STRATEGIES FOR RAPIDLY DEVELOPING PLASMA CHEMISTRY MODELS*

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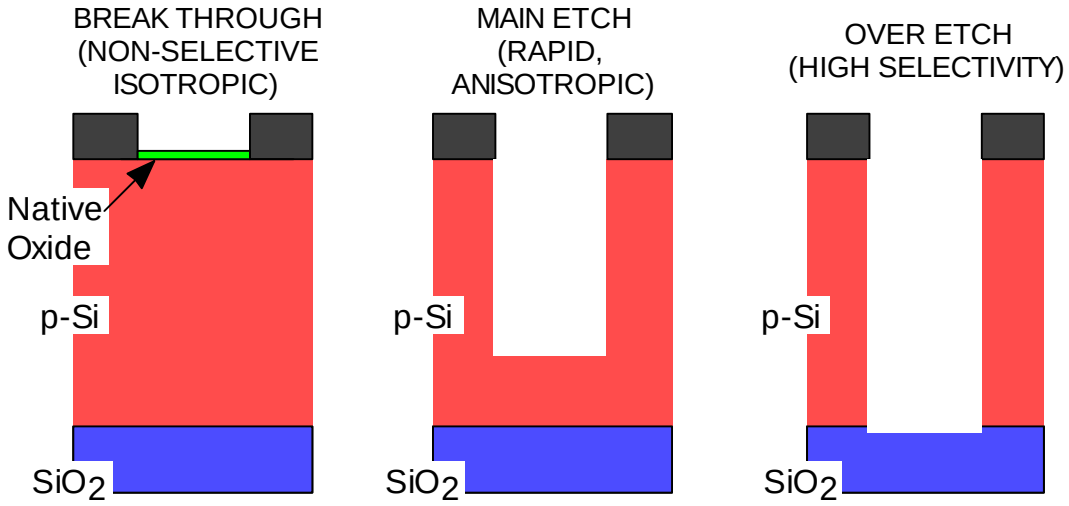
AGENDA

- Complex plasma chemistries for microelectronics fabrication
- What should you do if tasked with rapidly assessing a new chemistry?
- Components of your toolbox
- Sources of data
- If you must estimate or guess....
- Examples of rapidly assessed chemistries
- Concluding remarks

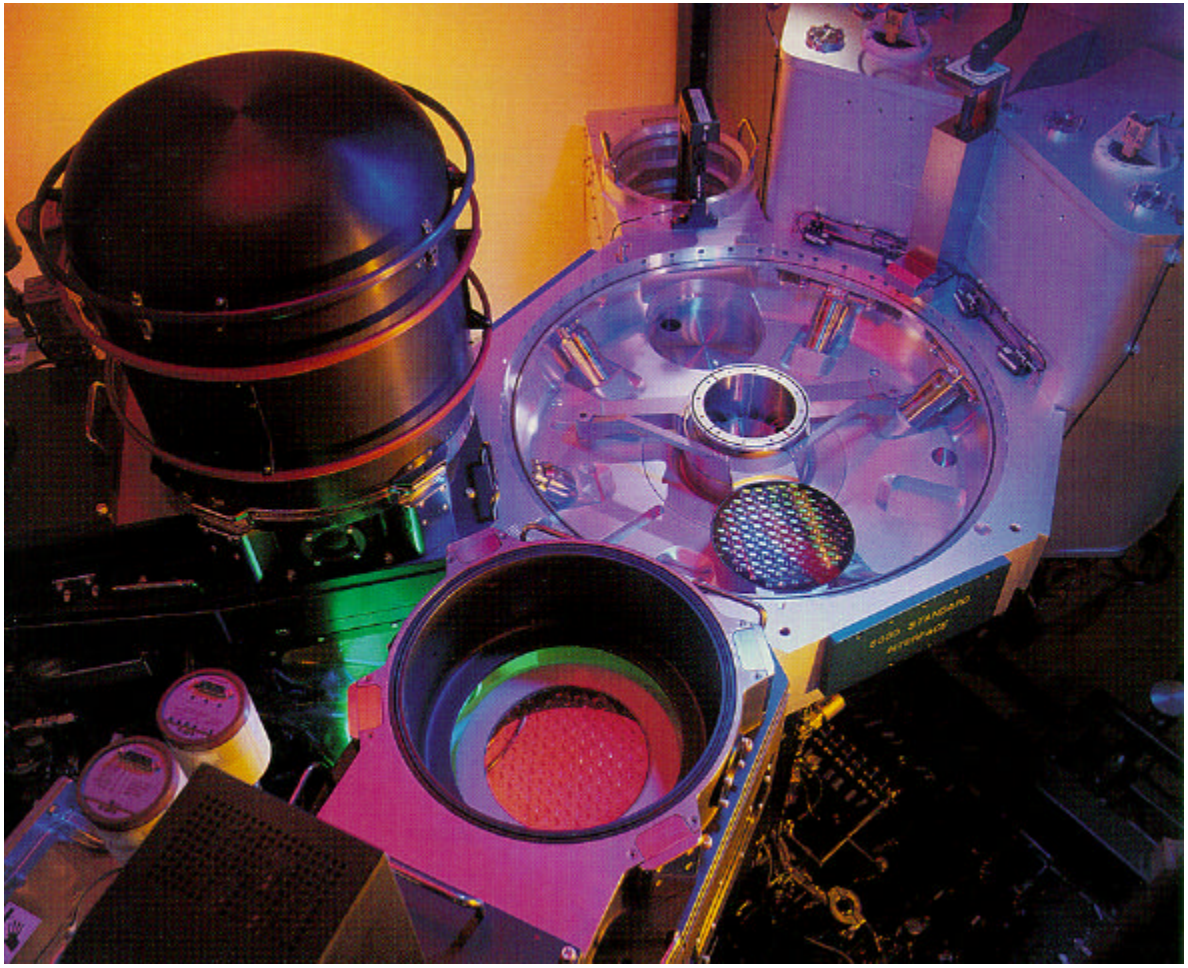
COMPLEX PLASMA CHEMISTRIES

- **Complex plasma chemistries for etching and deposition processes are everyday occurances in microelectronics fabrication.**
- **It is not unusual to have 4 or 5 component gas mixtures. (e.g., $Ar/Cl_2/BCl_3/N_2/HBr$)**
- **During a plasma etching process, it is not unusual for there to be 2-4 "recipe" changes.**



- **Recipe changes are different values of, for example, power, pressure, flow rate or gas mixture to address beginning, middle and end of the etch.**

COMPLEX PLASMA CHEMISTRIES



- **Most plasma processing tools have multiple chambers in which different chemistries (e.g., etch followed by clean) are used.**

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SCENARIO: QUICK EVALUATION OF A NEW PROCESS

- **You work for a semiconductor equipment manufacturer. Your boss tasks you with computationally evaluating a newly proposed process. You are given *3 days* to complete the job.**
  - **What should you have done *in preparation* for this request?**
  - **What should you ask *before* starting the job?**
  - **What is the *procedure* you should follow to fulfill the request?**

BEFORE YOU WERE TASKED: A TOOLBOX

- **In preparation of your task, you should have assembled a flexible computational toolbox.**

Databases ®

DataBase Processor®

Reaction Mechanisms ®

A "basic" global plasma model ®

Visualizer and post-processer

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COMPONENTS OF YOUR TOOLBOX

Databases:

- **Ion and Neutral transport coefficients**
- **Electron-impact cross sections**
- **Heavy particle reaction coefficients**
- **Gas/plasma-surface reaction probabilities**

- **Data should be in as "unprocessed" a form as possible. (e.g., cross sections are preferred over Townsend coefficients)**

- ***DataBase Processor:***
  - **Method to convert "raw" database to "model usable" coefficients (e.g., cross sections to rate coefficients)**
    - **Boltzmann solver**
    - **Maxwellian "integrator" of cross sections**

COMPONENTS OF YOUR TOOLBOX

- ***Reaction Mechanisms:***
  - **A collection of previously used (and hopefully validated) reaction mechanisms.**
  - **Scaling laws or IYMG (If you must guess) procedures for generating unavailable data.**
- ***A "basic" global plasma model***
  - **Rapid (and error-less) method to convert a reaction mechanism into ODE's or PDEs**
  - **Method to convert "power" into "excitation' (Circuit model, electromagnetics solver)**
  - **Robust integration technique**
  - **Higher dimensionality (2D) as required**
- ***Visualization and post-processing***
  - **A standardized, rapid way to display and manipulate the results.**

CONSTRUCTING YOUR DATABASE

- **The most reliable, most understood, most readily available, best formatted and most "comfortable" databases available are those you build *yourself* !**

- **Take FULL advantage of all external resources in building your database however devise a method of formatting, keeping track of references, revisions and updates which best suits *your* needs.**

- **(DON'T ALLOW YOUR ABILITY TO ACCOMPLISH YOUR GOAL BE LIMITED BY SOMEONE ELSE'S DECISION TO UPDATE THE FORMAT OF THEIR DATABASE...)**

- **In constructing your database, you will need to make value judgements on the goodness, appropriateness and validity of primary data sources or other databases.**

- **Make these decisions with some deliberate forethought as to what the database (or subsets of the database) will be used for.**

CONSTRUCTING YOUR DATABASE

- **Example: What data are required for:**
    - **Investigating the effects of anisotropic electron scattering on the EEDF in an argon rf discharge.**
    - **Evaluating the consequences of adding 1% H_2 to CF_2/C_2F_2 = 50/50**
- **These data requirements are very different BASED ON THE DESIRED OUTCOME.**
- **One requirement is not better or worse, just different. (Incomplete data is not a bad thing if it is not needed....)**

SOURCES OF DATA: ELECTRON-IMPACT

Publically Accessible Tabular Data:

- **Art Phelps (http://jilawww.colorado.edu/www/research/colldata.html)**

  [O_2, N_2, CO, CO_2, H_2, H_2O, NO, SF_6, He, Ne, Ar, Xe, Na, and Mg]

- **Skip Morgan/Kinema (http://www.sni.net/kinema/download.htm)**

  [N_2, O_2, H_2, Cl_2, HCl, F_2, CH_4, CF_4, SiH_4, SF_6, He, Ne, Ar, Kr, Xe]

- **NIST Electronics and Electrical Engineering Laboratory (J. Olthoff) (http://www.eeel.nist.gov/eeel_pages/811.html)**

  [CF_4, CHF_3, CCl_2F_2, C_2F_6, C_3F_8, Cl_2, SF_6]

- **University of Illinois (http://uigelz.ece.uiuc.edu)**

  [He, He*, Ne, Ne*, Ar, Ar*, Kr, Kr*, Xe, Xe*,N_2, N, O_2, O, H_2, H, Cl_2, Cl, F_2, F, SiH_4, Si_2H_6, CH_4, C_2H_6, CF_4, C_2F_6, H_2O, N_2O, NH_3, HCl, CCl_4, CCl_2F_2, NF_3 CO2, CO, SO_2, BCl_3, BF_3,Hg, Hg*, HgBr, Cu, Cu*, Al, Al*, Ti, Ti*]

SOURCES OF DATA: ELECTRON-IMPACT

- **C. Gorse, University of Bari, (cap@chimica.uniba.it): H_2(v),D_2(v)**

- **NIST Physics Division (Y.-K. Kim), Electron Impact Ionization (http://physics.nist.gov/PhysRefData/Ionization/Xsection.html)**

  [H, He, SiFx, SF_6, H_2, N_2, O_2, H_2O, CO, NO, CO_2, NH_3, CH, CH_2, C_2H_2, CH_3, CH_4, C_2H_4, C_2H_6, C_3H8, C_6H_6, SiF, SiF_2, SiF_3, SF_6, CS, CS_2, COS, H_2S, NO_2, N_2O, O_3, S_2, SO_2, SiH, SiH_2, SiH_3, SiH_4, Si_2H_6, $Si(CH_3)_4$, GeH, GeH_2, GeH_3, GeH_4, Ge_2H_6, CF_4, C_2F_6, CF_3]

- **ORNL "RedBooks" (He, H_2, D_2) (http://www-cfadc.phy.ornl.gov/redbooks/redbooks.html)**

<u>Publically Available Bibliographic Data</u>

- **GAPHYOR (http://gaphyor.lpgp.u-psud.fr/)**

SOURCES OF DATA: ELECTRON-IMPACT

- ***SWARM Data to unfold:***

  - **Unfolding swarm data to obtain cross sections is not a quick process, but nevertheless is an extremely a valuable source of cross sections.**

  - **Continue to collect all available swarm data to augment long term additions to your database. (Get a summer intern and a Boltzmann code.....)**

SOURCES OF DATA: NEUTRAL CHEMISTRY

- **Rate Coefficients:**
  - **NIST Chemical Kinetics Database (http://www.nist.gov/srd/nist17.htm)**
  - **International Journal of Chemical Kinetics (http://www.interscience.wiley.com/jpages/0538-8066/)**
  - **Journal of Physical Chemistry A (http://pubs.acs.org/journals/jpcafh/index.html)**
  - **Journal of Atmospheric Chemistry**
  - **Journal of Physical Chemistry Ref. Data (many, many compendia of rate coefficients for combustion and atmospheric chemistry)**
- **Reaction Mechanisms (Combustion literature)**
  - **Combustion and Flame (http://www.elsevier.com/inca/publications/store/5/0/5/7/3/6/)**
  - **International Journal of Chemical Kinetics**

SOURCES OF DATA: NEUTRAL CHEMISTRY

- eg: R. Fournet, et al "Experimental and Modeling of Oxidation of Acetylene, Propyne, Allene and 1,3-Butadiene", Int. J. Chem. Kinet. 31, 361 (1999).
- AIAA Journal (http://www.aiaa.org/publications/journals.html)
- Models outside your application area which use the same species
  - Excimer lasers (XeCl, XeF, KrF good source for halogen data)
  - Metal vapor lasers and MHD (good source for metal atom data)
  - Atmospheric chemistry (suprisingly, for C-H-O-N and Cl species)

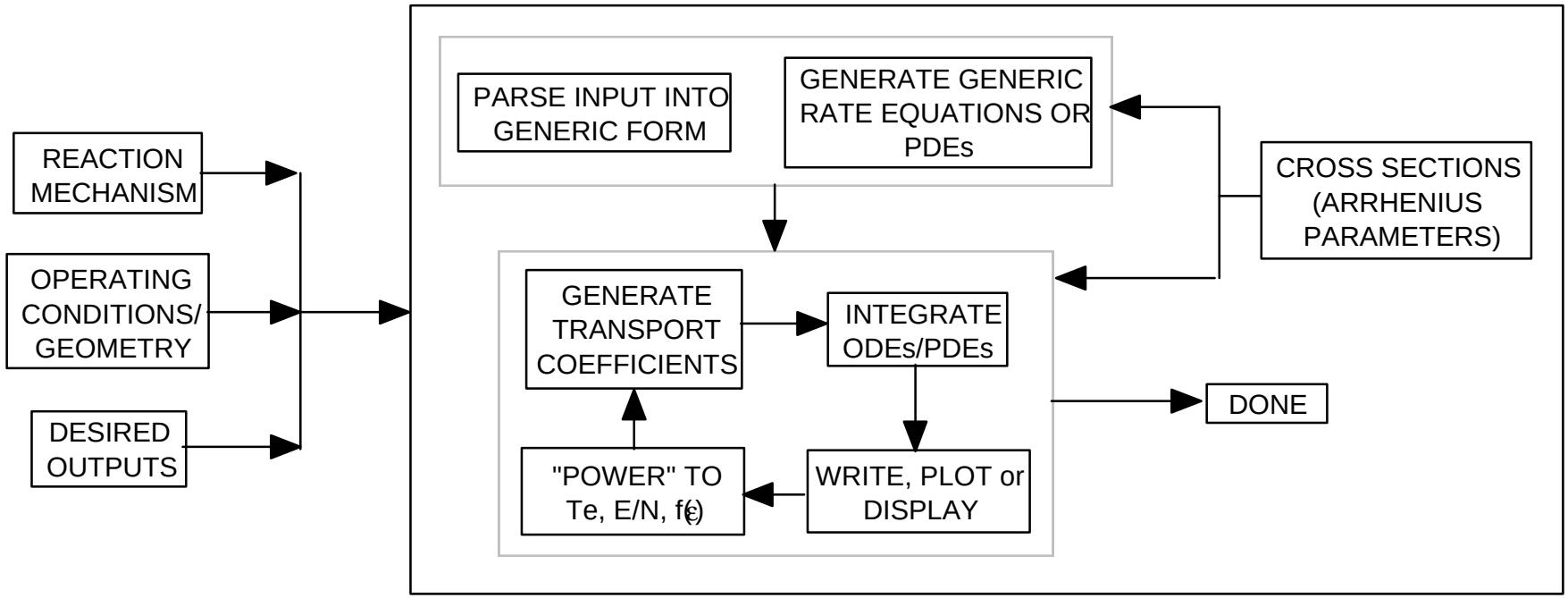
- Collect everything that key individuals have ever published in the field for specific chemistries (e.g., Jerome Perrin for silane plasma chemistry)

SOURCES OF DATA: ION MOLECULE AND ION TRANSPORT

- **Mobilities and diffusivities vs E/N (or T(effective))**
  - **H. W. Ellis, At. Data Nucl. Data Tables 17, 177-210 (1976); 22, 179-217 (1978); 31, 113-151 (1984)**
- **Ion-Molecule Rate coefficients compendia.**
  - **D. L. Albritton, At. Data Nucl. Data Tables 22, 2 (1978)**
  - **Y. Ikezoe, et. al. "Gas Phase Ion-Molecule Reaction Rate Constants Through 1986" (Mass Spectroscopy Society of Japan).**
  - **J. Phys. Chem. Ref. Data**

GENERIC LOW PRESSURE PLASMA CHEMISTRY MODEL

- **Your "toolbox" should hold a "generic" plasma chemistry model in which all parameters, chemistries and operating conditions are defined "from the outside" to facilitate rapid turnaround of reaction mechanisms.**



EXAMPLE OF "GENERIC INPUT FILE"

- **Defining the reaction mechanism should allow for rapid modifications in rates, processes and boundary conditions.**

Species, Boundary conditions

```
CL2          :  0  ;       70.00   &    0.0   ] 1 [ 0.0    @CL2       !
CL2^         :  1  ;       70.00   &    1.0   ] 1 [ 1.0    @CL2       !
CL           :  0  ;       35.50   &    0.005 ] 1 [ 0.0025 @CL2       !
>                         :5       &    0.1      [ 0.025  @SICL4     !
CL^          :  1  ;       35.50   &    1.0   ] 1 [ 1.0    @CL        !
CL*          :  0  ;       35.50   &    1.0   ] 1 [ 1.0    @CL        !
>                         :5       &    0.1      [ 0.025  @SICL4     !
CL-          : -1  ;       35.50   &    1.0   ] 1 [ 1.0    @CL        !
SICL4        :  0  ;      170.00   &    0.0   ] 1 [ 0.0    @SICL4     !
E            : -1  ;   5.444E-04   &    1.0   ] 1 [ 0.0    @E         !
*
```

Reactions, Rate coefficients, Links to database

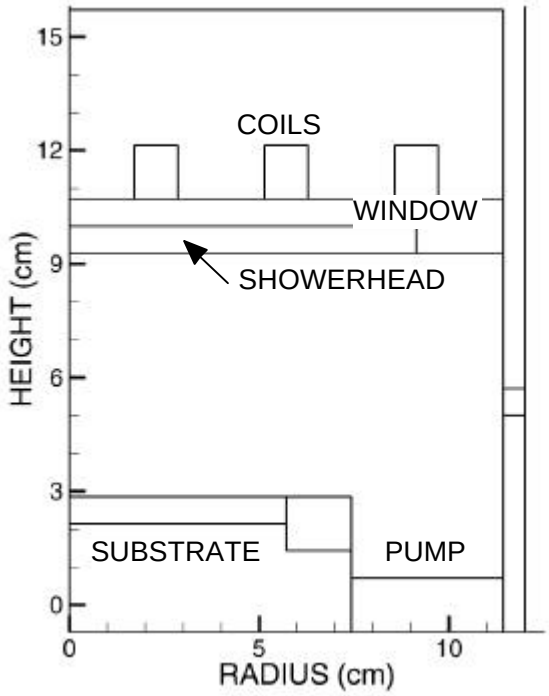
```
E + CL2 > CL + CL-                :   0.00E+00 ;                      771     !
E + CL2 > CL + CL + E             :   0.00E+00 ;                      774     !
E + CL2 > CL2^ + E + E            :   0.00E+00 ;                      776     !
E + CL > CL* + E                  :   0.00E+00 ;                      778     !
E + CL > CL* + E                  :   0.00E+00 ;                      779     !
E + CL > CL* + E                  :   0.00E+00 ;                      780     !
E + CL > CL* + E                  :   0.00E+00 ;                      781     !
E + CL > CL* + E                  :   0.00E+00 ;                      782     !
E + CL > CL* + E                  :   0.00E+00 ;                      783     !
E + CL > CL^ + E + E              :   0.00E+00 ;                      784     !
E + CL* > CL^ + E + E             :   0.00E+00 ;                      785     !
CL* > CL                          :   1.00E+05 ;                        1     !
E + CL- > CL + E + E              :   0.00E+00 ;                      788     !
E + CL2^ > CL + CL                :   1.00E-07 ;  -0.50 &  0.0   ]    -1     !
CL- + CL^ > CL + CL               :   1.00E-07 ;  -0.50 &  0.0   ]    -1     !
CL- + CL2^ > CL2 + CL             :   1.00E-07 ;  -0.50 &  0.0   ]    -1     !
CL + CL + CL2 > CL2 + CL2         :   5.40E-32 ;  -1.50 &  0.0   ]     1     !
CL^ + CL2 > CL2^ + CL             :   5.40E-10 ;   0.00 &  0.0   ]     1     !
```

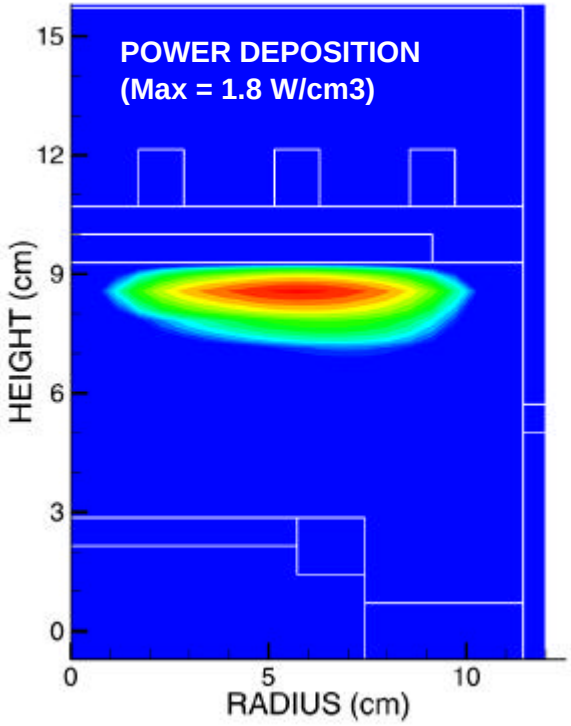
EXAMPLES OF "GENERIC" GLOBAL MODELS

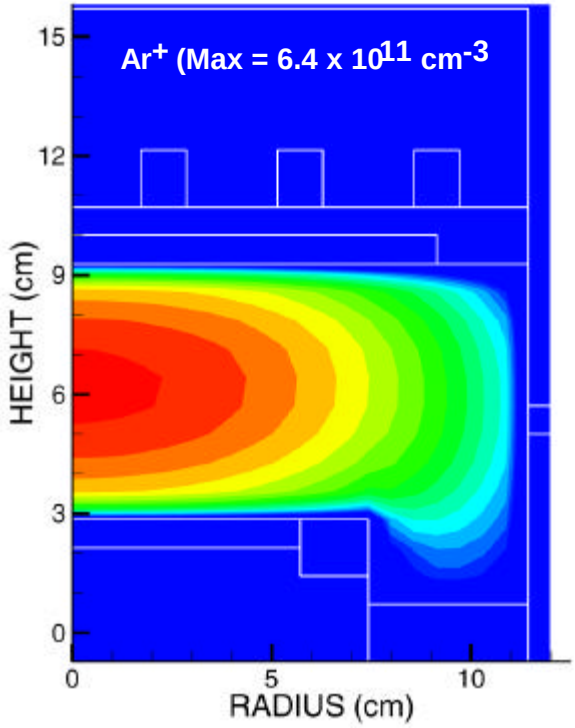
- **Commercial Products:**
  - **AURORA, Reaction Design, http://www.reactiondesign.com**
  - **KINEMA, Kinema Research and Software, http://www.sni.net/kinema/**
- **Literature Citations:**
  - **S. Ashida, C. Lee and M. A. Lieberman, "Spatially averaged (global) model of time modulated, high density argon plasmas", J. Vac. Sci. Technol. A, 13, 2498 (1995)**
  - **C. Lee, D. B. Graves, M. A. Lieberman and D. W. Hess, "Global Model of plasma chemistry in a high density oxygen discharge", J. Electrochem. Soc. 141, 1546 (1994)**
  - **E. Meeks and J. W. Shon, "Modeling of plasma-etch processes using well stirred reactor approximations and including complex gas-phase and surface reactions", Tran. Plasma Sci. 23, 539 (1995)**

DEMONSTRATION REACTOR

- **For demonstration and illustrative purposes, simulations will be performed in a small, inductively coupled plasma (ICP) reactor.**







- **Ar, 10 mTorr, 150 sccm, 400 W**

DEVELOP A REACTION MECHANISM WHICH ALIGNS WITH WHAT YOU NEED TO KNOW

- **The time required to develop a reaction mechanism scales with its size and complexity.**
- **The completeness of your reaction mechanism should correlate with the end product of your modeling activity.**
- **What do you really need to know *and to what accuracy*? What data is required to meet that goal?**
- **Example: The output of interest is uniformity of ion flux to the substrate.**

Reaction Mechanism 1	**Reaction Mechanism 2**
e, Ar(3s), Ar(4s), Ar(4p), Ar^+	**e, Ar(3s), Ar(4s), Ar^+**

- **How critical is Ar(4p) to "what I need to know" and, by implication, how important is it to know its cross sections (FOR THESE CONDITIONS!)**

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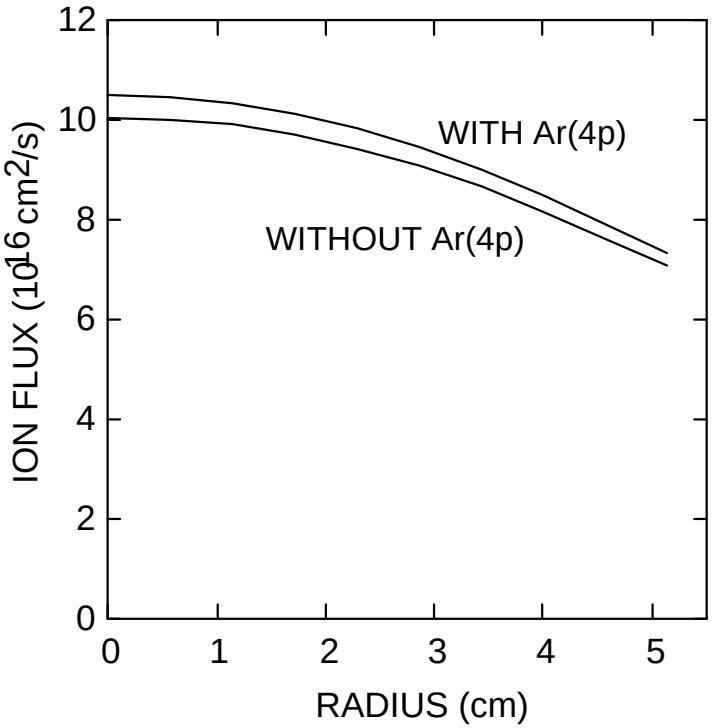
DEVELOP A REACTION MECHANISM WHICH ALIGNS WITH WHAT YOU NEED TO KNOW



- **Ar, 10 mTorr, 400 W, 150 sccm,**

- **If all you are interested in is the ion flux to the substrate, and are willing to tolerate a 5-10% error, a simple reaction mechanism serves your purpose.**

REMEMBER.....

YOU GOTTA HAVE THIS DONE IN 3 DAYS!!!!!

MAKE BACK OF THE ENVELOPE ESTIMATES TO REFINE (LIMIT) YOUR REACTION MECHANISM

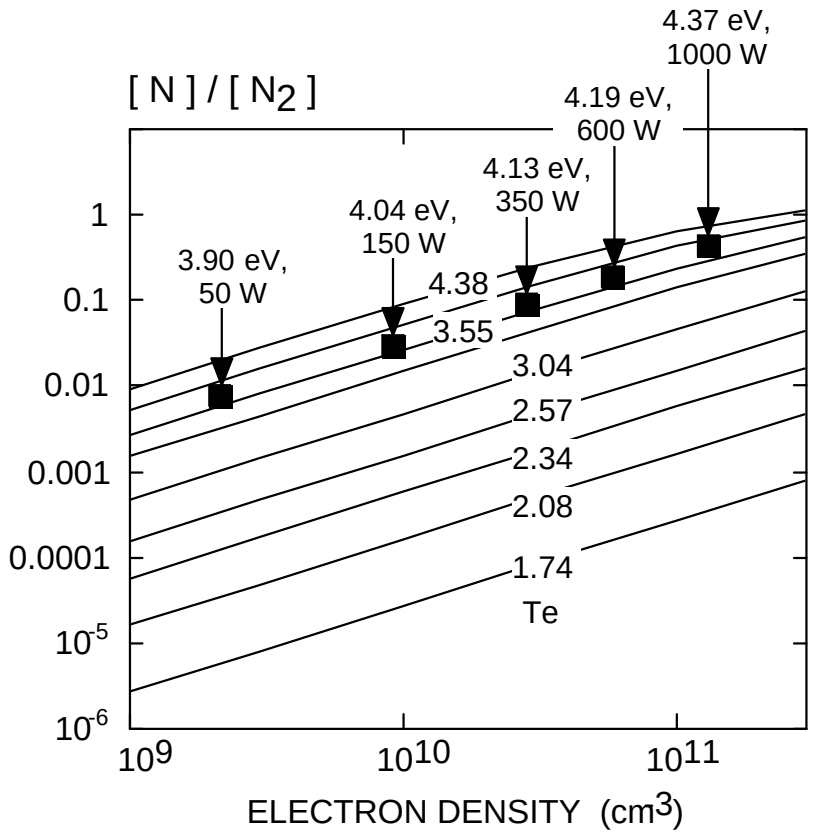
- **You always know the upper and lower bounds of reaction rate coefficients.**
  - **Ionization rate coefficients are never much bigger than 10^{-10} cm^3/s.**
  - **Momentum transfer rate coefficients are never much smaller than 10^{-10} cm^3/s**
- **Given these bounds, you can make back-of-the-envelope estimates to determine how much detail is required in your reaction mechanism?**
- **Example: In a N_2 plasma, do you need to include N atoms in the reaction mechanism?**

$$\frac{dN_2}{dt} = -n_e k_d N_2 + \frac{N_{2o} - N_2}{t_r} = 0, \qquad \frac{dN}{dt} = n_e k_d N_2 + \frac{N}{t_r} = 0$$

$$\frac{N}{N_{2o}} = \frac{2}{\frac{1}{n_e k_d t_r} + 1}$$

MAKE BACK OF THE ENVELOPE ESTIMATES TO REFINE (LIMIT) YOUR REACTION MECHANISM

- **Simple scaling shows regions where large electron densities and moderate electron temperatures produce significant N_2 dissociation.**
- **HPEM simulations for N_2 ICP plasmas confirm simple scaling.**
- **No need to include e-N processes for < 200-300 W.**



- **N_2, 10 mTorr, 150 sccm (0.05 s residence time)**

REMEMBER.....

YOU GOTTA HAVE THIS DONE IN 3 DAYS!!!!!

1% of MOLECULE "A" IN A MIXTURE OF MOLECULES "C" AND "D" DOESN'T MATTER.....sometimes

- In large part, if molecules are large enough, momentum transfer and the power deposited into a given component of a molecular gas mixture scales with its mole fraction.

- For example, if analyzing the consequences of adding 1% O_2 to CF_4/C_2F_6 = 50/50, the incremental change in momentum transfer by O_2 is neglible.

- WARNING! Small admixtures of molecular gases mixtures having deep and pronounced Ramsauer momentum transfer can have significant effects.

[R. Nagpal and A. Garscadden, Appl. Phys. Lett. 64, 1626 (1994)]

- The important consequences of adding O_2 to CF_4/C_2F_6 will be generating species WHICH WOULD NOT HAVE OTHERWISE NOT BEEN THERE!

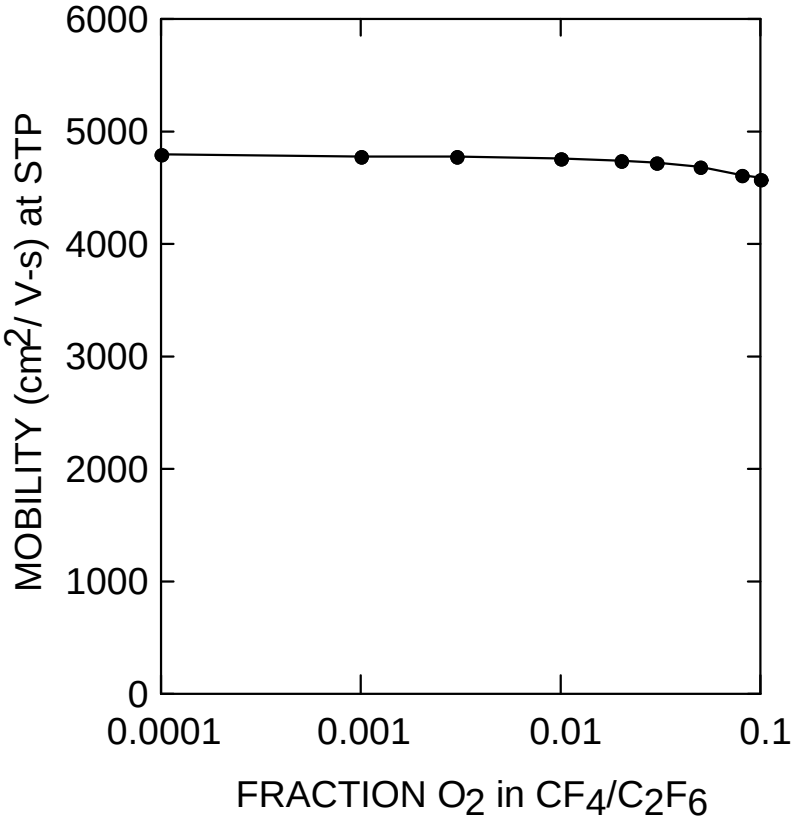
- These species are produced by INELASTIC processes (e.g., e + O_2 > O + O + e) or by excitation transfer (or chemical reactions) from the major mole fraction species.

1% of MOLECULE "A" IN A MIXTURE OF MOLECULES "C" AND "D" DOESN'T MATTER.....sometimes

- **Example: Electron mobility vs O_2 fraction in CF_4/C_2F_6 = 50/50 at 10 Td**

"The importance of O_2 in the gas mixture is the production of species which would not have otherwise been present...."

J. T. Verdeyen
said something like that



GENERAL SCALING LAWS: IF YOU HAVE *NO OTHER* INFORMATION
ION-ION NEUTRALIZATION

- **All negative ions neutralize with all positive ions provided that $E_{IP} > E_{EA}$.**
- **At thermal energies (and low pressures) neutralization is non-associative.**
- **Simple scaling laws are available. For example,**

$$s(e) = \frac{q^4}{4pe_0^2}\frac{1}{\Delta E^2}\left(1+\frac{\Delta E}{e}\right)F(e), \qquad \Delta E = E_I - E_A$$

$$F = \text{Landau} - \text{Zener transition probability}$$

[J. T. Moseley, R. E. Olson and J. R. Peterson, Case Studies in Atomic Physics, 4, 1, (1975)]

- **IYMG (If You Must Guess), $k = 10^{-7}\ cm^3s^{-1}$**

GENERAL SCALING LAWS: IF YOU HAVE *NO OTHER* INFORMATION
ELECTRON-ION RECOMBINATION

- **All molecular ions dissociatively recombine. If the electron temperature is not too low (< 300 K) or too high,**

$$s(e) = \frac{s_o}{e} \qquad k(T_e) = \frac{k_o}{T_e^{1/2}}$$

  - **Diatomics: s_o = 1-5 x 10^{-16} cm^2-eV. Polyatomic ions have larger s_o [J. B. A. Mitchell, Physics Reports 186, 215 (1990)]**

  - **IYMG, k = $10^{-7}/T_e(eV)^{1/2}$ cm^3s^{-1}**

- **In low pressure plasmas (< 100's mTorr) recombination of atomic ions can generally be ignored unless plasma densities are > 10^{12} cm^{-3}.**

  - **IYMG Radiative Recombination: k = 5 x $10^{-13}/T_e(eV)^{0.7}$ cm^3s^{-1}**
    Collisional Radiative Recombination: k = 7 x $10^{-27}/T_e(eV)^{4.5}$ cm^6s^{-1}

    [M. A. Biondi in "Principles of Laser Plasmas" edited by G. Bekifi (Wiley, New York, 1976)]

GENERAL SCALING LAWS: IF YOU HAVE *NO OTHER* INFORMATION
MOBILITIES

- **Heavy particle Mobilities (and Diffusion Coefficients)**

$$m = \frac{q}{m n_m}, \qquad \frac{n_m}{N} = s_m \left(\frac{8kT_{eff}}{p m_r} \right)^{1/2}, \qquad T_{eff} = T_{ion} + \frac{1}{3}\frac{Mv^2}{k}$$

$$\frac{1}{m_{j-mixture}} = \sum_i \frac{1}{m_{ij}}$$

  - **Neutrals: s_m is given by Lennard Jones parameters [R. A. Svehla, "Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures" NASA Technical Report R-132, 1962]**

  - **IYMG: Choose a LJ radius of a similar structured and sized molecule.**

Large molecules		Small Molecules		Small - Large Atoms	
$HgBr_2$	5.080 A	N_2	3.798 A	H	2.708 A
HgI_2	5.625	O_2	3.467	Cl	3.631
C_2H_6	5.349	F_2	3.357	Xe	4.047

GENERAL SCALING LAWS: IF YOU HAVE *NO OTHER* INFORMATION MOBILITIES

- **Use mixture rules from Hirschfelder, Curtiss and Bird "Molecular Theory of Gases and Liquids" (Wiley, New York, 1954) for additional accuracy.**

- **Ions: All ions undergo symmetric charge exchange with their neutral. Assume momentum transfer is dominated by charge exchange. If you have the charge-exchange cross section, use it for momentum transfer. Otherwise, assume gas kinetic rates.**

- **For "Non-resonant" ion transport (e.g., Hg^+ in He) s_m depends on the on the model of the interaction potential**

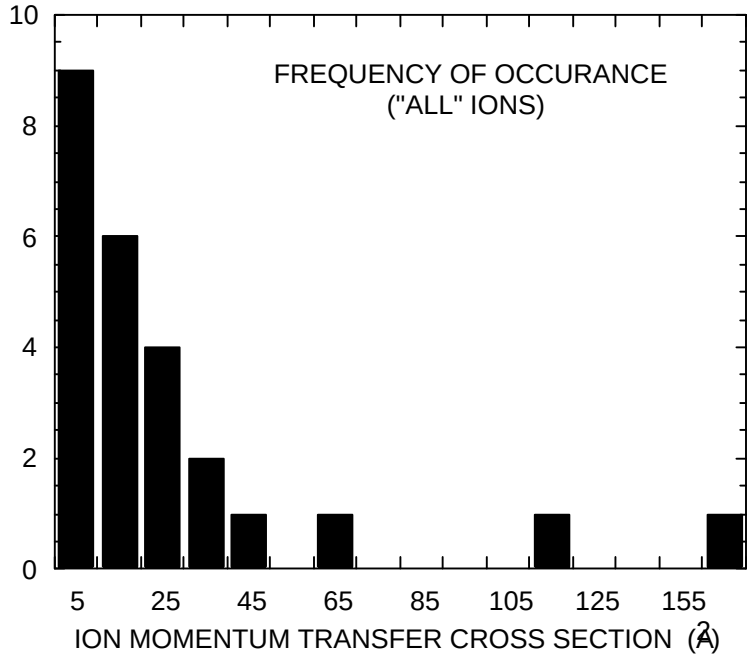
  [E. A. Mason and E. W. McDaniel, "Transport Properties of Ions in Gases" (Wiley, 1988)].

GENERAL SCALING LAWS: IF YOU HAVE *NO OTHER* INFORMATION MOBILITIES

- **If you have NO additional information, consult H. W. Ellis et al, for analogous ion-gas combinations.**

  [H. W. Ellis, At. Data Nucl. Data Tables 17, 177-210 (1976); 22, 179-217 (1978); 31, 113-151 (1984)]

- **With rare exceptions, at zero-field s_m range in 5-35 x 10^{-16} cm^2.**



REMEMBER.....

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GENERAL SCALING LAWS: IF YOU HAVE *NO OTHER* INFORMATION
ION MOLECULE, PENNING AND EXCITATION TRANSFER

- **If energetically allowed, charge transfer by positive ions to polyatomic molecules proceeds at the gas kinetic rate (there will always be a state available) and is dissociative.**

    - **Branchings are the same as electron impact at the IP of ion (if available) or estimated from appearance potentials of fragment ions from the parent molecule.**

    [S. G Lias et al, "Gas-Phase Ion and Neutral Thermochemistry", J. Phys. Chem. Ref. Data 17, Supplement 1, 1988]

- **If energetically allowed, Penning processes occur about about 0.2 gas kinetic.**

- **Quenching of excited states by polyatomic atoms is equivalent to electronic excitation at the same energy and is dissociative.**

GENERAL SCALING LAWS: IF YOU HAVE *NO OTHER* INFORMATION
ELECTRON IMPACT IONIZATION AND EXCITATION

- **Electron impact excitation and ionization cross sections are the most "species specific" of all data.**

- **On "casual inspection" it is difficult to predict or use analogy electron impact cross sections for complex molecules.**

- **So.....IF YOU MUST GUESS (IYMG)**

- **Use the same cross sections for fragments (CF_3 vs CF_4) until you REALLY feel really uncomfortable, and then deny you did it.**

- **At low gas pressures, only dissociative attachment is important for small molecules. Ignore 3 body processes (e.g., $e + O_2 + M > O_2^- + M$)**

  - **Thermal attachment may occur if $E_{EA} > E_{DISS}$ (e.g., F_2, Cl_2). Check the thermochemistry.**

- **Reduce threshold energies of excited species by vibrational or electronic energy**

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GENERAL SCALING LAWS: IF YOU HAVE *NO OTHER* INFORMATION
ELECTRON IMPACT IONIZATION AND EXCITATION

- **Electron impact ionization:**

  - **If you have the input, use the Kim cross sections (J. Chem. Phys 110, 3811 (1999) or, if not, resort to Gryzinski cross sections (binary encounter).**

$$s = 4\pi a_o^2 x_n \left(\frac{R}{I_n}\right)^2 g(u), \quad g(u) = \frac{1}{u}\left(\frac{u-1}{u+1}\right)^{3/2}\left(1+\frac{2}{3}\left(1-\frac{2}{u}\right)\ln\left(2.7+(u-1)^{1/2}\right)\right), \quad u = \frac{e}{I_n}$$

[T. D. Mark and G. H. Dunn, "Electron Impact Ionization" (Springer-Verlag, New York, 1985)]

- **Electron Imact Excitation: Born-Bethe formula (Drawin formulation) for optically allowed transition.**

$$s_{ij} = 4\pi a_o^2 x_n \left(\frac{R}{E_{ij}}\right)^2 f_{ij} a_{ij}\left(\frac{u_{ij}-1}{u_{ij}^2}\right)\ln\left(1.25 b_{ij} u_{ij}\right), \quad u = \frac{e}{E_{ij}}$$

REMEMBER.....

YOU GOTTA HAVE THIS DONE IN 3 DAYS!!!!!

EXAMPLE: H_2O ADDITION TO Cl_2/BCl_3 MIXTURES

- ***Task:*** **We have a "working" $Ar/Cl_2/BCl_3$ process in an ICP reactor (10 mTorr, 150 W, 150 sccm). What are the consequences of H_2O addition?**

- ***Response:*** **What do you really want to know? How much H_2O addition?**

- ***Refined Task:*** **What are the consequences on *ion flux to the substrate* for up to 10% H_2O addition?**

PROCEDURE:

- **Point of departure:**

  - **Working $Ar/Cl_2/BCl_3$ reaction mechanism**
  - **Working H_2O reaction mechanism**
  - **Combine them....**

EXAMPLE: H_2O ADDITION TO Cl_2/BCl_3 MIXTURES

- Examine neutral chemistry for important "cross reactions" (NIST Database). Addition of H_2O adds possibility of H, OH, O, O_2, H_2.

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H + CL2 > HCL + CL          :   2.00E-11 ;                  1   !
CL + H2O > OH + HCL         :   2.79E-11 ; 0.0 &  8670. ] 1   !
O + CL2 > CLO + CL          :   8.00E-12 ; 0.0 &  1368. ] 1   !
OH + CL2 > HOCL + CL        :   1.40E-12 ; 0.0 &   900. ] 1   !
OH + CL > O + HCL           :   9.80E-12 ; 0.0 &  2860. ] 1   !
```

- HCl will be a major product....Obtain HCl reaction mechanism from XeCl laser model [e.g., Ohwa and Obara, J. Appl. Phys. 59, 32 (1986)] by adding HCl, HCl(v)

- Mobilities of Cl^+, Cl_n^+, BCl_n^+ in H_2O, and OH^+, H_2O^+ in BCl_n, Cl_n are not known. Assume $s_m = 50\ A^2$.

- Assume all uknown dissociative recombination have $k = 10^{-7}/T_e^{1/2}\ cm^{-3}/s$.

- Assume all unknown ion-ion recombination have $k = 10^{-7}\ cm^{-3}/s$.

EXAMPLE: H_2O ADDITION TO Cl_2/BCl_3 MIXTURES

- Charge exchange cross sections for Cl^+, Cl_n^+, BCl_n^+ in H_2O, and OH^+, H_2O^+ in BCl_n, Cl_n are not known. Obtain thermochemistry from Lias et. al. and assume allowable reactions are gas kinetic.
- Ar/H_2O ion chemistry is known. Obtain from Ikezoe.

```
H2O^ + CL2 > CL2^ + H2O          :   1.00E-10 ;   1  !
H2O^ + CL2 > CL2^ + H2O          :   1.00E-10 ;   1  !
H2O^ + BCL2 > BCL2^ + H2O        :   1.00E-10 ;   1  !
H2O^ + BCL3 > BCL3^ + H2O        :   1.00E-10 ;   1  !
CL^ + H2O > H2O^ + CL            :   1.00E-10 ;   1  !
HCL^ + CL2 > CL2^ + HCL          :   1.00E-10 ;   1  !
HCL^ + CL2 > CL2^ + HCL          :   1.00E-10 ;   1  !
HCL^ + BCL2 > BCL2^ + HCL        :   1.00E-10 ;   1  !
HCL^ + BCL3 > BCL3^ + HCL        :   1.00E-10 ;   1  !
CL^ + HCL > HCL^ + CL            :   1.00E-10 ;   1  !
AR^ + H2O > ARH^ + OH            :   0.50E-09 ;   1  !
AR^ + H2O > AR + H2O^            :   1.50E-09 ;   1  !
AR^ + HCL > ARH^ + CL            :   1.28E-10 ;   1  !
AR^ + HCL > HCL^ + AR            :   1.00E-11 ;   1  !
```

- Lennard Jones parameters are available from Svehla. Use standard combination rules for neutral transport coefficients from HCB.

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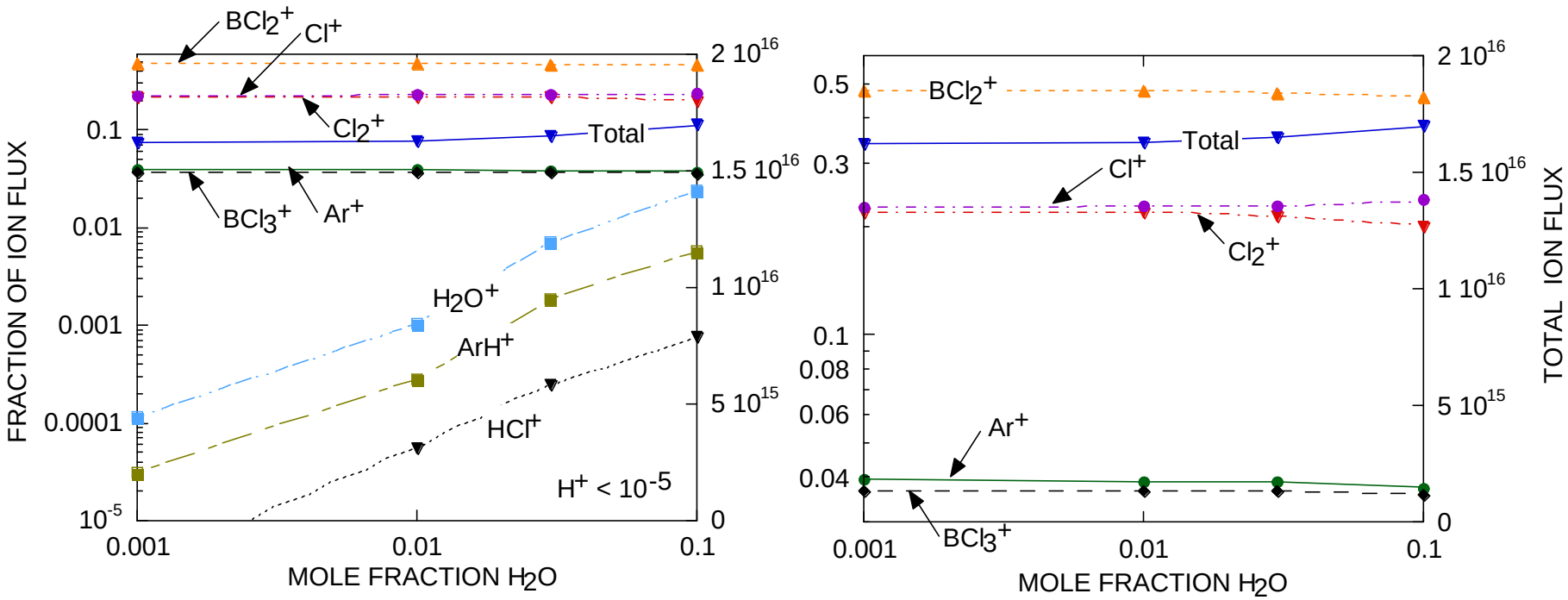
ION FLUX TO SUBSTRATE: $Cl_2/BCl_3/H_2O$ MIXTURES

- **$Ar/Cl_2/BCl_3/H_2O$ = 10/45/45/x process in an ICP reactor (10 mTorr, 150 W, 150 sccm).**



- **Contribution of "new ions" to flux scales less than the "impurity" mole fraction due to lower rates of ionization of H_2O and depleting charge exchange reactions.....Small increase in total ion flux.**
- **Elapsed Time: 4 hours**

EXAMPLE: O_2 ADDITION TO CF_4/C_2F_6 MIXTURES

- ***Task:*** **We have a "working" $Ar/CF_4/C_2F_6$ process in an ICP reactor (10 mTorr, 150 W, 150 sccm). What are the consequences of O_2 addition?**

- ***Response:*** **What do you really want to know? How much O_2 addition?**

- ***Refined Task:*** **What are the consequences on *ion flux to the substrate* for up to 10% O_2 and what new species are generated?**

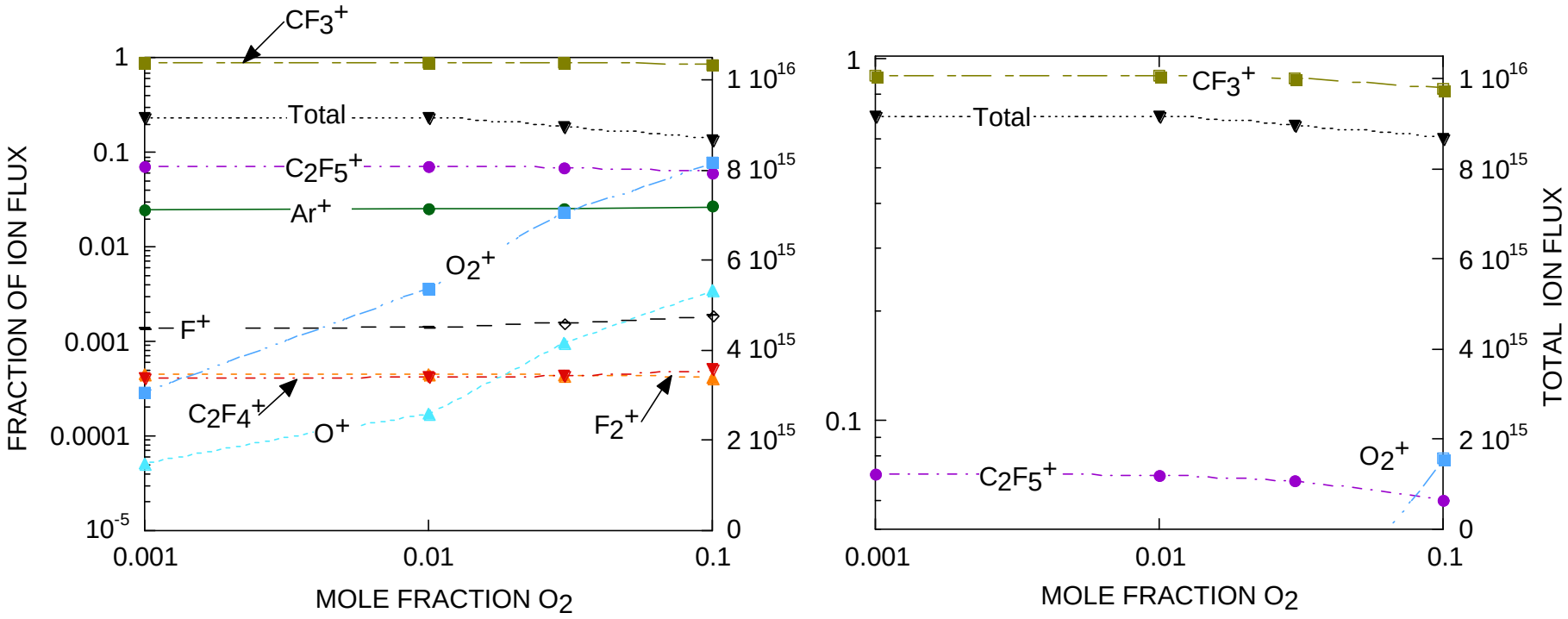
PROCEDURE:

- **Point of departure:**
  - **Working $Ar/CF_4/C_2F_6$ reaction mechanism**
  - **Working O_2 reaction mechanism**
  - **Combine them....**

- **Follow same procedure as for $Ar/Cl_2/BCl_3/H_2O$ with added benefit that others have looked at similar problems as this before...**

ION FLUX TO SUBSTRATE: $CF_4/C_2F_6/O_2$ MIXTURES

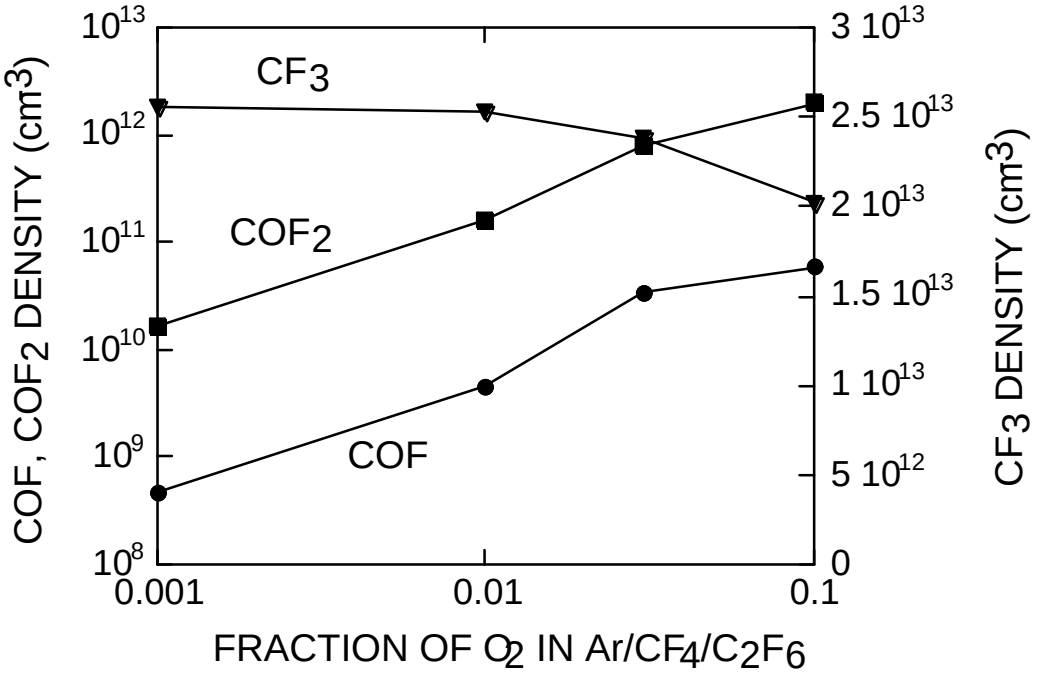
- **$Ar/CF_4/C_2F_6/O_2$ = 10/45/45/x process in an ICP reactor (10 mTorr, 150 W, 150 sccm).**



- **Contribution of "new ions" to flux exceeds the "impurity" mole fraction due to higher rates of ionization of O_2 and favorable charge exchange reactions.....Small decrease in total ion flux.**

"NEW SPECIES": $CF_4/C_2F_6/O_2$ MIXTURES

- **$Ar/CF_4/C_2F_6/O_2$ = 10/45/45/x process in an ICP reactor (10 mTorr, 150 W, 150 sccm).**



- **COF_2 and COF approach approximately 10% of the density of major radicals (e.g., CF_3).....**
- **Species which would have otherwise not been present....**

- **Elapsed Time: 4 hours**

CONCLUDING REMARKS

- **Scholarly assessment, analysis and investigation of plasma chemistries require timescales which often exceed industrial time scales.**
- **To respond to shorter timescales, strategies to assess new processes should be in place before the request is made .**
- **The most important component of this strategy is a well orchestrated "toolbox" which is rapidly adaptable to new chemistries.**
- **By leveraging and adding to existing reaction mechanisms and databases, simple scaling laws can often yield significant insight to complex chemistries.**

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