# Assembling and optimizing plasma chemistry sets using QDB

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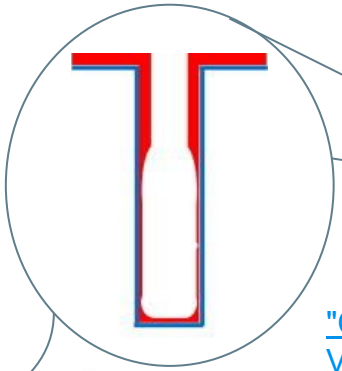
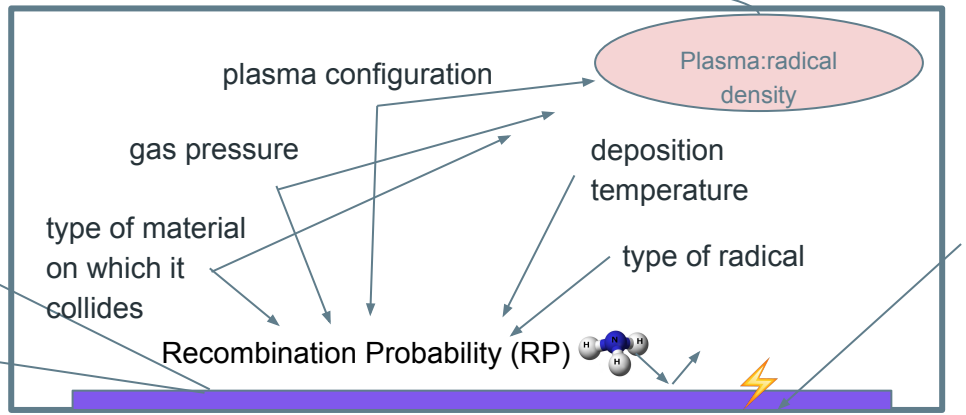
# Potential issues which can be addressed with simulations

Limited **conformality** in high aspect ratio structures






Potential plasma damage to the substrate

"Conformality in atomic layer deposition: Current status overview of analysis and modelling featured." V.Cremers, R.L. Puurunen and J.Dendooven, Applied Physics Reviews 6, 021302 (2019)

Higher radical densities lead to higher radical fluxes deeper in the trench, enhancing the conformality

# Problem statement

Every plasma simulation consists of two parts:

**Physical Model:**

Describes particle transport, electromagnetic fields etc.

Should be chosen to according to parameter space and specific balance of speed and accuracy:

PIC, Fluid, DSMC, Hybrid

Global, 1D, 2D, 3D

**Chemical Model:**

Describes the chemical reactions in a plasma via a set of species :

- Neutrals
- Excited states
- Positive and negative ions
- Electrons

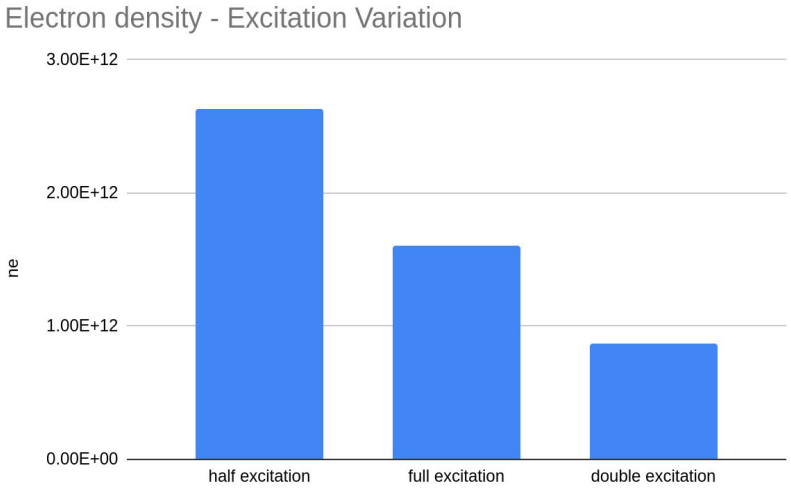
And reactions:

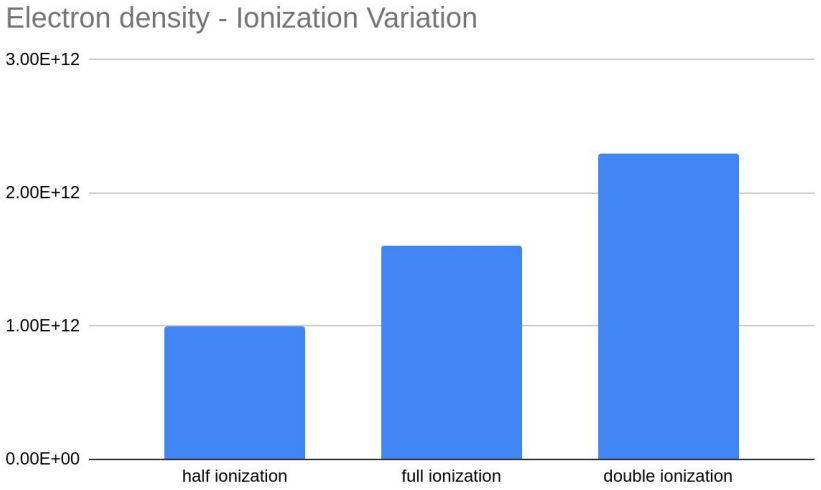
- Electron impact collisions
- Heavy particle collisions

# Overview of Electron impact collisions

- Elastic collision/momentum transfer: electron transport, gas heating
- Excitation: Determines density of excited states.
- Dissociation: Determines density of dissociation products.
- Dissociative Attachment: Determines electronegativity
- Electron detachment: Determines electronegativity
- Ionization: Determines ionization rate
- Recombination: Determines recombination rate

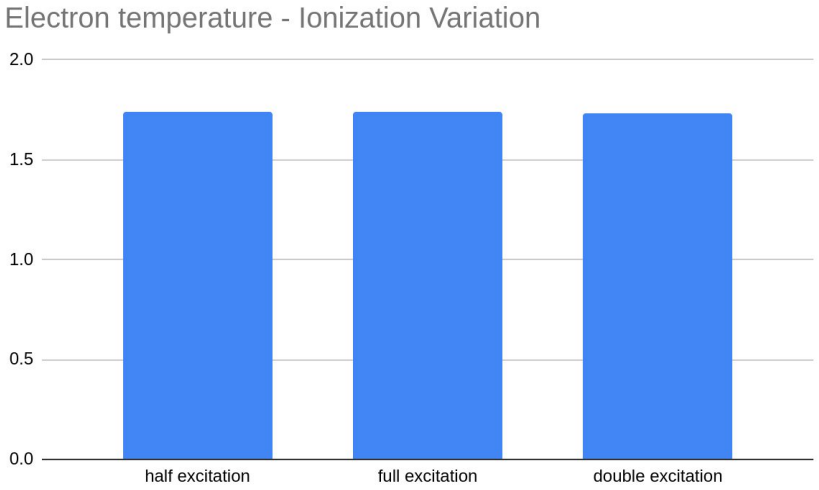
# Overview of Electron impact collisions

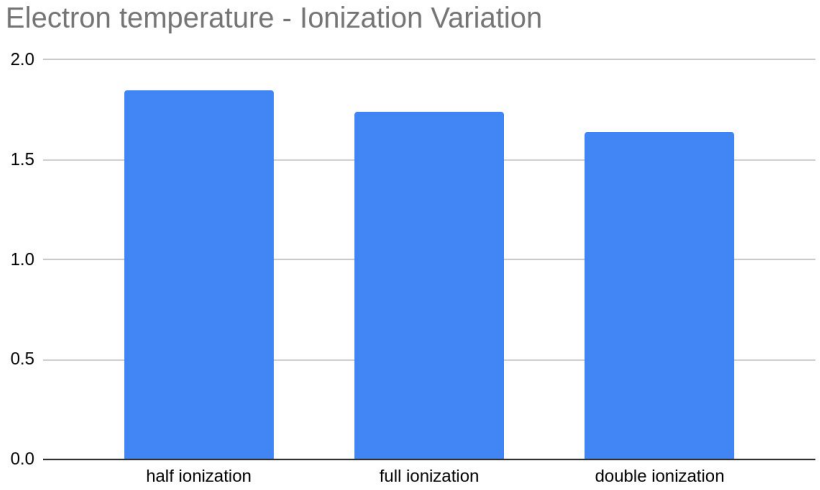



Excitation processes have a larger influence on electron density than the actual ionization processes.
→ If the electron density looks off, turn your attention to excitation and dissociation reactions!

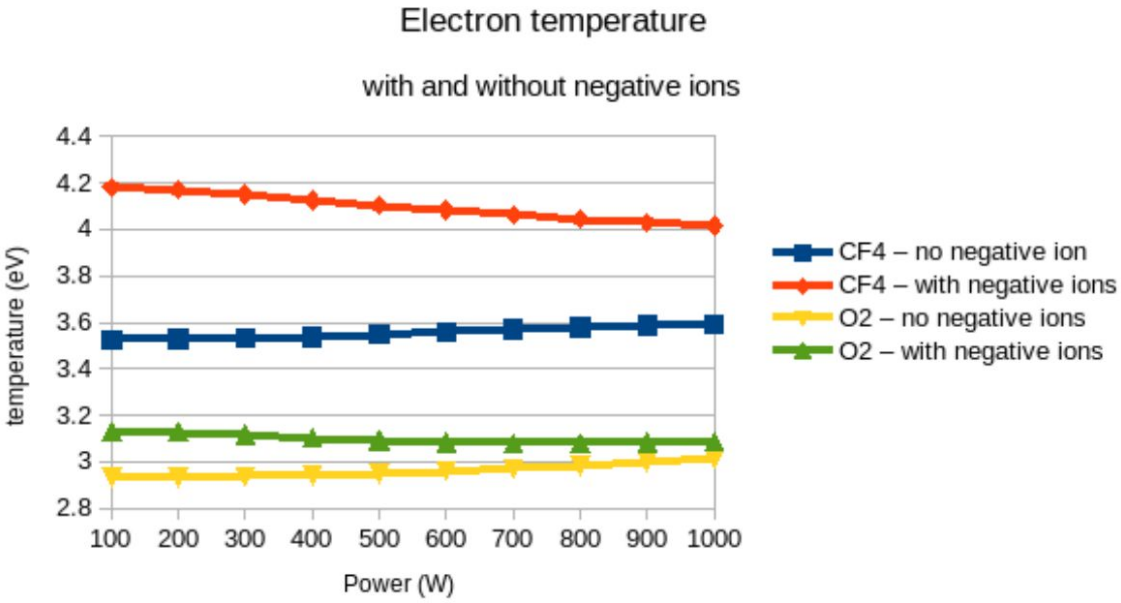
# Overview of Electron impact collisions




Only ionization processes significantly affect the electron temperature in a simple argon model.

# Overview of Electron impact collisions




The presence of negative ions generally increases the electron temperature.
→ If the electron temperature looks off, turn your attention to electron production and losses!

# Overview of Heavy Particle Collisions

- **Ion-Ion Recombination**
- Symmetric Charge Exchange
- Asymmetric Charge Exchange
- Neutral conversion
- Electron detachment
- Penning Ionization

$$A^+ + B^- \rightarrow A + B$$

$$AB^+ + C^- \rightarrow A + B + C$$

Vital for electronegative plasmas.

Typically represents the only efficient loss channel for negative ions.

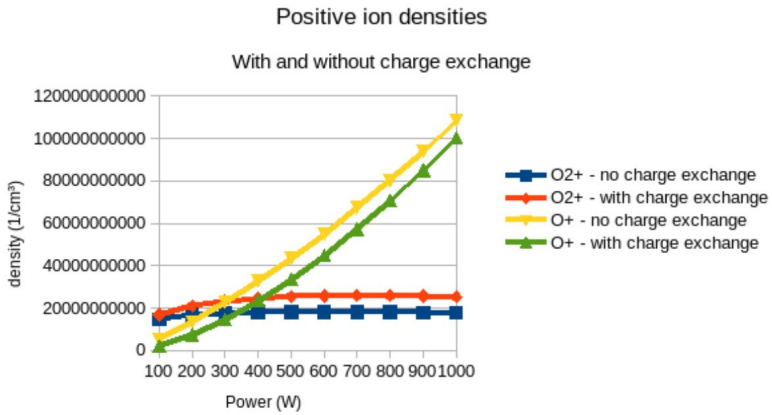
# Overview of Heavy Particle Collisions

- Ion-Ion Recombination
- Symmetric Charge Exchange
- **Asymmetric Charge Exchange**
- Neutral conversion
- Electron detachment
- Penning Ionization

$$A^+ + B \rightarrow A + B^+$$

$$A^+ + BC \rightarrow A + B + C$$

Asymmetric charge exchange affect the relative ion densities apart from heating neutrals.



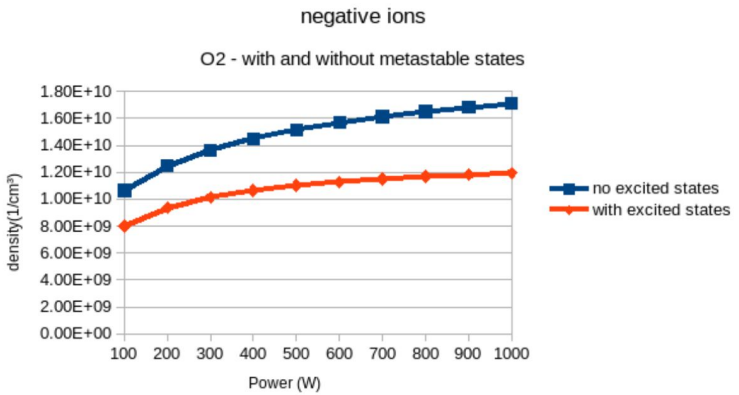
# Overview of Heavy Particle Collisions

- Ion-Ion Recombination
- Symmetric Charge Exchange
- Asymmetric Charge Exchange
- Penning Ionization
- Neutral conversion
- **Electron detachment**

$$A + B^- \rightarrow A + B + e$$

$$A^* + B^- \rightarrow A + B + e$$

Electron detachment can significantly influence the electronegativity of a plasma.



# Approaches to chemistry set design

## All-In

Simply collect all reactions and species found relevant for process parameters

Pro: Fast

Contra: Hard to identify problematic reactions, e.g. missing ones, duplicates etc.

Well suited for established sets with sufficient available data

## Step-by-Step

Start with one feed gas and add reactions. Identify “new” species, e.g. ions, excited states, dissociation products and reactions one by one.

Repeat for other feed gases.

Add cross-reactions and reactions for resulting species.

Pro: More control, easy to identify missing reactions etc.

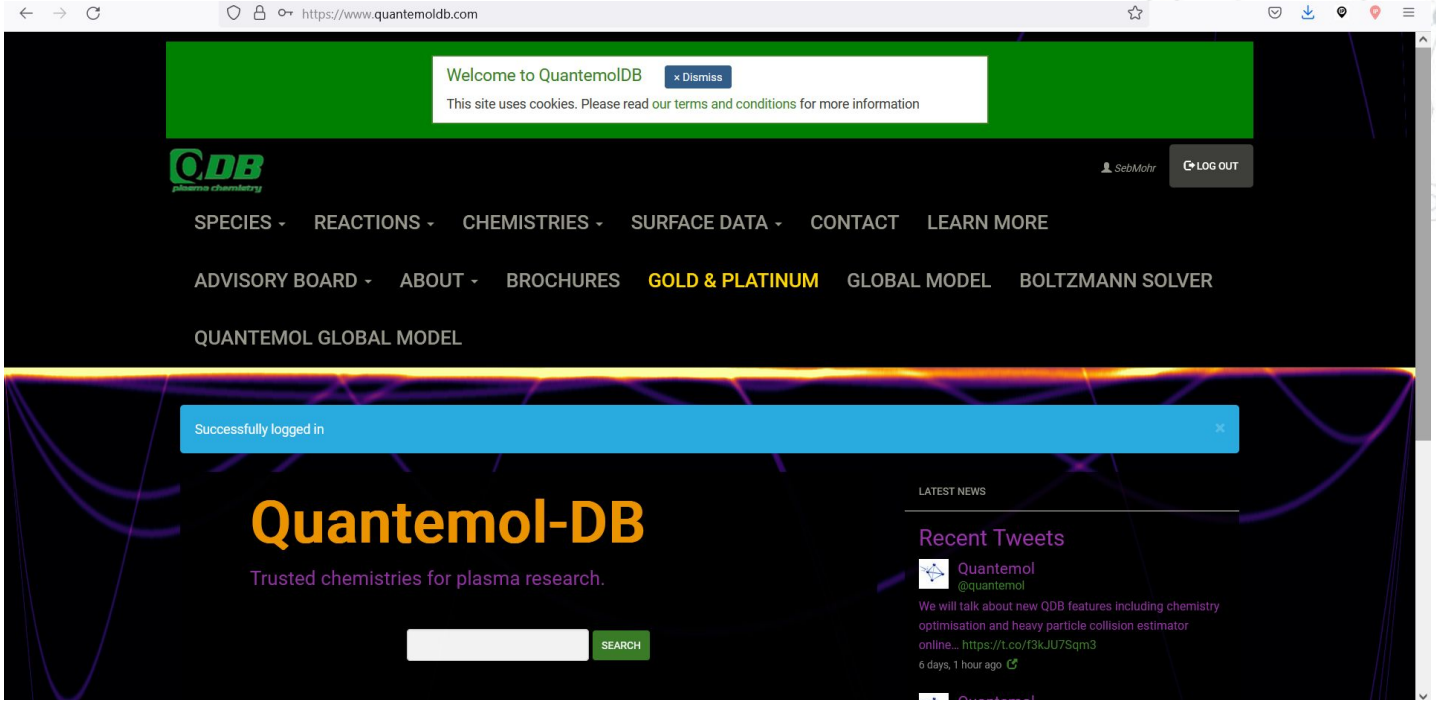
Contra: Needs more time

Suited for sets with “new” gases or data gaps.

# Where to get relevant data?

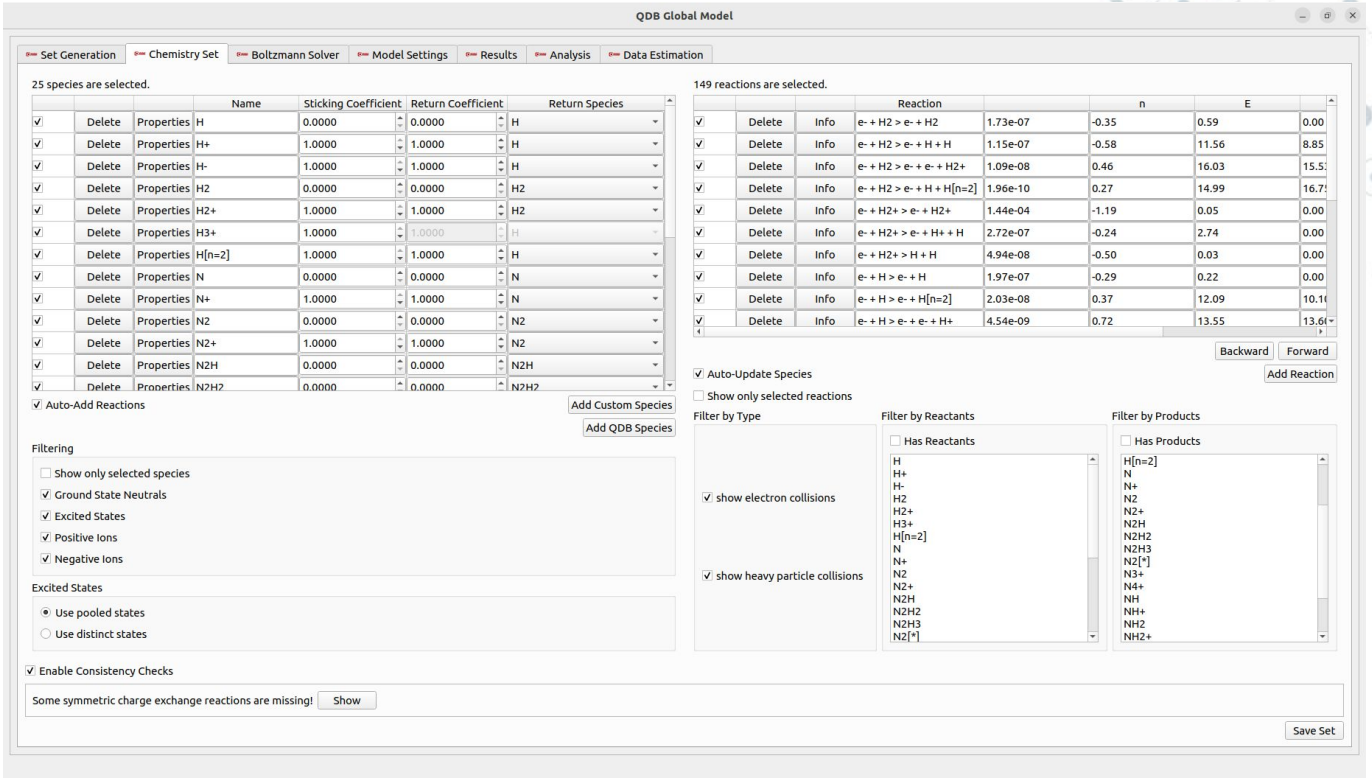
QDB offers access to cross-section and rate coefficients data for almost 30 000 reactions.

It also gives access to pre-assembled chemistry sets, species data such as enthalpies of formation, and some surface coefficients.



# Desktop app

Chemistry sets can be also be quickly created and tested via 0D simulations in the QDB desktop app.



# How to optimize sets for given process parameters

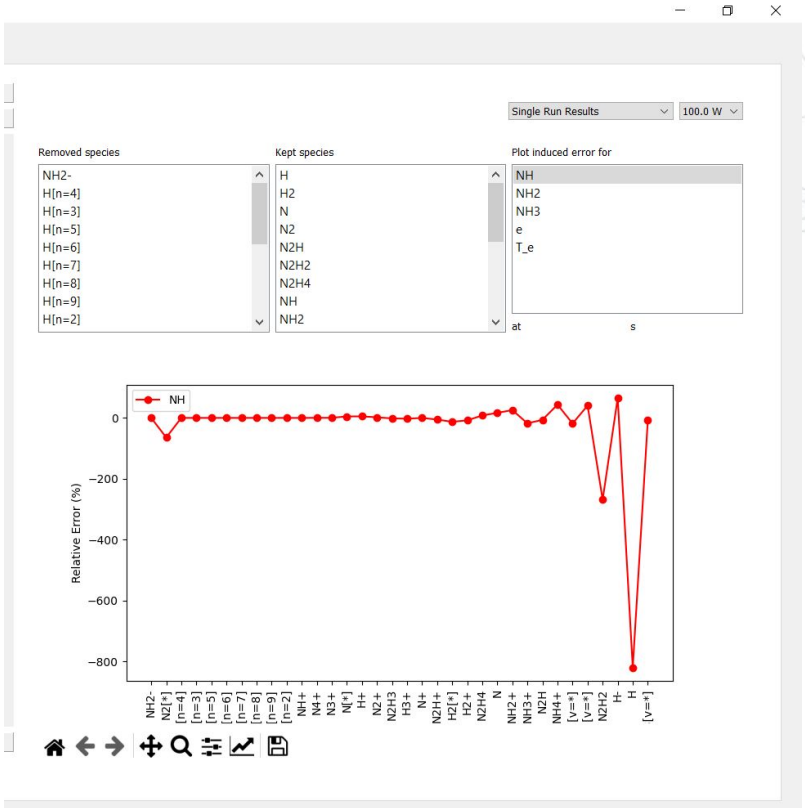
On the one hand, comprehensive sets usually contain more species/reactions than necessary to sufficiently predict important quantities such as the density of neutrals reacting with the surfaces.

On the other hand, important data such as coefficients describing surface processes might be missing/unknown/imprecise.

QDB offers tools to optimize sets and fill/calibrate missing data.

# Optimization - Set reduction

The desktop app now allows the user to reduce chemistry sets for given process parameters including variations of one parameter to the smallest set which reproduces chosen plasma parameters within a defined error margin compared to the full set. This allows to optimize sets before exporting them to multi-dimensional models.



# Optimization - Set reduction

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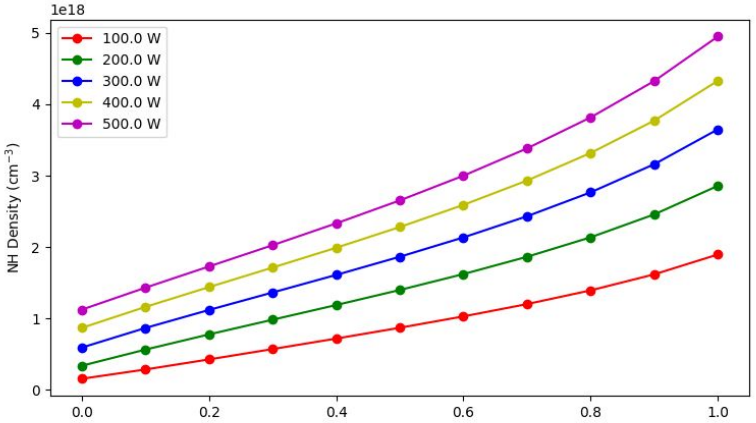
| | 100.0 W | 200.0 W | 300.0 W | 400.0 W | 500.0 W |
|---|---|---|---|---|---|
| H[n=5] | 0.42 % in e | -0.14 % in NH3 | -5.01 % in NH2 | -2.14 % in NH2 | -2.44 % in NH3 |
| H[n=6] | 0.44 % in e | -0.42 % in NH3 | -4.91 % in NH2 | -2.43 % in NH2 | -1.21 % in NH2 |
| H[n=7] | 0.45 % in e | -0.85 % in NH3 | -4.55 % in NH2 | -2.23 % in NH3 | -2.89 % in NH3 |
| H[n=8] | 0.45 % in e | -0.86 % in NH3 | -3.90 % in NH2 | -3.48 % in NH3 | -4.69 % in NH3 |
| H[n=9] | 0.46 % in e | -0.87 % in NH3 | -3.89 % in NH2 | -6.07 % in NH3 | -4.88 % in NH3 |
| H[n=2] | 0.93 % in e | -1.98 % in NH3 | -6.63 % in NH3 | -12.03 % in NH3 | -22.74 % in NH3 |
| NH+ | 0.96 % in e | -2.87 % in NH | -3.32 % in NH2 | -5.20 % in NH3 | -2.52 % in NH3 |
| N4+ | 0.84 % in e | -2.08 % in NH | -5.76 % in NH3 | -2.99 % in NH3 | -4.95 % in NH3 |
| N3+ | 0.86 % in e | 2.06 % in e | -6.88 % in NH3 | -5.22 % in NH3 | -8.75 % in NH3 |
| N[*] | 4.81 % in NH | 9.55 % in NH2 | -32.23 % in NH2 | 47.23 % in NH2 | 56.28 % in NH2 |
| H+ | 5.08 % in NH | 9.98 % in e | 11.18 % in e | -14.38 % in NH3 | -31.25 % in NH3 |
| N2+ | 6.71 % in e | 7.20 % in e | 8.28 % in e | 17.76 % in NH3 | 27.80 % in NH3 |
| N2H3 | 6.73 % in e | -2.76 % in NH | -1.82 % in NH | -1.32 % in NH | -1.30 % in NH2 |
| H3+ | 6.76 % in e | 10.09 % in e | 8.33 % in e | 2.02 % in e | 2.59 % in NH2 |
| N+ | 12.40 % in e | -13.20 % in NH2 | -11.13 % in NH3 | -10.62 % in NH3 | -17.47 % in NH3 |
| N2H+ | 6.93 % in e | 10.13 % in e | 27.73 % in NH3 | 68.75 % in NH3 | 68.36 % in NH3 |
| H2[*] | -12.91 % in NH | -11.64 % in NH | 11.63 % in NH3 | 5.72 % in NH2 | 6.92 % in NH2 |
| H2+ | 15.56 % in e | 21.85 % in NH2 | 19.81 % in e | 10.66 % in NH2 | 11.16 % in NH2 |
| N2H4 | -17.37 % in NH2 | -9.83 % in NH2 | -5.20 % in NH2 | -2.50 % in NH2 | -2.52 % in NH2 |

# Optimization - Surface Coefficient Variation

You can now run automated variations of surface coefficient for one absorbed/produced species pair, e.g. H producing NH at surfaces. Options are:

a) Vary only sticking coefficient
b) Vary only return coefficient
c) Vary both



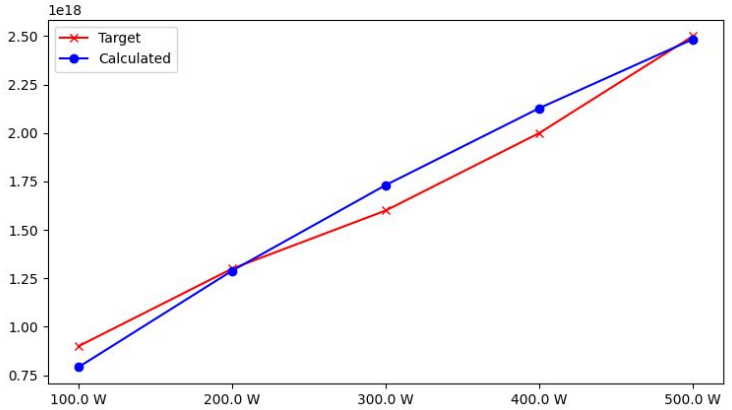

Here the return coefficient for NH produced by H with a constant sticking coefficient of H was varied.

# Optimization - Surface Coefficient Calibration

quantemol

You can also input target densities for the absorbed/produced species and find the coefficient (pair) which best reproduces these densities. Options are:

a) Optimize only sticking coefficient for absorbed species
b) Optimize only return coefficient for produced species
c) Optimize both for either or both densities.




The example shows again NH produced by H with a constant sticking coefficient for H; plotted are the calculated NH densities for the optimum coefficient as a function of pressure compared to the target densities.

# Estimating rate coefficients by Machine Learning

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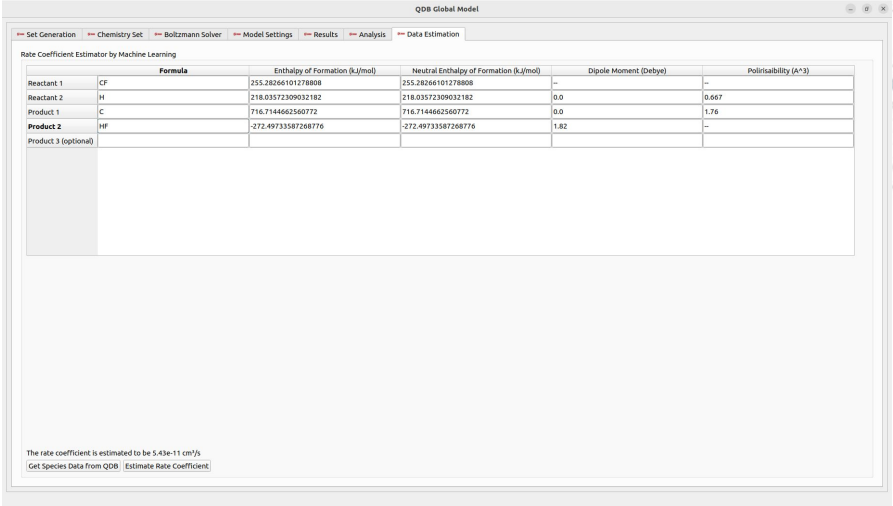
Martin Hanicinec has developed an ML model as part of his PhD to estimate rate coefficients for binary heavy particle collisions A + B > C + D. This algorithm is embedded into the website and available via the QDB desktop app.




The user inputs the desired reaction; used species parameters are displayed and can be changed manually.

# Radiative Process Database LIDB

A separate database for radiative processes, LIDB, has been developed. It currently contains mostly information about molecular transitions; once atomic data has been added, an API will be added to the desktop app to quickly add radiative processes to the chemistry sets.