Errors and uncertainty in oxygen chemistry

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Programme

- Best practice in plasma chemistry modelling: “Reaction mechanisms”
- Tools: Uncertainty quantification, sensivity analysis, dominant pathways
- Oxygen chemistry: Outcomes

Best practice? "Reaction Mechanisms"

- A "reaction mechanism" is a chemistry model with these features:
  1. Based on "curated" basic data
     (Sources of data identified, error bars (uncertainty) associated with data, multiple/contradictory sources critically evaluated to "best" value, *etc*)
  2. Validated against experimental "targets":
     (Some set of experiments to be reproduced, also critically evaluated, with error bars, *etc*)
  3. Optimized against "targets":
     (Uncertain rate constants systematically adjusted to minimise disagreement with targets.)

- Example:
  GRI Mech 3.0, optimised natural gas combustion model with ~ 325 reactions, ~ 50 targets

Developing a “Reaction Mechanism”

Curated Data | Basic → Optimisation ← Experimental Targets

↓

Reaction Mechanism

- Changes to basic data or targets trigger a reoptimisation
- Tinkering with an optimised model is unlikely to be a good idea

Present situation

- Our older literature contains examples of very good practice (by the standards of the time):
  Gordiets, *et al*, "Kinetic model of a low-pressure N_2-O_2 flowing glow discharge," J. Phys D 23, 750 (1995)
- But we don't seem to have improved since, and arguably there has been decline

Need for Curation: Quality of Data

- The reaction

$$\begin{aligned} O(^1D) + O_3 &\rightarrow 2O + O_2 \\ &\rightarrow 2O_2 \end{aligned}$$

  is the subject of about 10 experimental studies and three critical reviews (1987,2004,2011)
- The critical recommendation is

$$k = 2.4 \times 10^{-16}\ \mathrm{m}^3\ \mathrm{s}^{-1}$$

  with equal branching
  Established for almost 30 years!

- A look at nine models featuring this reaction shows:
  1. None cites a critical review as authority
  2. Seven have the wrong rate constant and/or branching ratio
  3. One has a rate constant almost 5 times too large
- Why?
  Misunderstanding complex sources, uncritical copying, unclear referencing

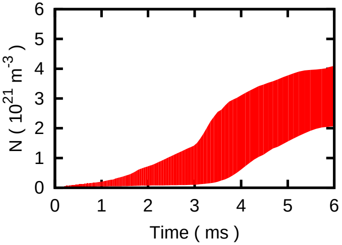
Oxygen Plasma Chemistry

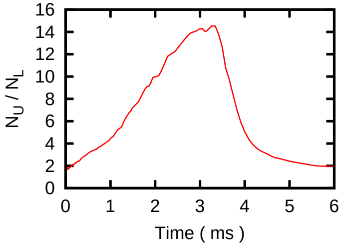
- Oxygen is clearly an important chemistry
  Perhaps dozens of species, hundreds of reactions, all with uncertain rate constants
- Models aim to predict (?), but predictive power is compromised by uncertain rate constants
- The predictive uncertainty involved can be large
  MMT, Plasma Source Sci. Technol. 24, 035027 (2015)
- What is an appropriate procedure for dealing with such models?

Uncertainty by Monte Carlo simulation

- He/O_2 chemistry, 373 reactions, 25 species
- Each rate constant has an error bar: $k \pm \Delta k$
- Monte Carlo procedure maps uncertainty in rates to uncertainty in density:

$$\mathbf{k} \pm \Delta\mathbf{k} \overset{\text{Monte Carlo}}{\longrightarrow} \mathbf{n} \pm \Delta\mathbf{n}$$





O_3

Sensitivity Analysis

- Which rate constants cause uncertainty?
- "Sensitivity analysis" aims to answer this question
- Basic concept:
  1. Isolate effects by changing a single rate constant in each trial (applying an "elementary effect")
  2. Obtain a global picture by averaging many such effects

So

$$\begin{pmatrix} k_1 \\ k_2 \\ \vdots \\ k_i + \Delta k_i \\ \vdots \\ k_N \end{pmatrix} \rightarrow \begin{pmatrix} n_1 + \Delta n_{1,i} \\ n_2 + \Delta n_{2,i} \\ \vdots \\ n_j + \Delta n_{j,i} \\ \vdots \\ n_M + \Delta n_{M,i} \end{pmatrix}$$

and

$$\mu_{j,i} = \langle \Delta n_{j,i} / \Delta k_i \rangle$$

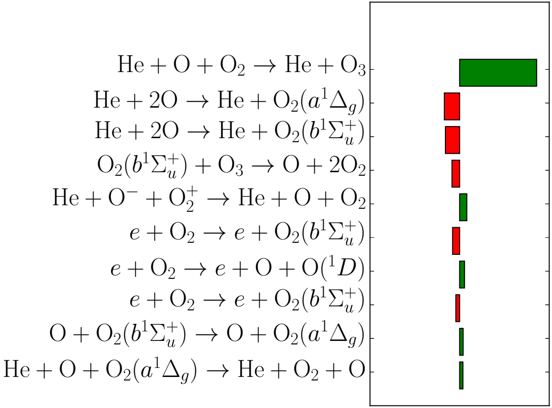
Sensitivity

- Outcome of sensitivity analysis is a "ranking":

  $\mu_{j,i} = \langle \Delta n_{j,i} / \Delta k_i \rangle$

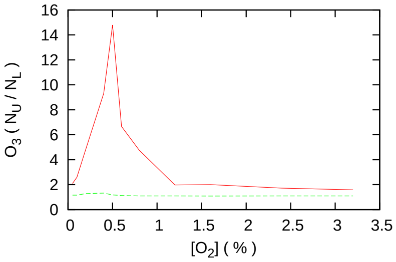
- *E.g.* Uncertainty in O_3 density is dominated by uncertainty in the rate constant for:

  $He + O + O_2 \rightarrow He + O_3$



Optimisation

- 9 sensitive reactions contribute most of the uncertainty
- Optimisation takes advantage of this sensitivity

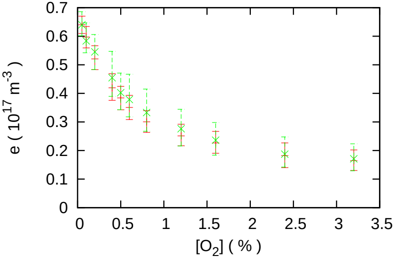


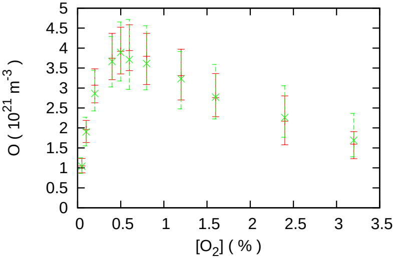
Did we need 373 reactions?

1. Limit the conditions of interest:

$$0.1\ \mathrm{W} < \quad P \quad < 10\ \mathrm{W}$$
$$0.05\ \% \leq \quad [\mathrm{O_2}]/[\mathrm{He}] \quad \leq 3\ \%$$

2. Limit the species of interest: O, $O_2(a^1\Delta_g)$, O_3
3. Discard all reactions contributing < 5 % to any time derivative
4. $N : 25 \rightarrow 12,\ M : 373 \rightarrow 51$





See also: Peerenboom *et al*, Plasma Sources Sci. Technol. 24, 025004 (2015)

Procedure

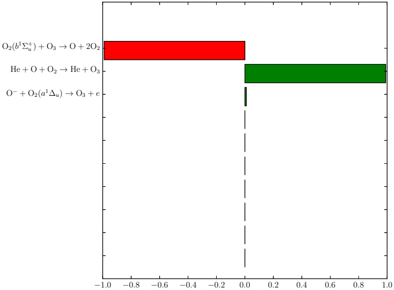
- Clarity of purpose:
  1. What species densities do we aim to predict?
  2. Under what conditions?
- Model construction:
  1. Gather data (provenance!)
  2. Model reduction $\Rightarrow$ Selection of relevant processes
  3. Sensitivity analysis $\Rightarrow$ Identification of problematic data
- Validation:
  1. Relevant species densities measured
  2. Critical comparison of model and experiment
  3. Optimisation

Dominant Pathways

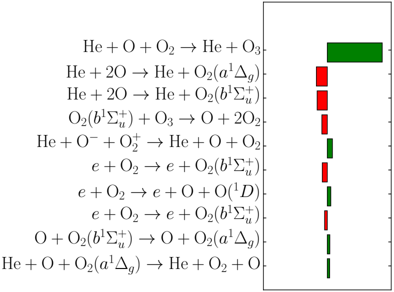
- We can ask: Which reactions dominantly control species densities?
- A separate question from sensitivity analysis
- Pumpkin is a useful tool

O_3

Dominant pathways

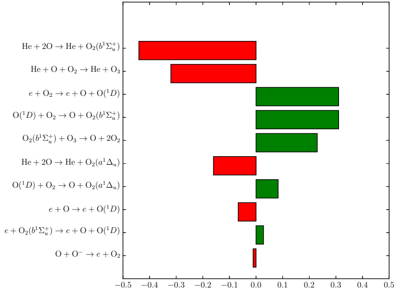


Sensitivity

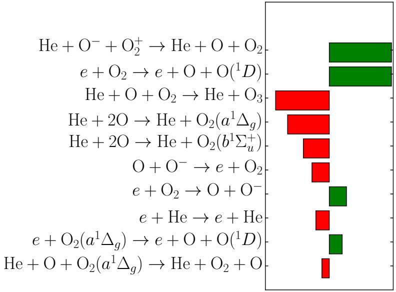


O

Dominant Pathways

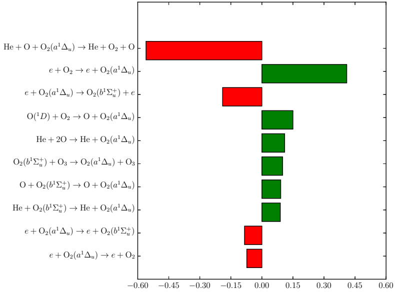


Sensitivity

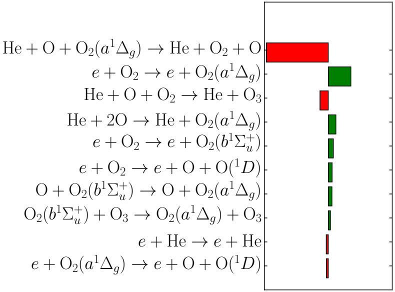


$O_2(a^1\Delta_g)$

Dominant pathways



Sensitivity



Sensitive Reactions

- Of 373 original reactions, only 9 contribute more than 10 % to the uncertainty of any species of interest:

$$e + O_2 \rightarrow e + O + O(^1D)$$
$$e + O_2 \rightarrow e + O_2(a^1\Delta_g)$$
$$e + O_2 \rightarrow e + O_2(b^1\Sigma_u^+)$$
$$O_2(b^1\Sigma_u^+) + O_3 \rightarrow O + 2O_2$$
$$He + 2O \rightarrow He + O_2(a^1\Delta_g)$$
$$He + 2O \rightarrow He + O_2(b^1\Sigma_u^+)$$
$$He + O + O_2 \rightarrow He + O_3$$
$$He + O + O_2(a^1\Delta_g) \rightarrow He + O_2 + O$$
$$He + O^- + O_2^+ \rightarrow He + O + O_2$$

Conclusions

- A reaction mechanism is the outcome of a big effort:
  1. Clear aims
  2. Curated data with provenance
  3. Sensitivity analysis and model reduction
  4. Validation
  5. Optimisation
- The unit of consideration should be a "reaction mechanism" (and not individual rate constants)
- A "reaction mechanism" can often be drastically reduced (important for multi-dimensional models)