IDTs for n-pentane, JSR data for pentane mole fraction, well captured by previous model (dashed lines).
- Cyclic ether mole fractions very poor – requiring an update in rate constants for their formation from QOOH.
- Leads to slight increase in reactivity in NTC – due to lowering rate of propagation vs. chain branching reactions.
- Significant improvement in prediction of two major cyclic ethers formed (2-methyltetrahydrofuran and 2,4-dimethyloxetane)
- **NOTE: High level of theory required due to stated deficiencies of CBS-QB3 (Bugler, 2017).**



2-methyltetrahydrofuran (black), and 2,4-dimethyloxetane (red).

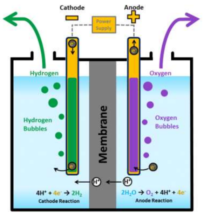
Comparison of sensitivities for different targets (Burke, 2012)



Normalized sensitivity coefficients to A-factors of reaction rate constants for H_2/O_2 combustion.

Overview of validation studies

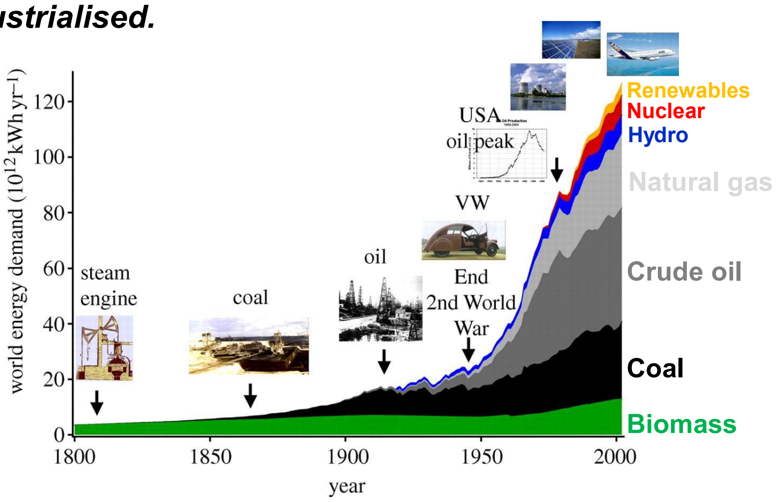
- Each type of experiment tests a chemical model in different ways and a general model should be applicable for all scenarios.
  - **Sensitivity analysis crucial for identifying constraints offered by experiments.**
- Low *T*, **IDT** really mainly depends on predicting **relative rate of branching to 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.
  - Can add heat release rates and speciation to targets.
- **LBV measurements** add high temperature targets for models of relevance to **flame extinction** and turbulent flame propagation within engines.
- **Speciation measurements** in flames, STs 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 5
FUTURE FUELS

Challenges of future fuels

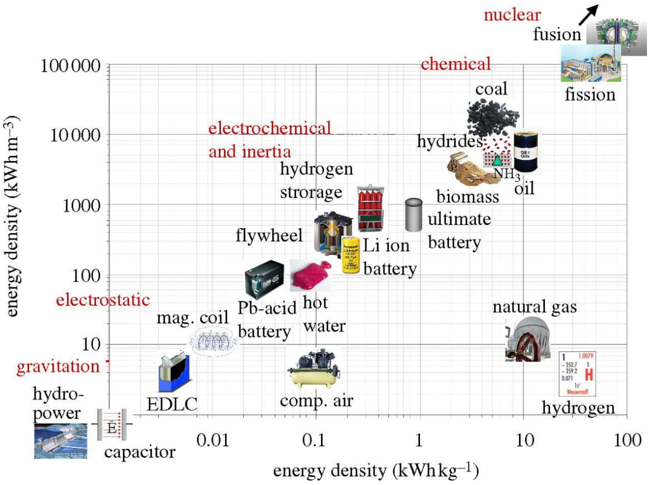
Energy demand has grown rapidly since 1950s as economies have industrialised.



Challenges of future fuels

Solid and liquid fuels provide effective energy storage in terms of mass and volume.

Liquids good for transportation?



Züttel, 2010

Or do they lock us into existing technologies?

Challenges of future fuels

- Change in energy economy from fossil energy carriers to renewable energy fluxes is **necessary**.
- Main challenge to efficiently convert renewable energy into electricity and store it or produce synthetic fuel.
- **Hydrogen** produced from water through electrolysis.
  - **Pros:** Novel storage methods include using hydrides and salt caverns, gas networks are existing infrastructure that could be used for heat provision, no CO_2/CO/soot emissions, low NOx strategies required.
  - **Cons:** Storage is a challenge, system energy density is significantly smaller than liquid and solid fuels.
- **Synthetic hydrocarbons** can be produced from hydrogen and CO_2 extracted from the atmosphere.
  - **Pros:** almost CO_2 neutral, energy dense, stored like fossil fuels, conventional engines and turbines can be used, suitable for hard to electrify sectors (aviation, shipping).
  - **Cons:** High cost, poor overall system efficiency.

Challenges of future fuels

Biofuels – liquid fuels that can be generated from biomass e.g. biodiesel, ethanol, butanol, HVO, ethers, furans.

- Can be generated from a variety of biomass sources including:
  - **First generation**: corn, sugar cane and beets, soya, vegetable oils.
  - **Second generation:** lignocellulosic feedstock classified as not suitable for human consumption e.g. grasses, Jatropha and other seed crops, waste food and vegetable oil, municipal solid waste, waste wood, corn stover.
  - **Third generation:** Algal sources.

Pros:

- Many have similar energy densities to petroleum fuels.
- Can often be used or blended for use in engines without modifications.
- Can lead to lower particulates reducing need for after-treatment.

Cons:

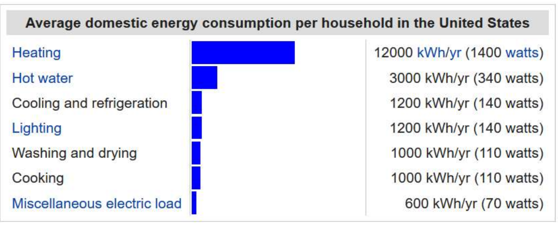
- 1st gen compete with food. EU stipulating increase in 2nd gen components (RED II).
- 2nd/3rd gen more difficult and expensive to produce – breaking down complex bonds. More costly than fossil fuels. Can lead to less stable oils (algae).
- Available biomass resource is not limitless.
- Time-scales are involved in recapturing CO_2 through growth and photosynthesis.
- Potential to encourage mono-cultures.

HYDROGEN

Combustion challenges and opportunities

Opportunities

- Heat is a major sector in energy use.



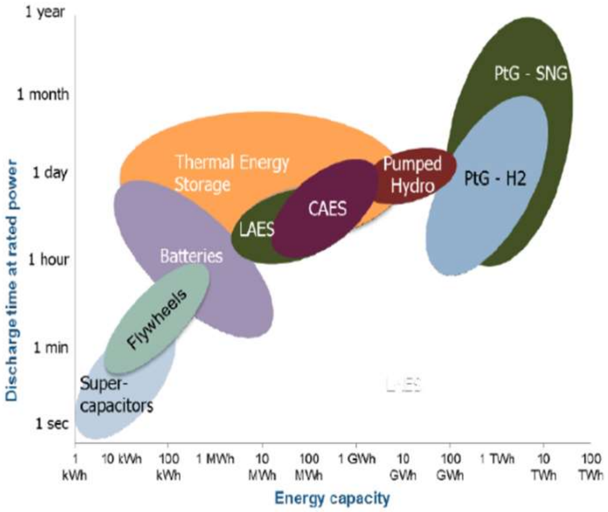
Average domestic energy consumption per household in the United States

Heating	12000 kWh/yr (1400 watts)
Hot water	3000 kWh/yr (340 watts)
Cooling and refrigeration	1200 kWh/yr (140 watts)
Lighting	1200 kWh/yr (140 watts)
Washing and drying	1000 kWh/yr (110 watts)
Cooking	1000 kWh/yr (110 watts)
Miscellaneous electric load	600 kWh/yr (70 watts)

DOE, 2016

- Currently provided by natural gas, biomass, electricity (directly or via heat pumps).
- Decarbonising requires transporting more electricity or carbon free gas.
- Hydrogen can be blended up to 20% by volume with NG without changing infrastructure (HyDeploy project).
- Large CO_2 reductions however, need much bigger volumes.

Storage time-scales



Source: World Energy Council, 2016

Long term storage needed for winter heat.

Hydrogen a possibility.

Controversial topic!

Important Combustion/ other Properties of H_2

- **High flame speeds** and **adiabatic flame temperatures**.
- **Wide flammability** limits. But long IDTs (high RON).
- Materials **embrittlement**.
- Very light/diffusive.
  - efficient storage requires high pressure cylinders or very low (below −253 °C) temperature at 1 atm.
  - Leaky, but disperses quickly if leaked.
- Odourless.
- Premixed flames have **low visibility**.
- Higher heating value (HHV) of hydrogen =13 MJ/Nm^3, whereas that of NG = 40 MJ/Nm^3.
  - To satisfy same energy demand, volume of H_2 transported 3 x that of NG.
- Differences in density result in approximately same pressure drop for H_2 and NG, a critical parameter in pipeline network.

Source: Robert Schefer, Sandia National Laboratory

Table of properties (in air, stoich)

	H_2	CH_4	Propane
Adiabatic Flame Temperature	2380 K	2226 K	2267 K
Diffusivity (m^2/s) x 10^5	6.11	1.60	1.00
Flammability limits	4-75%	5.3-15 %	2.2-9.5 %
LHV (MJ/Kg)	120	50	46.4
Energy density (MJ/m^3)	9.6	32.5	81.2
RON (with uncertainties)	130	120	
MIT	845 K	905 K	766 K
Min. Ignition Energy (10^{-5} J)	2.0	33	30.5
Fuel Volume Fraction %	29.5%	9.48%	4.03%

Wobbe Number of Fuels

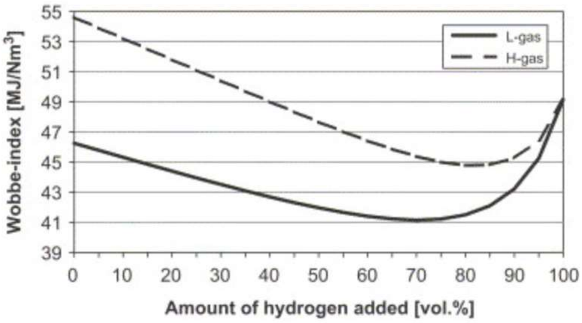
- The Wobbe-index W_s is a measure of the exchangeability of gases in gas burners:
- $W_s = \frac{H_s}{\sqrt{d}}$, where H_s is the HHV, MJ/Nm^3, and *d* the relative density compared to air, dimensionless.
- Compared to NG the lower HHV value for hydrogen is compensated by its lower density.
- **What about mixtures?**

Wobbe Index of NG/H_2 mixtures

Boundaries for Wobbe number:

- Rich NG burners 48-58 MJ/Nm^3
- Lean NG burners 41-47 MJ/Nm^3
- ~99% H_2 can match both these ranges whereas 75% cannot.

Suggests that hydrogen burners can be designed with similar operation to NG?

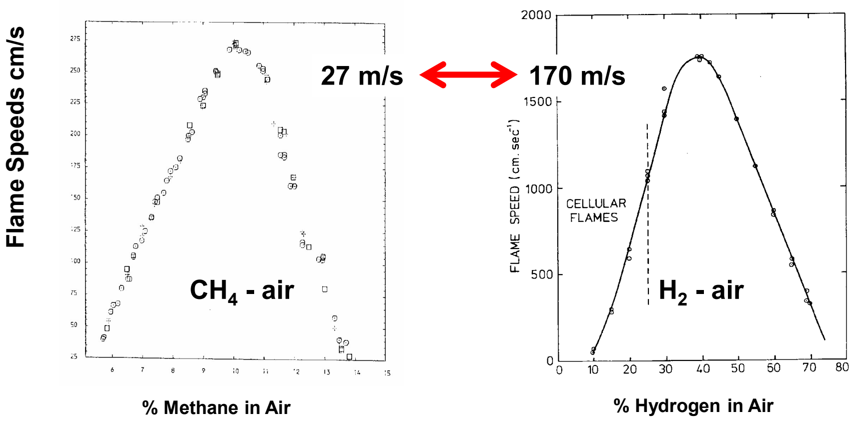


H-gas: high calorific gas
L-gas: low calorific gas

Haeseldonckx and D'haeseleer, 2006

Combustion challenges

- Flame speeds and adiabatic flame temperatures are much higher for H_2 than NG and hydrocarbons.
- Combustors of all types will have to be redesigned for H_2.



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

Measured in a 0.5 m diameter by 0.5 m long closed vessel, 1 atm

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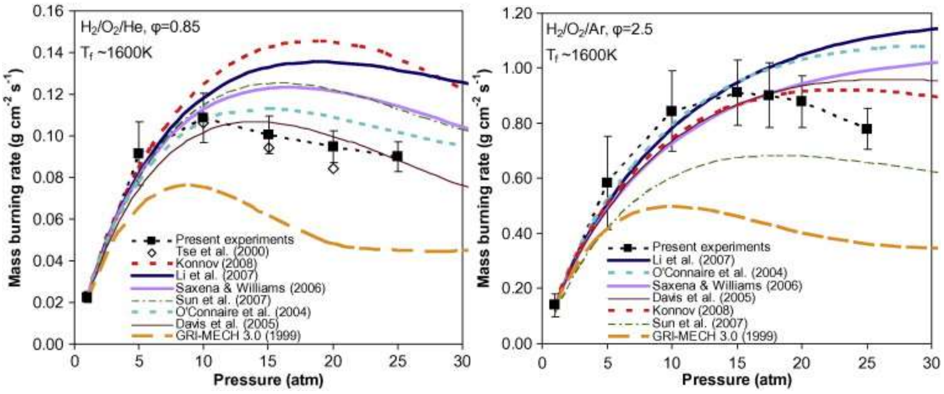
How well can we model the mass burning rate for H_2?

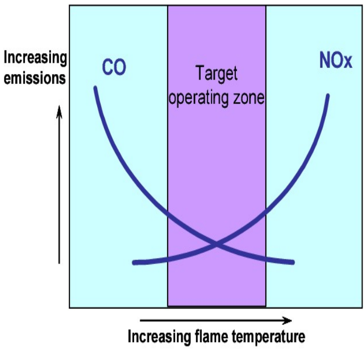
- Burke (*Western States Section of the Combustion Institute Spring Technical Meeting 637-648, 2010*) showed significant variation between models.
- Updates to reaction chemistry discussed earlier need to be incorporated.
  - Models are constantly changing and being updated. If we're lucky…



How to control for thermal NOx?

- Controlling excess air – **lean operation**.
- Reducing temperatures – **heat transfer** through impingement on surfaces: burner, coals etc..
- Affecting transit times in hot/rich zones through mixing (e.g. swirl).

- In an NG burner, conflict between lowering temperatures to reduce NOx and producing incomplete combustion (soot and CO).
- Hydrogen burners cannot have a CO problem. Or unburnt HC, or soot…
  - Duel fuel devices (i.e. will burn either fuel) may have to deal with these issues.
  - Duel fuel devices could enable much faster penetration into market.

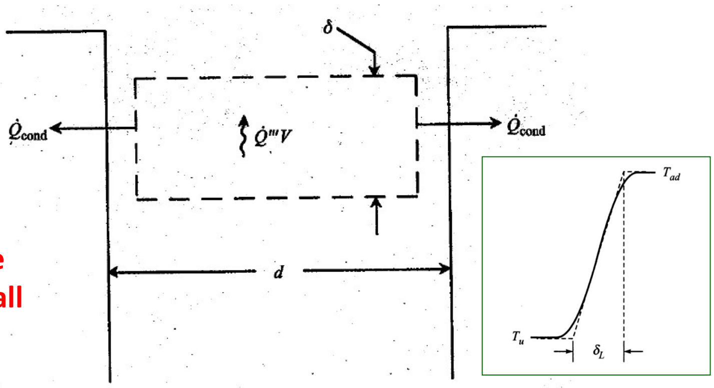


Quench distance and prevention of flashback

Quench Distance (QD) – largest characteristic distance (tube diameter *d*) that prevents the propagation of a flame.

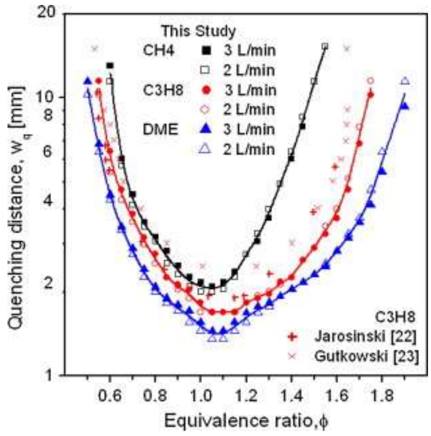
Condition: $Q_{loss} >= Q_{gen}$

Increasing the Q_{loss} to the wall can create quenching.

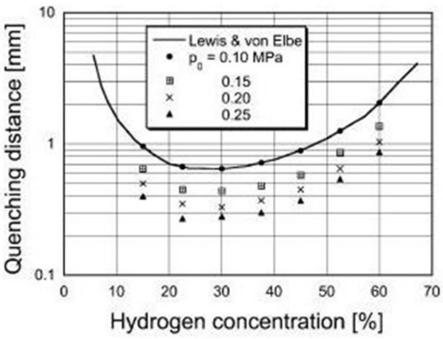


QDs for various fuels

QD for hydrogen ~ 10 times lower than for CH_4.



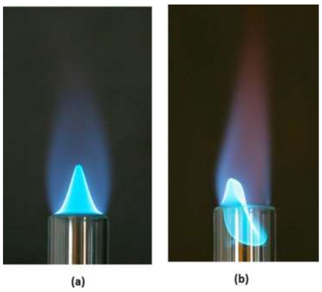
Liu and Kim 2014



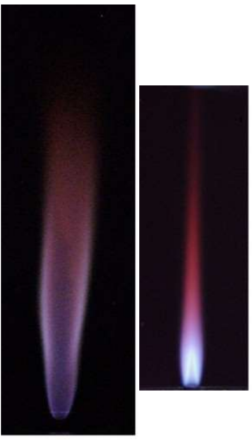
Yang et al. 2003

Flashback

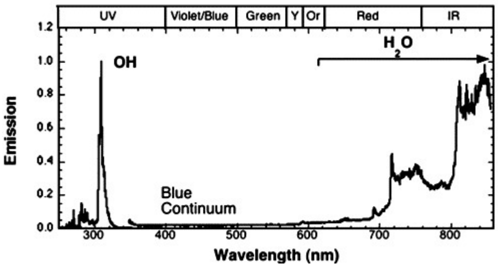
- In the design of burners prevention of flashback critical.
- Ability of flame to travel back down fuel supply leads to safety risk.
- For premixed burners the risk is higher (O_2 available).
- Low QD for hydrogen requires change in design compared to methane to prevent flashback risk.
  - Smaller burner nozzles.
  - Diffusion rather than premixed flames i.e. non-aerated burners.


(a) (b)

Flame visibility



- Common thinking is that hydrogen burns with an invisible flame.
- Partially true for premixed flames.
- Schefer et al. (2009) suggested a factor of 45 increase in emission intensity for diffusion H_2–air flames compared to premixed.
- Emissions in the visible (red-orange) spectrum.



Design principles for H_2 fire

- Non-premixed
  - visibility and flash back avoidance.
- Impingement cooling
  - reducing flame temperatures and NOx.
- Balance between flame visibility and NOx emissions.
- Small burner nozzle size
  - flash back avoidance.
- Repeated experiments tweaking design was not ideal.
- Needed time/funding to develop CFD model with detailed chemistry, flow and transport.

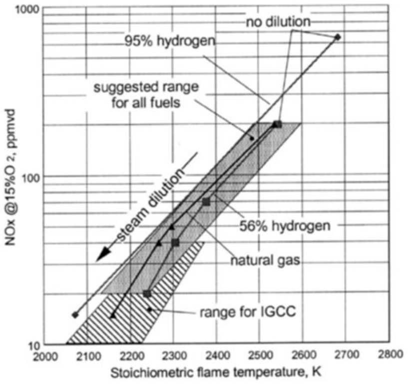
Challenges for gas turbine operation on H_2

- NOx emissions – high flame *T* leading to thermal NOx formation.
- Potential for oscillations – due to high flame speeds, instabilities.
- Flashback – QD and flame speed issues.

- MHPS, a joint venture between Japanese giants Mitsubishi Heavy Industries and Hitachi is addressing such problems.
  - "diffusion combustor" based on low-NO_x technology that injects fuel to air. Steam injection used to control NOx.
- GE also operating turbines with high %H_2 in fuel mix.

Challenges for gas turbine operation on H_2

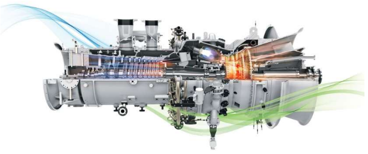
- NOx traditionally controlled in GTs using premixing
  - Lean operation in primary zone reducing *T*s.
- Switching to hydrogen makes premixing highly questionable
  - larger flammability limits (Chiesa et al. 2005)
  - lower ignition temperatures of hydrogen with respect to NG.
- Diffusion burners almost exclusively used.



Combustion research opportunities

- Since all devices would need to be redesigned CFD for reacting flows + NOx formation could be vital.
  - Gas turbines.
  - IC engines.
  - Boilers, fires, cooker burners.
  - H_2 injection systems.
  - Control systems.

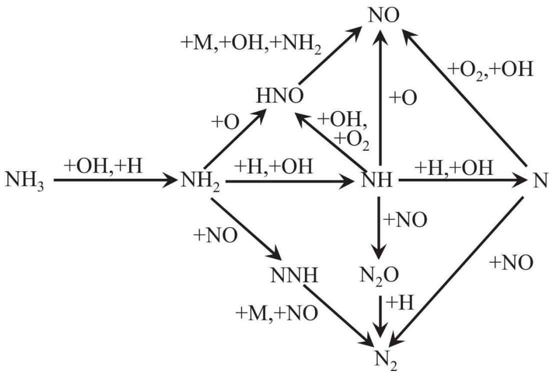
- Rate coefficients and transport properties important.
- Mixed fuels or dual fuel systems even more challenging.



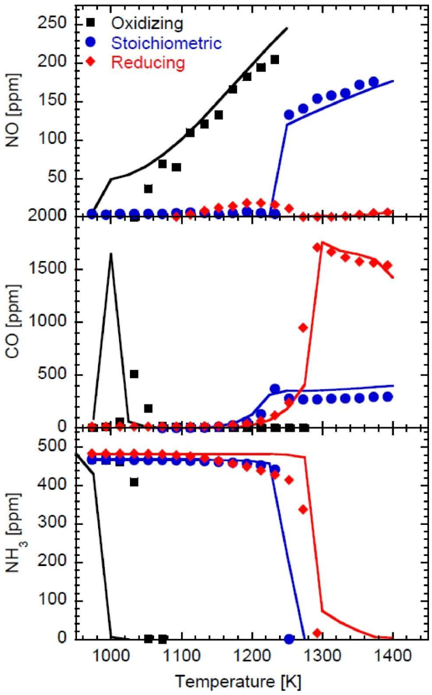
AMMONIA (Kobayashi, 2019, Glarborg, 2018)

- **Why?** Economic storage and transport of H_2 remain challenging especially in countries and regions currently lacking NG pipelines infrastructure.
- Ammonia in liquid form at room temperature (25°C) when pressurized to 9.90 atm or temperature of −33.4°C at atmospheric pressure.
- Easier to transport and higher energy density than H_2. Could be used as a direct fuel or a hydrogen carrier.
  - equipment designed for the storage and transport of propane is likely applicable also for ammonia.
- **Challenges:** high ignition temperature and low maximum burning velocity. Emissions.

Kinetics of oxidation



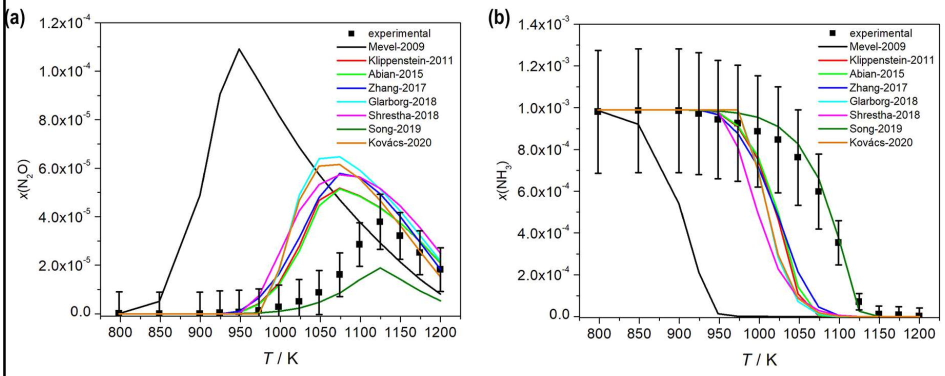
- Emissions of NOx and unburnt NH_3 key.
- Both contribute to atmospheric particulates and acidification.
- Reactor conditions will strongly determine selectivity of products.



Example of model performance, (Glarborg, 2018)

- CH_4 = 2508 / 2513 / 2515 ppm, O_2 = 3480 / 5040 / 40100 ppm, NH_3 = 484 / 468 / 468 ppm; balance N_2. All experiments were conducted in a 12 mm inner diameter alumina reactor at 1.05 atm with a residence time in the isothermal zone of 1296/T(K).

N_2O and NH_3 concentration measurements of Caton et al. (pressure 102 kPa, inlet mole fractions $\boldsymbol{x}(NH_3) = 0.00099$, $\boldsymbol{x}(O_2) = 0.150$, $\boldsymbol{x}(N_2) = 0.84901$) and the simulation results with all investigated mechanisms. The indicated error bars belong to $3\boldsymbol{\sigma}$.



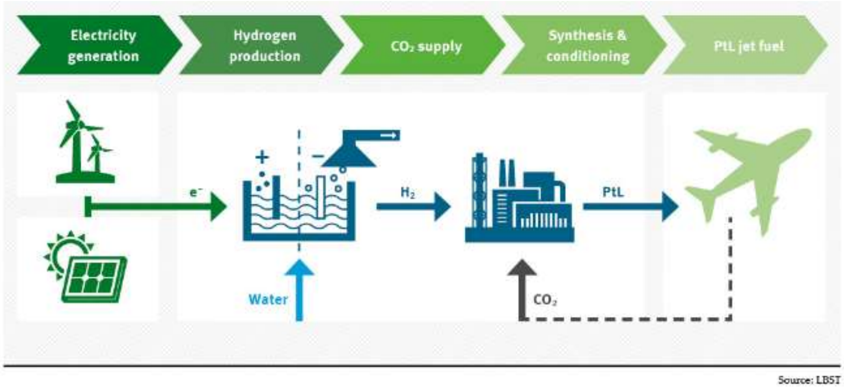
Kawka et al. (2020) compared recent mechanisms and ability to reproduce IDTs and flow reactor concentrations – **see later for error analysis**.

Renewable electricity to liquid fuels

Power to liquid fuels (PtL fuels)

- IF (big if currently…) we have abundant renewable electricity, excess can be used to create liquid fuels as storage method.
  - Create H_2 from electrolysis (TRL 5-8, depending on process type).
  - Capture CO_2 from ambient air (TRL 6).
  - Synthesis of liquid hydrocarbons with subsequent upgrading and refining (TRL 8-9).
- Why bother? Why not just store electricity or H_2?
  - High energy densities in terms of volume and weight.
  - Well suited to current infrastructures.
- Applications? Aviation, heavy goods, shipping?

Overall process



Source: LBST

PtL vs. advanced biofuels

Advantages

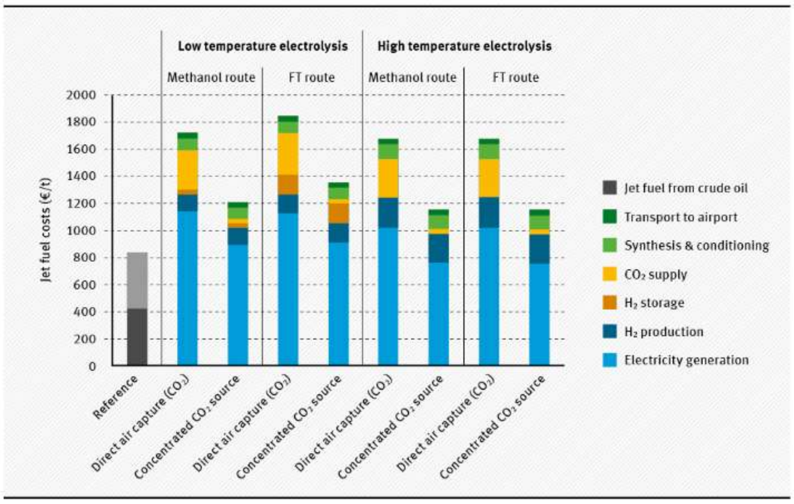
- High energy density.
- Low land requirements.
- Low water requirements.
- Huge renewable power potential.
- Lower aromatics and zero sulphur compared to traditional fuels and cleaner to burn.
- “Drop-in” capabilities.

Disadvantages

- Cost: H_2 production, Air CO_2 capture.
- Readiness of systems integration.
- Overall efficiency low – in terms of land higher than biofuels.
- Non-zero air pollutants (NOx, PM).
- Could lead to lock in for traditional engines preventing development of zero emission innovations.

Costs

Jet fuel costs projected for future PtL plants in 2050 (jet fuel reference price: 42–95 US$/bbl; renewable electricity costs: 40 €/MWh$_e$; equivalent full-load period: 3750 h$_{eq}$/yr)



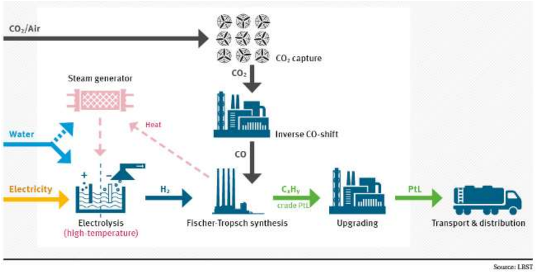
Source: LBST

Production of PtL fuels

(German Environment Agency (2016))

- Two principle production pathways:
  - ➢ Fischer-Tropsch (FT) synthesis and upgrading.
  - ➢ Methanol (MeOH) synthesis and conversion.
- ASTM jet fuel standard already allows for a 50 % blend of FT synthetic fuel. PtL via the methanol pathway is not yet approved

FT process



Source: LBST

- Already commonly used in biomass-to-liquid (BtL), gas-to-liquid (GtL) and coal-to-liquid (CtL) processes.
- Requires CO which in PtL has to be obtained from CO_2.

- CO_2 converted to CO via inverse CO-shift reaction using the **reverse** water gas shift process.

  $CO + H_2O \rightleftharpoons CO_2 + H_2$

- Or, high-temperature electrolysis may allow for co-electrolysis of steam and CO_2, producing H_2 and CO in single step.

Simplified model

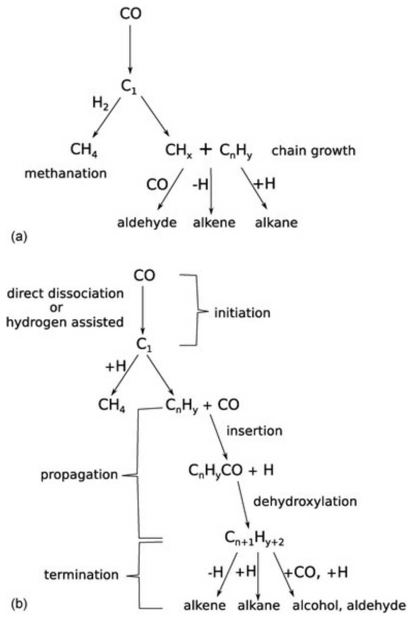
FTS can be simplified as a combination of the FT reaction and the WGS:

$$CO + \left(1 + \frac{m}{2n}\right) H_2 \rightarrow \frac{1}{n} C_nH_m + H_2O \quad (R_{FT})$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (R_{WGS})$$

where *n* is the average carbon number and *m* is the average number of hydrogen atoms of the hydrocarbon products.

FT process



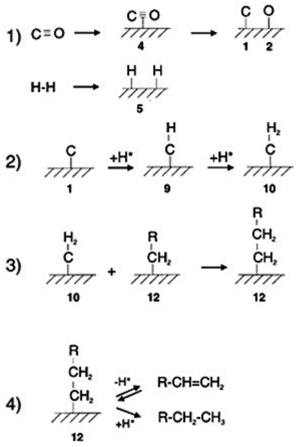
Van Santen, 2013

- Catalytic process at *T* = 200–300° C and *P* = 10–60 bars with choice of catalyst (e.g. cobalt, iron, ruthenium) depending on H_2 to CO ratios.
- Main products linear paraffins, α-olefins, alcohols.
- **Possibility for selectivity of final products based on process conditions.**
- Lack of detailed heterogeneous reaction kinetics potentially a limitation to optimal reactor design and product selectivity (Van Der Laan, 2011).

Example for linear hydrocarbon formation

Polymerization reaction with following steps:

1. Reactant adsorption
2. Chain initiation
3. Chain growth (e.g. by CH_2 insertion)
4. Chain termination (abstraction of hydrogen to an olefin or addition of a CH_3 species or hydrogen to form a paraffin)
5. Product desorption
6. Readsorption and further reaction



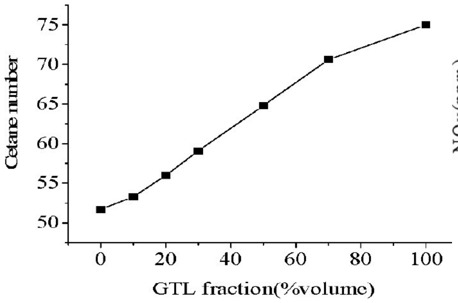
Combustion of FT fuels

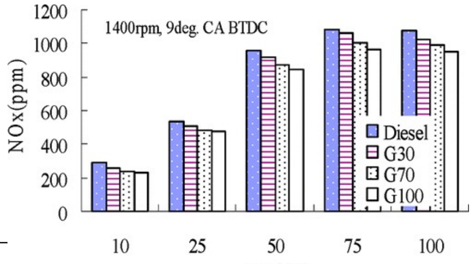
- Features of FT fuels:
  1. high cetane number
  2. low aromatics, C/H ratio and sulphur
  3. unwanted oxygenates can be removed through upgrading
- Advantages
  1. facilitates lower pressures and temperatures due to shorter IDTs – lowering NOx formation potential.
  2. low catalyst poisoning due to low sulphur, low soot formation due to lack of aromatics. However also leads to low lubricity which can be improved with additives.
  3. low oxygen content an advantage for aviation applications due to required energy densities.
- Overall synthetic fuels have emission benefits in the reduction of HC, CO, NO_x and PM.
- Lower volumetric energy density than diesel may require updated injection system.

Gill et al., 2011

Cetane number

- Higher cetane number means shorter IDT.
- Fraction of fuel burnt under pre-mixed conditions reduced lowering *T*s, *P*s and *P* gradients.
- Lowers production of thermal NOx.
- Shorter IDT gives more time for complete combustion and particle oxidization potentially also lowering PM.

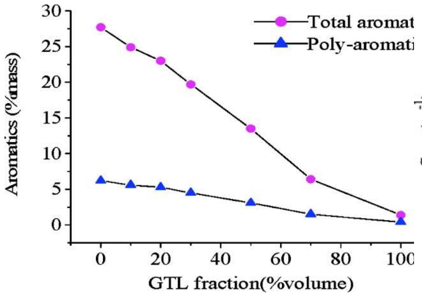


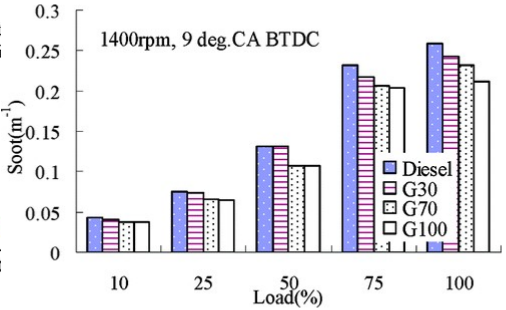


Wu et al. 2007

Aromatics

- Aromatics involved in early stages of soot formation.
- Lowering aromatics lowers PM formation potential.
- Aromatics also have higher adiabatic flame temperatures than paraffinic equivalents.
  - lower *T* – lower NOx.





Wu et al. 2007

Biofuels

Range of biofuels

Feedstocks

- 1st generation
  - corn, wheat, sugar cane, beet
  - palm oil, rapeseed, soybean, sunflower
- 2nd generation
  - copice, forest residue, miscanthus, corn stover, bagasse.
  - jatropha, camelina, used cooking oil/tallow.
- 3rd generation
  - Algae.

Fuel

- 1st generation
  - ethanol, butanol
  - biodiesel, HVO.
- 2nd generation
  - ethanol, butanol
  - biodiesel, HVO.
- 3rd generation
  - range of products incl. biodiesel.

Other proposed biofuels?

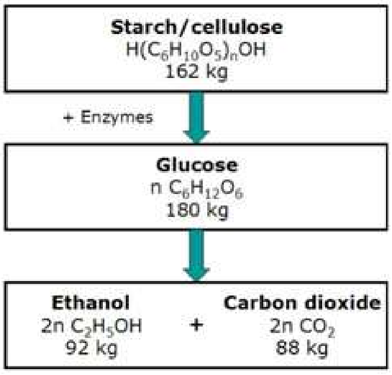
- Furans e.g. from corn stove
  - 2-methylfuran (MF)
  - 2,5-Dimethylfuran (DMF)
  - tetrahydrofuran (THF)
  - 2-methyltetrahydrofuran (MTHF)
- Ethers (DME, DEE, DBE)
- Levulinates
- Biofuel blends

Not at high TRL stage apart from DME.

Production bio-ethanol

Limayem and Ricke 2012

- Ethanol from 1st gen crops is produced via acid hydrolysis and sugar fermentation using yeast + distillation/deyhdration.
- Conversion of lignocellulosic biomass more difficult than hydrolysis of starch due to carbohydrate polymers: **cellulose** composed of glucose molecules bonded together in long crystalline chains, **hemicellulose** consisting of a mixture of xylose, mannose, galactose, or arabinose and **lignin**.
- Not soluble in water.
- Currently higher production costs that could be reduced by G-engineered strains or use of thermochemical methods.

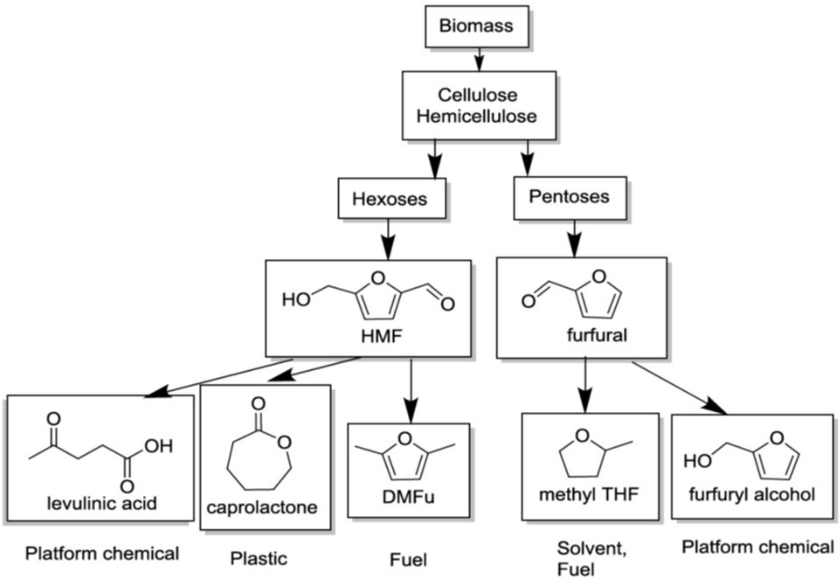


Production bio-butanol

Amiri and Karimi 2019

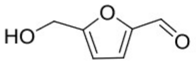
- Currently based on similar production process to ethanol but more costly to produce with lower yields.
- E.Coli strains developed with genes coding for 2 enzymes that converted keto-acids into aldehydes, and aldehydes into 1-butanol.
  - Able to produce butanol at much higher efficiencies.
  - Strain less sensitive to butanol concentration.

Production - furans

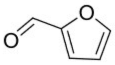


Production - furans

- Lignocellulosic biomass consists of polymeric sugars - can be converted into furans by rearrangement to fructose and elimination of water using an acid at elevated temperatures
  → hydroxylmethylfurfural (HMF) and furfural,



HMF

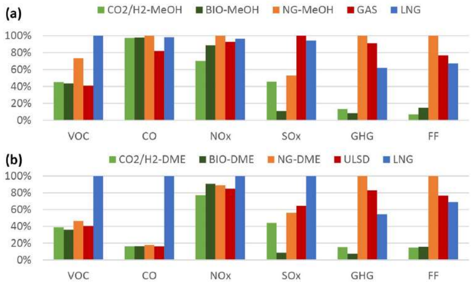


furfural

- HMF can then be used to produce biofuels such as MF and DMF.
  - Currently achieved at the lab scale but not the commercial scale.

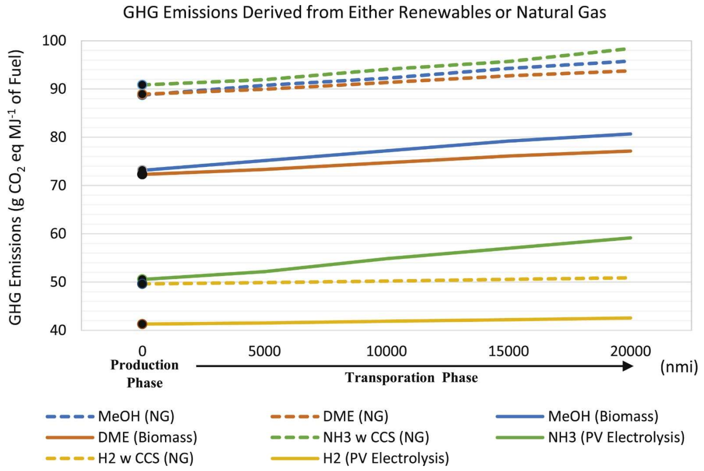
DME production

- Can be produced from lignocellulosic biomass.
  - Gasification to produce syngas.
  - Syngas to methanol.
  - Dehydration of methanol. $2\ CH_3OH \rightarrow (CH_3)_2O + H_2O$.
- Can also be produced from wind-based electrolytic hydrogen and captured carbon dioxide (air capture or ethanol fermentation process) .
  - Potentially lower lifecycle GHG and NOx, SOx emissions cf. biomass.



Matzen, 2016

Carbon footprint of fuels (Al Breiki, 2021)



Sensitivity analysis on various distances of a full life cycle of energy carriers derived from either renewables (solar PV and biomass) or natural gas covering production, transportation, and utilization phases

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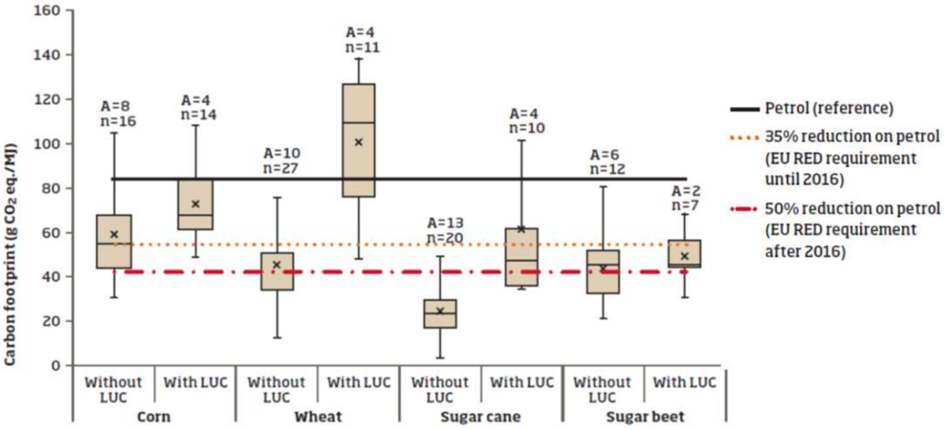
Important properties of biofuels

- Must meet stipulated CO_2 reductions e.g. from EU Renewable Energy Directive (RED II).
- Physical properties need to be suitable for replacing or blending with petroleum derived equivalents.
  - Viscosity, flash point, density, energy density, hygroscopy etc.
- Non-toxicity.
- Chemical properties need to be suitable for replacing or blending with petroleum derived equivalents.
  - Cetane number, octane number and sensitivity, heating value, flame speeds, NOX, PM, UHC, CO emissions.
- High yields from biomass source.
- Cost competitive (controversial point since strongly affected by subsidy and taxation regimes).

Carbon footprint

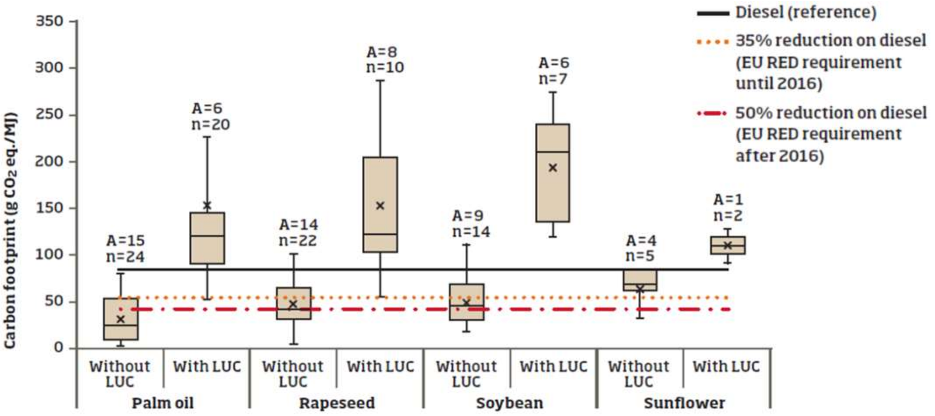
Data from Royal Academy of Engineering
report: Sustainability of
liquid biofuels, 2017.

C foot-print bioethanol – 1st gen



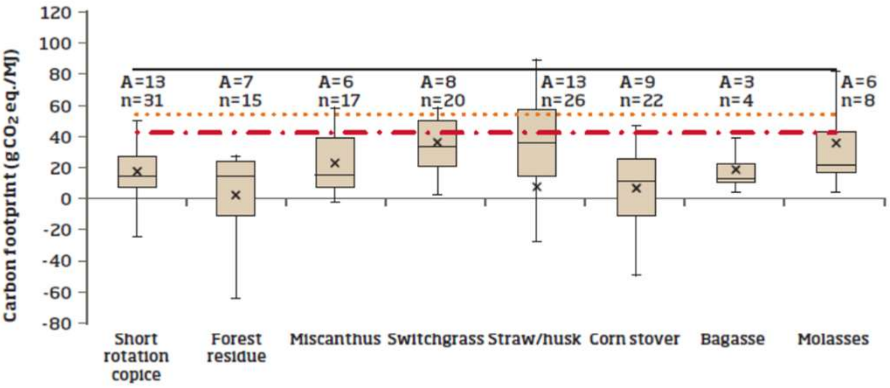
If land use change is used then no source meets the EU RED apart from sugar cane. N_2O from fertiliser use a problem.

C foot-print biodiesel – 1st gen



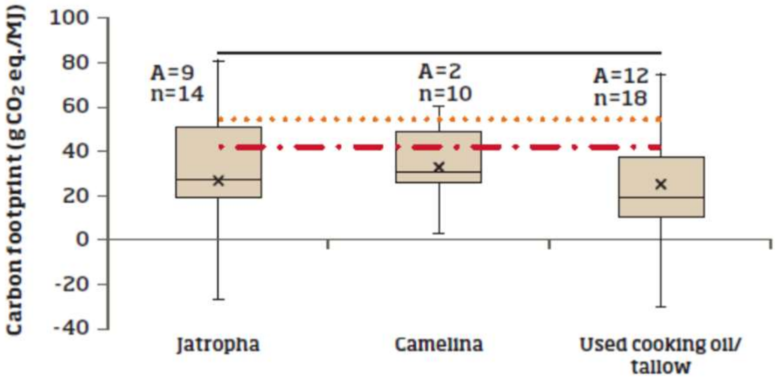
If land use change is used then no source meets the EU RED for biodiesel.

C foot-print bioethanol – 2nd gen



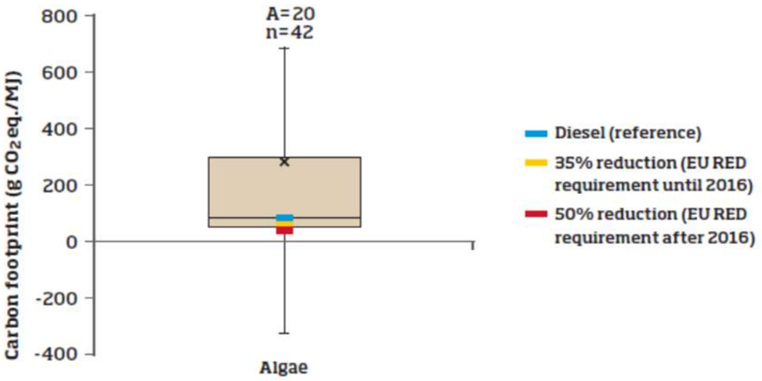
Much lower LCA CO_2 than 1st gen due to lower fertilisers and use of waste materials e.g. forest residue or co-product allocation.

C foot-print biodiesel – 2nd gen



Note the range of uncertainties due to differing assumptions on yields and co-product allocation.

C foot-print biodiesel – 3rd gen



Massive range of uncertainty for algae. Significant savings depend on using waste CO_2, nutrient recycling and cane sugar as nutrient feedstock.

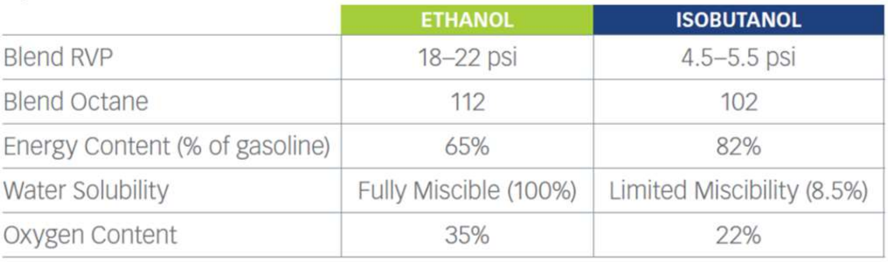
Fuel properties

Wide range of physical/combustion properties to be matched for drop-in fuel, etc!

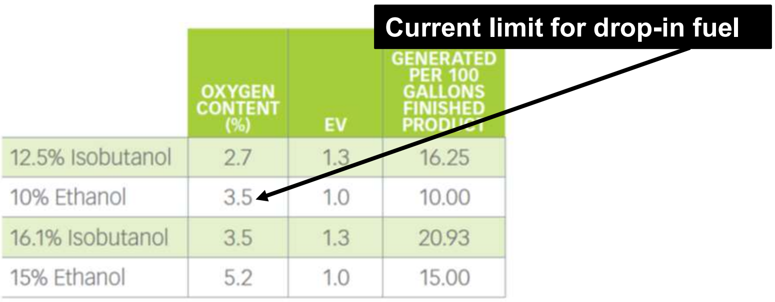
Property	Standard	Base fuel	Standard Limits
Ignition Delay Time		Gasoline	
Cetane Number	EN 590	Diesel	51
RON	EN 228	Gasoline	95
MON	EN 228	Gasoline	85
Emissions	Euro VI	Both	
Viscosity at 40 C	EN 590	Diesel	2000 - 4500 mm^2/s
Density	EN 590 EN 228	Diesel	820 - 845 kg/m^3 720 - 775 kg/m^3
Cloud Point	EN 590	Diesel	-10 to -34 C depending on class
Lubricity	EN 590	Both	Wear scar diameter 460 μm
Copper Strip Corrosion	EN 590, EN 228	Both	Class 1
Materials Compatibility		Both	
Oxygen content	EN 228	Both	3.7 % m/m
Heating Values			
Toxicity ….. Etc. ↓			

Vom Lehn, 2021 - database

Property comparison



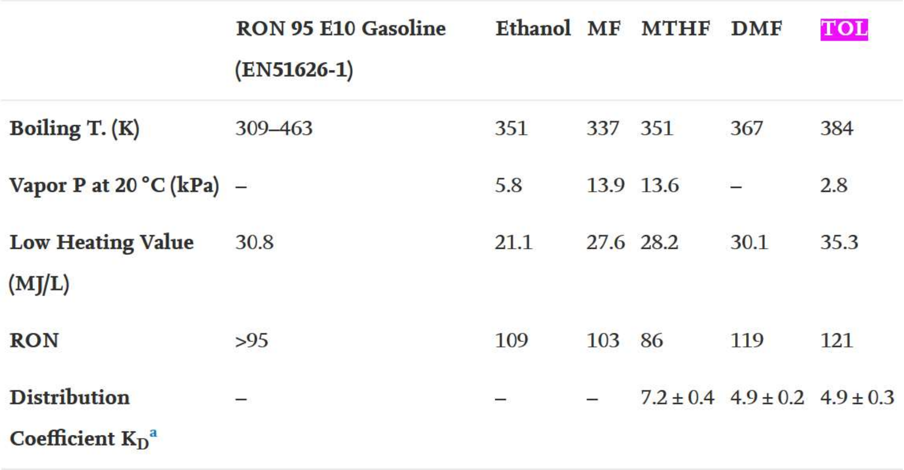
	ETHANOL	ISOBUTANOL
Blend RVP	18–22 psi	4.5–5.5 psi
Blend Octane	112	102
Energy Content (% of gasoline)	65%	82%
Water Solubility	Fully Miscible (100%)	Limited Miscibility (8.5%)
Oxygen Content	35%	22%



Current limit for drop-in fuel

	OXYGEN CONTENT (%)	EV	GENERATED PER 100 GALLONS FINISHED PRODUCT
12.5% Isobutanol	2.7	1.3	16.25
10% Ethanol	3.5	1.0	10.00
16.1% Isobutanol	3.5	1.3	20.93
15% Ethanol	5.2	1.0	15.00

Properties of furans and ethanol vs. RON 95 gasoline



	RON 95 E10 Gasoline (EN51626-1)	Ethanol	MF	MTHF	DMF	TOL
Boiling T. (K)	309–463	351	337	351	367	384
Vapor P at 20 °C (kPa)	–	5.8	13.9	13.6	–	2.8
Low Heating Value (MJ/L)	30.8	21.1	27.6	28.2	30.1	35.3
RON	>95	109	103	86	119	121
Distribution Coefficient K_D[a]	–	–	–	7.2 ± 0.4	4.9 ± 0.2	4.9 ± 0.3

Gandarias 2018

Ethanol vs. Butanol for gasoline blending?

- ✓ Higher yield.
- ✓ Lower production costs.
- ✓ Currently higher global production capcity.
- ❖ Low upper blending wall without engine modification.

- ✓ Less miscible with water.
- ✓ Higher energy content.
- ✓ Lower Reid vapour pressure.
- ✓ Higher legal blending wall (16% bio-butanol blend is legal equivalent to E10 in US)
- ✓ Lower oxygen content.
- ✓ Lower corrosion.
- ❖ Lower octane number.
- ❖ Lower yield.
- ❖ Higher cost.
- ❖ Higher toxicity.

Flash point of biofuels

- Gasoline is very volatile and in a fuel tank the vapour is
- too rich to be flammable – **very low flash point**.
- Adding **ethanol** to petrol **will change the lean/rich limits and could make it flammable** at ambient temperature**.**
- **Limits the potential blend walls.**

**** Henry Persson et al. Fuel vapour composition and flammability properties of E85,SP Technical Research Institute of Sweden SP Report 2008:15***

Flash point of biofuels

- Typically gasoline will not form a flammable mixture until the ambient temperature is below -20°C, which is the rich limit.
- However, when ethanol is added the higher flash point and different stoichiometry make an explosion more likely at ambient temperature.
- Measurements in Sweden have recently shown that E85 has a flammable mixture at 2-5^{o}C (rich limit) and down to -18^{o}C (lean limit or flash point).
- Longer carbon chains increase the flash point, potentially making longer chain alcohols more suitable for diesel blending.

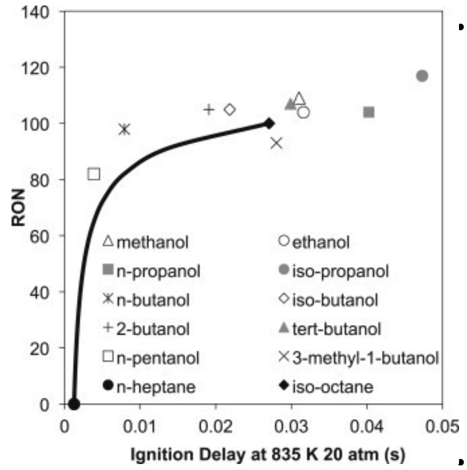
Flashpoint of example fuels

Fuel or fuel component	Flashpoint
Gasoline	~ -65° C
Diesel	>52 °C
Biodiesel	>130 °C
Jet fuel	>38 °C
Ethanol	16.6 °C
N-butanol	35 °C
Iso-butanol	28 °C
1-pentanol	49 °C
DMF	−1 °C
MF	−22 °C
DME	−41 °C

For alcohols, 5 carbons are needed to reach realm of diesel. Could affect storage, safety issues.

COMBUSTION PROPERTIES OF SELECTED ALTERNATIVE FUELS

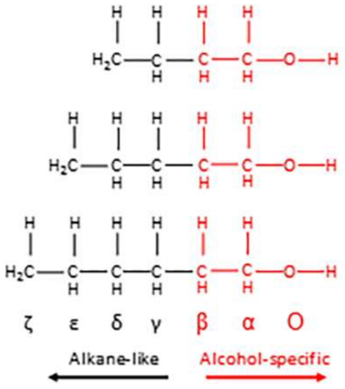
Effect of alcohol addition on RON

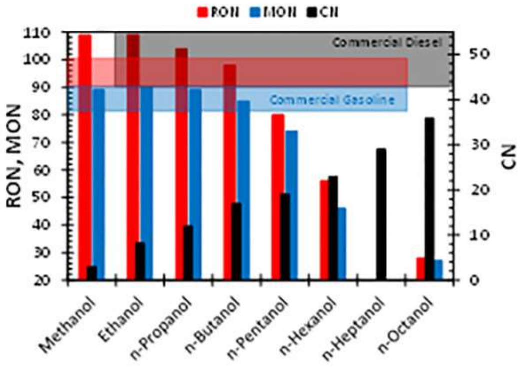


- Varies according to C number and bond structure with iso-propanol showing greatest knock resistance.
  - Lower molecular weight alcohols have highes ONs – suitable for blending with gasoline type fuels.
  - C_5 and higher have lower ONs and display significant low- and NTC-temperature reactivity, making them more suitable for CI engine applications.
- BUT are there temperature effects of reductions in low *T* reactivity ?

(Sarathy et al, 2014)

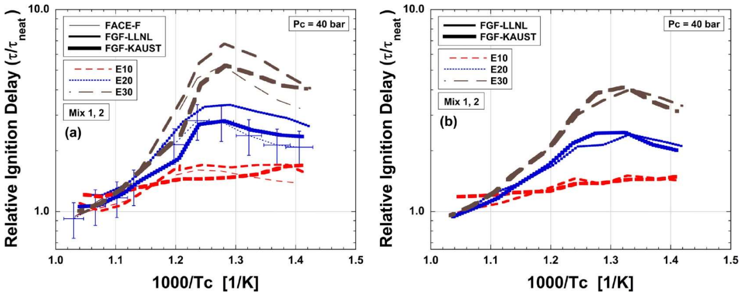
Alcohol octane numbers, (Pelucchi, 2020)





- Suggests different C number alcohols relevant for diesel vs. gasoline blending.

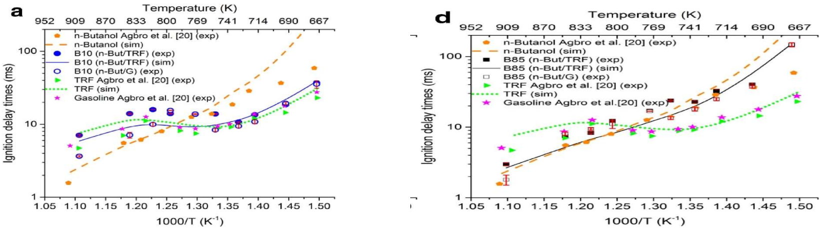
Effects on IDTs – alcohol blending



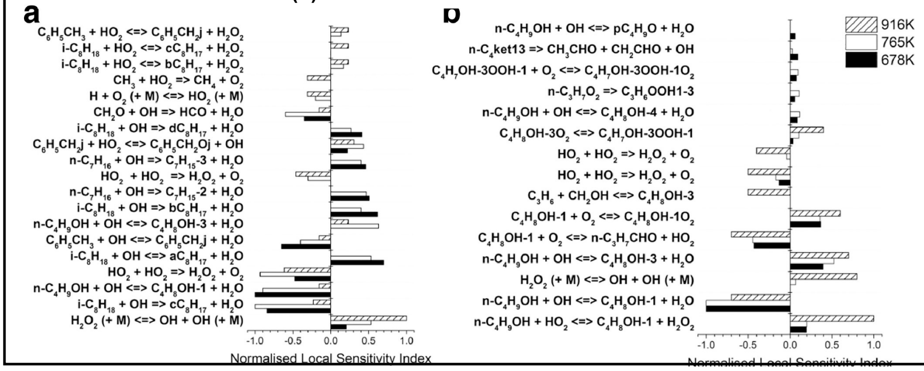
Experimental (a) and modelled (b) relative main IDTs for different blends (Cheng 2021)

- **Ethanol** reduces ignition delays across all *T*, compared to RON94 FACE, although a small cross over for one surrogate.
  - On edge of NTC.

Butanols – n-butanol (Gorbatenko, 2019)

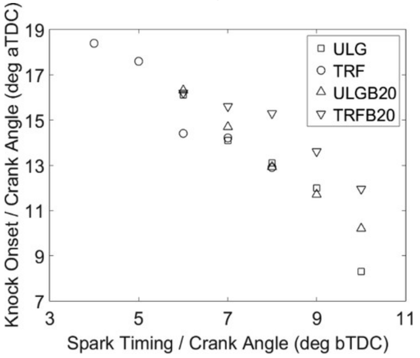


Brute force local sensitivity indices for ignition delay time for (a) 10% vol n-butanol+TRF blend and (b) 85% vol n-butanol +TRF blends



N-butanol - *T* effects

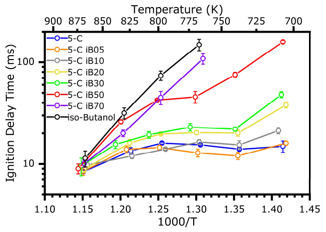
- At high *T*, n-butanol supresses NTC causing a decrease in IDTs relative to gasoline and an increase in reactivity.
- **Cross over *T* exists.**
- At low *T* n-butanol acts as anti-knock agent.
- Impact in engine will depend on *T* regime.

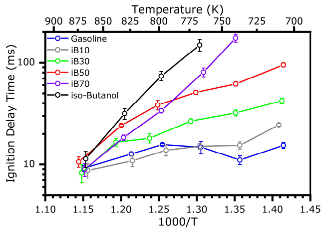


- Cross over of behaviour of IB20 compared to gasoline in SI engine.

Agbro (2018)

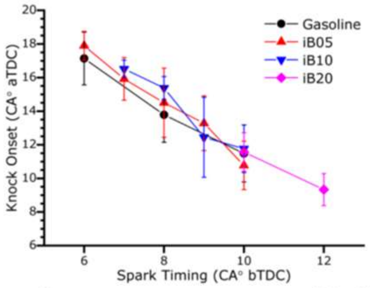
Butanols – iso-butanol (Michelbach, 2021)



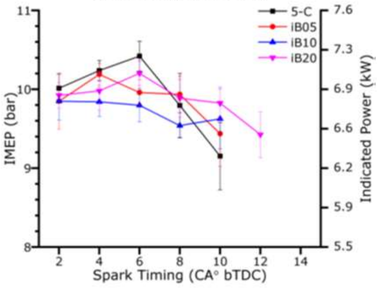


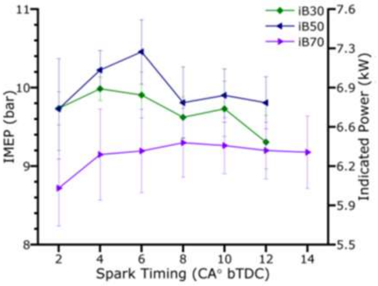
- At high *T* all IB blends lead to longer IDTs.
- At low *T*, IB5, IB10 are actually more reactive.
- Hence, anti-knock qualities will depend on in cylinder temperatures of engine.
- IB20 upwards < IDT.
- Only IB70, IB100 show Arrhenius type behaviour.
- All other blends have shallow NTC.

Knock onset on blending - IB



- IB blending delays knock onset for all blends. No knock from > IB20.
- Also decreased knock intensity.
- There is however, a decrease in indicated power for low blends.
- Returns for higher blends due to ability to avoid knock and therefore change spark advance.

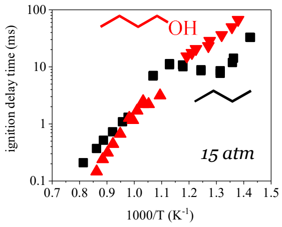




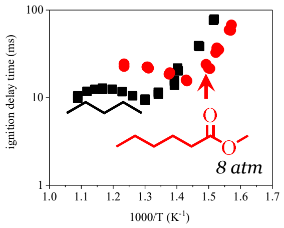
General Oxygenates – thanks to Brandon Rotavera

Functional Groups Alter Chemical Mechanisms of Ignition

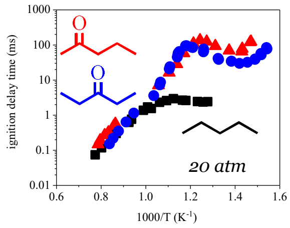
UNIVERSITY OF GEORGIA



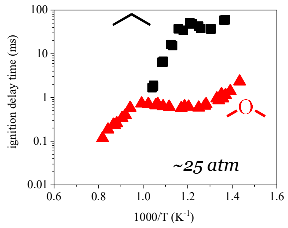
1-butanol/n-butane



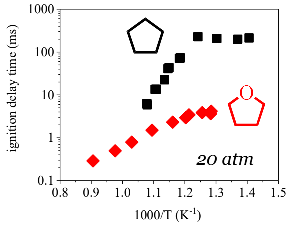
methyl hexanoate/n-pentane



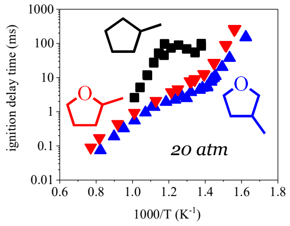
3-pentanone/2-pentanone/n-pentane



dimethyl ether/propane



tetrahydrofuran/cyclopentane



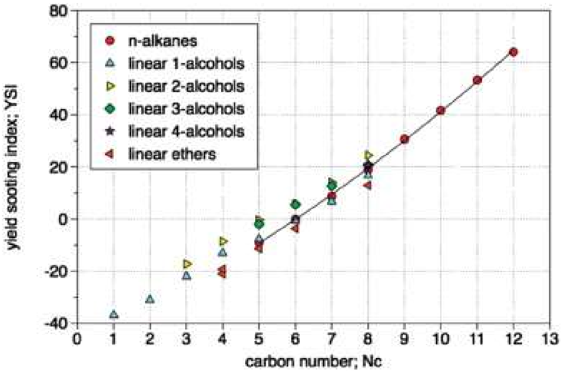
2-methyltetrahydrofuran/toluene

You can also watch Brandon's Webinar

Ignition Delay Time Citations

- 1-butanol/n-butane
  - Weber et al., Combust. Flame, 158 (2011) 809-819 – UConn
  - Vranckx et al., Combust. Flame, 158 (2011) 1444-1455 – RWTH Aachen University
  - Healy et al., Combust. Flame, 157 (2010) 1526-1539 – Texas A&M University / NUIG
- methyl hexanoate/n-pentane
  - HadjAli et al., Proc. Combust. Inst., 32 (2009) 239-246 – Université de Lille
- 3-pentanone/2-pentanone/n-pentane
  - Minwegen et al., Proc. Combust. Inst., 36 (2017) 561-568 – RWTH Aachen University
  - Fenard et al., Combust. Flame, 216 (2020) 29-44 – RWTH Aachen University
  - Bugler et al., Combust. Flame, 163 (2016) 138-156 – NUIG
- dimethyl ether/propane
  - Li et al., Energy & Fuels, 27 (2013) 2811-2817 – RPI
  - Gallagher et al., Combust. Flame, 153 (2008) 316-333 – NUIG
- tetrahydrofuran/cyclopentane
  - Uygun, Combust. Flame, 161 (2014) 2519-2530 – RWTH Aachen University
  - Al Rashidi et al., Combust. Flame, 183 (2017) 372-385 – NUIG / KAUST

Emissions Characteristics

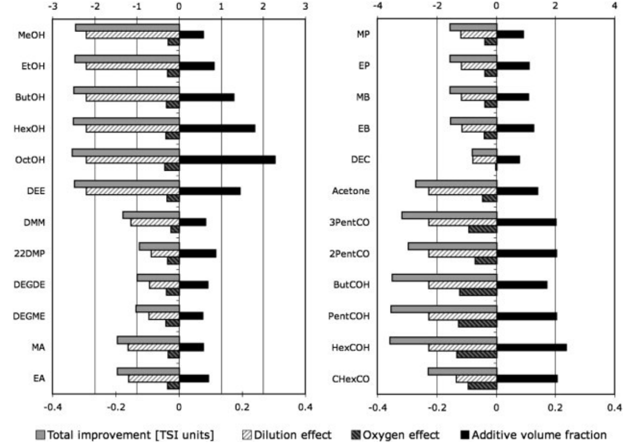


- Expect alcohol and ethers to reduce sooting tendencies compared to petroleum type fuels which contain alkanes and aromatics.
- Effects of carbon chain length and oxygen vs aromatic content.

(Sarathy, 2014)

Effects of oxygen content and dilution on TSI improvements cf diesel, (Pepiot-Desjardins, 2008)

- Smoke point measurements and modelling of n-heptane/toluene/oxygenate mixtures. Methane flames and rich homogeneous reactors.

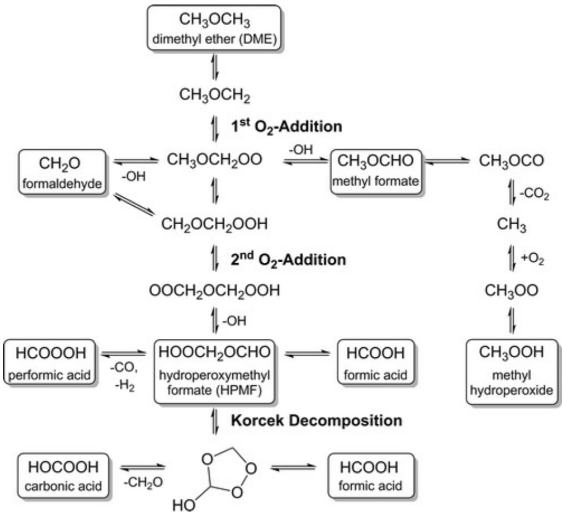


- Dilution effect depends on relative TSI of blended fuel.
    - Could be +ve or -ve
- Oxygenated groups were found to reduce sooting tendency of base fuel depending strongly on the nature of these groups.

Dimethyl ether (DME) as a fuel?

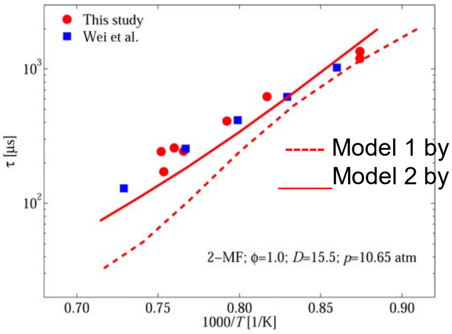
- DME (CH_3OCH_3) interest as alternative fuel
  - high cetane number (≥55)
  - its combustion produces very low gaseous and particulate emissions.
- It has a low vapour pressure.
  - Dedicated engine but low required injection pressure.
- DME's energy density is lower than diesel, but overall engine thermal efficiency is same or higher.
- Can be generated from residual forestry biomass or as an E type fuel (see earlier).

DME oxidation

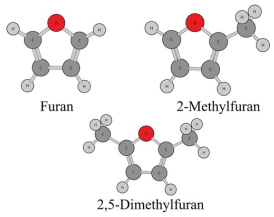


Moshammer et al. 2016

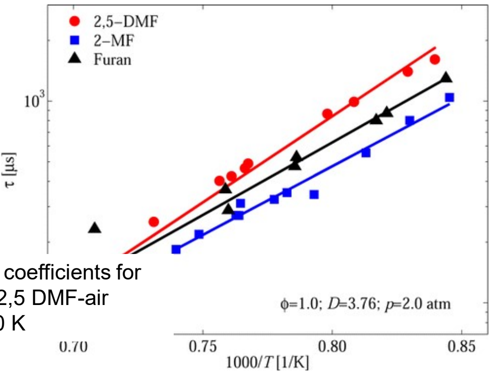
Furans

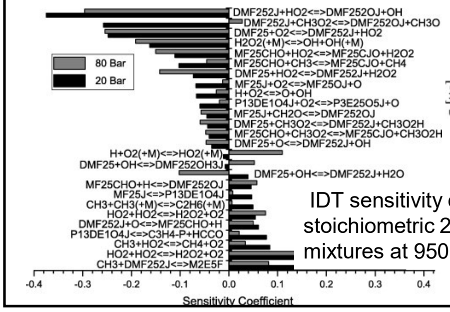


----- Model 1 by Sirjean et al.
_____ Model 2 by Somers et al.



Eldeeb and Akih-Kumgeh (2014), Somers (2013)





IDT sensitivity coefficients for stoichiometric 2,5 DMF-air mixtures at 950 K

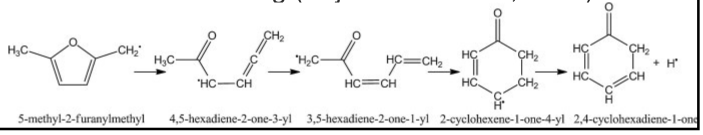
Remember earlier discussion on utility of different targets?

Somers (2013)

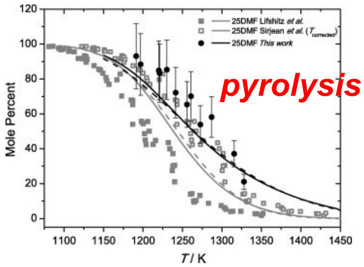
2,5 DMF investigation

- A single pulse shock tube to investigate the pyrolysis of 2,5 DMF.
- A low pressure shock tube to measure ignition delay times of dilute 2,5 DMF/O_2/Ar mixtures.
- A high pressure shock tube to measure ignition delay times of non-dilute 2,5 DMF/O_2/N_2 mixtures, representing “fuel in air”.
- A jet-stirred reactor to quantify mole fractions of reactants and products for the oxidation of dilute 2,5 DMF/O_2/N_2 mixtures.
- A flat-flame burner (heat-flux method) to determine laminar burning velocities of atmospheric pressure 2,5 DMF/O_2/N_2 mixtures as a function of equivalence ratio and unburnt gas temperature.

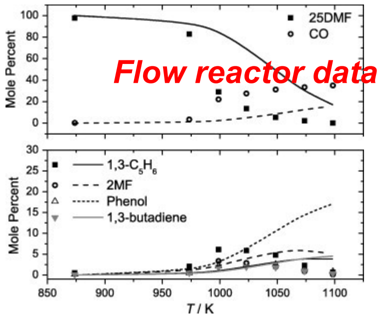
Includes new data on thermal decomposition of 25DMF2R radical from CBS-QB3 calculations and RRKM/ME modelling (Sirjean & Fournet, 2012)



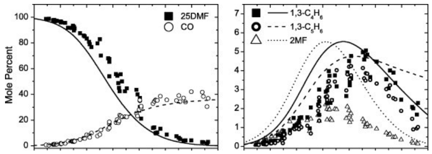
Evaluation data



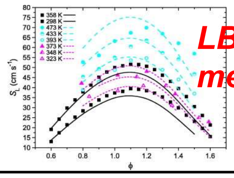
pyrolysis



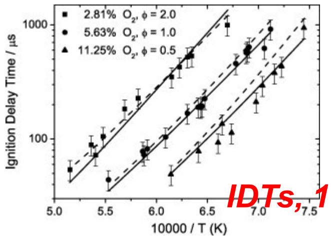
Flow reactor data



Shock tube speciation

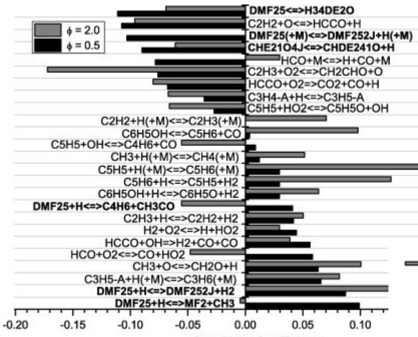


LBVs, heat flux method



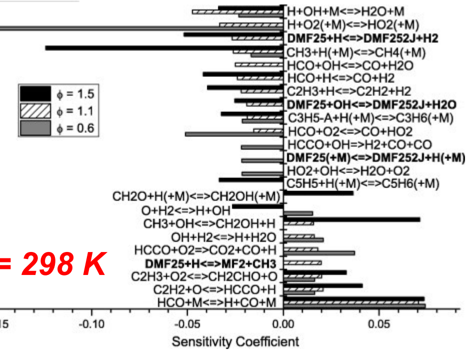
IDTs, 1 atm

Sensitivity analysis



- Good agreement shock tube.
- Good agreement effect of O_2 on IDT.
- LBV good except for rich conditions.

IDTs, 1 atm



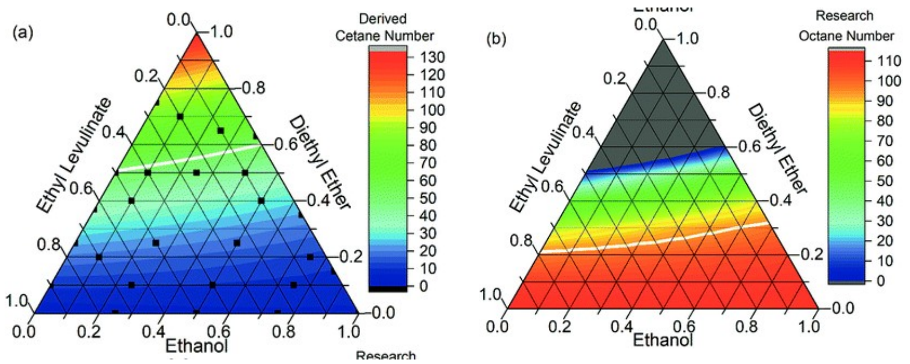
LBVs at 1.0 atm and T_i = 298 K

Tailoring fuel mixtures?

- Biofuel and PTL fuel products can be selected through optimisation of process conditions during production process.
- Gives the opportunity to tailor fuel mixtures to obtain desired properties for drop in fuels/blends.
  - A lot of properties to optimise…
  - RON, CN, IDTs, flashpoints, emissions, physical properties, flame speeds etc.
- Depending on combustor and replacement fuel (gasoline, diesel, propane, etc.) characteristics may vary.
  - Higher carbon numbers more similar to diesel.
  - Lower carbon numbers more similar to gasoline.
- Adjustments of RON may allow increased compression ratios.

Example for ethanolic gasoline mixtures

- Biofuel blends derived from lignocellulosic biomass.
- CN and RON can be tailored (Howard, 2019).



Section 6
Model uncertainties, sensitivity analysis and optimisation

Sources of data for chemical models and their uncertainties

Intro

- We have seen from earlier examples that presenting uncertainties in experimental data is far more common than for modelling results.
- But we need to know the robustness of our models to use them in design and decision making e.g. for use of new fuels.
- Need methods for **uncertainty quantification**.
  - Emerging field of UQ in combustion modelling.
  - Need first to estimate uncertainties in
    - Input parameters
    - Model structure.
  - Efficient methods for **propagating** through model to provide uncertainties on target outputs.

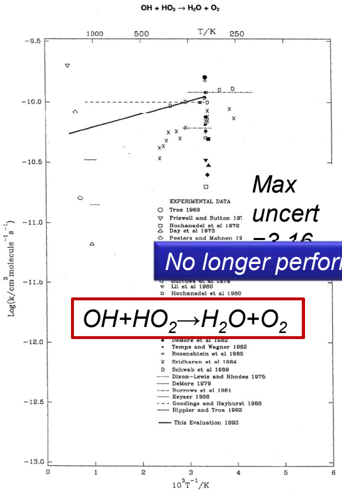
Sources of model input data and uncertainty information

- 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)

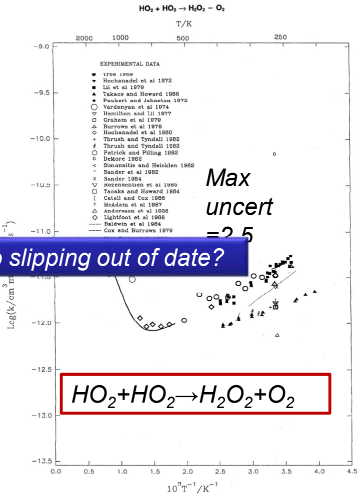
Δlogk = ±0.2 (300K) ±0.5 (2000K)

Δlogk = ±0.15 (550-800K) ±0.4 (1250K)



Max uncert =3.16

$OH+HO_2 \rightarrow H_2O+O_2$



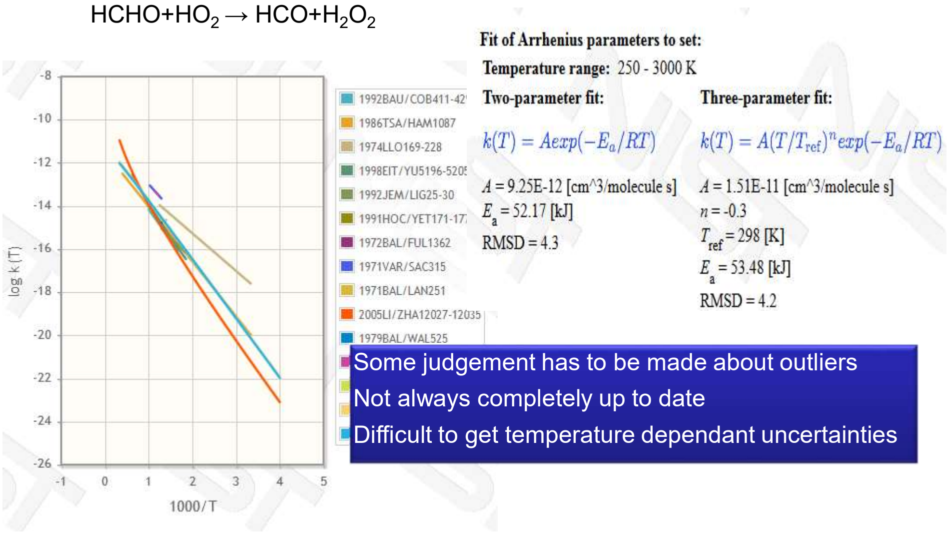
Max uncert =2.5

$HO_2+HO_2 \rightarrow H_2O_2+O_2$

No longer performed so slipping out of date?

NIST data base

$HCHO+HO_2 \rightarrow HCO+H_2O_2$



Fit of Arrhenius parameters to set:

Temperature range: 250 - 3000 K

Two-parameter fit:

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

A = 9.25E-12 [cm^3/molecule s]
E_a = 52.17 [kJ]
RMSD = 4.3

Three-parameter fit:

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

A = 1.51E-11 [cm^3/molecule s]
n = -0.3
T_{ref} = 298 [K]
E_a = 53.48 [kJ]
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

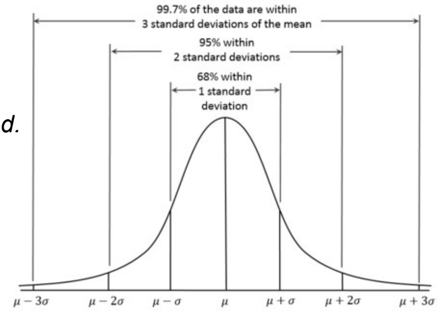
- Depends of level of knowledge about a particular parameter.
- If evaluation available then *f* value may be given.

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

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

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

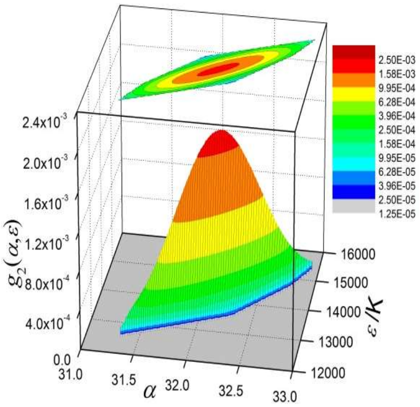
where m is the level of uncertainty suggested.
m = 2, 2σ deviation or 95 %ile,
m= 3, 3σ deviation or 99.7 %ile



Examples of levels of uncertainty

uncertainty parameter *f*	multiplication factor of 3σ uncertainty limits	σ($\log_{10}$ k)	σ(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

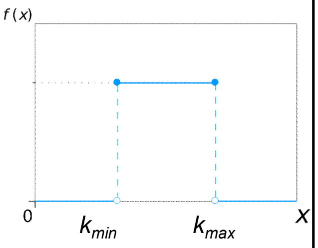


- All available current information on a system is used fit a joint pdf of parameters
  - ➢ e.g. 2,3 parameter Arrhenius
- Provides highly detailed data on parameter correlations etc.

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 guestimate 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 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 (**see earlier**) to reduce uncertainties in data (Burcat & Ruscic, 2005).
- Network of Computed Reaction Enthalpies to Atom-Based thermochemistry **(NEAT)** **(***Csaszar and Furtenbacher, 2010)*
- **Results in highly correlated parameters – be careful of the effects of neglecting such correlations!**

Species Name	Formula	$\Delta_f H°$(0 K)	$\Delta_f H°$(298.15 K)	Uncertainty	Units	Relative Molecular Mass	ATcT ID
Dihydrogen	H2 (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	C7H16 (l)	-201.46	-223.91	± 0.74	kJ/mol	100.2019 ± 0.0057	142-82-5*500
Octane	C8H18 (l)	-226.61	-249.73	± 0.79	kJ/mol	114.2285 ± 0.0065	111-65-9*500
2,2,4-Trimethylpentane	(CH3)2CHCH2C(CH3)3 (l)	-224.4	-258.9	± 1.5	kJ/mol	114.2285 ± 0.0065	540-84-1*500

Part of a thermo-chemical network showing the basic ideas

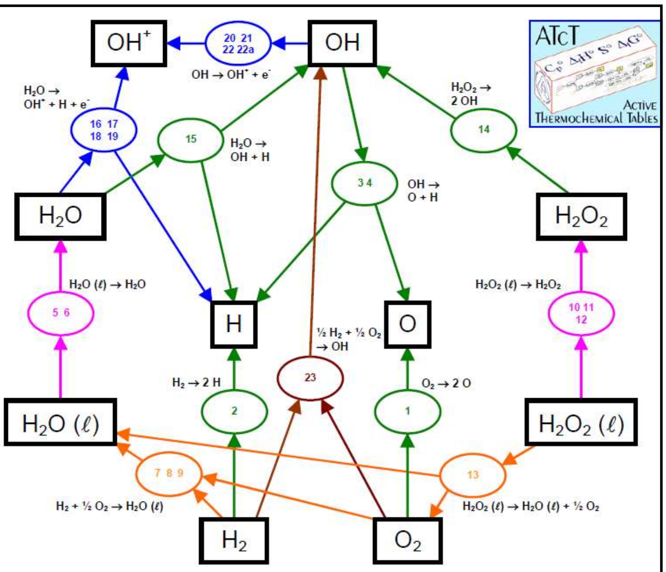
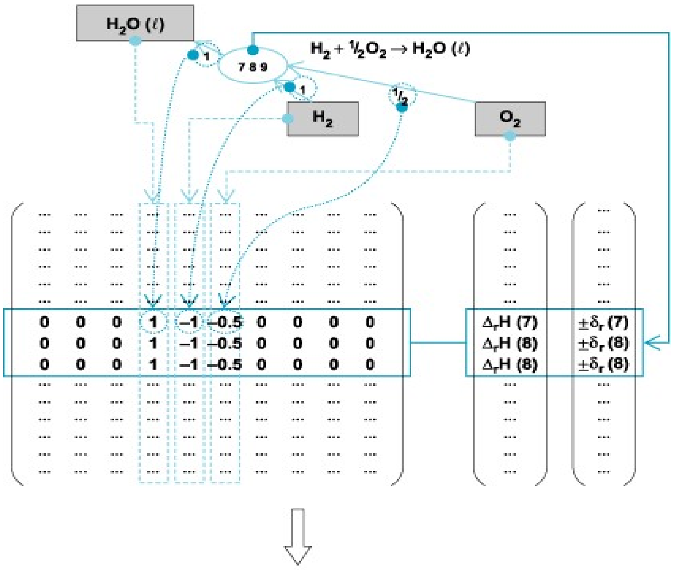


Figure 1. A small subsection of the current Core (Argonne) Thermochemical Network. The full network currently contains >600 primary vertices and >3200 secondary vertices. See text for further details



…

Eq. (7): $\Delta_f H(H_2O <\ell>) - \Delta_f H(H_2) - 0.5\ \Delta_f H(O_2) = \Delta_r H\ (7) \pm \delta_r\ (7)$

Eq. (8): $\Delta_f H(H_2O <\ell>) - \Delta_f H(H_2) - 0.5\ \Delta_f H(O_2) = \Delta_r H\ (8) \pm \delta_r\ (8)$

Eq. (9): $\Delta_f H(H_2O <\ell>) - \Delta_f H(H_2) - 0.5\ \Delta_f H(O_2) = \Delta_r H\ (9) \pm \delta_r\ (9)$

…

Example: CH_3

Formula	$\Delta_f H°$(0 K)	$\Delta_f H°$(298K)	Uncertainty	Units
CH_3(g)	149.788	146.374	± 0.08	kJ mol^{-1}

95% uncertainty limits

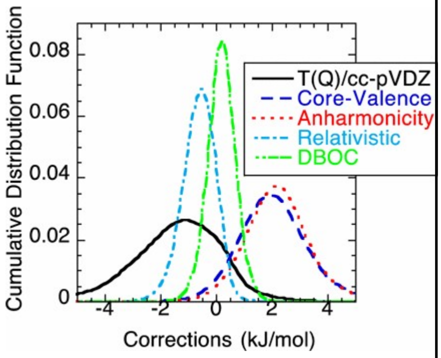
- **Top contributors to the provenance of $\Delta_f H°$ of CH_3 (g):** The top **20** contributors account only for **72.5%** of the provenance of $\Delta_f H°$ of CH_3 (g). A total of **99** contributors would be needed to account for **90%** of the provenance.
- Link to latest version of ATcT: https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php

Ab Initio Computations and Active Thermochemical Tables Hand in Hand: Heats of Formation of Core Combustion Species

Klippenstein, 2017

- High level ab initio electronic structure based predictions of $\Delta_f H^o(0\ K)$ for 348 C, N, O, and H containing species - essentially all core combustion species with 34 or fewer electrons.

- Accuracy of theoretical predictions is explored through
(i) examination of the magnitudes of the various corrections,
(ii) comparisons with other high level calculations, and
(iii) through comparison with the ATcT values.
- Inclusion of theoretical results into ATcT thermochemical network expected to significantly improve the thermochemical knowledge base for less-well studied species.



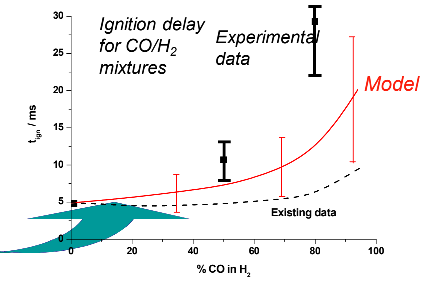
RESPECTH
Reaction Kinetics, Spectroscopy, Thermodynamics database

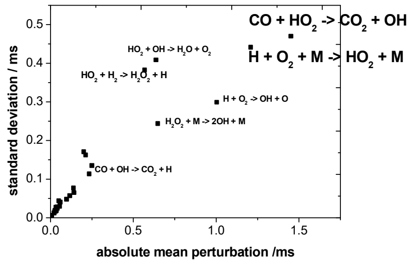
- http://respecth.chem.elte.hu/respecth/
- Thermodynamics section:
  - Thermochemical data calculated by the method NEAT;
  - High-accuracy thermochemical data for $H_2{}^{(16)}O$;
  - A mirror of Burcat's thermochemistry database – which incorporates ATcT values where available. .
  - **Always check your data sources and uncertainties!**

```
CH2O  FORMALDEHYDE  SIGMA=2 A0=9.40546 B0=1.295407 C0=1.134216
NU=2782.4,1746.1,
1500.1,1167.2,2843.2,1249.1   HF298=-109.164+/-0.1 kJ     REF=ATcT C
2011.
C4H10O-N 1-BUTANOL SIGMA=1  STATWT=1 IA=4.4899  IB=42.7094  IC=45.1130
NU=3300,2950(9),1470,1450(4),1294(7),1250,1070,1050,955(4),890(3),446,3
92,350
REF=Chao et. al, JPCRD 15,(1986),1369  HF298=-275.981+/-8. kJ
REF=Burcat G3B3
```

Sensitivity and uncertainty analysis

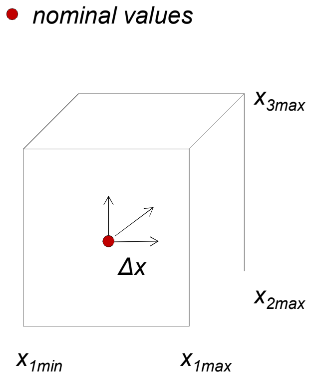
- **Uncertainty quantification (UQ)** estimates the overall predictive uncertainty of a model given the state/or lack of knowledge about its input parameters.
- UQ puts error bars on predictions.





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

Local sensitivity coefficients



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.

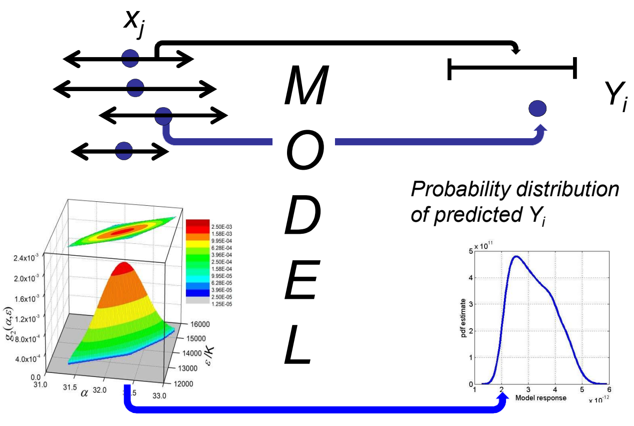
Contributions to uncertainty?

- 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


x_j

M O D E L

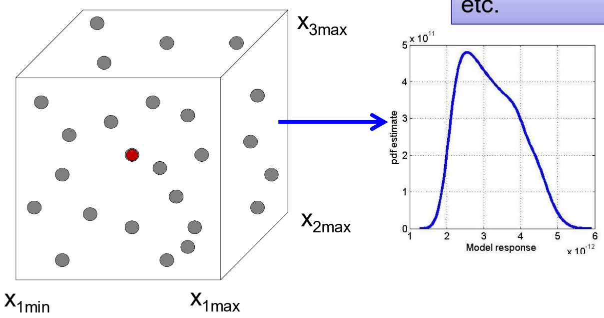
Y_i

Probability distribution of predicted Y_i

Global sensitivity/uncertainty methods

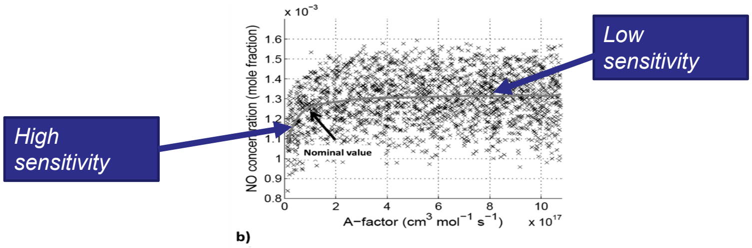
Global - attempts to cover whole input space using a sampling method.

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**.


High sensitivity

Low sensitivity

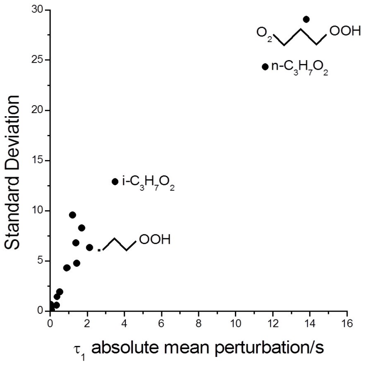
Disadvantages of global methods

- 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 x 2, rv x 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, useful for targets such as IDTs.
- **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

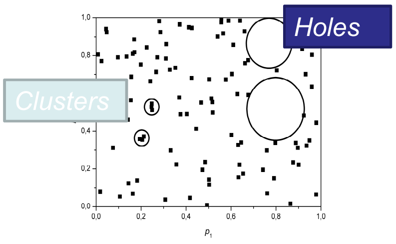


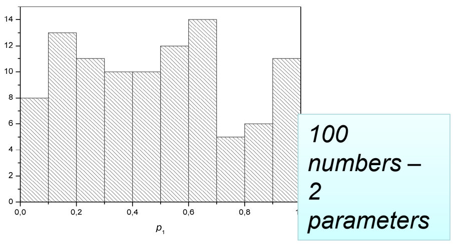
- *Note the high standard deviation of the outputs compared to the mean.*
- *Very nonlinear responses requiring large sample size to converge.*

Morris analysis for species ΔH_f^o with respect to ***time to cool flame for propane oxidation****. T= 593 K, equimolar C_3H_8+O_2 at 53.4 kPa, diluted by N_2 to 101.3 kPa (Hughes et al., 2006)*

Global sampling methods
Monte Carlo

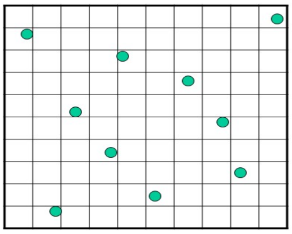
- For a global sampling method it is important to get good coverage of the input parameter space – which may be high dimensional.
- Typical random sampling methods can lead to clustering and holes.





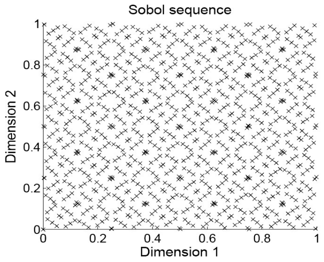
Structured sampling

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



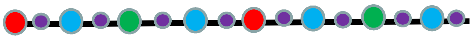
d)

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

Sobol sequence

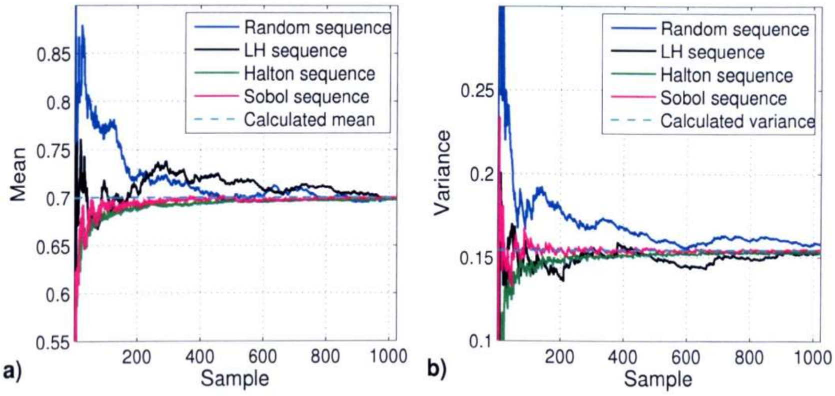
Sobol sequences use a base of two to form successively finer uniform partitions of the unit interval and then reorder the coordinates in each dimension.

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.

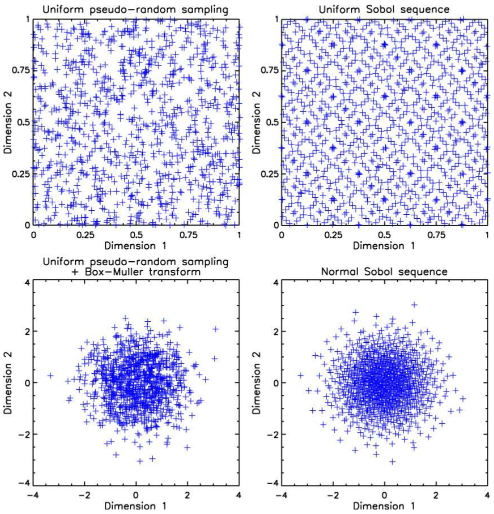
Comparison of convergence properties of different sampling strategies for a simple test model: $f(x) = x_1 + x_2^4$



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).

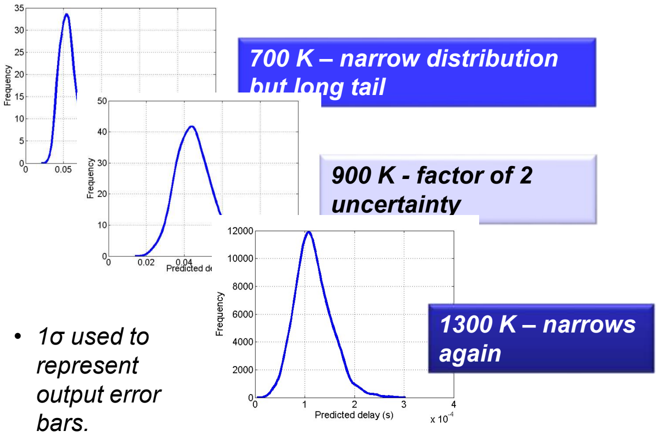


What parameters to include?

- *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)



700 K – narrow distribution but long tail

900 K - factor of 2 uncertainty

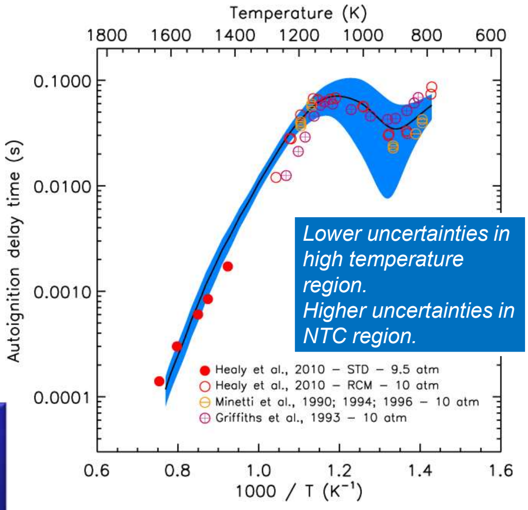
1300 K – narrows again

- *1σ used to represent output error bars.*

(Hébrard et al., 2015)

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)



Lower uncertainties in high temperature region.
Higher uncertainties in NTC region.

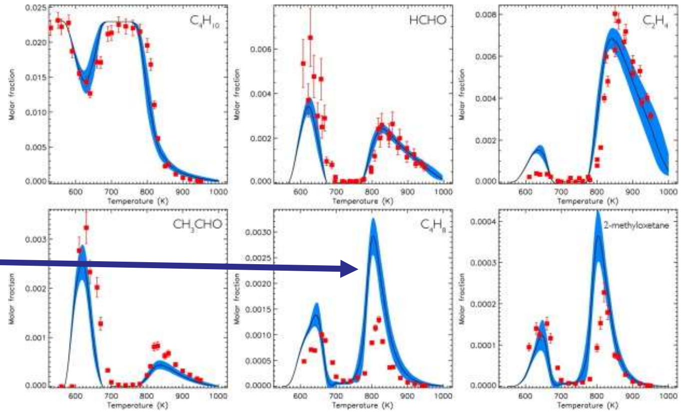
Reasonable agreement between model and shock tube and RCM data if uncertainties are taken into account.

JSR data

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

Missing reaction steps?

Other uncertainties not identified?



We learn about missing parts of the model.

(Hébrard et al., 2015)

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 $Y_i = f_i(x_1, x_2, ..., x_N)$ is influenced by independent random parameters, then the joint pdf of the parameters $P(x_1, x_2, \ldots, x_N) = \prod_{j=1}^{N} p_j(x_j)$.
- The mean or expected value $E(Y_i)$ of the calculated result Y_i is then given by: $E(Y_i) = \iint \ldots \int f_i(x_1, x_2, \ldots, x_N) \prod_{j=1}^{N} p_j(x_j)\,\mathrm{d}\,x_j$
- while the variance $V(Y_i)$ of the calculated result Y_i is specified as:

$$V(Y_i) = \iint \ldots \int (f_i(x_1, x_2, \ldots, x_N) - E(Y_i))^2 \prod_{j=1}^{N} p_j(x_j)\,\mathrm{d}\,x_j$$

$$= \iint \ldots \int f_i^2(x_1, x_2, \ldots, x_N) \prod_{j=1}^{N} p_j(x_j)\,\mathrm{d}\,x_j - E^2(Y_i)$$

- 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:

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

- 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:

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

- 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 us 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 **x** as follows:

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

Nominal value

- 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 **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 **x** may be expressed as a polynomial expansion of basis random variables $\boldsymbol{\xi}$:

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

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 **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 ½ $\mathbf{I}_m$, 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:

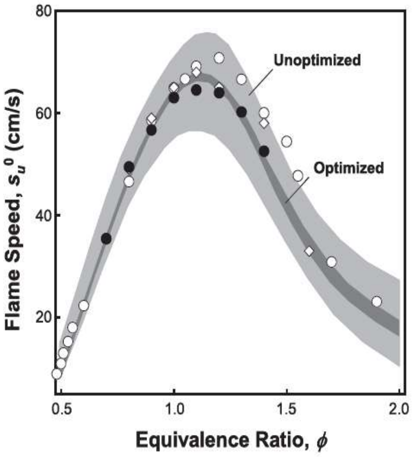
$$\eta_r(\boldsymbol{\xi}) = \eta_r(\mathbf{x}^{(0)}) + \sum_{i=1}^{m} \hat{\boldsymbol{\alpha}}_{r,i}\xi_i + \sum_{i=1}^{m}\sum_{j\geq i}^{m} \hat{\boldsymbol{\beta}}_{r,ij}\xi_i\xi_j + \ldots,$$

$$\hat{\boldsymbol{\alpha}}_r = \tfrac{1}{2}\mathbf{I}_m\mathbf{a}_r \qquad \hat{\boldsymbol{\beta}}_r = \tfrac{1}{4}\mathbf{I}_m^T\mathbf{b}_r\mathbf{I}_m$$

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

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

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):

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

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

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

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

- 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.

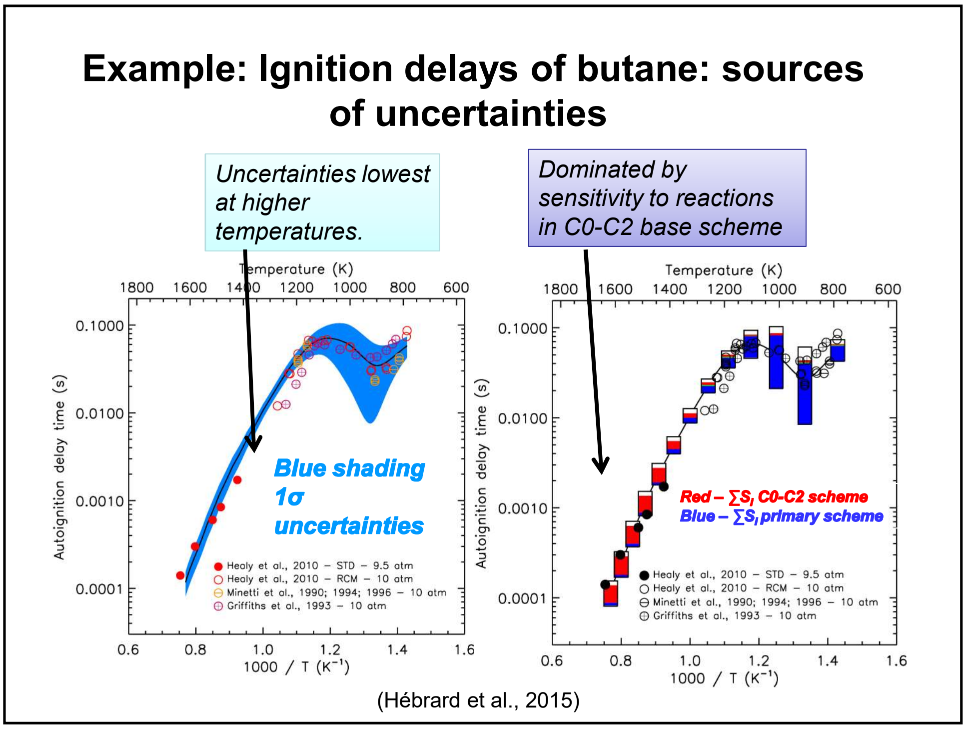
QRS-HDMR

- **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

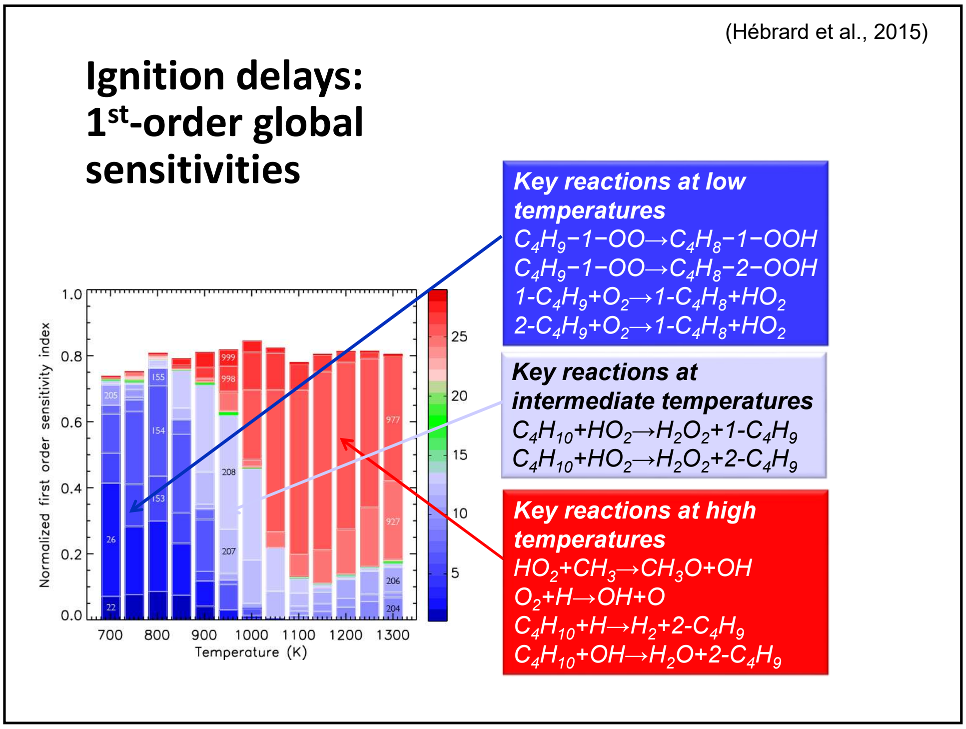
Uncertainties lowest at higher temperatures.

Dominated by sensitivity to reactions in C0-C2 base scheme

Blue shading 1σ uncertainties

Red – ∑Si C0-C2 scheme

(Hébrard et al., 2015)



(Hébrard et al., 2015)

Ignition delays: 1st-order global sensitivities

Key reactions at low temperatures

C_4H_9−1−OO→C_4H_8−1−OOH
C_4H_9−1−OO→C_4H_8−2−OOH
1-C_4H_9+O_2→1-C_4H_8+HO_2
2-C_4H_9+O_2→1-C_4H_8+HO_2

Key reactions at intermediate temperatures

C_4H_{10}+HO_2→H_2O_2+1-C_4H_9
C_4H_{10}+HO_2→H_2O_2+2-C_4H_9

Key reactions at high temperatures

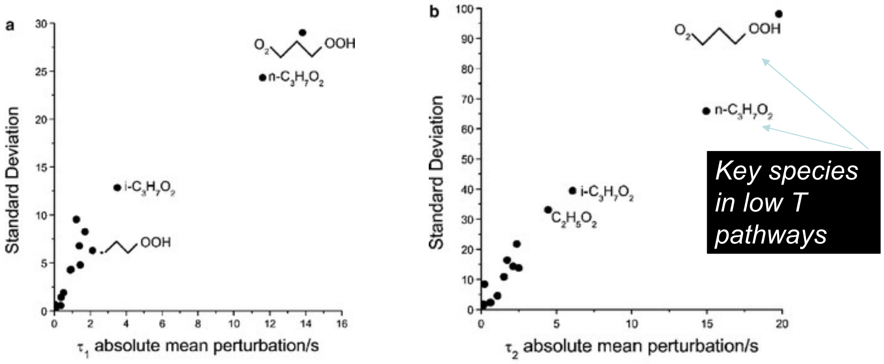
HO_2+CH_3→CH_3O+OH
O_2+H→OH+O
C_4H_{10}+H→H_2+2-C_4H_9
C_4H_{10}+OH→H_2O+2-C_4H_9

Importance of uncertainties in thermodynamic data

- Many sensitivity studies focus only on a local analysis of A factors for reactions.
  - Tells us about importance of different reaction steps but not really sufficient for full uncertainty propagation.
- Effects of thermo data often ignored but can be critical for predicting e.g.
  - Heat release
  - Equilibrium between important species in low T reactions such as RO_2, QOOH
- At simplest level **should involve variability in heats of formation**.
- In reality where data from ATChT – data is highly correlated.

Some examples

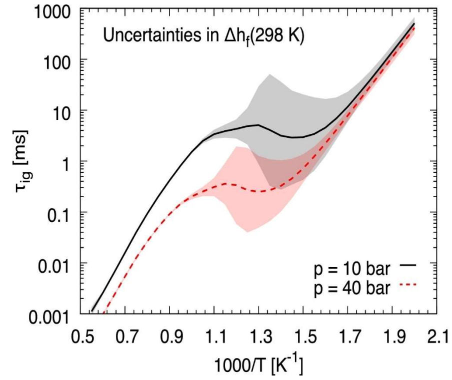
- 2 stage ignition delay times for **stoichiometric propane oxidation**.
- Morris method (Hughes, 2006).
- Variations in ΔH_{f° from NIST Chemistry WebBook where possible.
- Where no quoted error, ±5, +10 or +15 kJ mol^{-1}, used depending on complexity of species.



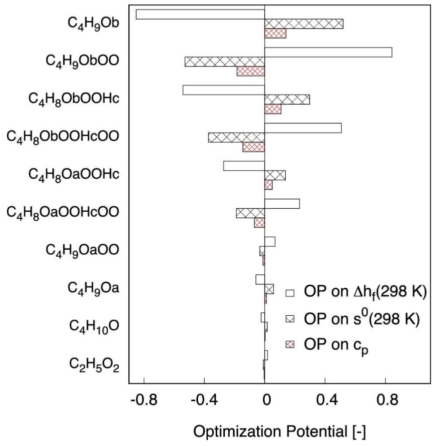
Key species in low T pathways

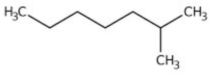
Impact of thermo uncertainties on diethyl ether oxidation (Vom Lehn, 2019)

- Highest prediction uncertainty observed in the NTC regime.

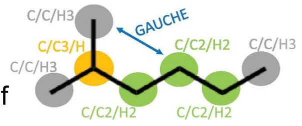


Optimization potential of τ_{ign} for uncertainties in Δh_f(298 K), s^0(298 K), and c_p for a stoichiometric DEE/air mixture at T=769 K and 10 bar.

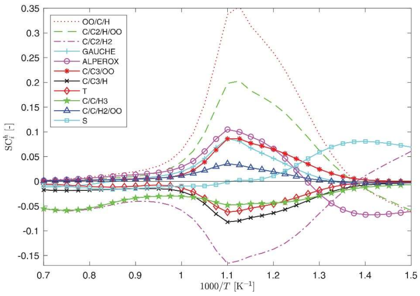


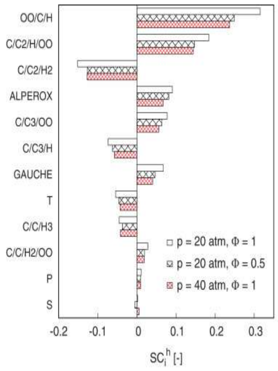


Impacts of group additivity values on kinetic model predictions (vom Lehn, 2020)



- 2 methyl heptane, shock tube ignition delays.
- Non-dimensionalized sensitivity coefficients of ignition delay time with respect to group parameters ψ_j defined as:
- $SC_j^{\Psi} = \dfrac{\partial \tau_{ign}}{\Psi_j} \dfrac{\Psi_{norm}}{\tau_0}$

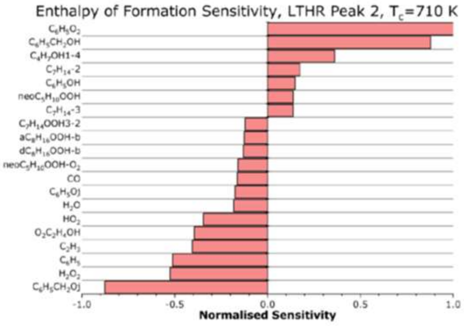


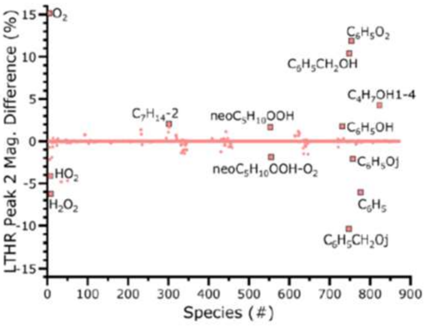


Sensitivity coefficients of ignition delay time on the group values of Δh_f(298 K)

Impact of thermo uncertainties (+5 kJ mol^{-1}) **in prediction of LTHR for gasoline surrogate**

Michelbach, thesis 2020





- Competition between 2 benzyl reaction pathways involving relatively unreactive benzyl alcohol ($C_6H_5CH_2OH$) and more reactive $C_6H_5CH_2O$j.
- Reverse true for increase in enthalpy of formation for the benzyloxy radical

Optimisation methods for constraining model uncertainties.

Range of data types available:

Direct measurements:

- Determination of the rate coefficient of a single elementary reaction.
- Rate coefficients are published at a given temperature, pressure, and bath gas. Sometimes Arrhenius expressions developed.

Theoretical (direct) determinations:

- TST/master equation calculations.
- The rate coefficients are published at given T, P.
- Parameterized T, P dependence of rate coefficient k.

Indirect measurements:

- A property of the whole combustion system is measured.
- Interpretation is based on a detailed mechanism.
- *Examples:* Laminar burning velocities, ignition delays, concentration profiles.

Traditional approach is to develop k(T,P) using first two methods and evaluate using third.

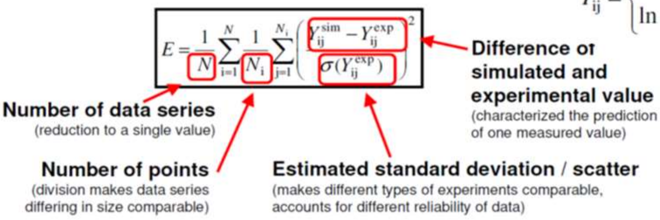
Evaluation

- More effective to automate mechanism evaluation via codes that perform many simulations over all available indirect experiments.
- Normalised error measures needed to rank accuracy of mechanisms and to evaluate which are the key reactions and species within them.
  - i.e. not just eyeballing results.
- Examples from Eötvos group:

Absolute deviation of a single data point

$$D = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{N_i}\sum_{j=1}^{N_i}\left(\frac{\boxed{Y_{ij}^{\mathrm{sim}} - Y_{ij}^{\mathrm{exp}}}}{\sigma(Y_{ij}^{\mathrm{exp}})}\right)$$

$$Y_{ij} = \begin{cases} y_{ij} & \text{if } \sigma(y_{ij}^{\mathrm{exp}}) \approx \text{constant} \\ \ln y_{ij} & \text{if } \sigma(\ln y_{ij}^{\mathrm{exp}}) \approx \text{constant} \end{cases}$$



$$E = \frac{1}{\boxed{N}}\sum_{i=1}^{N}\frac{1}{\boxed{N_i}}\sum_{j=1}^{N_i}\left(\frac{\boxed{Y_{ij}^{\mathrm{sim}} - Y_{ij}^{\mathrm{exp}}}}{\boxed{\sigma(Y_{ij}^{\mathrm{exp}})}}\right)^2$$

Difference of simulated and experimental value
(characterized the prediction of one measured value)

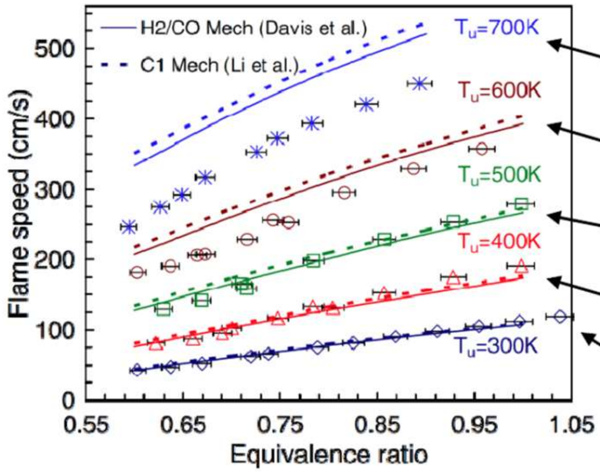
Number of data series
(reduction to a single value)

Number of points
(division makes data series differing in size comparable)

Estimated standard deviation / scatter
(makes different types of experiments comparable, accounts for different reliability of data)

Zsely

Example



E	D
998	+62.6
1603	+79.6
21.94	+29.2
39.96	+40.2
1.46	+4.3
2.72	+11.2
3.29	+0.5
4.67	+4.7
2.15	+1.1
5.19	+3.5

Optimisation

- What then if we can **vary the parameters** within **uncertainty bounds** to minimise such error functions and improve overall fit with available data:
  - Optimisation.
  - Error function used as objective function in minimisation process.
- First used for development of GRI mech for methane combustion (Frenklach and co-workers).
- BUT available data sets grow in size over time, new parameter estimations developed, uncertainties change.
- **Mechanisms are not static** and we shouldn't get stuck with old mechanisms out of convenience.

Example for hydrogen combustion

- First: comparison of mechanisms using available data..

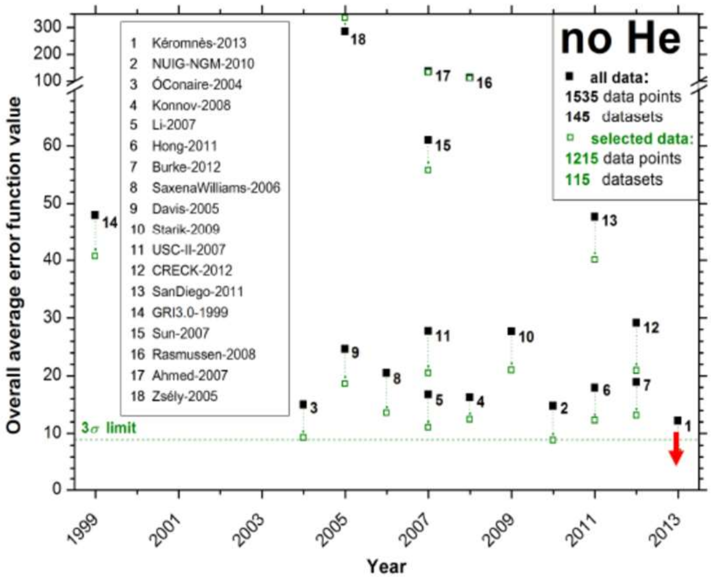
• Ignition delays – shock tube	770 data points in 53 datasets
• Ignition delays – RCM	229 data points in 20 datasets
• Laminar burning velocities	631 data points in 73 datasets
• Species profiles – JSR	152 data points in 9 datasets
• Species profiles – flow reactor	389 data points in 17 datasets

Wide range of conditions

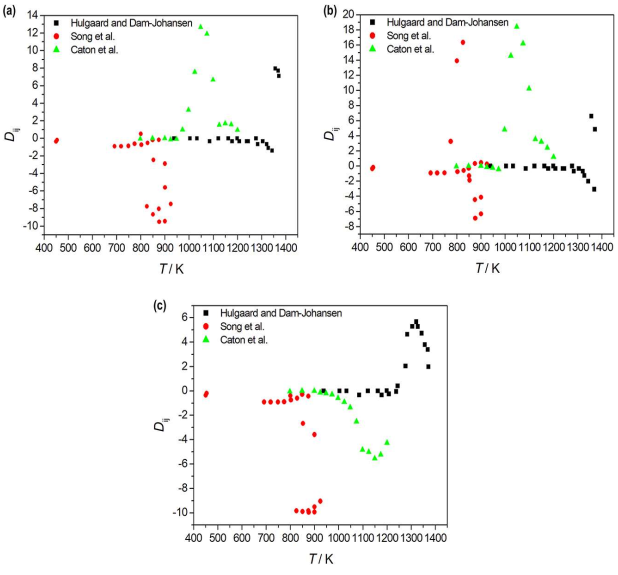
• Temperature:	800 K – 2300 K	Pressure	0.1 bar – 65 bar
• Equivalence ratio	0.2 – 5.0		

C. Olm, I. Gy. Zsély, R. Pálvölgyi, T. Varga, T. Nagy, H. J. Curran, T. Turányi
Comparison of the performance of several recent hydrogen combustion mechanisms
Combustion and Flame, **161**, 2219-2234 (2014)

Available mechanisms and error functions over time



Ammonia example (Kawka, 2020)



- Plot of the $\boldsymbol{D}_{ij}$ values versus temperature calculated by mechanisms Klippenstein-2011 (a), Glarborg-2018 (b) and Song-2019 (c) for the N_2O concentration measurements.

Methods used for optimisation

- Frenklach and co-workers
  - Most influential (**active**) parameters identified via sensitivity analysis (often local method).
  - **Response surfaces models** used for each optimization target to express the simulation result as a function of values of active parameters.
  - Minimise error function by varying active parameters.
  - **LATER** with penalties for distance from evaluated nominal values - MUM-PCE.
  - $\Phi = \sum_r [(\mu_{r,\, expt} - \mu_{r,\, calc})/\sigma_r]^2 + \sum_k 2xk^2$
- Wang and co-workers
  - Use of polynomial chaos expansions to provide covariance matrix of fitted parameters.

Validity of optimised mechanism

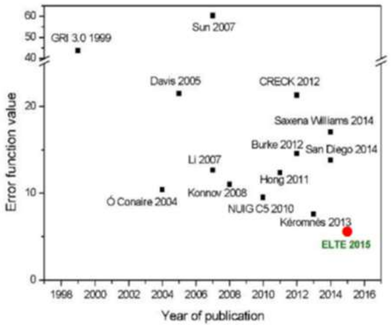
- Limited set of targets makes **extrapolation** of mechanism to new conditions dangerous.
- **Must be based on sensitive parameters** or others will be changed with no basis.
- Sets of targets can in principle include:
  - Direct measurements
  - Theory
  - Indirect measurements
- Very large number of simulations required hence use of surrogate models – see later.
- Can also use hierarchical approach:
  - First, most influential parameters optimized roughly.
  - Reactions (and corresponding experiments) added one by one and optimized first separately, later altogether.

Example: Keromnes mechanism

- Thousands of samples required.
- Orthonormal polynomial response surface used.

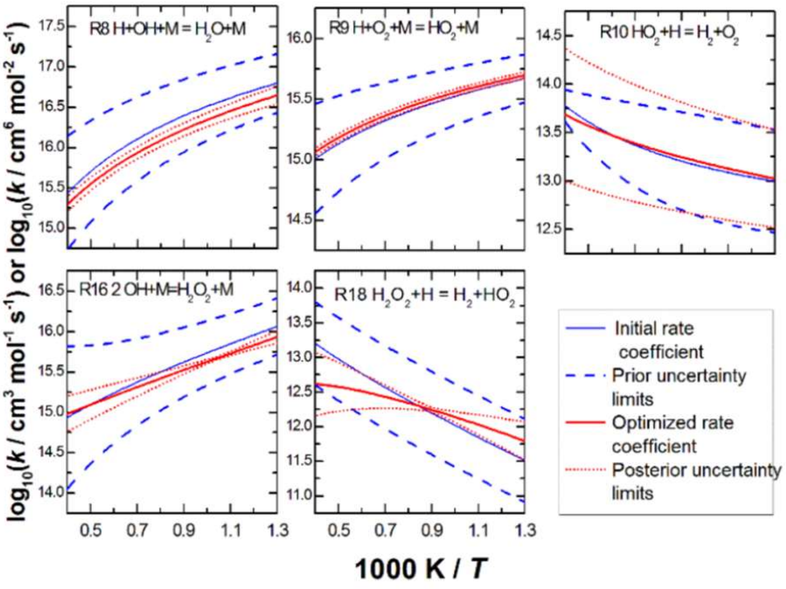
Final set of optimization targets

• Ignition measurements in shock tubes	566 data points in 43 datasets
• Rapid compression machines	219 data points in 19 datasets
• Burning velocity measurements	364 data points in 59 datasets
• Direct rate coefficient measurements	1749 data points in 59 datasets



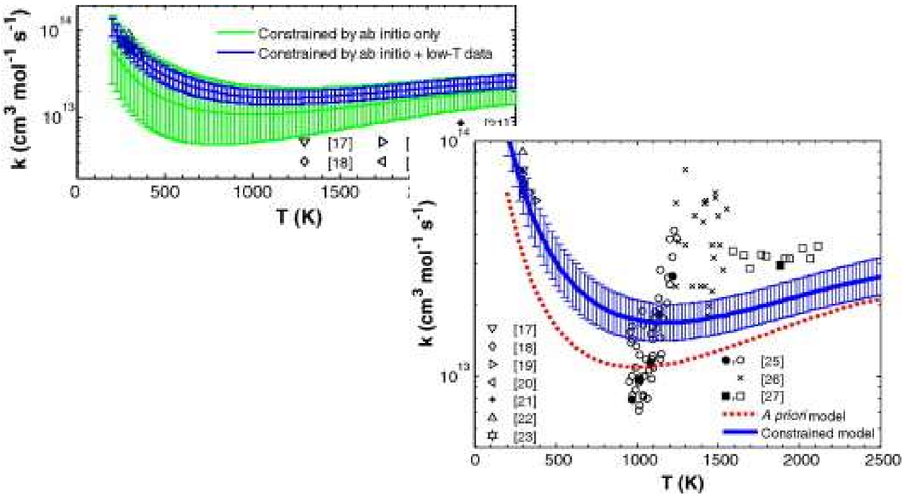
Measurement type	Kéromnès mechanism	Optimized mechanism
Shock tube	1.081	1.043
RCM	1.400	0.600
Burning velocities	3.115	1.770
Direct measurements	2.254	0.924
Total	7.851	4.338

Prior and posterior uncertainties



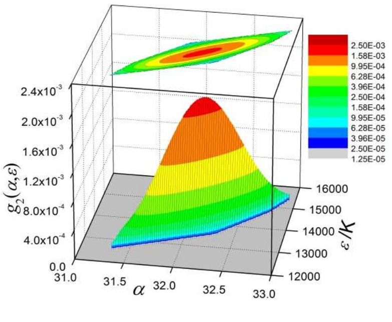
$OH + HO_2 = H_2O + O_2$
An example of multi-scale modelling

- Remember from earlier?
- In this case theory was used but with more limited experimental data.



Correlated sensitivities

- The result of optimisation of reaction/thermodynamic networks is a joint probability distribution of parameters.
- Correlations must be accounted for when propagating uncertainties or final predictive uncertainties will be overestimated.



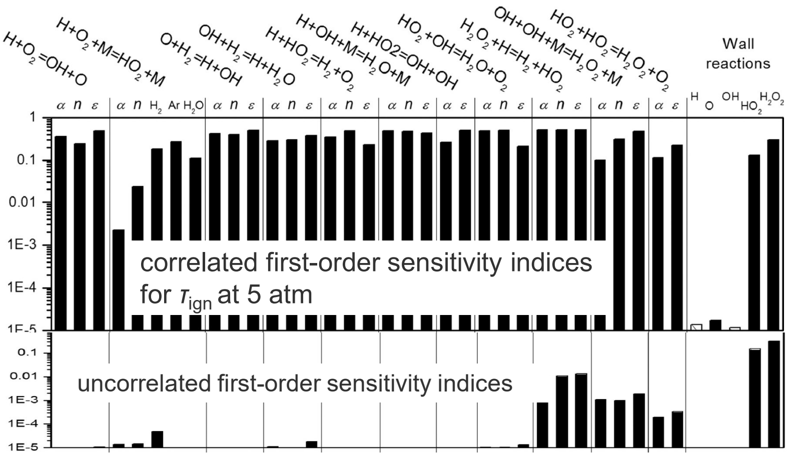
- Straightforward for uncertainty propagation – just sample from **joint probability distribution**.
- Need a way to account for correlations in sensitivity analysis.
  - Trickier.

Example for optimised hydrogen combustion mechanism (Valko, 2017)

- HDMR method used (see earlier) to calculate sensitivities as contributions to overall variance in target outputs.
- Rosenblatt transformation used to create an uncorrelated sample from the correlated one.
- Results in sets of correlated sensitivities, plus hierarchical set of marginal sensitivities where correlated effects of previous parameters in sequence are neglected.
- Marginal sensitivity indices represent partial correlations and depend on selection order.
- In last step obtain totally uncorrelated contribution of parameter x_n to the variance of $f(\mathbf{x})$.

Effect of correlations

- Similarity of correlated sensitivity indices indicates that rate parameters act as a **correlated group** rather than through individual effects.
- Predictive power of model could be improved by decreasing uncertainty of almost any rate parameter, if fed back to optimization.



Information content and design of experiments (DoE)

- High correlations perhaps suggests a different approach for determining new experiments of value.
- Instead of designing experiments to isolate and improve accuracy of individual reactions, need to think about **minimising uncertainty of system as a whole through optimisation.**
- Methods from information theory useful.
  - Particularly for alternative fuels where little data exists and species are large (limiting application of high level theory).
- Optimal experiments are chosen iteratively one by one.
  - Giving high priority experiments and their order.

We are not used to simulating experiments before we perform them but we should do it!

Example for DME combustion (Vom Lehn, 2021)

- Posterior covariance matrix **Σ*** of **x** is estimated based on a linearization of the response surface in the neighbourhood of their posterior values **x*** where $\mathbf{J}_r^*$ is local gradient of model response r with respect to **x**, evaluated at **x*.**

$$\mathbf{\Sigma}^* = \left[\sum_{r=1}^{n} \frac{\mathbf{J}_r^* \mathbf{J}_r^{*\mathrm{T}}}{\left(\sigma_r^{\mathrm{obs}}\right)^2} + 4\mathbf{I}\right]^{-1}.$$

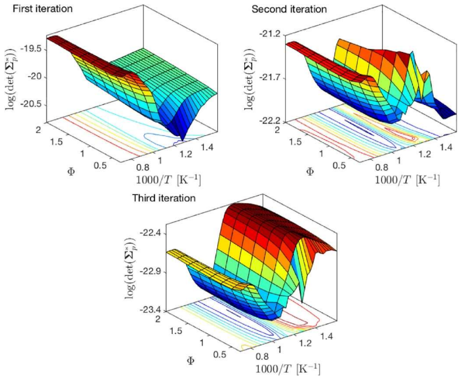
Aim: *efficient minimization of joint parameter uncertainties.*

- Each iteration starts with evaluation of all not yet selected conditions p in terms of covariance matrices that would result if the experiment p were selected.
- Nominal model prediction from previous iteration assumed as hypothetical experimental value of experiment *p* to determine Σp*. Sum includes all previous exp.

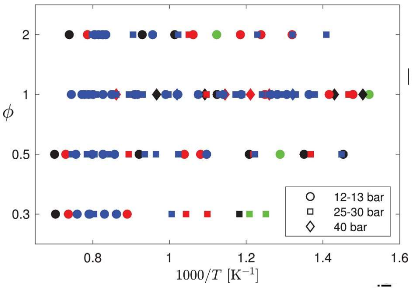
Example for DME combustion (Vom Lehn, 2021)

- Equivalent to D-optimal design.
  - select the experiment which minimizes the Shannon entropy of the multivariate normal distribution of model parameters in each step.
- Shannon entropy in this context measures the variability of the multivariate normal distribution of the model parameters.
- Minimization is equivalent to minimizing the determinant of the expected covariance matrix after inclusion of the new experiment

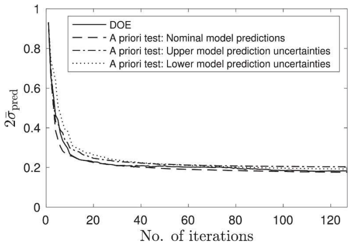
$$\Psi(p) = \min_p \left(\det\left(\mathbf{\Sigma}_p^*\right)\right)$$

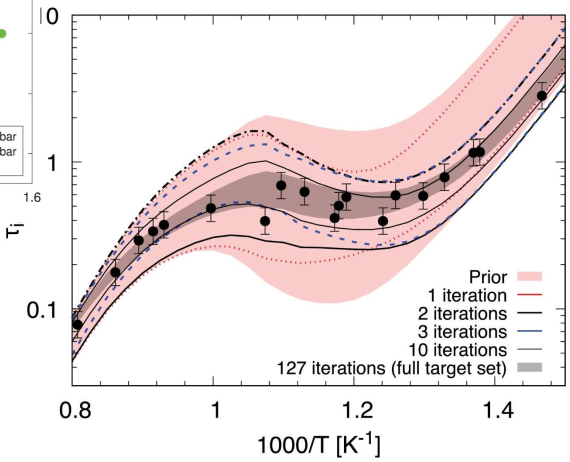


Example for DME combustion (Vom Lehn, 2021)



● 1-5, ● 6-20,
● 21-50, ● 50-127





2σ prediction uncertainties after different DOE iteration steps

Doing things optimally

- Requires collaboration as a community!
- To combine modelling, experimental design and expertise, statistical methods.
- To think about what experiments/theory calcs are required to reduce system uncertainty and not just what we fancy/might be easiest…

SECTION 7
CHEMICAL MODEL REDUCTION

Why is it necessary?

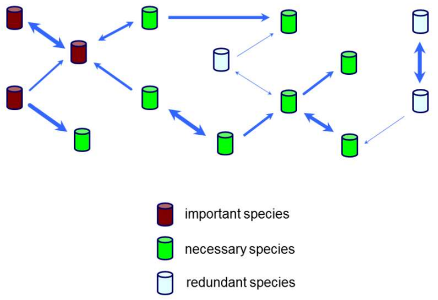
- Reactive flow models may involve resolving complex 3D turbulent flows within complex geometries.
- In order to achieve realistic computational times something has to be sacrificed:
  - **Spatial resolution**
  - **Highly averaged turbulence models**
  - **Use of simplified chemistry.**
- Detailed chemistry 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 loose 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 someway and store the results for use in CFD.

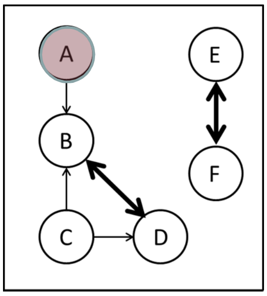
Skeletal reduction

- 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.

$$R_{i\to j}^{(\mathrm{Lu})} = \frac{\sum_{\alpha\in C(i,j)} \left|\nu_{i\alpha} r_\alpha\right|}{\sum_{\alpha\in R(i)} \left|\nu_{i\alpha} r_\alpha\right|}$$

threshold

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

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, $\nu_{i\alpha}$ is the stoichiometric coefficient of species *i* in reaction *α*, and r_α is the net reaction rate

Examples of variants of DRG

$$R_{i\to j}^{(\mathrm{Luo})} = \frac{\max_{\alpha\in C(i,j)}\left|\nu_{i\alpha} r_\alpha\right|}{\max_{\alpha\in R(i)}\left|\nu_{i\alpha} r_\alpha\right|}$$

- 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.

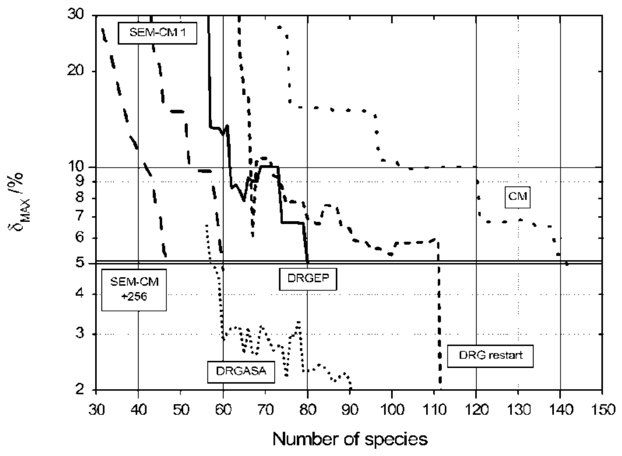
Simulation Error Minimization Connectivity Method (SEM-CM)

- Connectivity determined iteratively using: $B_i = \sum_j \left(\left(y_i / f_j \right) \left(\partial f_j / \partial y_i \right) \right)^2$
- Shows the effect of a change in the concentration of each species on the concentrations of all **important + necessary** species, *j*.
- Gaps in B_i 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)

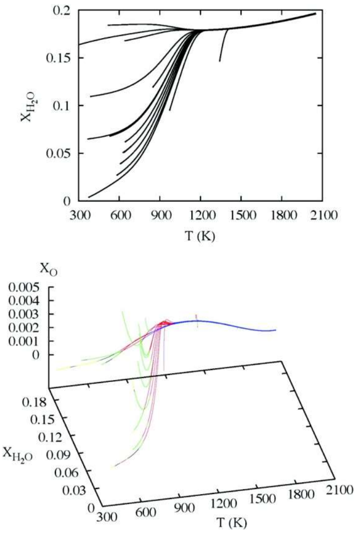
methane partial oxidation mechanism



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??

Davis & Tomlin, 2008

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).

$$\Delta Y_i = \left(-\frac{\mathrm{d}\,Y_i}{\mathrm{d}\,t}\right)\left(-\frac{1}{J_{ii}}\right)$$

- Or for coupled groups of QSS species: $\frac{\mathrm{d}\,\mathbf{Y}^{(QSS)}}{\mathrm{d}\,t} = \mathbf{J}^{(QSS)}\Delta\mathbf{Y}^{(QSS)}$
- 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.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C\,.$$

- If QSSA applied to B

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

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

B can be removed providing the global reaction step: A → C

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

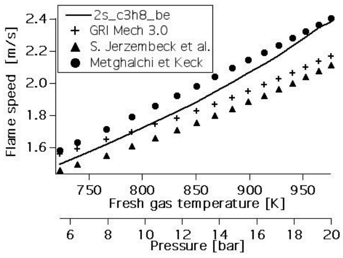
- In other cases numerical iteration methods are needed.

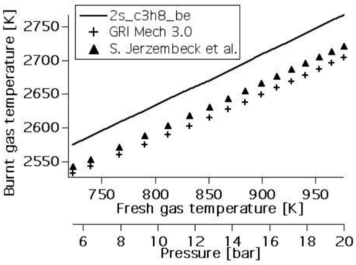
Global reaction schemes

- 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. **WARNING – such expressions are often out of date from a kinetics perspective.**

Example from CERFACS – note non-integer stoichiometries:

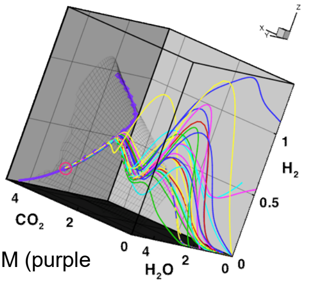
```
# Reaction 1 reaction( "C3H8 + 3.5 O2 => 3 CO + 4 H2O", [5.82320E+12, 0,
34000], order = " C3H8:0.8 O2:0.86 ")
# Reaction 2 reaction( "CO + 0.5 O2 <=> CO2", [2.00000E+09, 0, 12000])
```





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 hyper-surfaces 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:

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

where $\psi = (\psi_1, \psi_2, \ldots, \psi_{S+2})^T$ is the thermokinetic state, $\psi = (h, p, w_1, \ldots, w_S)^T$, 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:

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

$$\tilde{Z}_c\frac{\partial\psi}{\partial t} = \tilde{Z}_c F(\psi)$$

$$\tilde{Z}_s\frac{\partial\psi}{\partial t} = \tilde{Z}_s F(\psi)$$

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

Equilibrate fast time-scales

$$\tilde{Z}_f F(\psi) = 0$$

Project onto slow subspace

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

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

Rate-controlled constrained-equilibrium method (RCCE)

- Based on assumption that fast chemical processes lead to an equilibrium state, subject to the conditions that some major species have concentrations which evolve according to kinetics.
- Major species evolve according to differential equations involving detailed chemical kinetics, whilst equilibrated species are determined by **minimising the free energy of the mixture**, subject to ***additional constraints*** (i.e. in addition to the conservation of mass, energy and elements).
- **Constrained species often equivalent to non-QSS species**.

RCCE

- System dynamics takes place on the constrained equilibrium manifold.
  - Analogous to other invariant manifolds.
- In the limit that the number of constraints equals the number of species in the problem, the RCCE model becomes equivalent to a detailed mechanism.
- Also suggested that the relationship between an RCCE model and a detailed mechanism is analogous to that between statistical mechanics and molecular dynamics in applications to thermodynamics and reaction rate theory (Miller, 2021).
  - Need to have ways to define constraint species optimally.

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

$$F_\psi = \left(Z_c\, Z_s\, Z_f\right) \cdot \begin{pmatrix} N_c & & \\ & N_s & \\ & & N_f \end{pmatrix} \cdot \begin{pmatrix} \tilde{Z}_c \\ \tilde{Z}_s \\ \tilde{Z}_f \end{pmatrix},$$

$$|\lambda_i(N_c)| < \tau_c, \quad \lambda_i^{\text{real}}\left(N_f\right) < \tau_s < \lambda_i^{\text{real}}(N_s)$$

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):

.

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.*

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 “loose” 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 O_2 to form HO_2 and conjugate olefins.
  3. Direct and reverse O_2 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 HO_2 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.

$R_1 + O_2 \rightarrow R_1OO \quad k_1$

$R_2 + O_2 \rightarrow R_2OO \quad k_2$

$R_3 + O_2 \rightarrow R_3OO \quad k_3$

$R_4 + O_2 \rightarrow R_4OO \quad k_4$

The lumped alkyl radical is then defined by:

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

with the corresponding lumped reaction given by:

$R + O_2 \rightarrow ROO \qquad k_5$

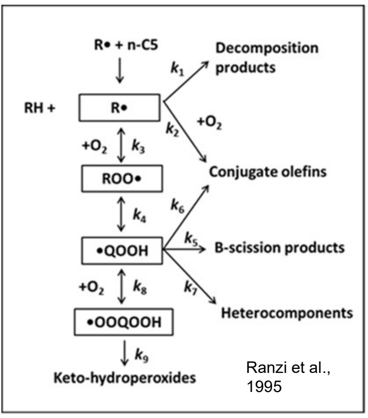
Lumped rates defined by **fitting** with respect to experimental data or with respect to the complex full model (MAMOX, Milan) or **weighted averages** for the different component isomers depending on the relative **weights** within the initial fuel or from the **weighted mean of the elementary rate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

$$k_5 = \frac{k_1[\mathrm{R}^\bullet{}_1] + k_2[\mathrm{R}^\bullet{}_2] + k_3[\mathrm{R}^\bullet{}_3] + k_4[\mathrm{R}^\bullet{}_4]}{[\mathrm{R}^\bullet]}$$

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.
- Q7OOH → OH + 0.3HCHO + $0.32C_5H_{10}$ + $0.3C_4H_8$ + $0.35CH_3CHO$ + $0.31C_3H_6$ + $0.35C_2H_5CHO$ + $0.4C_2H_4$ + $0.06C_7H_{14}$



Ranzi et al., 1995

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).

(i,1)	$A_i + H \leftrightarrow A_i^{\cdot} + H_2$
(i,2)	$A_i^{\cdot} + C_2H_2 \leftrightarrow A_iCHCH^{\cdot}$
(i,3)	$A_iCHCH^{\cdot} + C_2H_2 \rightarrow A_{i+1} + H$
(i+1,1)	$A_{i+1} + H \leftrightarrow A_{i+1}^{\cdot} + H_2$
(i+1,2)	$A_{i+1}^{\cdot} + C_2H_2 \leftrightarrow A_{i+1}CHCH^{\cdot}$
(i+1,3)	$A_{i+1}CHCH^{\cdot} + C_2H_2 \rightarrow A_{i+2} + H$
(i+2, i+3, …, n)	… etc.

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:

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

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

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

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

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

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

… *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 $M_o = [A_i] + [A_i^{\cdot}] + [A_iCHCH^{\cdot}] + [A_{i+1}] + \dots$.

- 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.

$$\frac{d\mathrm{M}_1}{dt} = \left(m_o \frac{d[\mathrm{A}_i]}{dt} + m_o \frac{d[\mathrm{A}_i^{\cdot}]}{dt} + (m_o + 2)\frac{d[\mathrm{A}_i\mathrm{CHCH}^{\cdot}]}{dt} + (m_o + 4)\frac{d[\mathrm{A}_{i+1}]}{dt} + \cdots . \right)$$
$$= m_o r_o + 2k_2[\mathrm{C_2H_2}]\sum_i [\mathrm{A}_i^{\cdot}] - 2k_{-2}\sum_i [\mathrm{A}_i\mathrm{CHCH}^{\cdot}] + 2k_3[\mathrm{C_2H_2}]\sum_i [\mathrm{A}_i\mathrm{CHCH}^{\cdot}]$$

where $M_1 = m_o[\mathrm{A}_i] + m_o[\mathrm{A}_i^{\cdot}] + (m_o + 2)[\mathrm{A}_i\mathrm{CHCH}^{\cdot}] + (m_o + 4)[\mathrm{A}_{i+1}] + (m_o + 4)[\mathrm{A}_{i+1}^{\cdot}] + \cdots,$

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:

$$\hat{c}_1 = \sum_i [\mathrm{A}_i]$$
$$\hat{c}_2 = \sum_i [\mathrm{A}_i^{\cdot}]$$
$$\hat{c}_3 = \sum_i [\mathrm{A}_i\mathrm{CHCH}^{\cdot}]$$

- The corresponding lumped equation system is then given by:

$$\frac{d\hat{c}_1}{dt} = r_o - k_1[\mathrm{H}]\hat{c}_1 + k_{-1}[\mathrm{H_2}]\hat{c}_2 + k_3[\mathrm{C_2H_2}]\hat{c}_3$$

$$\frac{d\hat{c}_2}{dt} = k_1[\mathrm{H}]\hat{c}_1 - k_{-1}[\mathrm{H_2}]\hat{c}_2 - k_{-2}\hat{c}_3$$

$$\frac{d\hat{c}_3}{dt} = k_2[\mathrm{C_2H_2}]\hat{c}_2 - k_{-2}\hat{c}_3 - k_3[\mathrm{C_2H_2}]\hat{c}_3$$

- 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 **Y** to a new transformed variable vector $\hat{\mathbf{Y}}$ using the transformation function **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:

$$\frac{\mathrm{d}\hat{\mathbf{Y}}}{\mathrm{d}t} = \hat{\mathbf{f}}\left(\hat{\mathbf{Y}},\hat{\mathbf{k}}\right) \qquad \hat{\mathbf{Y}}(t_0) = \hat{\mathbf{Y}}_0$$

Linear Lumping

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

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

where **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 $\hat{Y}_1 = Y_1$.

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

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.

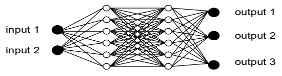
1. Δt is selected to achieve good resolution of the characteristic system time-scale.
2. Several thousand, spatially homogeneous simulations carried out with series of initial concentrations and/or T, representative of circumstances of final applications.
3. $\mathbf{Y}(t)$, $\mathbf{Y}(t+\Delta t)$ 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.

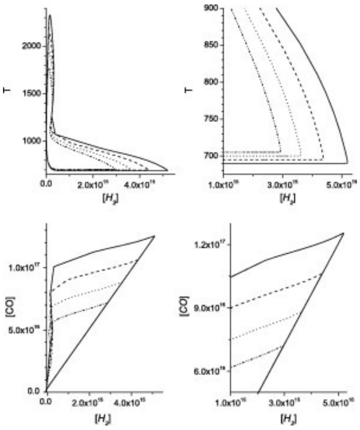
Different approaches

- 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 H_2/air mixtures over wide ranges of temperatures and pressures ($1000 < T0 < 1500$ 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-H_2 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.
- [H_2], [O_2], [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)

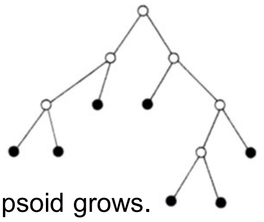
- Polynomial approach (Tonse et al., 1999) whereby fitted polynomial functions are ***developed during the calculation***, and then ***reused*** when the region of composition space is revisited in subsequent time steps or different spatial regions (c.f. ISAT later).
- Uses **second-order polynomials** 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).

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**.

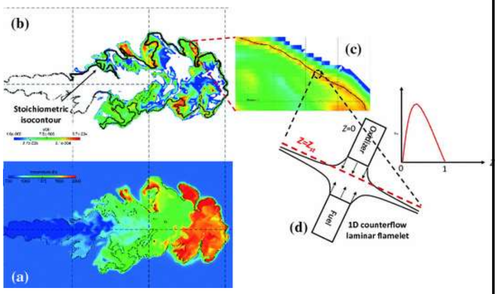
In situ adaptive tabulation (ISAT), (Pope, 1997)

- 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 les 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*;**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 on reduction methods

- 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.

Final overall considerations

- All this work has required an enormous human effort.
- New fuels are likely to be more complex/varied than the ones we know.
- Devices will need to be redesigned and optimised to work with new fuels/blends.
- We need to get a move on to be relevant.
  - ➢ net zero by 2050!

Fully automated luxury communism for kinetics?

- Automated laboratories.
  - High throughput/accuracy.
  - Conditions chosen by DOE.
- Automated big data analysis.
  - For evaluation of mechanisms, optimisation.
  - **Effective sharing** of data, including raw.
- Automated theory calculations (Elliot, 2021).
  - Large number of reactions for new fuels.
  - Hierarchical approach in terms of level of accuracy.
- Automated optimisation.
- Automated model reduction for inclusion into CFD design codes.

➢ **SOLVE GRAND CHALLENGE PROBLEMS.**