

Reduction of Complex Chemistry Tutorial



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Presentation Overview

- Plasma discharges can vary greatly in complexity depending on gas mixture and application
- Modelling is a necessary step to fine tune many processes. This is gated however by an understanding of the chemistry
- Since chemistry is an integral component to model run time and stability, we should be able to reduce chemical complexity per application

Work Flow of Modelling in Plasma Physics



INNOVATION

- Chemistry Modelling in 0D**
- Use QDB
 - Remove geometrical complexity
 - Concentrate on plasma chemistry

- Reactor Modelling in 2D/3D**
- Generally use Ar or O₂
 - Concentrate on Power, Pressure, flow & frequency effects on plasma parameters

- Full Reactor and Chemistry Modelling in 2D/3D**
- Input reduced chemistry set
 - Input chosen set of reactor inputs

Process Outputs

- Fluxes
- EDFs
- Densities
- Etch/Deposition Rates
- Feature Profile Modelling



Quantemol database

- Developed for people working on plasma modelling with complex chemistries.
- Supports and compares multiple data sets.
- Quantemol has developed a plasma chemistry database to establish a trusted resource for plasma chemistry information.
- Chemistry sets could be used in different plasma modelling software via API.



Quantemol database provides:

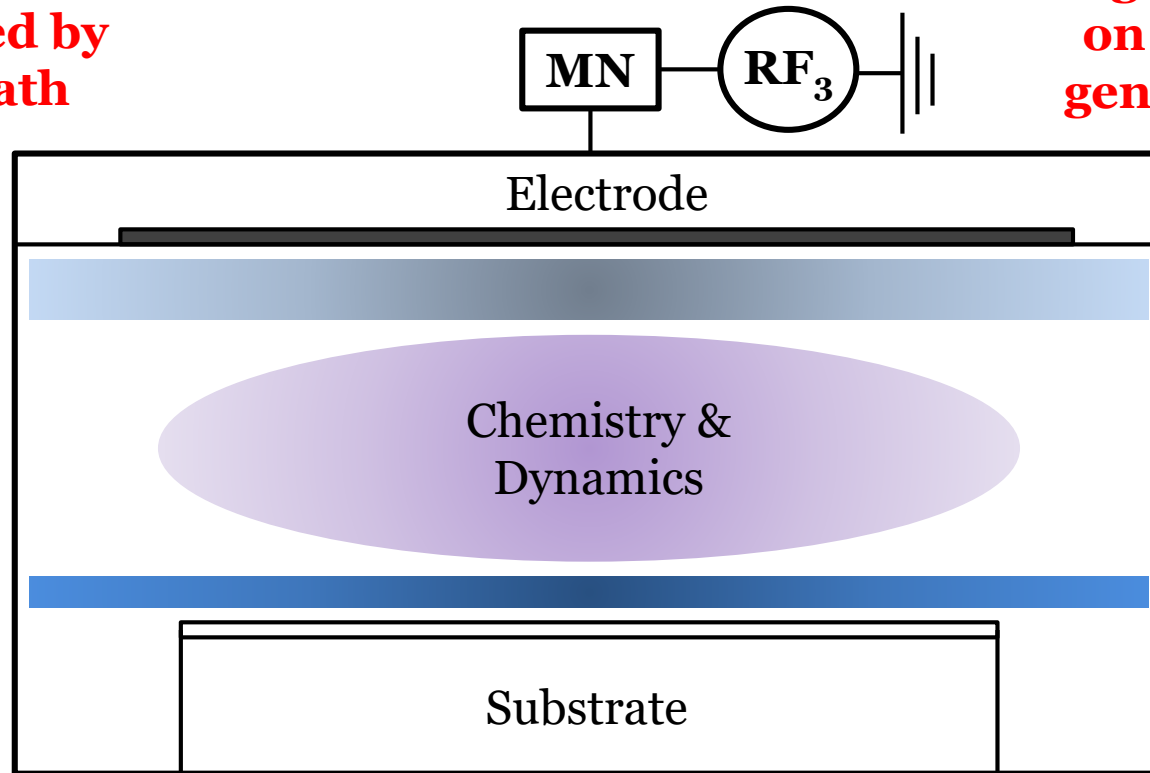
- On going data updates and support
- Self consistent and validated chemistry sets
- One place to exchange data and research ideas

www.QuantemolDB.com

Simple Example (1)

**Plasma electrons
are accelerated by
high RF sheath**

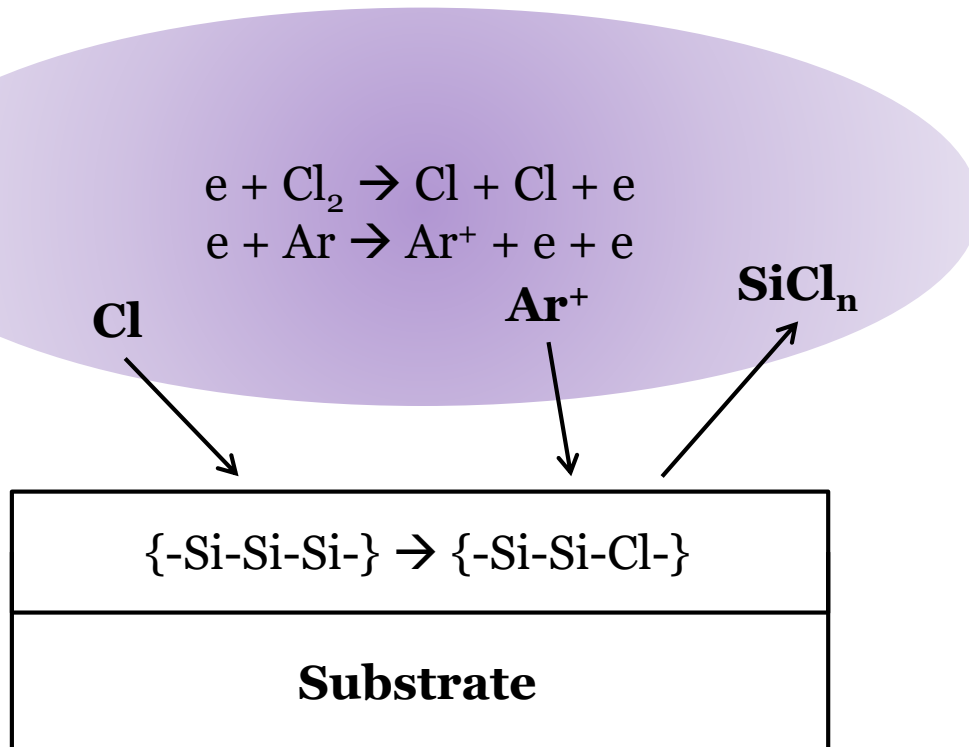
**Higher frequency
on electrode to
generate plasma**



**Positive ions
accelerated by low
frequency sheath**

**Multiple
frequencies on the
substrate designed
to accelerate ions**

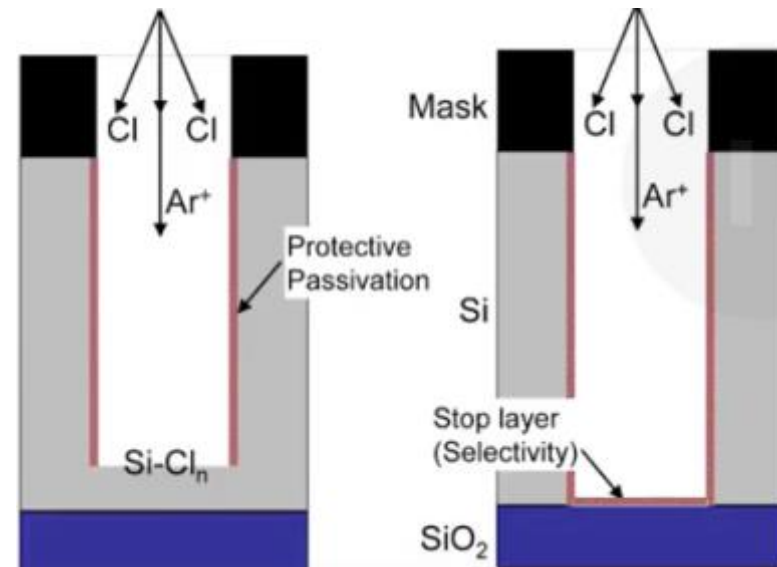
Simple Example (2)



A 'simple' etching process depends on being able to control of neutral radicals and anisotropic, energetic ions. The information needed for a solver to be able to model this, depends on knowledge of the plasma chemistry

Selectivity of Si and SiCl depends on chemistry and ion energy

Made more complicated when considering dielectric substrates and fluoro-carbon gases.



Ways to Model

- 0D Modelling
 - Plasma-R
 - Global-kin

No geometrical complexity. Cannot investigate reactor behaviours. No set limit to chemistry. Fast computation times
- 2D Modelling
 - Q-VT (HPEM)
 - Vizglow

Very accurate. Works best with symmetrical reactors. Modular and multiphysical. Depending on the make (QVT), easily computes chemistry and geometry
- 3D Modelling
 - COMSOL
 - Opera-D
 - CFD-ACE+

The most accurate. Can investigate asymmetrical effects. Multiphysics. Computationally expensive – multiplied by inputs. Limited to ~ 50 reactions

TESV Cleaning post-DRIE Etching with a Trymax Reactor (1)

During the powerbase project, Quantemol Ltd was tasked with carrying out 0D chemistry modelling and 2D reactor modelling for Trymax

Reactor: Microwave

Power Range: 0 – 2000 W

Pressure Range: 1 – 1000 mTorr

Gas: CF₄/O₂/N₂/H₂

Percentage: 0.1/85/14.15/ 0.75

Total Gas Flow: 3780 SCCM

TESV Cleaning post-DRIE Etching with a Trymax Reactor (2)

- Plasma processes are a lot more complex than simply using Argon
- The gas mixture for the TESSV Cleaning was:
 - $\text{CF}_4/\text{N}_2/\text{O}_2/\text{H}_2$
- Before one even attempts to understand the TESSV clean process and this chemistry, one needs to be aware of how different plasma conditions may affect the species densities
 - This is the first step in understanding how modular the plasma modelling work flow is

CF₄/O₂/N₂/H₂

Used in:

- Remote plasma chemical etching
- Direct plasma etching with CF₄/O₂ of poly-Si and SiO₂
- Dry reactive ion etching in TSV cleaning

Current reaction set is 396 reactions. This is A LOT of reactions.

The aim is to make this reaction set useable in software by reducing it based on application

Some Power and Pressure Variations With the Entire Reaction Set

It is noted that increasing power generally increases dissociation due to a strong relationship with electron density

- Electron temperature is not very much affected
- Species are more likely to be fractionated and ionized.
- Discharge is strong electropositive

Increasing pressure on the other hand increases collisionality

- Electron temperature is greatly dependent on the mean free path
- Attachment and dissociative attachment mechanisms become common
- Charge transfer and neutralization collisions more prevalent
- Heavy neutral collisions become comparable to electron collision processes

Important Information

The following results were obtained using:

- Arrhenius Coefficient data from QDB (www.quantemoldb.com)

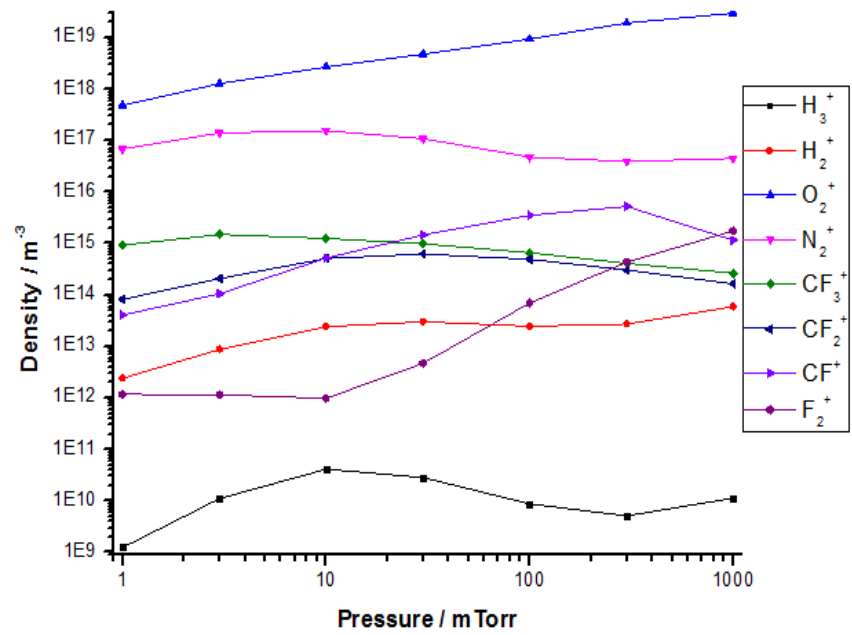
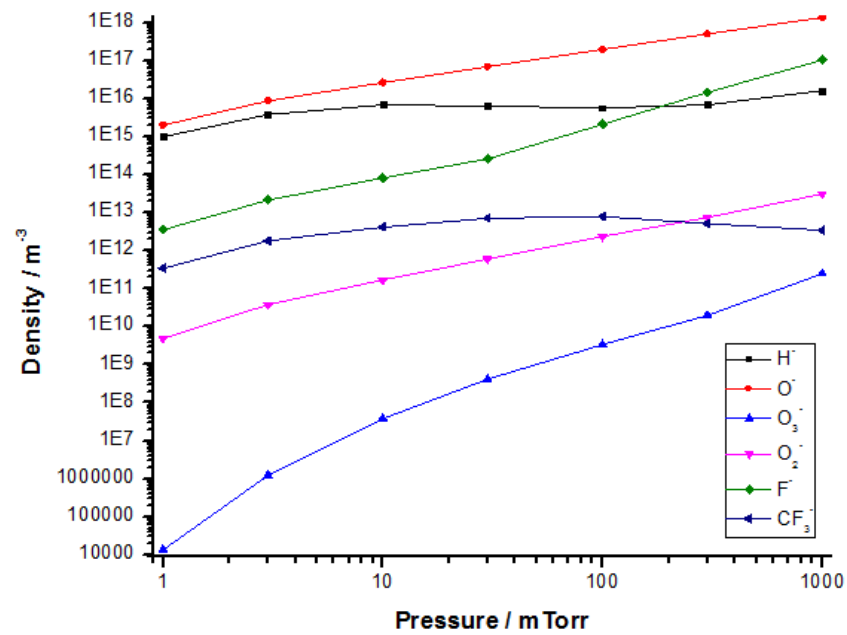
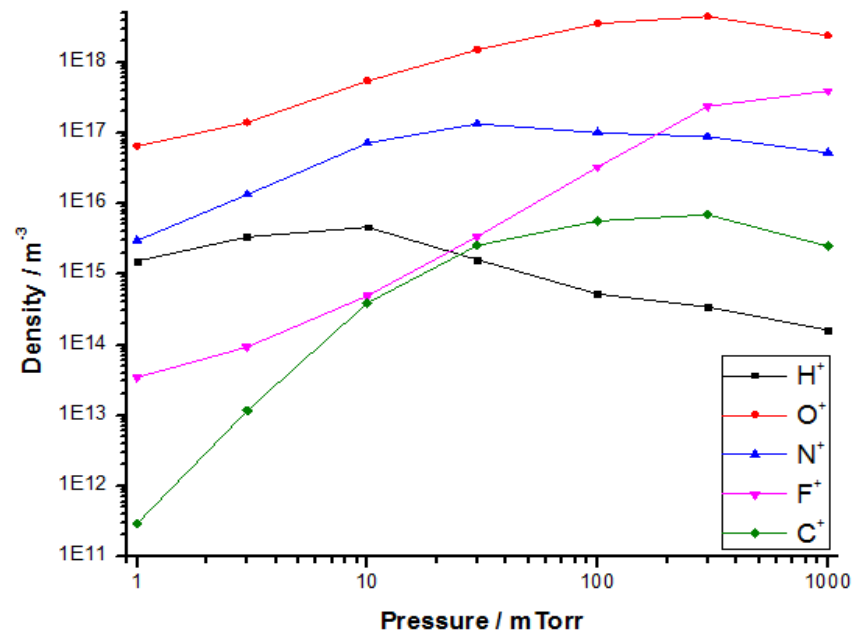
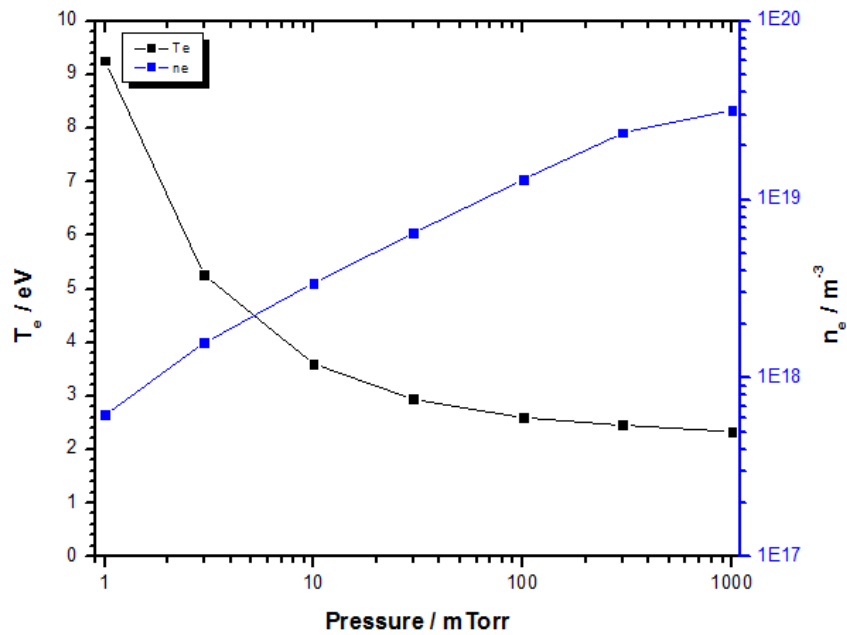
$$R = AT_e^n e^{-\frac{c}{T_e}}$$

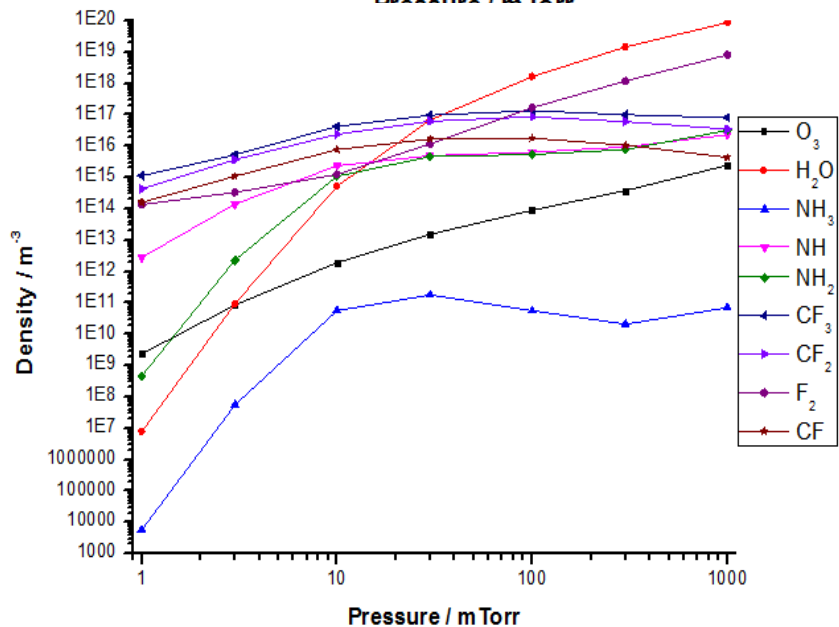
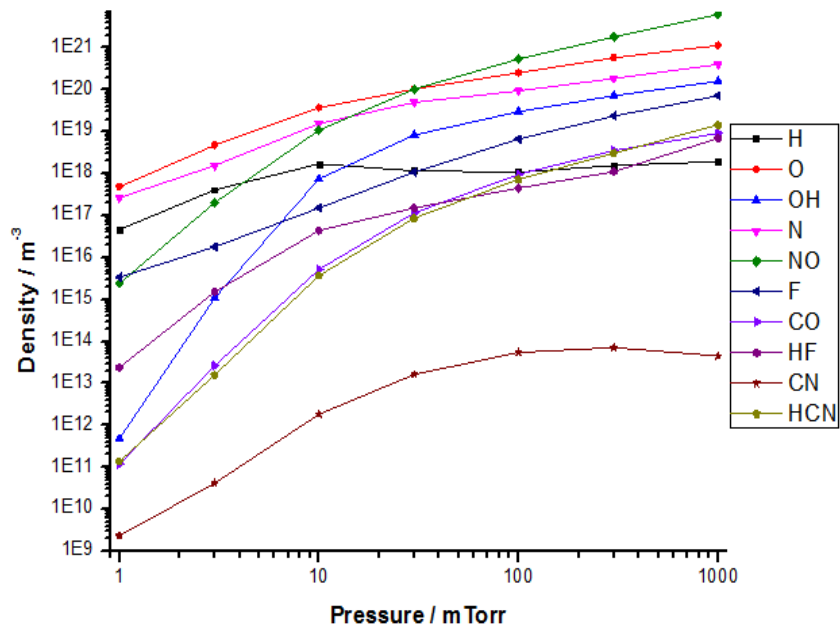
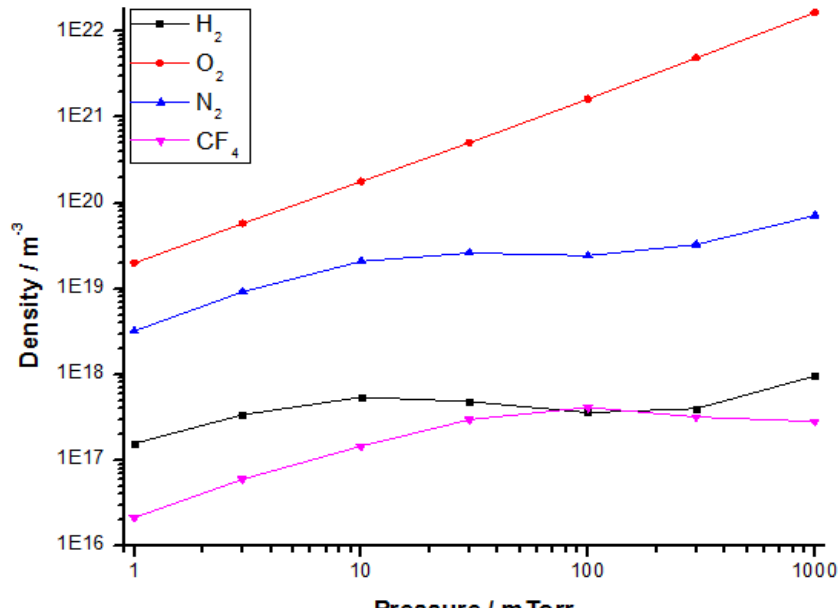
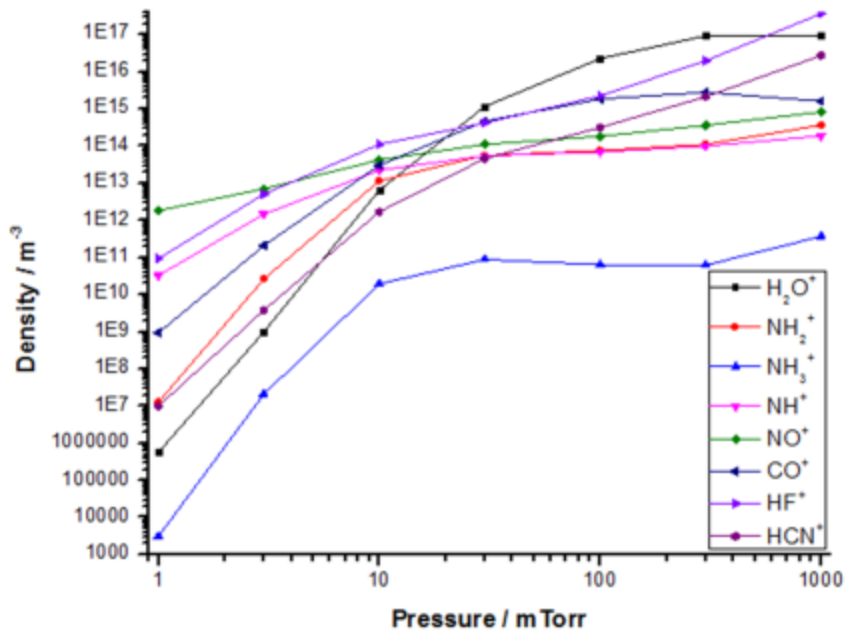
- π lasma-R 0D modelling code

G. Kokkoris, A. Goodyear, M. Cooke and E. Gogolides, J. Phys D: Applied Physics 41 (19) “A global model for C₄F₈ plasmas coupling gas phase and wall surface reaction kinetics”, 2008

G. Kokkoris, A. Panagiotopoulos, A. Goodyear and M. Cooke, J. Phys D: Applied Physics 42 (5) “A global model for SF₆ plasmas coupling reaction kinetics in the gas phase and on the surface of the reactor walls”, 2009

Pressure Variation

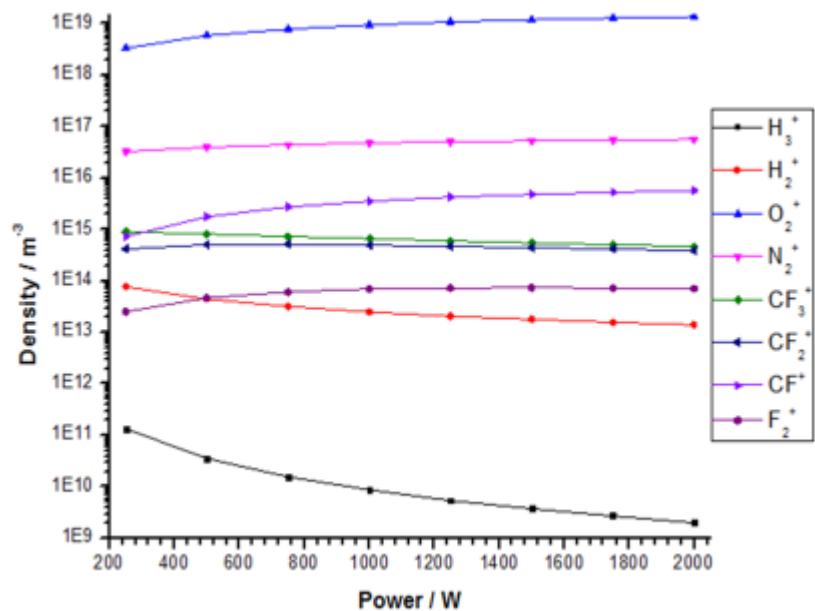
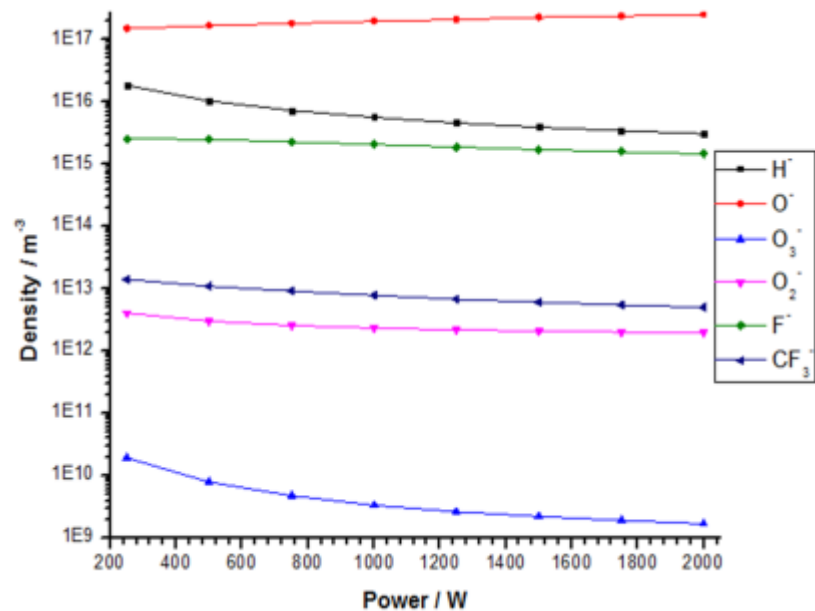
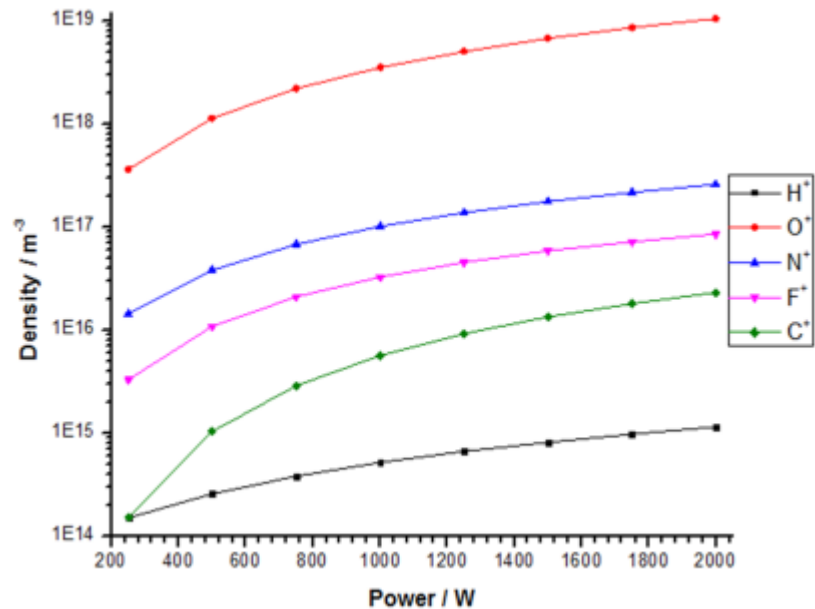
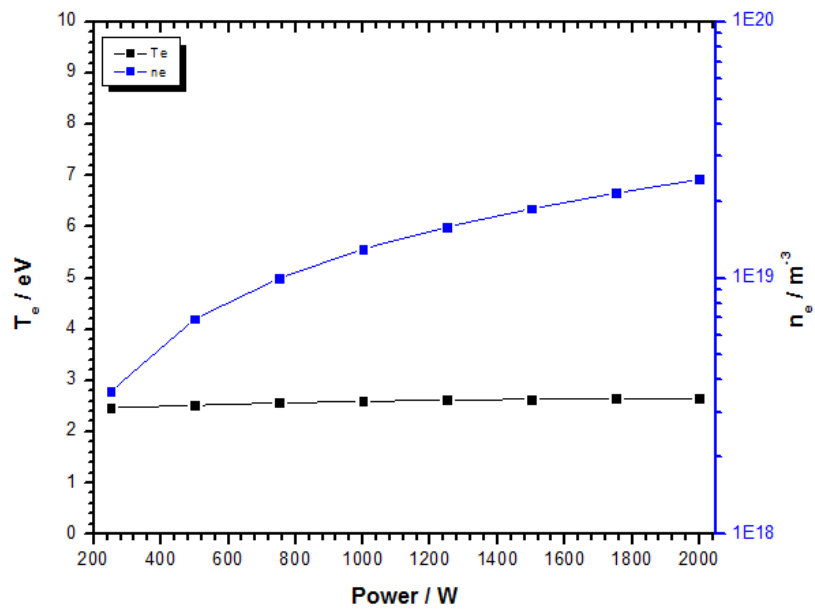


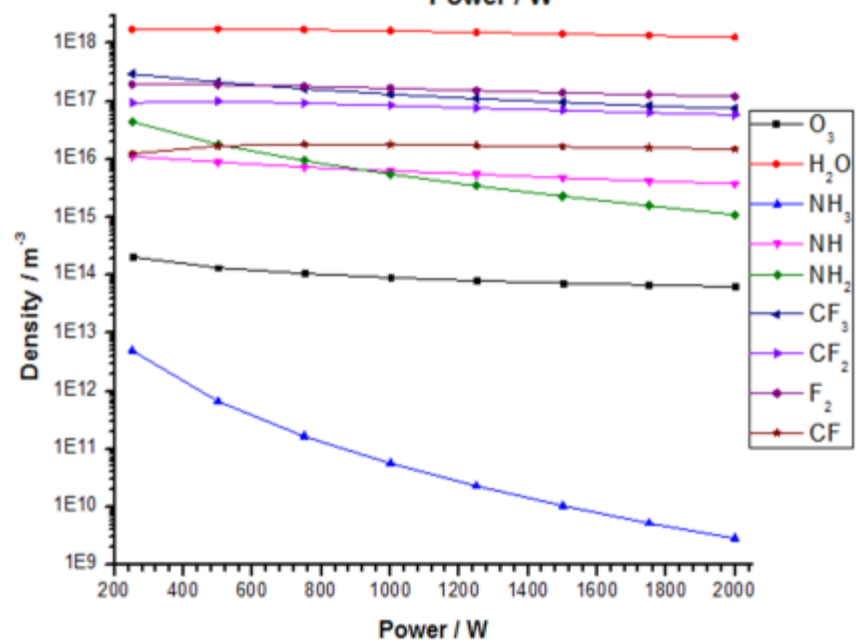
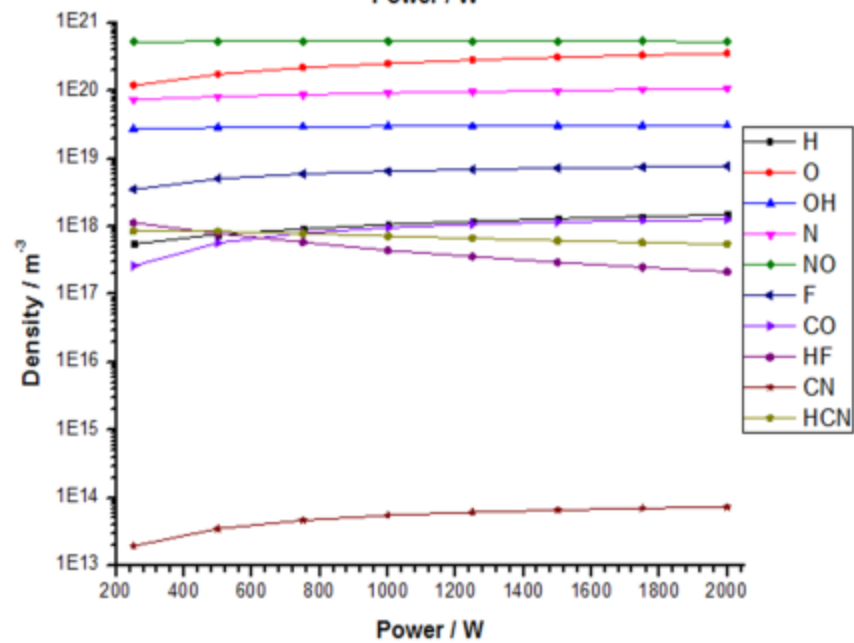
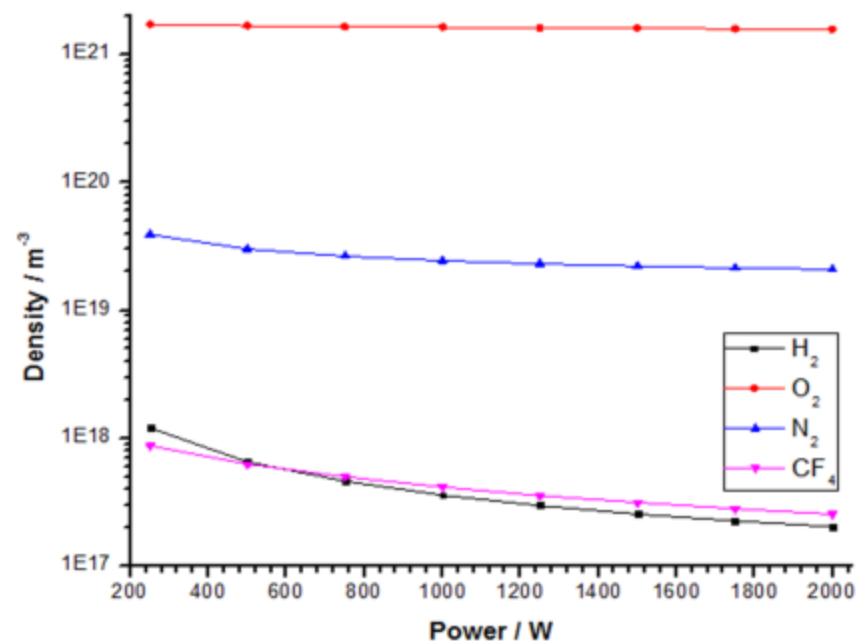
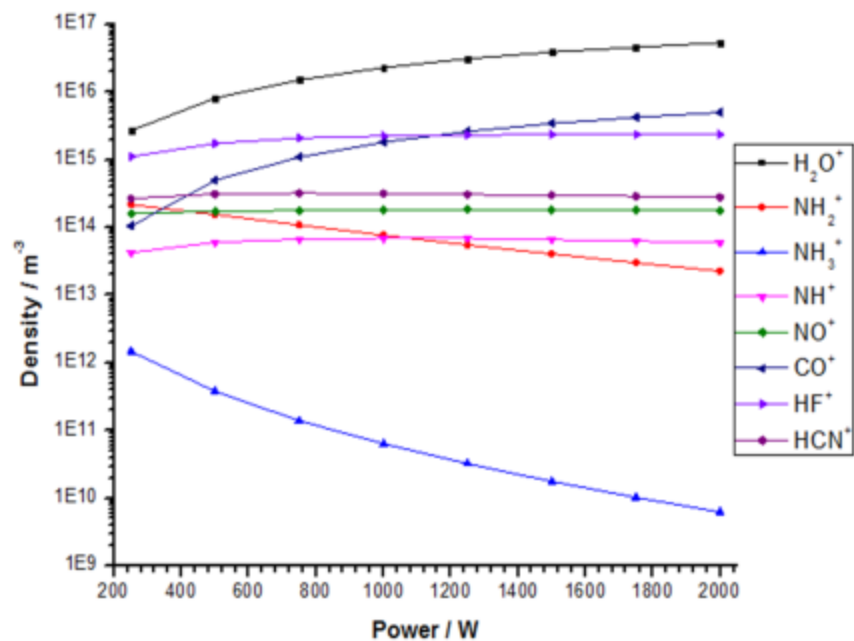


Notes on Pressure

- Increasing the pressure increases the density of feed gas – less of them are being consumed in electron impact collisions/more of them are recombined
- The discharge becomes more electronegative and electron density also rises as singlet positive ion density drops
- The electron temperature notably lowers as the pressure is increased due to lower effective volume for electron acceleration
- There is a sweet (medium pressure) spot where singlet positive ions have their highest densities

Power Variation





Notes on Power

- Varying the power does little to affect the electron temperature but has a similar affect to pressure on the plasma density.
- Dissociation is encouraged
- Positive ion density is increased and the electronegativity of the plasma decreases

Modelling

- Although the entire chemistry set was modelled using 0D (Plasma-R), it is extremely difficult to try and do this in 2D and 3D modelling codes.
- Not only would computational times be unacceptable, the stability of the simulation is limited by how well it resolves the energy and mass balances of every single species.
- Computational time is strongly dependent on the amount of species present in the calculation

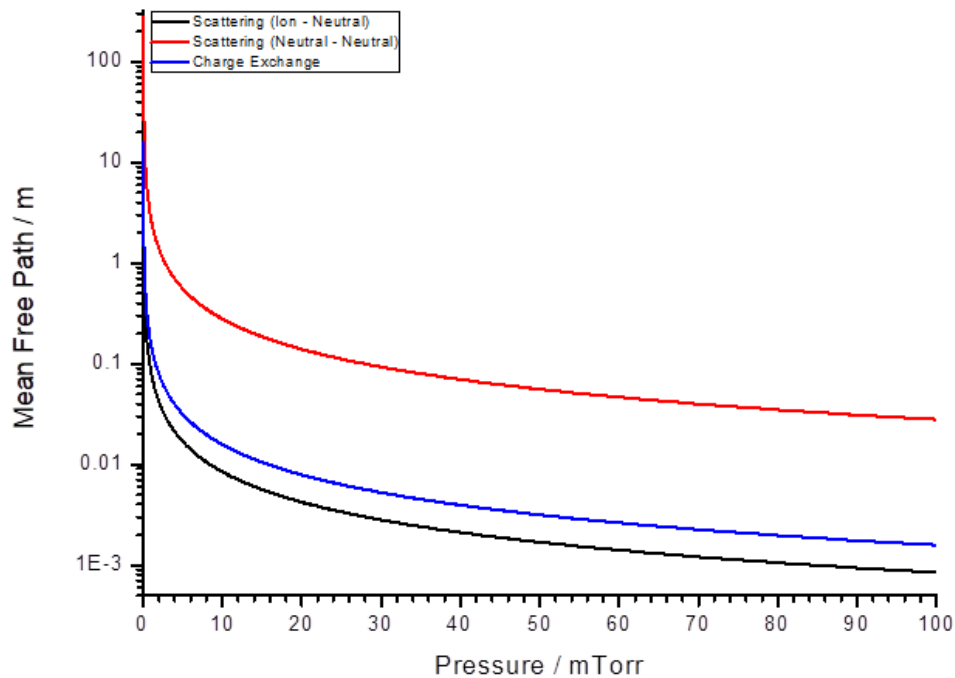
How do we Reduce such a Chemistry Set? (1)

- **Choose a pressure that matches application**
 - Very Low pressure = 1 - 30 mTorr – Ion bombardment etching
 - Low pressure = 30 – 100 mTorr – ion etching with some neutral assistance
 - Medium pressure = 100 – 500 mTorr – some ion etching with neutral coverage
 - High pressure = 500 – 1000 mTorr – neutral deposition
- **Choose a power to tune application conditions**
 - High powers boost singlet positive ion density and electron density
 - Comparatively, most negative ion density reduces
 - Heavy negative ions are more likely to be dissociated and/or dissociation processes are more favourable at high powers

How do we Reduce such a Chemistry Set? (2)

- **Let's choose very low pressure and reasonable power (10 mTorr and 1000 W)**
 - No neutral-neutral collisions due to large mean free paths ^a
 - No negative heavy ions due dissociation processes dominating
 - Heavy collisions are dominated by charge-exchange
 - 1000 W ensures enough dissociation for positive ion bombardment
 - Negative ions aren't expected to leave the plasma unless pulsed ^c
 - 10 mTorr ensures a low enough mean free path for anisotropic, energetic ions
 - Relatively few collisions in the bulk and in the sheath on their way to the substrate ^b

^a Mean Free Paths of Collisions Varying as Pressure



- Collision cross-section between neutral species is $1.3 \times 10^{-20} \text{ m}^2$
- Resonant Charge-exchange cross-section is $20 \times 10^{-20} \text{ m}^2$
- Charge-exchange cross-section is $44 \times 10^{-20} \text{ m}^2$

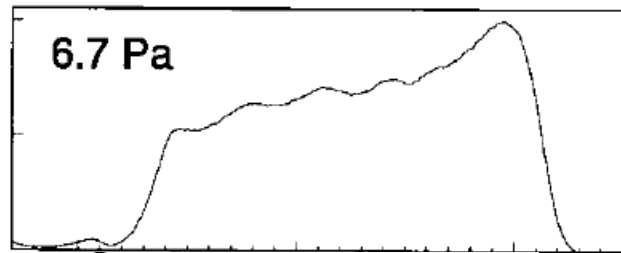
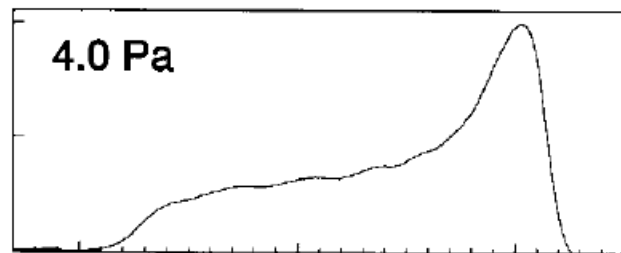
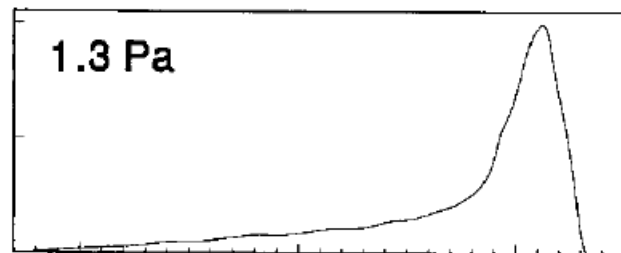
- ***“Cross-sections and Swarm Coefficients for Nitrogen Ions and Neutrals in N₂ and Argon Ions and Neutrals in Ar for Energies from 0.1 eV to 10 keV”***, A. Phelps

“Energetic Binary Collisions in Rare Gas Plasmas”, R. Robinson, 1979

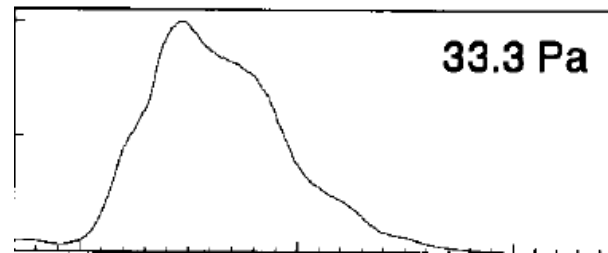
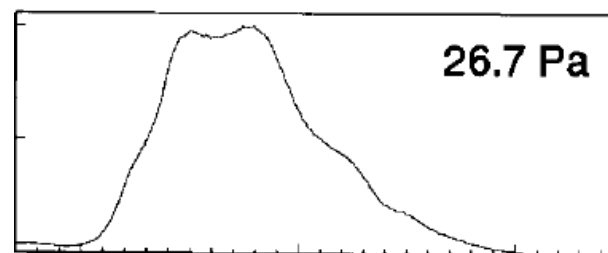
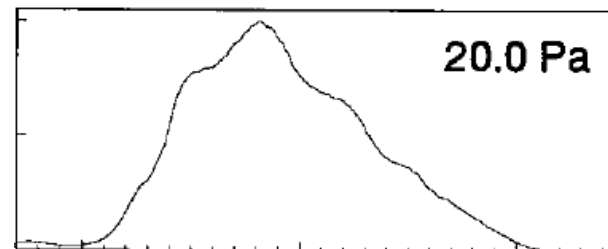
- ***“Basic Data of Plasma Physics: The Fundamental Data on Electrical Discharges”***, S. Brown, 1966

^b Ar⁺ Energy Distributions from a GEC cell varying with Pressure

- *“Studies of Ion Kinetic-Energy Distributions in the Gaseous Electronics Conference RF Reference Cell”, J. K. Olthoff, 1995*

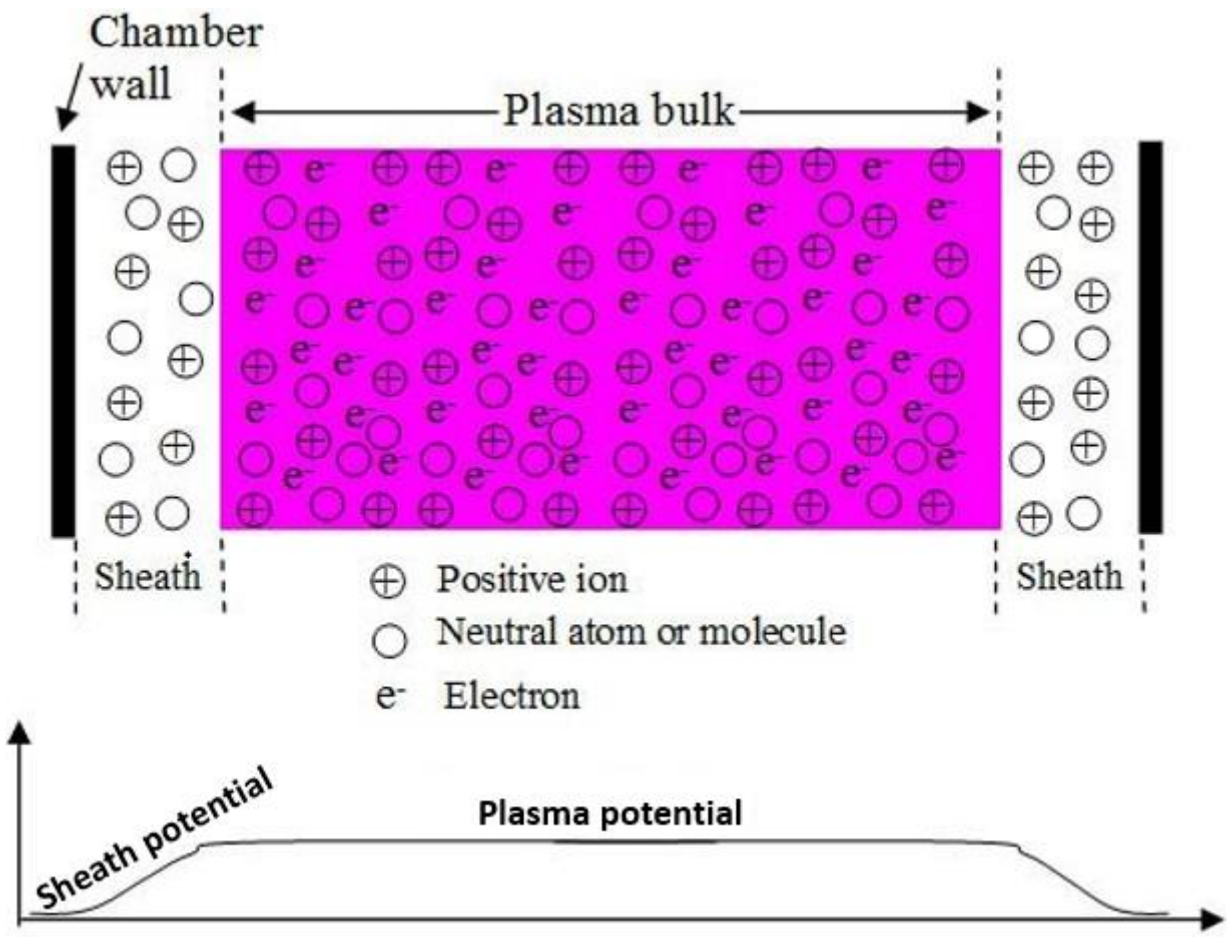


Ion Energy (eV)



Ion Energy (eV)

• Variation of Charge Density and Potential from the Bulk of the Plasma to a Surface



Removal (1)

- O_3^- , O_2^- and CF_3^-
 - As they are heavy negative ions and dissociative processes dominate.
- C and C^+
 - As they are more suited to a deposition process
- H_2O , H_2O^+ , CO , CO^+ , CN , HCN , HCN^+ HF , HF^+
 - As the ground states are the products of gas phase neutral collisions which won't be happening very often at a pressure of 10 mTorr.

Comparison at 10 mTorr (1)

Species	Reduced Set	Full Set
H ₃ ⁺	5.69E+10 m ⁻³	4.11E+10 m ⁻³
H ₂	5.96E+17 m ⁻³	5.43E+17 m ⁻³
H ⁺	5.17E+15 m ⁻³	4.59E+15 m ⁻³
H	2.39E+18 m ⁻³	1.72E+18 m ⁻³
H ₂ ⁺	2.72E+13 m ⁻³	2.45E+13 m ⁻³
H ⁻	4.78E+15 m ⁻³	6.85E+15 m ⁻³
O ₂	1.82E+20 m ⁻³	1.78E+20 m ⁻³
O ⁻	2.71E+16 m ⁻³	2.64E+16 m ⁻³
O	4.07E+19 m ⁻³	3.70E+19 m ⁻³
O ₂ ⁺	2.63E+18 m ⁻³	2.67E+18 m ⁻³
O ⁺	5.62E+17 m ⁻³	5.45E+17 m ⁻³
O ₃	2.02E+12 m ⁻³	1.88E+12 m ⁻³
OH	2.13E+16 m ⁻³	7.45E+17 m ⁻³
N ₂	3.01E+19 m ⁻³	2.08E+19 m ⁻³
N	7.73E+18 m ⁻³	1.54E+19 m ⁻³
N ₂ ⁺	2.07E+17 m ⁻³	1.57E+17 m ⁻³
N ⁺	3.28E+16 m ⁻³	7.20E+16 m ⁻³
NH ₂	4.10E+11 m ⁻³	2.35E+15 m ⁻³
NH	8.06E+15 m ⁻³	1.09E+15 m ⁻³

Comparison at 10 mTorr (2)

Species	Reduced Set	Full Set
NH ₂ ⁺	1.42E+11 m ⁻³	1.15E+13 m ⁻³
NH ⁺	6.31E+13 m ⁻³	2.28E+13 m ⁻³
NO ⁺	2.48E+13 m ⁻³	4.30E+13 m ⁻³
NO	6.80E+15 m ⁻³	1.09E+19 m ⁻³
CF ₄	1.90E+17 m ⁻³	1.45E+17 m ⁻³
F ⁻	7.26E+13 m ⁻³	8.17E+13 m ⁻³
CF ₃	1.39E+16 m ⁻³	4.29E+16 m ⁻³
F	1.03E+17 m ⁻³	1.50E+17 m ⁻³
CF ₂	1.83E+16 m ⁻³	2.36E+16 m ⁻³
CF ₃ ⁺	1.32E+15 m ⁻³	1.26E+15 m ⁻³
F ⁺	3.16E+14 m ⁻³	4.89E+14 m ⁻³
CF ₂ ⁺	3.55E+14 m ⁻³	5.12E+14 m ⁻³
F ₂	7.16E+14 m ⁻³	1.24E+15 m ⁻³
CF ⁺	6.25E+14 m ⁻³	5.25E+14 m ⁻³
CF	1.67E+16 m ⁻³	7.73E+15 m ⁻³
F ₂ ⁺	5.26E+11 m ⁻³	9.81E+11 m ⁻³
T _e	3.57 eV	3.60 eV
n _e	3.41E+18 m ⁻³	3.42E+18 m ⁻³

First Round Comments

- There is a very close agreement between the species densities of both the reduced and full set with the exception of OH, NH₂, NH₂⁺ and NO
- Reaction set is now 194 reactions which is still quite a lot, but better than 396
- Depending on power, we can go 1 step further and completely remove heavier species based on their number densities and the likelihood of them being formed. **For this, it is 'ok' to neglect species more than 3 orders mag less than the highest species in its class**
- Suspect H⁻, O₃, NH₂, NH₂⁺, H₂⁺, H₃⁺, NO, NO⁺, F₂⁺ and F₂. Remove them and compare with the full set at 10 mTorr again

Removal (2)

- H^- and F^-
 - As they are more than 3 magnitudes lower than the electron density. At this power and pressure, negative charge density is dominated by electrons. Only O^- ions are noticeable
- O_3
 - As its dissociation processes are most likely to be dominant
- NH , NH^+ , NH_2 , NH_2^+ , NH_3 and NH_3^+
 - As not only do they illustrate unnatural jumps in density, the removal of H^- means no production of NH for heavier NH_x formation
- H_2^+ and H_3^+
 - The high degree of dissociation sees an extremely large density of H atoms. If H_2^+ is removed, H_3^+ must therefore be removed also.
- F_2 and F_2^+
 - As their production seems pressure dependent

Sensitivity Analysis

Removal of NO

- Express particle loss and gains as an equality
 - $k_{\text{diss}} n_e n_{\text{NO}} = k_{\text{neu}} n_{\text{N}_2} n_{\text{O}_2^+}$
 - $k_{\text{neu}} = 1 \times 10^{-23} \text{ m}^3 \text{ s}^{-1}$, $n_e = 1 \times 10^{18} \text{ m}^{-3}$, $k_{\text{diss}} = 1.27 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$, $n_{\text{N}_2} = 3 \times 10^{19} \text{ m}^{-3}$, $n_{\text{O}_2^+} = 2.67 \times 10^{18} \text{ m}^{-3}$
 - $n_{\text{NO}} \sim 6.31 \times 10^{14} \text{ m}^{-3}$
- Although this is comparable to CF_x^+ densities, because the production of NO comes from NO^+ , we need to consider the loss and gain of NO^+

Loss and Production Channels for NO⁺

Production

Reaction	Rate Constant / m ³ s ⁻¹	Reaction Rate / m ⁻³ s ⁻¹
$O + N_2^+ \rightarrow N + NO^+$	1.4×10^{-16}	1.25×10^{21}
$N + O_2^+ \rightarrow O + NO^+$	1.5×10^{-16}	3.05×10^{21}
$O^{++} + N_2 \rightarrow N + NO^+$	1.2×10^{-18}	2.03×10^{19}
$N_2 + O_2^+ \rightarrow NO + NO^+$	1×10^{-23}	8×10^{14}

Losses

Reaction	Rate Constant / m ³ s ⁻¹	Reaction Rate / m ⁻³ s ⁻¹
$e + NO^+ \rightarrow N + O$	2×10^{-10}	2.94×10^{22}
$O^- + NO^+ \rightarrow O + O + N$	1×10^{-13}	2.72×10^{17}
$O^- + NO^+ \rightarrow O + NO$	1×10^{-13}	2.72×10^{17}

Losses are clearly > production mechanisms. This is not including losses of NO⁺ to the surface

Further Checking – H⁻

- H⁻ was noted to be very low when compared to the densities of O⁻ and n_e
- A loss process for H⁻ was:
$$\text{N} + \text{H}^- \rightarrow \text{e} + \text{NH}$$
- The removal of the ammonium species (NH_x) means that this loss process is no longer prevalent and could affect the H⁻ density



Production



Loss



Loss



Loss



Loss



Loss



Loss




Loss



Loss



Loss



H⁻ density in validation shown to be important in correctly calculating the electron temperature and density even at low pressure:

Yang et. al, "A Global Model Study of the Population Dynamics of Molecular Hydrogen and the Generation of Negative Hydrogen Ions in a Low-pressure Discharge with an Expansions Region: Effects of EEPF", 2018

Must check!

H⁻ Density before removal of NH: **6.85E+15 m⁻³**

H⁻ Density after removal of NH: **5.71E+15 m⁻³**

Loss processes are overwhelming large due to charge-neutralization of O & N species

Comparison at 10 mTorr (3)

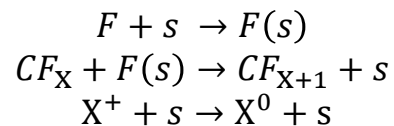
If we discount surface reactions, our gas phase reaction set is now 56 reactions, all the way down from 396.

Te and ne are within 5% agreement between the full set and reduced set

Species	Reduced Set	Full Set
H ₂	1.04E+18 m ⁻³	5.43E+17 m ⁻³
H	1.54E+18 m ⁻³	1.72E+18 m ⁻³
H ⁺	2.45E+15 m ⁻³	4.59E+15 m ⁻³
O ₂	1.82E+20 m ⁻³	1.78E+20 m ⁻³
O ⁻	2.72E+16 m ⁻³	2.64E+16 m ⁻³
O	4.09E+19 m ⁻³	3.70E+19 m ⁻³
O ₂ ⁺	2.67E+18 m ⁻³	2.67E+18 m ⁻³
O ⁺	5.65E+17 m ⁻³	5.45E+17 m ⁻³
N ₂	3.01E+19 m ⁻³	2.08E+19 m ⁻³
N	7.63E+18 m ⁻³	1.54E+19 m ⁻³
N ₂ ⁺	2.20E+17 m ⁻³	1.57E+17 m ⁻³
N ⁺	3.85E+16 m ⁻³	7.20E+16 m ⁻³
CF ₄	1.93E+17 m ⁻³	1.45E+17 m ⁻³
F	9.67E+16 m ⁻³	1.50E+17 m ⁻³
CF ₃	1.27E+16 m ⁻³	4.29E+16 m ⁻³
CF ₂	1.82E+16 m ⁻³	2.36E+16 m ⁻³
CF ₃ ⁺	1.31E+15 m ⁻³	1.26E+15 m ⁻³
F ⁺	2.98E+14 m ⁻³	4.89E+14 m ⁻³
CF ₂ ⁺	3.48E+14 m ⁻³	5.12E+14 m ⁻³
CF ⁺	5.66E+14 m ⁻³	5.25E+14 m ⁻³
CF	1.07E+16 m ⁻³	7.73E+15 m ⁻³
T _e	3.56099 eV	3.60342 eV
n _e	3.47E+18 m ⁻³	3.42E+18 m ⁻³

Reaction Scheme

Charge	Species	Reactions
Positive	CF_3^+ CF_2^+ CF^+ F^+ O_2^+ O^+ N_2^+ N^+ H^+	Ionization Charge Exchange Charge Neutralization
Negative	e^- O^-	Dissociation Charge Neutralization
Neutral	CF_4 CF_3 CF_2 CF F O_2 O N_2 N H_2 H	Elastic Ionization Dissociation Recombination Charge Exchange



Important To Know (1)

- Reducing chemistry means simplifying reaction set without changing the actual plasma characteristics, namely the electron temperature (T_e) and electron density (n_e).
- These **should not be varying wildly**.
- Some leeway can be allowed for differences in species densities after reduction – so long as they are not varying by orders of magnitude.

Important To Know (2)

- Chemistry reduction should be carried out within a space of minimal/no geometrical complexity i.e. 0D modelling.
- In 0D modelling, the focus is entirely on chemistry and plasma chemical behaviour as plasma settings are varied.
- Most 2D modellers and 3D modellers cannot handle large reaction sets. So the workflow should aim to reduce large/complex chemistries in 0D, then transfer to the 2D/3D modelling suite.

Conclusions

- Using 0D modelling in conjunction with validated data from QDB enables the study of simple to complex chemistries for process development.
- Process development and general innovation follows a workflow that is often gated by an understanding of the chemistry.
- The study of the chemistry can be made more trivial...
- ...By considering pressure regimes, power depositions and general application...
- ...Which then allows a focus of reactor/plasma dynamics in 2D/3D with minimal complication.