



TUESDAY 2-1 (ALISON TOMLIN)

Chemical kinetics data:

Mechanism generation and sources
of data



DEVELOPING KINETIC MECHANISMS FOR COMBUSTION



Main source material for this section

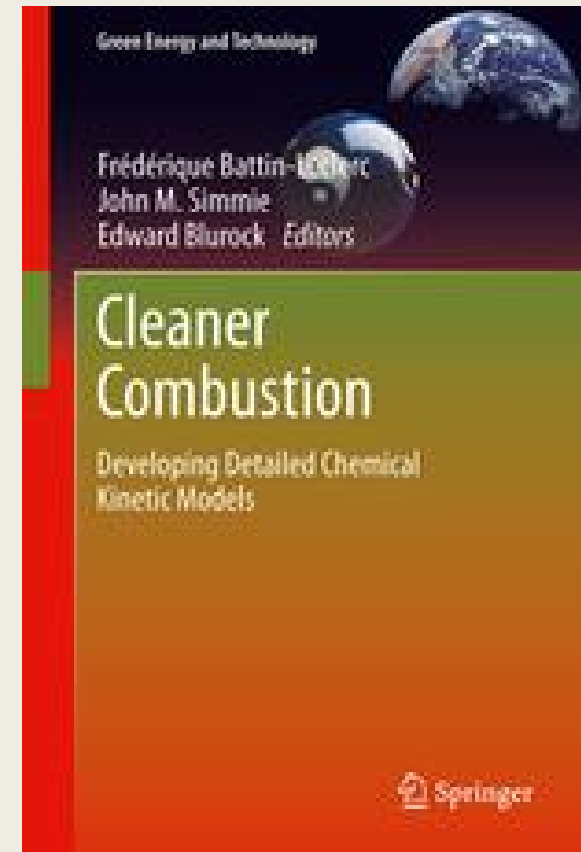
- **Cleaner Combustion**

Developing Detailed Chemical Kinetic Models

Editors: **Battin-Leclerc, Frédérique, Simmie, John M., Blurock, Edward (Eds.)**

Springer, 2013

- **Chapters 1-3**



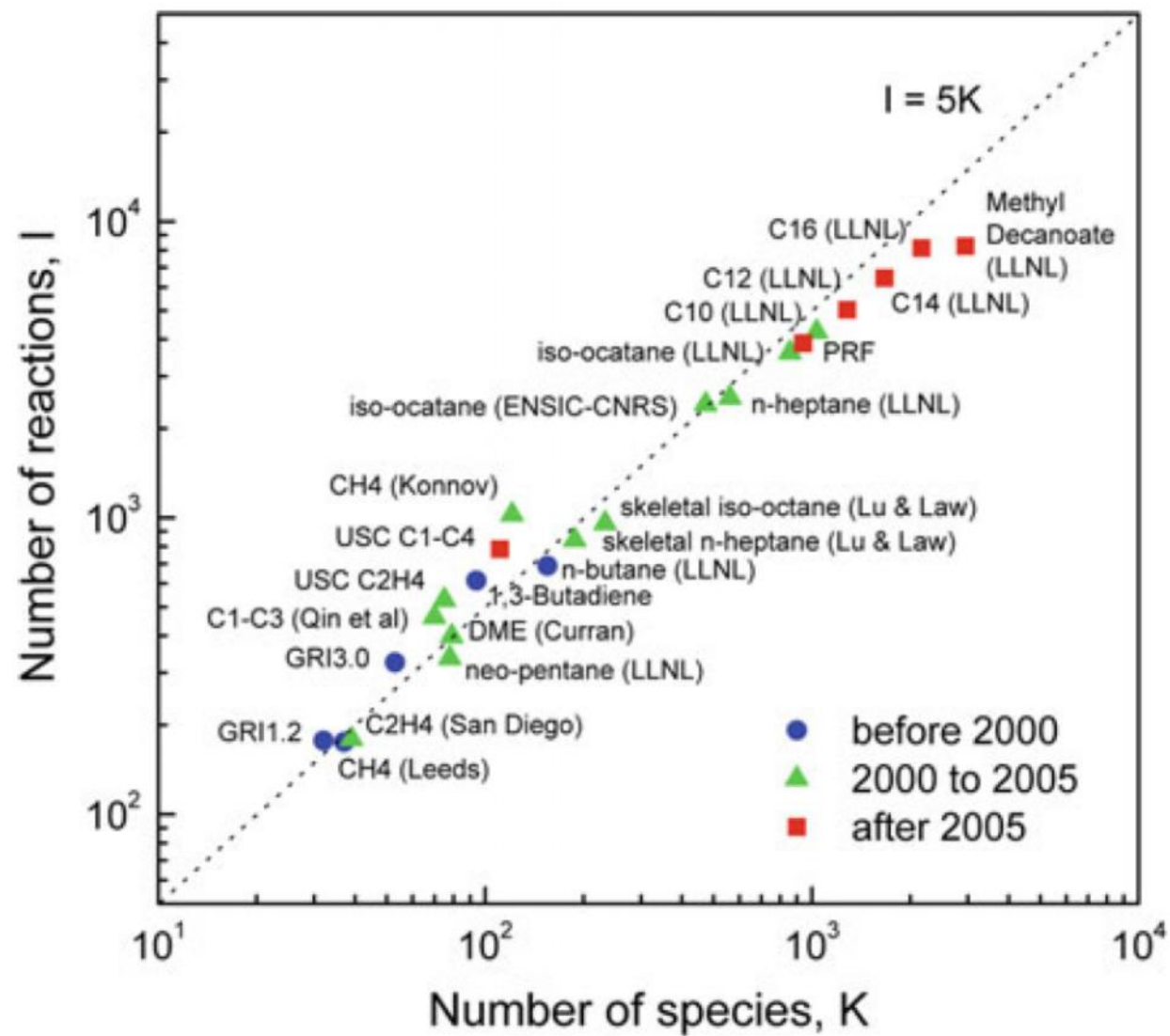
What is the purpose of a model?

- A model is an interpretation and an approximation of physical reality.
- In one sense it is a construction which helps us to understand the governing principles behind the physical/chemical phenomena we are trying to describe.
- We also need it to make predictions about physical behaviour. Prediction in this sense means telling us *things we do not yet know or have not yet measured*.
- 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.
- In addition, 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, 2013)

- The more complex the model, the larger number of parameters contains and therefore a lot of work has to be done to quantify these parameters.
- In combustion, the tendency has been for models to become more and more complex as our understanding of fundamental processes improves.
- Faraday's early work in "The Chemical History of the Candle" (Faraday 1861) describes the interactions of the fundamental thermodynamics and chemical aspects of a flame.
- Much later, 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.

Lu and Law
(2009)



Manual construction

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

Detailed Chemical Mechanisms

- A detailed chemical mechanism is usually considered to be composed of *elementary reaction steps* (no macroscopically observable intermediate between the reactants and the products).
- The molecular structures of the species involved are not always stable molecules, but in many cases free radicals (or even atoms), e.g. uncharged species with an unpaired electron.
- Reactions involving free radicals can be divided in four types:
 - **Initiation**: those creating radicals from fuel,
 - **Termination**: those consuming radicals,
 - **Propagation**: those transforming a radical into another one,
 - **Branching**: those creating new radicals from a radical or an unstable product (degenerate branching steps).
- Processes like ignition depend on the relative importance of these steps.
- The rate constant associated with each elementary reaction is derived from the molecular structure and is not dependent on conditions under which it is measured, except temperature and in some cases pressure.
- Many rate constants relevant to combustion can be obtained from databases (e.g., Baulch et al. 1992; Tsang & Hampson 1986), evaluating experimental measurements and theoretical calculations.

The concept of reaction classes (Blurock and Battin-LeClerc, 2013)

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

How to define reaction classes

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

Examples of high temperature reaction classes (Sarathy et al., 2011)

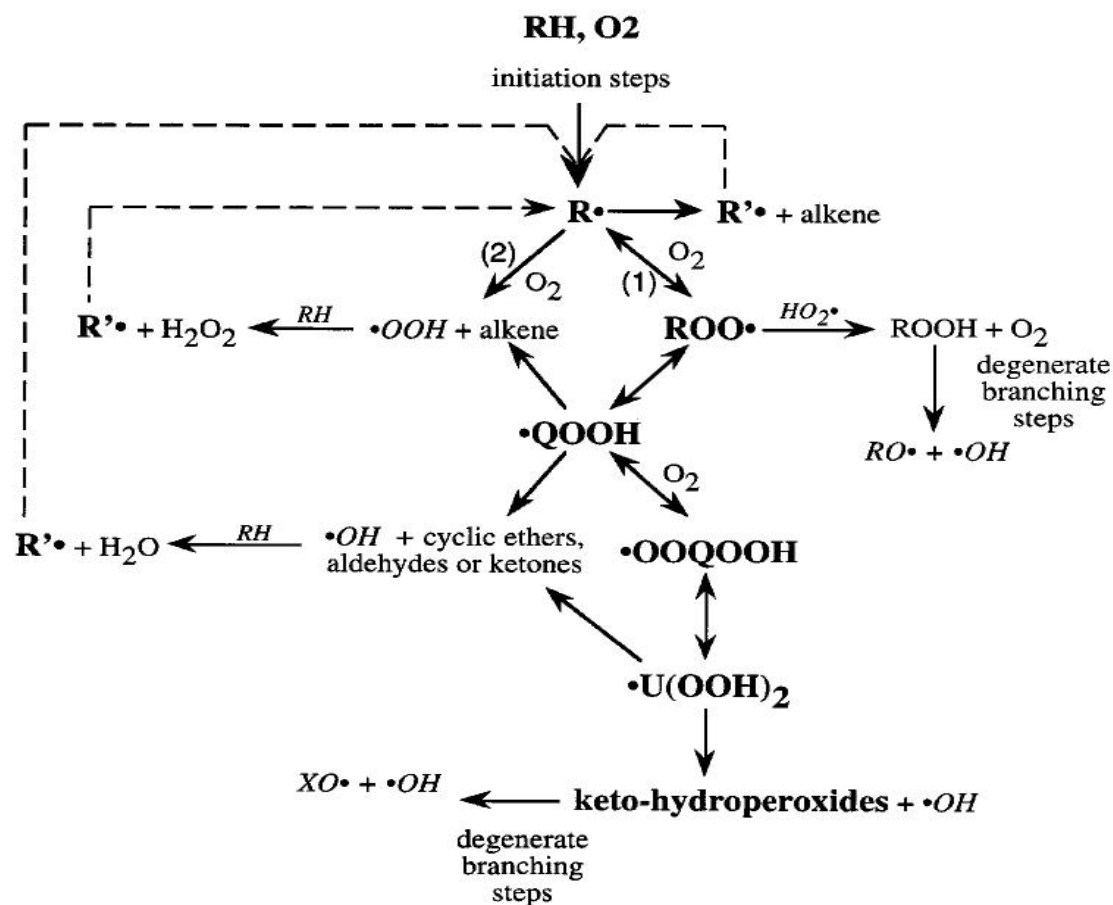
1. Unimolecular fuel decomposition
2. H-atom abstraction from the fuel
3. Alkyl radical decomposition
4. Alkyl radical isomerization
5. H-atom abstraction reactions from alkenes
6. Addition of radical species O and OH to alkenes
7. Reactions of alkenyl radicals with HO_2 , CH_3O_2 , and $\text{C}_2\text{H}_5\text{O}_2$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

Examples of Low Temperature Reaction Classes (Sarathy et al. 2011)

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 ($ROO = \text{alkene} + HO_2$)
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. $QOOH = \text{cyclic ether} + OH$ (cyclic ether formation)
24. $QOOH = \text{alkene} + HO_2$ (radical site beta to OOH group)
25. $QOOH = \text{alkene} + \text{carbonyl} + OH$ (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

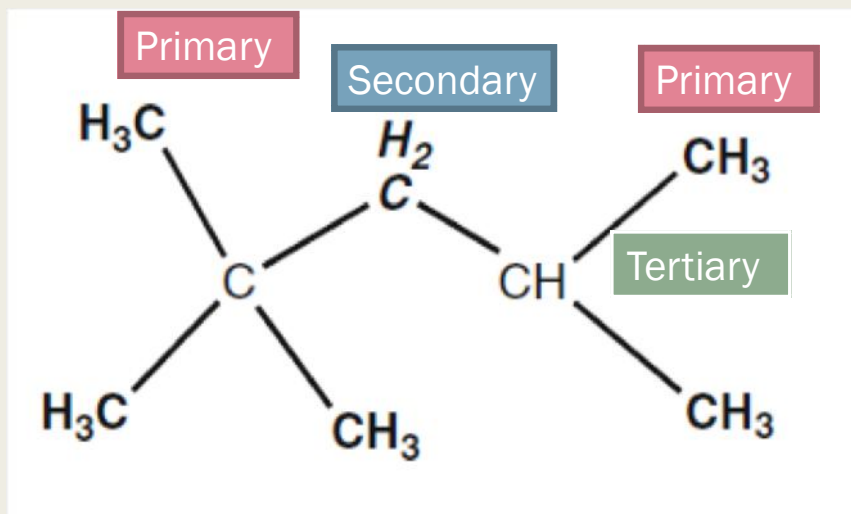
Example of protocol based upon low temperature reaction classes



Simplified scheme for the primary mechanism of oxidation of alkanes (broken lines represent metatheses with the initial alkane RH) ([Warth et al. 2000](#))

Rate constants and functional groups

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



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

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

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

H-abstraction	Primary H			Secondary H			Tertiary H		
	lg A	b	E	lg A	b	E	lg A	b	E
O ₂	12.84	0	ΔH_r	12.84	0	ΔH_r	12.84	0	ΔH_r
·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
·CH ₃	-1	4	8200	11.0	0	9600	11.00	0	7900
HO ₂ ·	11.30	0	17000	11.30	0	15500	12.00	0	14000

The structure of reaction mechanisms

- We saw that reaction classes can vary with temperature and hence the size of a required mechanism can be reduced by, for example, restricting to low temperature classes (e.g. ignition problems), or high temperature mechanisms (e.g. flame propagation).
- Additional classification of sub-mechanisms can be based on several types of criteria.
- **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** is concerned by the reactions of the initial reactants and of the directly derived radicals.
 - The **secondary mechanism** consumes the products of the 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.

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 already been validated under the conditions being considered.
- Estimated rate constants are not usually used within base mechanisms, rather data is obtained from *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).
- The developer or modeller determines which sub-mechanisms and reaction classes should be generated.
- Therefore the expert system is based on similar rules and reaction classes discussed earlier but these are now encoded rather than applied by hand.
- This should reduce errors and apply rules in a systematic way.
- If rate constants are changed for a whole class then should be easier to regenerate the mechanism.

Examples of automatic generation codes

- EXGAS – Developed at CNRS Nancy (Côme et al. 1997).
- RMG – Developed at MIT (Green et al. 2001; Van Geem et al. 2006).
- REACTION – Developed by Ned Blurock (Blurock 1995; Moreac et al. 2006).
- MAMOX++ – Developed by Milan (Ranzi et al. 1995).

Each is based on a set of common principles but application may be different for different codes.

Structure of an Automatic Generator (Blurock et al, 2013)

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

Iterative Generation Process

Generator will start from parent molecules generating new reactions using inputs from the species pool at each stage of the iteration.

1. **Initialisation.** Fill the reaction pool with initial reactants(e.g. fuel, oxygen etc.).
2. **Generate reactions.** Using the information in the reaction class database, create a new set of reactions and molecules using the species pool as input. Add the generated molecules and reactions to the mechanism.
3. **Update the species pool.** Update the species pool with the newly generated species from step 2.
4. **Check termination criteria.** If the algorithm is done, then exit, otherwise iterate to step 2. Termination could mean that small enough species have been reached to feed into the *Base Mechanism*, or that no new species are added to the mechanism.

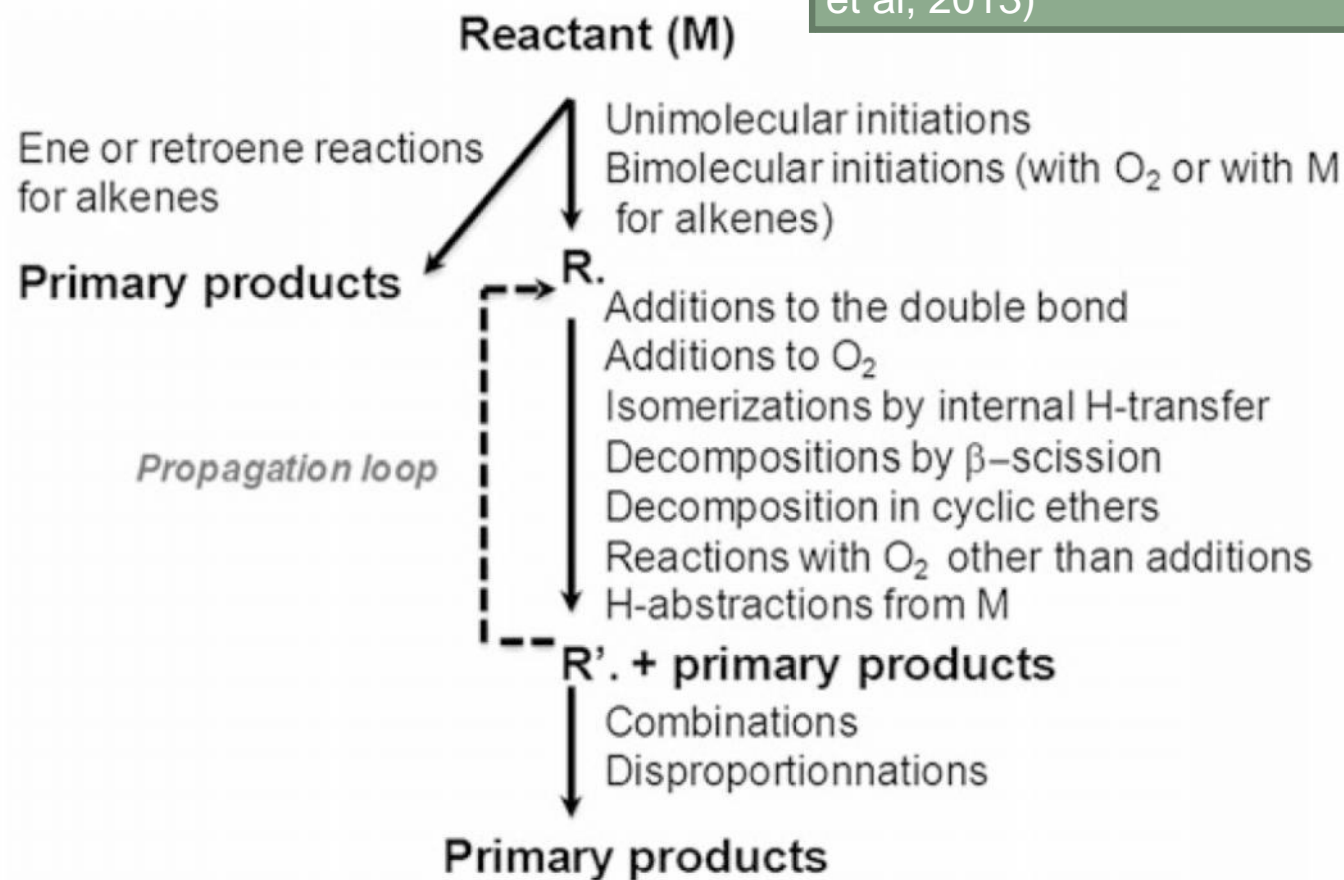
Initialisation

- Input to the algorithm is the fuel molecule or molecules.
- These species are added to the species pool.
- Sub-mechanism generated is considered as the *primary mechanism*.
- The *Generate Reactions* step uses the species pool as input to generate the next set of reactions.
- The initialisation process may require some “extra” reactants, such as small radicals used in some reactions have to be added to the species pool. These are taken from the molecule database.

Generate Reactions

- Current species pool is analysed and those reaction classes from the reaction class database which are valid are applied.
- A reaction class is valid for a species (or set of species) if the **functional groups** required by the reaction class are present.
- A method is therefore required to identify the presence of functional groups.
 - E.g. graph isomorphism
- Some filtering may be done here of important reaction classes e.g. to keep the size of the mechanism to a minimum.
 - *If the relative rates for a class are low compared to competitors. If the reaction is too endothermic. Generation of bi-radical inhibited. etc.*
- New set of reactions and molecules is collected. A crucial algorithm here is the determination of **which molecules and reactions are equivalent**. Only newly generated reactions and molecules should be added to the mechanism.

Algorithm of generation used to generate the primary mechanisms of alkanes and alkenes in EXGAS (Blurock et al, 2013)



Update the species pool

- The species pool is updated with the new set of generated species via essentially two algorithms:
 - **Exhaustive.** *The (filtered) set of generated molecules is added to the species pool, creating a larger pool.*
 - Reactions are applied (in the Generate Reaction step) until no new species are produced.
 - **Progressive.** *The species pool is initialised and the (filtered) set of species is added at each step.*
 - Only selected species are used in the next step e.g. only newly generated species are applied in the next step as in REACTION code.

Termination and Convergence of the Algorithm

- Additional criteria usually have to be applied to prevent the produced mechanism from reaching an infinite size or from entering into an infinite loop.
 - *E.g. EXGAS limits the size of the largest molecule that can be obtained e.g. through recombination steps.*
 - *For isomerisation steps, a given molecule can only have a finite number of isomers, and a reaction class producing another isomer can only be applied a finite number of times (though the number of isomers can be very large for large molecules).*

Defining Molecules

- A molecule is a complex object with many models and representations.
- A fundamental task is to give each molecule a unique name so that two molecules with same name have same structure. Important for defining functional groups.
- Usually, representation of the molecule is a 2D graph (Balaban 1985, 1995).
 - *The atoms are graph nodes with additional information such as atomic number, charge, radical, etc.*
 - *The graph bonds are essentially the full covalent bonds of the molecule.*
- Finding a unique name, or a canonical form, for a graph is a complex task and is connected to identifying whether or not graphs are identical (graph isomorphism (Balaban 1985)).
 - *Essential for identifying identical species within the generation process.*
- Standard IUPAC nomenclature uses a linearisation of this graph based structure.
 - E.g. iso-octane has the IUPAC name of 2,2,4-trimethylpentane.

Chemical Mark-up Language (CML)

- The use of canonical names may not be efficient for use in computer codes searching for similarities in chemical structure or the transformations of species creating a reaction.
- Chemical Markup Language (CML) (Murray-Rust and Rzepa 1999) is a specialisation for physical and organic chemistry of the Extensible Markup Language (XML).
- There is a chemical data structure directly associated with the CML format.
- Represents 2D information about atom connectivity within molecules, bond description etc.
- This type of information important in determining if two molecules are identical since a textual comparison of IUPAC names cannot be used for this purpose.

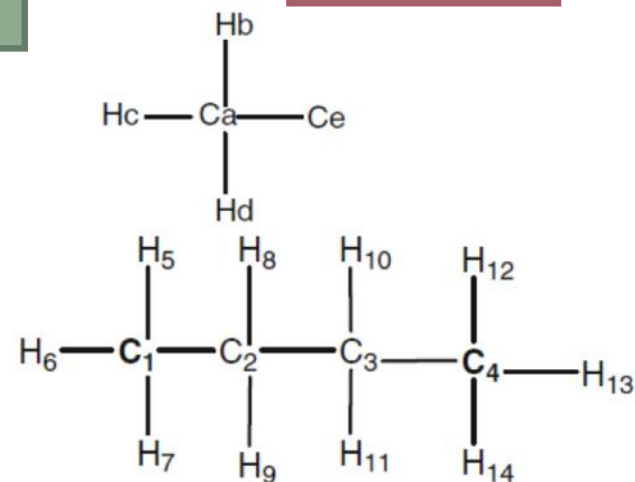
Sub-structure Search

- In order to determine whether a particular reaction class can be applied to a species then the appropriate functional groups need to be searched for within the molecule.
- Again, graph isomorphism, i.e. the atom-to-atom correspondence between graphs, is used.

Atom to atom correspondences for a primary methyl group in n-butane. There are 12 combinations. Due to symmetries – 6 reactions would be generated.

	Carbon atom1						Carbon atom4					
	b5		b6		b7		b12		b13		b14	
a	1	1	1	1	1	1	4	4	4	4	4	4
b	5	5	6	6	7	7	12	12	13	13	14	14
c	6	7	5	7	5	6	13	14	12	14	12	13
d	7	6	7	5	6	5	14	13	14	12	13	12
e	2	2	2	2	2	2	3	3	3	3	3	3

H abstraction
of Hb



Different AMG codes and specificities

■ MAMOX ++

- *Produces a hierarchy of (highly) lumped mechanisms derived numerically from automatically generated detailed mechanisms (see later for lumping methods).*

■ EXGAS

- *Has a very comprehensive reaction class database and a large choice given to user for mechanism tailoring: e.g. low temp vs high temp, 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.*
- *Only 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.*

The use of Reaction Pathways

- The **REACTION** code uses the concept of reaction pathways with the intention of mimicking better, how a combustion modeller actually thinks.
- Instead of applying recursively a pool of reaction classes, the reaction classes are arranged in pathways, i.e. a linear sequence of sets of reaction classes.
- The reaction classes of the current step are only applied to products of the last step
- The primary reasons are:
 - *A more controlled form of generation which inhibits the combinatorial explosion of possible reactions.*
 - *It mimics more closely the way a modeler thinks and builds a complex detailed mechanism.*
 - *It provides a means of introducing a generation strategy without hard-coding the strategy in the generation engine.*
- Produced a similar *n*-hexadecane mechanism as that generated by hand in Westbrook et al. (2009).
- REACTION also has a database of standard molecules with corresponding 2D graphical information

Problems with mechanism formulations

■ Notation!

- *A large number of different notation systems are used by different mechanism developers making it very difficult to combine mechanisms from different groups.*
- *A mark up language like CML would help here.*

■ Provenance

- *The sources of rate data and thermodynamic data should be given but are not always easy to trace.*

■ Uncertainties

- *It is rare for a mechanism to be circulated with estimated uncertainties in the data it contains – unless for example it is the product of an optimisation procedure (lectures of Zsely).*

Types of fuels covered by AMG

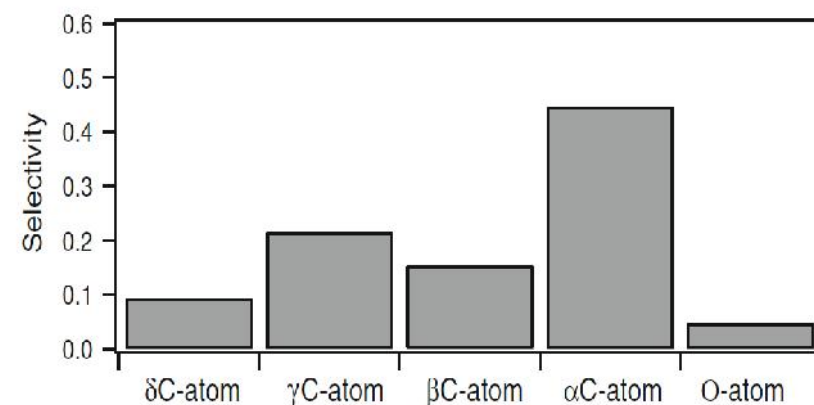
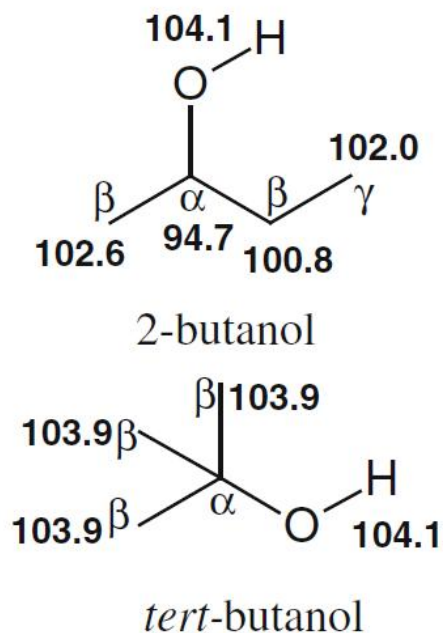
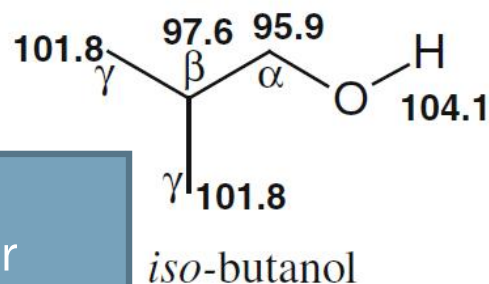
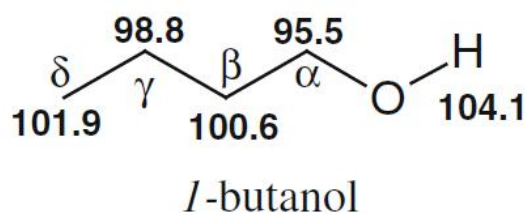
- Linear and branched alkanes up to high C numbers covered by all codes.
- Linear alkenes up to C7 now covered e.g. in EXGAS.
- Cycloalkanes.
- New work has started to cover oxygenated fuels
 - *Of relevance for biofuel combustion.*

Particular Challenges Posed by Biofuels

- 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*
- Molecules contain oxygen and have different functional groups compared to e.g. alkanes.
- Modifications need to be made in terms of
 - *Reaction classes*
 - *Relevant rate data for existing classes compared to alkanes, alkenes*
 - *Species present*
- The existence of measured data for the reactions of such compounds is SCARSE!

Example of H abstraction Reactions

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



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

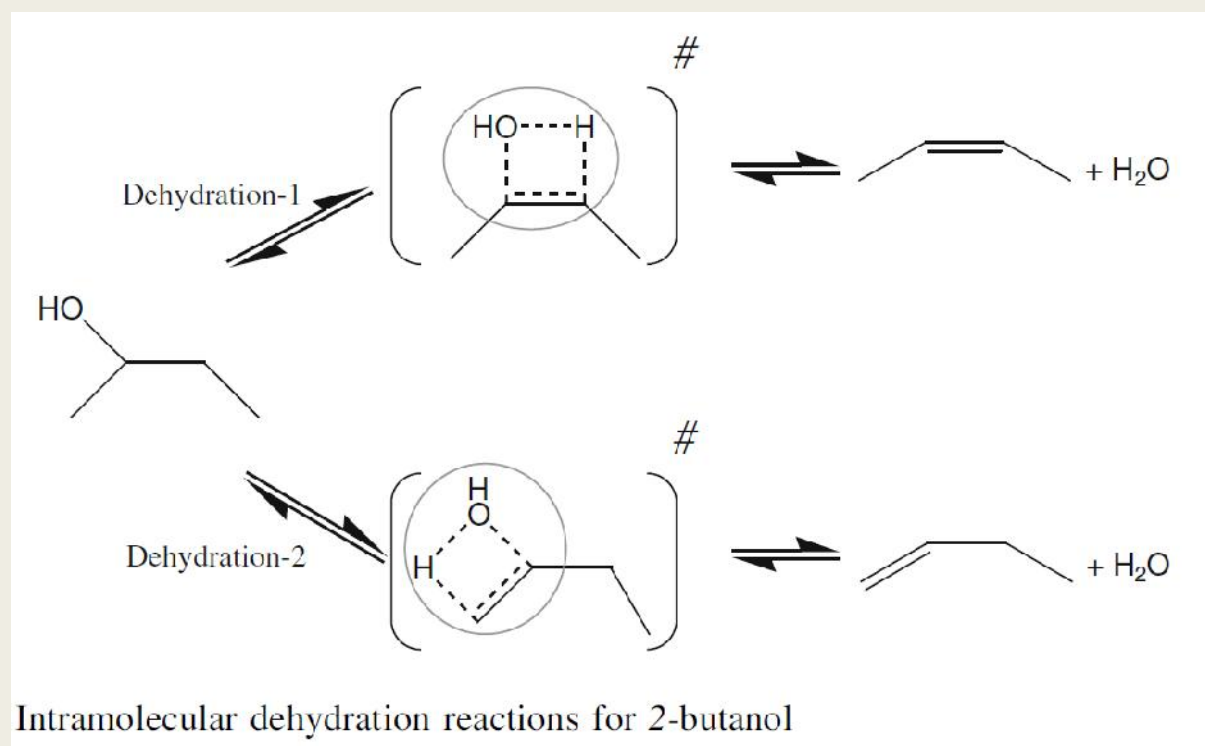
C-H bond
energies for
butanol isomers

Rate constant determination

- Abstraction from α site close to BDE to tertiary carbon in iso-butene.
- BUT - Zhou et al. (2011) found that, in considering abstraction by oxygenated radicals such as OH and HO₂ from oxygenated molecules, it is not accurate to assume similarity with abstraction from alkanes, as hydrogen bonding between the radical and the molecule in the transition state generally lowers the activation energy for abstraction but also ties up a rotor in the molecule.
- Thus rate constants for abstraction from alcohols by OH (Zhou et al. 2011) and HO₂ radicals (Zhou et al. 2012) have been shown to be generally faster at lower temperature (due to the decrease in activation energy for abstraction) but slower at higher temperature (due to the decrease in entropy change) compared to alkanes.

Molecular dehydration and dehydrogenation reactions for alcohols

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



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

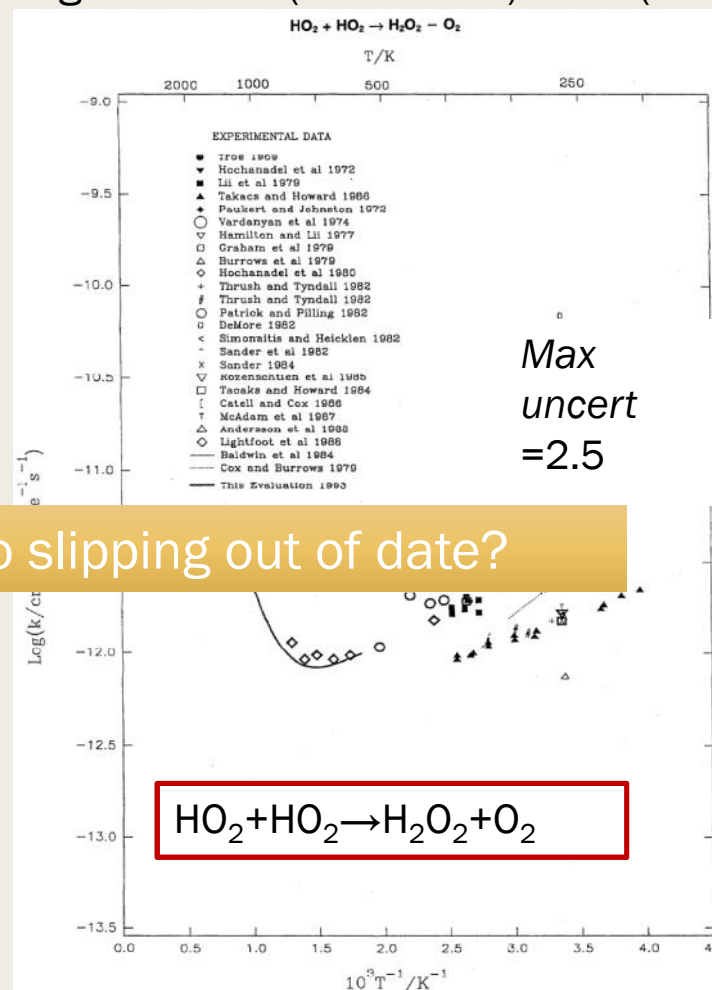
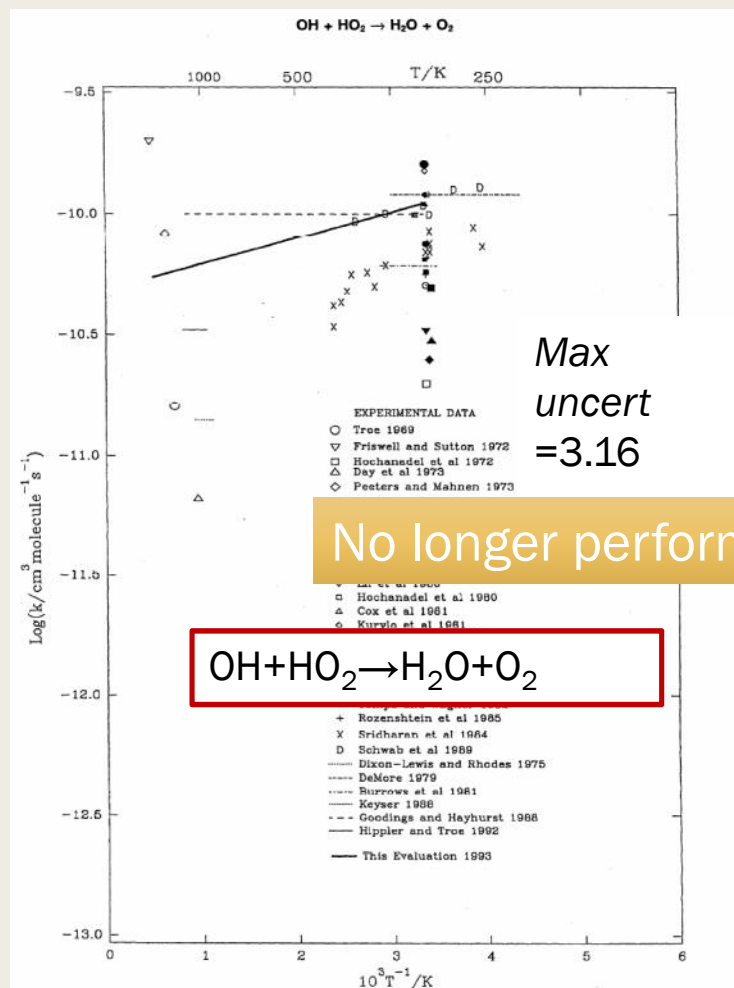
Sources of model input data and uncertainty information

- Kinetic evaluations (e.g. Baulch, Tsang, Atkinson).
- NIST data base
- Output from theoretical studies
- Trawling literature....
 - *Time consuming!*
- Detailed statistical studies
 - *Active tables for thermodynamic data (Ruscic et al.)*
 - *Optimisation studies for reaction mechanisms (Nagy et al.)*
- What to do about estimated parameters?

Evaluated data (Baulch et al. 1994)

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

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

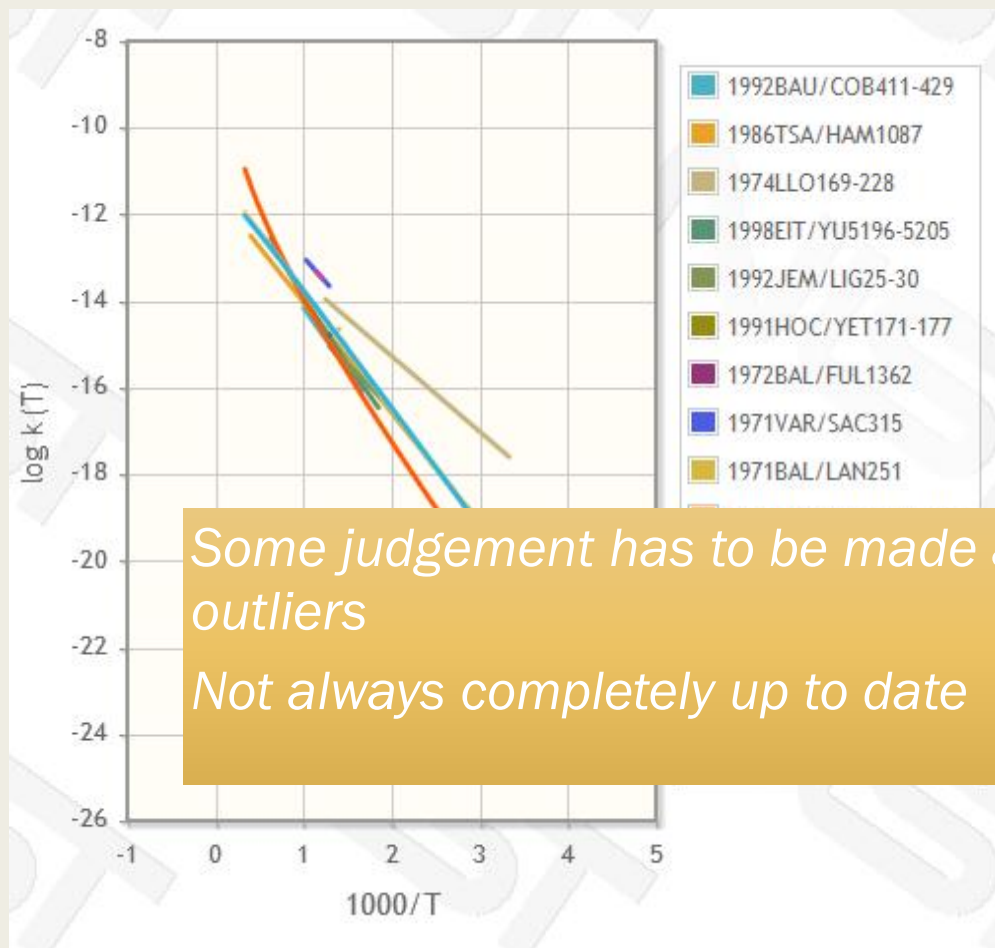
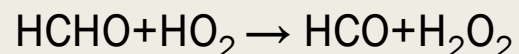


No longer performed so slipping out of date?

Sources of model input uncertainty information

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- **NIST data base**
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 - *Time consuming!*
- Detailed statistical studies
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- What to do about estimated parameters?

NIST data base



Some judgement has to be made about outliers

Not always completely up to date

Fit of Arrhenius parameters to set:

Temperature range: 250 - 3000 K

Two-parameter fit:

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

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

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

$$\text{RMSD} = 4.3$$

Three-parameter fit:

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

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

$$n = -0.3$$

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

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

$$\text{RMSD} = 4.2$$

Representations of Uncertainty

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

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

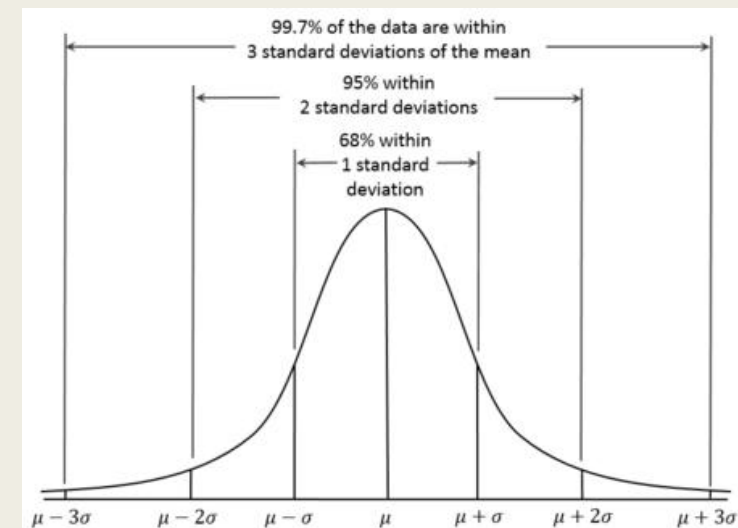
- k_0 recommended value of rate coefficient. k_{\min} , k_{\max} extreme values.

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

where m is the level of uncertainty suggested.

$m = 2$, 2 \dagger deviation or 95 %ile,

$m = 3$, 3 \dagger deviation or 99.7 %ile



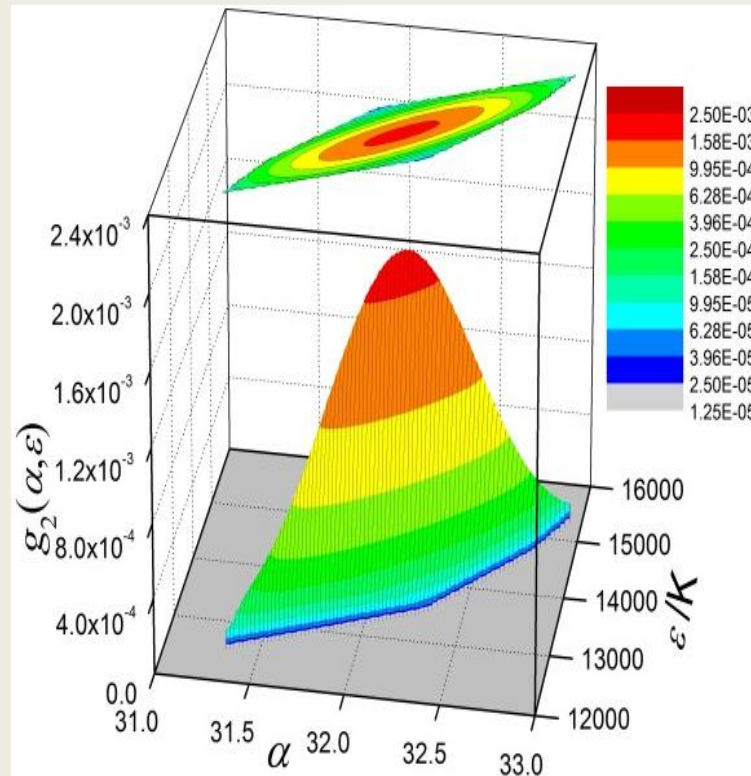
Examples of levels of uncertainty

uncertainty parameter f	multiplication factor of 3 [†] uncertainty limits	[†] (log ₁₀ k)	[†] (ln k)	multiplication factor of 1 [†]	multiplication factor of 2 [†]
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

Sources of model input uncertainty information

- Kinetic evaluations (e.g. Baulch, Tsang, Atkinson).
- NIST data base
- Output from theoretical studies
- Trawling literature....
 - *Time consuming!*
- **Detailed statistical studies**
 - *Active tables for thermodynamic data (Ruscic et al.)*
 - *Optimisation studies for reaction mechanisms (Nagy et al.)*
- What to do about estimated parameters?

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 and wet CO oxidation (Nagy et al).

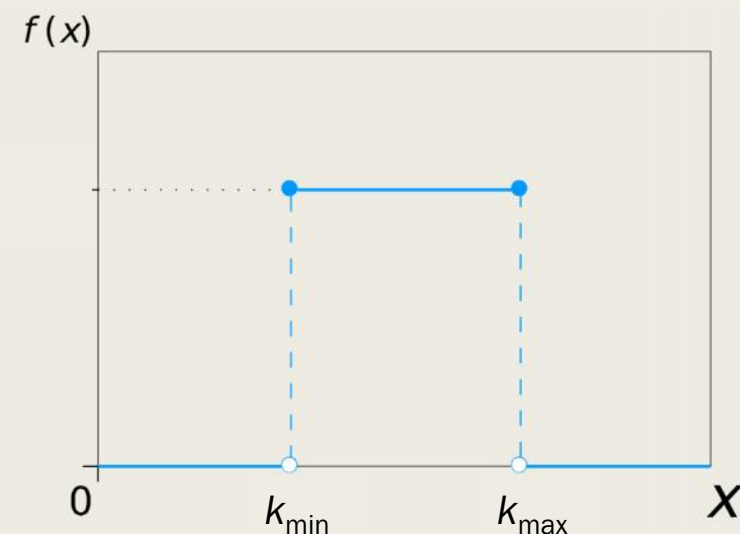
See lectures of Zsely.

Sources of model input uncertainty information

- Kinetic evaluations (e.g. Baulch, Tsang, Atkinson).
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- **What to do about estimated parameters?**

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 would be used since no probabilistic information is likely to be available.
- In the 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?*



Thermo-dynamic Data

- „Extended Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables” of Elke Goos, Alexander Burcat and Branko Ruscic.
 - Available from DLR, and Technion
 - Mirrored on RESPECTH including plotting function for heat capacity, enthalpy of formation, entropy.
- Includes ideal gas thermodynamic data in polynomial form, for species used in combustion and air pollution.

```
74-82-8
CH4 METHANE  STATWT=1. SIGMA=12.  IA=IB=IC=0.52410356  NU=2916.7,1533.295(2),
3019.491(3),1310.756(3)  X11=-26 X12=-3 X13=-75 X14=-4 X22=-.4,X23=-9 X24=-20
X33=-17 X34=-17 X44=-11  ALFA1=.01 ALFA2=-.09 ALFA3=.04 ALFA4=.07 D0=1.10864E-4
HF298=-74.6+/-0.3 KJ HF0=66.63 kJ REF=TSIV 91 {HF298=-74.554+/-0.60 kJ  REF=ATcT
C}  MAX LST SQ ERROR CP @ 1300 K 0.54%.
CH4  ANHARMONIC  g 8/99C  1.H  4.    0.    0.G  200.000  6000.000  B  16.04246  1
  1.65326226E+00 1.00263099E-02-3.31661238E-06 5.36483138E-10-3.14696758E-14    2
-1.00095936E+04 9.90506283E+00 5.14911468E+00-1.36622009E-02 4.91453921E-05    3
-4.84246767E-08 1.66603441E-11-1.02465983E+04-4.63848842E+00-8.97226656E+03    4
```

Active Tables, Argonne National Labs (Branko Ruscic)

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

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

Advantages of Active Tables (Ruscic et al, 2005)

- Explicitly exposes the maze of inherent interdependencies normally ignored by conventional treatment of thermochemistry allowing a statistical analysis of the individual measurements that define the thermochemical network (TN).
- Extracts best possible thermochemistry, based on optimal use of all the currently available knowledge.
- Provides uncertainty limits and information about cross correlations.
- New knowledge (data) can be easily propagated through all affected thermochemical values.
- Allows hypothesis testing and evaluation, as well as discovery of weak links in the TN - providing pointers to new experimental or theoretical determinations that can most efficiently improve the underlying thermochemical body of knowledge.

Summary of lecture 2-1

- We looked at how oxidation mechanisms for fuels are developed both manually and automatically.
- Both utilise the concepts of *reaction classes* and *structural similarities* between species to suggestion reaction pathways and to provide rate constant estimates for larger molecules.
- Oxygenated fuels lead to additional possible reaction classes and changes in rate constants compared to alkanes.
 - *Data tends to be sparser.*
- Rate constant data are available from a variety of sources.
 - *Estimated uncertainties are less commonly presented.*
 - *Where possible full *optimisation* or *active table* approaches provide the highest quality information on uncertainties but have yet to be carried out for larger fuel molecules.*