



Steady-State Chlorine Plasma

APP-Plasma-1 (v2.0) August 30, 2010

Summary

This application note provides an example of modeling a low-pressure plasma reactor as a steady-state Perfectly Stirred Reactor.

Project Description

The plasma pressure is 5 mtorr and pure chlorine gas flows into the reactor at 35 sccm. The energy equation and the electron energy equation are solved, and a heat-transfer correlation is used to account for heat loss through the wall of the reactor.

This chemistry set is for a pure chlorine plasma without surface etching reactions, and is based on work published by Meeks and coworkers.^{1,2}

The gas-phase chemistry in the chlorine plasma is relatively simple. The element list contains three elements: E (the electron), Cl and Si. Si does not actively participate in any chemical reactions, as it only appears in the surface chemistry file, *surf.inp*, in the composition of surface species on the wall material, but it still needs to be included in the element list in the GAS-PHASE KINETICS input file. The gas-phase species list contains seven species: Cl₂, Cl, Cl* (chlorine atoms in a metastable electronically excited state), Cl₂⁺, Cl⁺, Cl⁻ and E. The gas-phase reactions include electron collisions with Cl₂ leading to vibrational and electronic excitation, dissociation, ionization, and dissociative attachment. Electron reactions with Cl include electronic excitation into a number of excited states, including Cl* formation, and ionization. The gas-phase reaction mechanism also includes electron collisions with Cl⁻ leading to electron detachment, electron collisions with Cl* leading to ionization, and gas-phase neutralization of Cl⁻ with Cl⁺ and Cl₂⁺ ions. All the reactions are irreversible as is typical of non-thermal plasmas. In low-pressure plasmas, ionization and dissociation are balanced primarily by surface recombination reactions. The rates for the electron-impact reactions depend on the electron energy, rather than the neutral gas temperature.

The surface mechanism for reactions occurring on the reactor wall is also fairly simple. It only involves neutralization of Cl⁺ and Cl₂⁺ with electrons (subject to the Bohm criterion), de-excitation of Cl* and

¹"Modeling of Plasma-Etch Processes Using Well Stirred Reactor Approximations and Including Complex Gas-Phase and Surface-Reactions", E. Meeks and J. W. Shon, *IEEE Transactions On Plasma Science*, **23**(#4):539-549 (1995).

²"Effects of Atomic Chlorine Wall Recombination: Comparison of a Plasma Chemistry Model With Experiment," E. Meeks, J. W. Shon, Y. Ra, P. Jones, *JVSTA* **13**(#6):2884-2889 (1995).

radical recombination reactions for Cl to Cl₂. The neutralization and de-excitation reactions are non-site specific, but the recombination reactions are described in terms of open and Cl-covered sites. Although this example problem does not include surface etching reactions, surface recombination and neutralization reactions can be quite important in determining the overall composition of these kinds of low-pressure plasmas. All the surface reactions are irreversible. The thermodynamic properties for surface species, therefore, provide the elemental composition of the surface species, but the polynomial fitting parameters are considered placeholder values and are not used in the simulation.

Project Setup

The CHEMKIN project file is called *plasma_psr__chlorine.ckprj*. The data files used for this sample are located in the CHEMKIN-created directory *samples\plasma_psr__chlorine*. This reactor diagram contains one gas inlet, one plasma PSR, and one outlet.

To specify the reactant gas mixture, which is pure Cl₂ in this case, go to the Species-specific Property tab of the C1_Inlet1 panel. The initial guess for the steady-state gas composition, which is input on the Initial Gas Fraction subtab of the Species-specific Data tab of the C1_Plasma PSR panel, is quite important. A good initial guess (one that is close to the steady-state solution) will result in fast convergence, while a poor initial guess can at worst lead to failure of the simulation.

You can enter the problem type and reactor parameters such as pressure, temperatures, volume, area, heat loss, and plasma power on the Reactor Physical Property tab of the C1_Plasma PSR panel. Solving the electron energy equation requires that an initial guess for the electron temperature be input on this tab, as well as an inlet electron temperature on the Stream Property tab of the C1_Inlet1 panel. The latter has no impact on the solution unless there are electrons in the inlet gas mixture. The Sheath Loss parameter describes the ion energy gained crossing the sheath and you may specify it differently for each material in the system. On the Solver panel, skipping the intermediate fixed-temperature solution is usually more robust for plasma simulations than trying to solve it first.

Project Results

Figure 1 shows the electron temperature as a function of power for this chlorine plasma. The electron temperature shows only small changes over the large variation in plasma power, since most of the power is transferred into ionization and dissociation rather than electron heating. However, as the plasma power drops the electron temperature rises as the plasma nears extinction, since there are fewer electrons and electron-driven events. The mole fractions of the electrons and positive ions increase steadily with increasing plasma power, as shown in *Figure 2*, but the chlorine negative ions show a maximum at intermediate powers. *Figure 3* shows that the net dissociation of molecular chlorine to atomic chlorine steadily increases with increasing plasma power, as expected.

Figure 1 Steady-state Chlorine Plasma—Electron Temperatures vs. Power

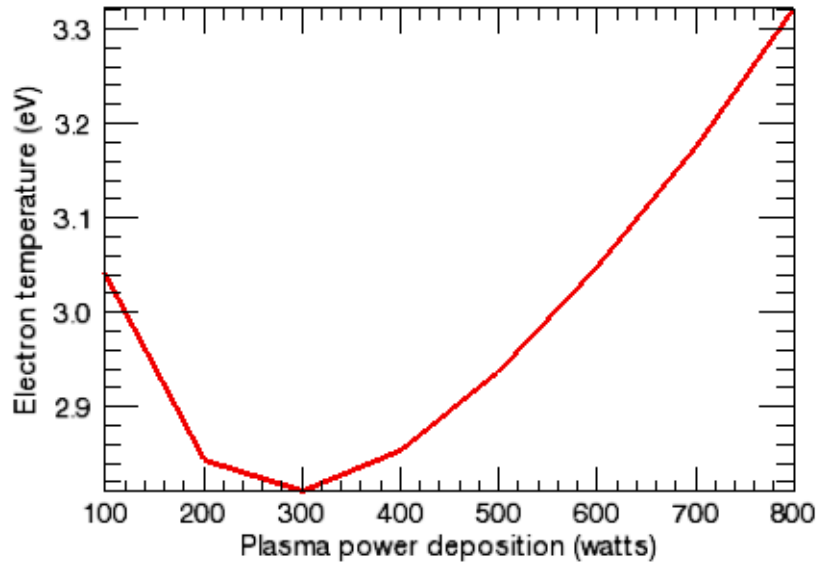


Figure 2 Steady-state Chlorine Plasma—Mole Fractions

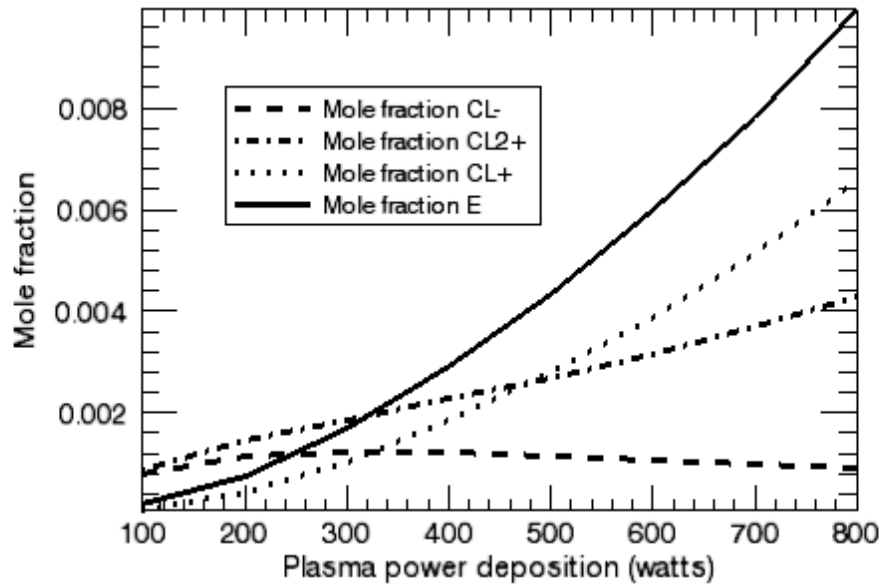


Figure 3 Steady-state Chlorine Plasma—Cl and Cl₂ Mole Fractions

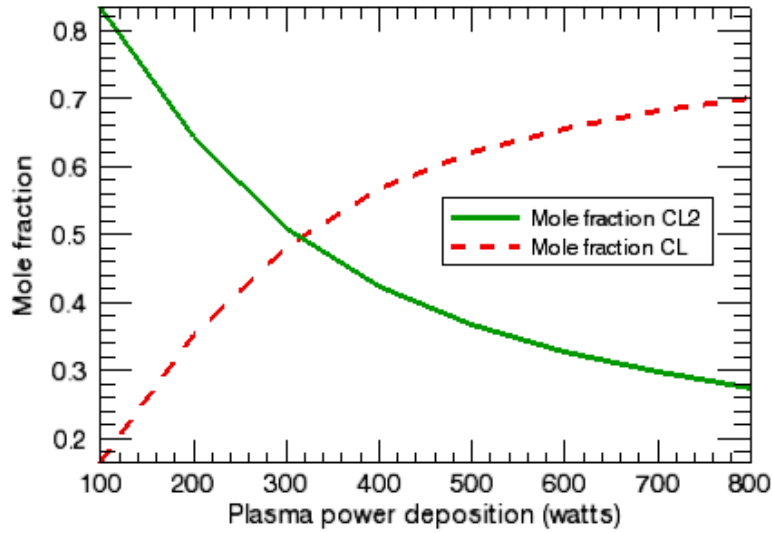
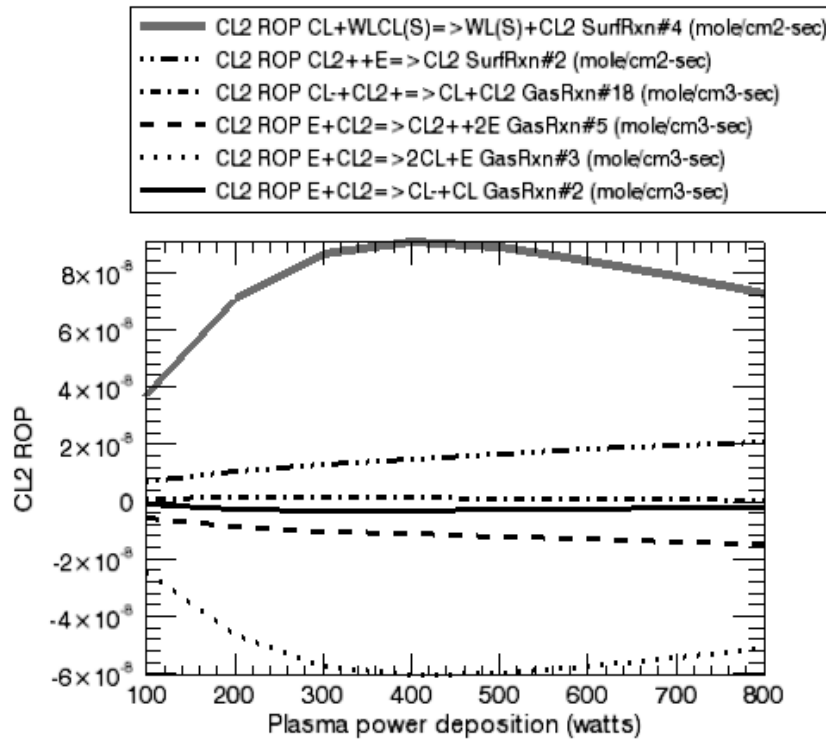


Figure 4 Steady-state Chlorine Plasma—ROP Analysis shows a rate-of-production analysis for the input gas Cl₂. In this case, there are clear major and minor pathways. The primary reaction consuming molecular chlorine is gas-phase reaction #3, which is the electron-impact dissociation to two Cl atoms. Gas reactions #5 and #2, the electron-impact ionization and dissociative attachment reactions of Cl₂, respectively, are minor channels for Cl₂ consumption. The primary reaction producing Cl₂ is surface reaction #4, the reaction between gas-phase and adsorbed Cl atoms producing molecular chlorine in the gas phase. Gas reaction #18, the neutralization reaction between Cl⁻ and Cl₂⁺, and surface reaction #2, the neutralization of Cl₂⁺ on the wall, are minor channels for Cl₂ production.

Figure 4 Steady-state Chlorine Plasma—ROP Analysis



About Reaction Design

Reaction Design helps transportation manufacturers and energy companies rapidly achieve their Clean Technology goals by automating the analysis of chemical processes via simulation and modeling solutions. Reaction Design is the exclusive developer and distributor of CHEMKIN, the *de facto* standard for modeling gas-phase and surface chemistry that provides engineers ultra-fast access to reliable answers that save time and money in the development process. Reaction Design also offers the KINetics software module, which brings detailed kinetics modeling to other engineering applications, such as Computational Fluid Dynamics (CFD) programs. Reaction Design’s world-class engineers, chemists and programmers have expertise that spans multi-scale engineering from the molecule to the plant. Reaction Design serves more than 350 customers in the commercial, government and academic markets.

Reaction Design can be found online at www.reactiondesign.com.

CHEMKIN® and Reaction Design® are registered trademarks of Reaction Design. KINetics and Model Fuels Consortium are trademarks of Reaction Design.