



Iodine as an Alternative Fuel for Electric Propulsion

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Iodine as an Alternative Fuel for Electric Propulsion

by

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Abstract

The targeted goal of this research is to quantify propellant-materials impacts on spacecraft when using iodine as a propellant.

Iodine is an attractive replacement for xenon in electric space propulsion for volume constrained satellites due to its high density at standard condition. Iodine provides similar performance characteristic as xenon, but presents reactivity issues for many commonly used spacecraft materials. Much of the previous research on iodine reactions was performed fifty to one hundred years ago, and focuses primarily iodine and pure metal reactions. This research focuses on iodine plasma and its interactions with spacecraft materials. Two feed systems were built: one for the material testing apparatus and one for cathode testing. Three different cathode configurations provided by Plasma Controls LLC were tested with iodine. A tantalum cathode with a graphite liner was tested for a total of **44 hours**. Based on test results, this cathode design is promising for future long duration testing.

Current electric propulsion devices have proven their worth and won their place for large, conventional satellites. These high-efficiency devices do not meet mission requirements for small, volume constrained space vehicles, though. Trade studies using iodine as a propellant show superior system-level performance when compared to existing xenon based systems. Iodine stores at three times the density without the need for a high pressure vessel/system, making it possible for small satellites (<180 kg) to accomplish large satellite missions (e.g. lunar

reconnaissance, near-Earth asteroid visits). As a halogen, iodine introduces a chemical reactivity issue not present in xenon plasmas. This issue is now just starting to be explored.

Current electric satellite thrusters employ xenon propellant stored in high pressure (14 MPa, ~ 1.6 g/cm³) tanks limiting the amount of total impulse available to the satellite. Iodine is easily stored as a solid at room temperatures and pressures; iodine impulse density is nearly three times that of xenon. The low pressure storage and propellant delivery system also has the potential to significantly reduce the cost of large, telecommunication satellites (orbit transfers and station keeping) which could lead to decreased costs of satellite-based services.

The focus of this research is to develop an iodine plasma material interactivity model at high temperatures for refractory metals typically used in hollow cathodes. Hollow cathodes present a unique challenge for use with reactive plasmas because they require conductive materials (metals) to make them work. These materials are typically more prone to corrosion than ceramics and are operated at extreme temperatures. Electric propulsion systems do not function without a cathode. The duty cycle of electric propulsion requires the cathode to operate for long periods of time at temperatures as high as 1700 K. The most acceptable materials meeting these system demands include tungsten, tantalum, molybdenum and rhenium.

Iodine plasma material interactions consist of two facets: chemical reactivity and physical erosion. Reactivity is affected by physical properties (i.e. surface properties) thermodynamics (free energy) and kinetics (valence bonds). The physical erosion is a function of particle impact

velocity and angle of incident (kinetic removal of material). This research effort aims to separate the physical from the chemical effects and identify the impact of erosion individually.

The current experiment has been designed and is currently being demonstrated. Further refinements to the experimental test setup are being conducted to make improvements to the process, ensuring accurate, defensible results for the spacecraft materials of interest. Material samples will be separately exposed to iodine vapor and iodine plasma to determine erosion rates and how the addition of plasma affects erosion. This fundamental approach is expected to quantify erosion rate quantities directly attributed to plasma effects.

Table of Contents

1	Introduction.....	4
1.1	Research Motivation and Concept Overview	4
1.2	Research Objectives.....	7
1.3	Research Limitations	7
2	Material Interactions	8
2.1	Introduction.....	8
2.2	Basics of Material Interactions	8
2.2.1	Structure of Metals.....	12
2.2.2	Metal Thermodynamics	18
2.2.3	Kinetic Processes in Metals	18
2.2.4	Transport Properties.....	21
2.3	Iodine Properties	26
2.4	Iodine Chemical Reactivity.....	29
2.4.1	Scale Formation	32
2.5	Gas/Plasma and Solid Surface Interactions	36
2.6	Properties of Specific Metals and Associated Iodides.....	40
2.6.1	Stainless Steel	40
2.6.2	Tungsten.....	41
2.6.3	Molybdenum	42
2.6.4	Tantalum	42
2.6.5	Rhenium.....	43
2.6.6	Miscellaneous	44

2.7	Characterization Devices	47
2.7.1	Scanning Electron Microscopy	47
2.7.2	X-ray Diffractometry	51
2.7.3	X-ray Photoelectron Spectroscopy	53
3	Inductively Coupled Plasma Sources.....	56
3.1	Plasma Physics Basics	56
3.1.1	Ionization	56
3.1.2	Quasi-neutrality and the Debye Length	59
3.1.3	Sheath Formation	62
3.2	Inductively Coupled Plasma Source	64
3.2.1	Introduction.....	64
3.2.2	Applications of Inductively Coupled Plasma Sources.....	66
3.2.1	Model	67
3.2.2	Plasma Heating	69
3.2.3	Radio Frequency Impedance Matching	70
3.3	Hollow Cathodes.....	73
3.3.1	Hollow Cathode Operating Conditions.....	76
3.4	Plasma Characterization.....	77
3.4.1	Langmuir Probe	77
3.4.2	Spectroscopy	88
4	Experimental Setup	95
4.1	Material Exposure Apparatus.	95
4.1.1	Radio Frequency Inductively Coupled Plasma Source.....	97
4.1.2	Langmuir Probe	98

4.1.3	Spectral Measurements	99
4.1.4	Resistance Measurement.....	100
4.2	Cathode Testing Chamber.....	105
4.2.1	Cathode Setup and Gas Feed System.....	105
4.2.2	Electrical Setup	107
4.2.3	Test Procedure	108
4.2.4	Cathode Configurations	110
5	Test Plan.....	111
5.1	Introduction.....	111
5.2	Characterization Phase.....	111
5.3	Testing.....	114
5.3.1	Startup Procedure.....	115
5.3.2	Shut-down Procedure.....	116
5.4	Statistical Significance.....	117
6	Results.....	118
6.1	Preliminary Results	118
6.2	Feed Lines and Vacuum Chamber	118
6.3	Cathode	119
6.4	PC-I3 and PC-I4.....	121
6.5	PC-120	122

1 Introduction

1.1 Research Motivation and Concept Overview

Spacecraft propulsion technology has been gradually shifting from chemical-based propulsion methods to higher efficiency electric propulsion techniques. Electric propulsion technology in the United States has matured to an operational level but has not yet become a mainstream propulsion solution for manufacturers or deep space researchers. Electric propulsion devices do not provide superior system level performance when compared to existing propulsion systems but using iodine as a propellant eliminates some of this shortfall.

Other electric propulsion devices employ xenon propellant. Xenon has a relatively high atomic mass, low ionization energy, is not toxic, can be stored long-term (albeit high pressure), and is compatible with most materials. ^[1] As demands for more payload mass and more orbit transfers increase the spacecraft will become increasingly volume limited due to the increased propellant onboard. A higher thrust density propellant such as iodine would alleviate this limitation.

Iodine provides similar atomic mass (126.9 amu, vs. xenon's 131.3 amu), low ionization energy, and long-term storage performance characteristics. Iodine excels in its storage density, 4.9g/cm³ at room temperature and pressure. Xenon is only 1.6g/cm³ at room temperature and requires a pressure vessel capable of 14.0 MPa. ^[2] Iodine is stored as a solid and requires a small amount of energy to vaporize; 183° C yields 1.0 atm of iodine vapor. ^[2]

The advantage of using iodine is also evident in the amount of energy consumed in the ionization process. Iodine has shown it will first dissociate (1.5 eV) and then preferentially ionize as a single positive ion (9.4 eV). ^[3] Therefore, the use of iodine will produce the same thrust and

specific impulse as xenon using less ionization energy (10.5 eV total versus the 12.1 eV required for xenon).^[2] Adding to the benefits of singly ionizing iodine, the dimer ionization ($I_2 + e \rightarrow I_2^+$) only requires 9.4 eV.^[2] Previous work has shown as high as 3% of the plasma consists of particles having an effective mass of 254 amu, implying dimer ionization.^[2] The combination of a lower ionization and the higher atomic mass results in a 15% higher thrust to power ratio with similar specific impulse to that of xenon.^[3]

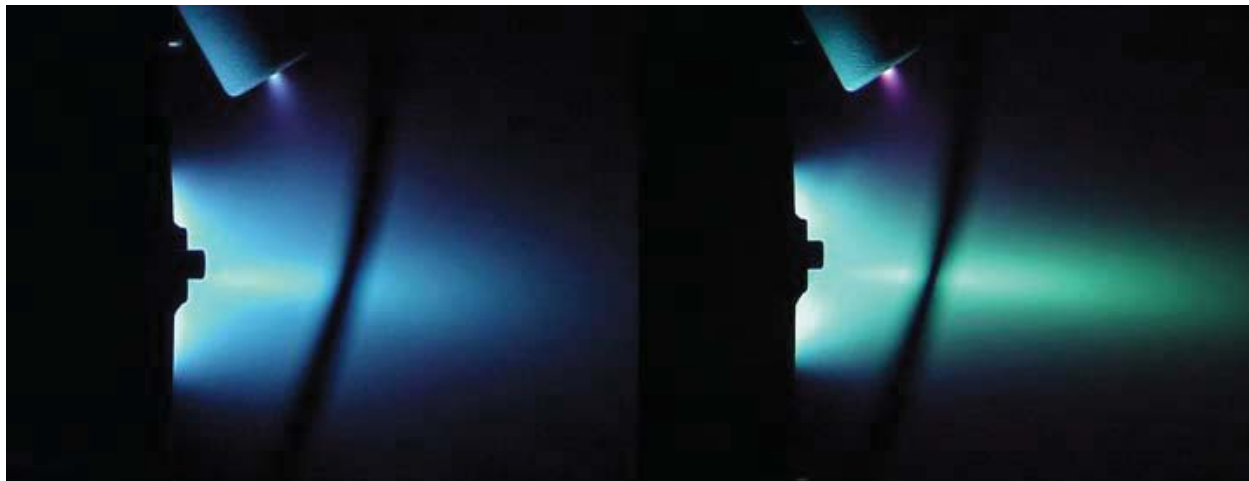


Figure 1: Busek 200W Hall Effect Thruster with xenon (left) and iodine (right)



Figure 2: Busek 200W HET after Operating on Iodine: Left – Anode just after Shutdown (Glowing Hot), Right – Anode Extensively Corroded.

As a halogen, iodine introduces two issues not present with xenon plasmas, negative ionization and high reactivity. The higher reactivity directly limits the lifespan of the cathode. Cathodes are used in ion thrusters to first ionize the neutral gas and then in the exhaust to

neutralize the plasma. Without a functional cathode most electric propulsion systems will not properly function. So, identifying acceptable materials is a major milestone for use of iodine in electric propulsion. Hollow cathodes present a unique challenge for use with reactive plasmas because they require conductive materials (metals) operating at extreme temperature, which are typically more prone to corrosion than ceramics.

Iodine will also commonly take on an extra electron, negative ion, in the monatomic state as is typical with halogens. The proven ionization process used by space propulsion devices introduces high energy electrons from a cathode. These electrons do influence the diatomic iodine to disassociate and create a negative ion in some instances, but the electronegativity of iodine (2.5 eV for the diatom and 3.0 eV for the monatom) is a relatively low level compared to the ionization energies (10.4 eV monatom and 9.4 eV diatom). Negatively charged ions hurt the performance and efficiency of the thruster as the electric field attempts to accelerate negative charges in the reverse direction, potentially resulting in damage to the anode. ^[4]

Iodine plasma material interactions consist of two facets: chemical reactivity and physical erosion. Reactivity is typically explained using physical properties (i.e. surface properties, coatings) thermodynamics (free energy) and kinetics (valance bond theory). In pure substances, increased exposure (surface area and time) will result in increased reactions.

Thermodynamically, the chance of a reaction of two substances increases if the final products have a lower free energy. According to valance bond theory, the outer shell electrons can help explain the probability of a reaction. Each of these physical approaches to explaining the reactivity is important in explaining the mechanisms involved. The physical erosion of a spacecraft surface is directly related to the momentum exchange once the ionized species are accelerated by the applied electric and/or magnetic fields.

The focus of this research will be to develop an iodine plasma material interactivity model at high temperatures for typical refractory metals used in hollow cathodes while taking into account the various ionized species expected in the plasma (positive and negative).

1.2 Research Objectives

This research will develop an iodine plasma material interactivity (erosion and reactivity) model and compare it to xenon models. The research will produce and characterize iodine plasma, determine the composition accurately, and then characterize the effect on the erosion rate due to chemical and plasma impacts.

The key objectives of this research focus on the impacts of iodine vapor and iodine plasma on spacecraft materials:

1. Design, construct, and validate an iodine inductively coupled plasma source
2. Expose various cathode materials to iodine vapor and plasma at cathode operating conditions
3. Characterize cathode materials erosion rates (added)
4. Characterize chemical reactivity (added)
5. Test and Characterize iodine fueled hollow cathode

1.3 Research Limitations

The primary limitations of this research effort stem mainly from the difficulty with in-situ measurements of the materials samples. Ideally, the characterization techniques would be performed during or immediately after exposure. Some of the reaction species are likely to be pressure and/or temperature dependent, so changes in the conditions due to sample transfer may ultimately change the measured erosion rates and reactivity determinations.

2 Material Interactions

2.1 Introduction

The primary goal in this work is to investigate how iodine vapor and iodine plasma interacts with various materials. In order to understand how the materials in question are being impacted, it is important to understand the material properties and potential mechanisms that lead to variations. Important basics of materials are reviewed. Important properties of iodine and halogen reaction mechanisms are presented. The materials used in this research are identified and a review of previous iodine erosion studies are presented. The best approach to characterize material erosion and chemical reactivity is explained.

2.2 Basics of Material Interactions

The fundamental building block of any material is the elements that make up its composition. Each element is an atom composed of a close packed nucleus with some number of neutral neutrons and positively charged protons with a cloud of negatively charged electrons. The cloud of electrons is distributed by discrete distances and shapes based on their respective energy levels. The behavior of the electrons and nucleus gives rise to a variety of properties that determine material characteristics.

As described by quantum mechanical theory, electrons form “shells” orbiting around the nucleus. Each shell has a specific energy level, defining the amount of energy needed to move an electron between shells. The outer shell is commonly called the valence shell; every atom aims to have eight electrons in its valence shell. The outer shell of electrons is the primary driver of inter-atomic interactions. Due to the behavior of seeking eight electrons in the valence shell,

atoms with valence shells closest to complete octets generally are the most reactive, for example fluorine in the halogen group or sodium in the alkali metal group.

Elements are frequently described by their ionization energy, atomic radius, electron affinity, and electronegativity. The ionization energy, or ionization potential, is the energy required to remove one electron from the valence shell of an atom. The electron affinity is the energy either gained or released when an atom gains an electron. The atomic radius is the distance from the center of the nucleus to the edge of the electron cloud. Atomic radii are defined based on the type of bonds: covalent, ionic, metallic, and van der Waals. Covalent radii follow a relatively predictable trend where they decrease along the period and decrease down each group of the periodic table. The radius dramatically increases from noble gas to the next alkali metal, due to a higher energy electron shell (higher orbit radius for the outer electron). The radius decreases across the period because the number of protons in the nucleus increases, the electrons are added to same outermost shell and the Coulomb force between the positive and negative charges increases the electron cloud is smaller. Electron affinity and ionization potential are both defined with respect to isolated atoms and do not provide any information on how atoms interact. So, electronegativity was introduced as a way to measure the attraction an atom has for the electrons in another atom. The most common measure of electronegativity was developed by Linus Pauling: ^[5]

$$\chi = \frac{0.31(n + 1 \pm c)}{r} + 0.5 \quad (1)$$

From electronegativity the excess binding energy between atoms is defined:

$$\Delta_{A-B} = 96.5(\chi_A - \chi_B)^2 \quad (2)$$

The excess binding energy can also be determined from the measurable bond dissociation energy.

$$\Delta_{A-B} = DE_{AB} - [DE_{AA}DE_{BB}]^{\frac{1}{2}} \quad (3)$$

The bond dissociation energy, DE_{ij} , is the energy needed to separate two bonded atoms.^[5] The larger the difference in the electronegativity corresponds to a larger excess binding energy, providing a good way of describing and characterizing bond strength and type. Excess binding energy provides a useful metric for connecting the bond dissociation energy and electronegativity.

Bond types are divided into two categories: primary bonds and secondary bonds. Primary bonds consist of ionic, covalent, polar covalent, and metallic bonds. Secondary bonds consist of hydrogen bonding, dipole-dipole interactions, and van der Waals forces.

Ionic bonds form when electrons are transferred from one atom to a more electronegative atom, typically when the electronegativity difference is greater than 2 (e.g. Na and F). Covalent bonds form when one or more electrons are shared by two atoms, typically at electronegativity differences less than 0.4 (e.g. HCl). In cases where the electronegativity is between 0.4 and 2.0 a polar covalent bond is formed, where the bond is somewhere in between covalent and ionic with electron sharing but also some charge distribution. Metallic bonds occur in a collection of homonuclear atoms, where the bonding electrons are shared by a group of positive nuclei.

Of course, the ionic bonds are of significant interest to this research. Previous research has provided several important characteristics to describe these physical phenomena such as bond length and bond potential energy. For ionic bonds, the equilibrium separation distance for a bond is given by :

$$r_0 = \left(\frac{nb}{ma} \right)^{\frac{1}{n-m}} \quad (4)$$

The equilibrium potential energy for an ionic bond is given by :

$$U_0 = \left(1 - \frac{1}{n} \right) \left(-\frac{e^2}{4\pi\epsilon_0 r_0} \right) + \Delta E_{ions} \quad (5)$$

ΔE_{ions} is the energy required to form an ion. In an ordered assembly of atoms, referred to as a lattice, each atom can have more than one bond. The result is an increased interionic spacing, which is characterized by introducing a constant called the Madelung constant. The Madelung constant is based on the structure of the crystal, the charge of the ions, and the relative size of the ions.

$$U_L = \left(\alpha_M - \frac{1}{n} \right) \left(-\frac{e^2}{4\pi\epsilon_0 r_0} \right) + \Delta E_{ions} \quad (6)$$

The Madelung constant, α_M , is determined empirically. The structure of a covalent bond is significantly more complicated and is represented by using molecular orbital theory. In the simplest case of the hydrogen molecule, the two atomic orbitals (1s) overlap to form two molecular orbitals: one bonding orbital ($\sigma 1s$) and one antibonding orbital ($\sigma^* 1s$). Antibonding orbitals weaken the bond and bonding orbitals strengthen the bond. The reason for this description is to ensure agreement with the long held Pauli Exclusion Principle; two electrons in a molecule cannot have the same set of quantum numbers. So, when the atomic orbitals overlap they split into one with an energy lower than the atomic orbital and one with a higher energy. The antibonding orbital doesn't have to be occupied. In a molecule like hydrogen the two shared electrons occupy the bonding orbital, which results in a molecule more stable than a single atom.

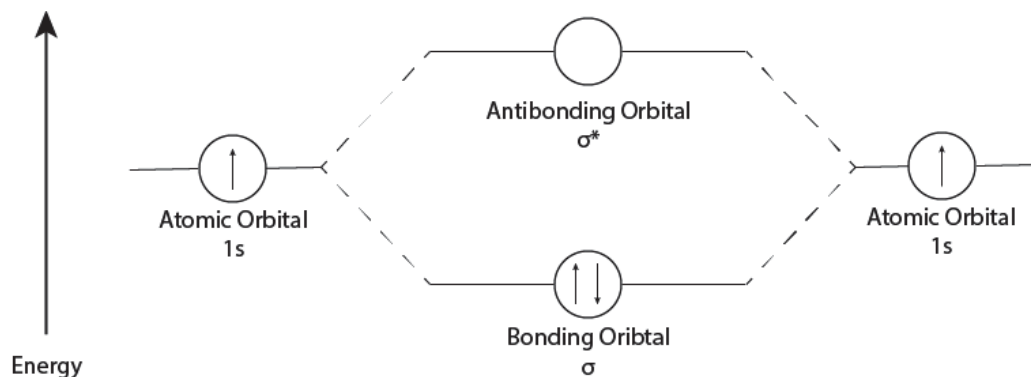


Figure 3 – Molecular Orbital Diagram

Metallic bonds present an additional challenge since they have the tendency to form large groups of atoms that share valence electrons. A collection of atoms, N , have N atomic orbitals and form N molecular orbitals. Many of the molecular orbitals are degenerate. The result is a very large number of orbitals so closely spaced that they effectively form a continuum, referred to as an energy band. The highest occupied band is known as the valence band. The lowest unoccupied band is known as the conduction band.

2.2.1 Structure of Metals

In metallic bonds the electrons are decentralized and provide minimal limitations on how close atoms can pack together, resulting in close-packed arrangements. A close-packed arrangement is one where the maximum number of atoms directly in contact with one another is achieved. The maximum number of atoms that can be in contact with a center atom is twelve; six in the same plane, three above and three below.

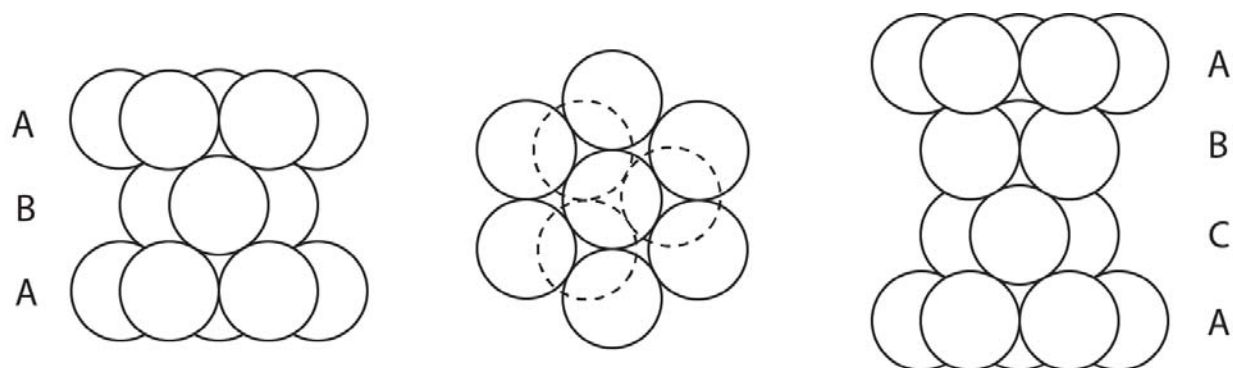


Figure 4 – Close Packed Configurations

Atoms can stack themselves into two different configurations while still maintaining a close-packed structure (*Figure 4*). The ABAB structure is known as hexagonal close-packed and the ABCABC structure is known as face-centered cubic.

The resulting structure created by the interaction of the atoms is referred as the crystal structure. The crystal structure, and flaws in the crystal structure, give rise to a significant number of material properties. In the context of this work, crystal structure impacts material diffusion and the likelihood of forcible ejection of atoms from sputtering.

Crystal structures have an associated number of nearest surrounding atoms, called a coordination number. In either close-packed arrangement, the coordination number is 12. The coordination number defines the number of atoms associated with a unit cell but does not describe how those atoms connect to the surrounding arrangements. The description of the crystal structure defines each unit cell but is continuously connected to adjacent unit cells without a break.

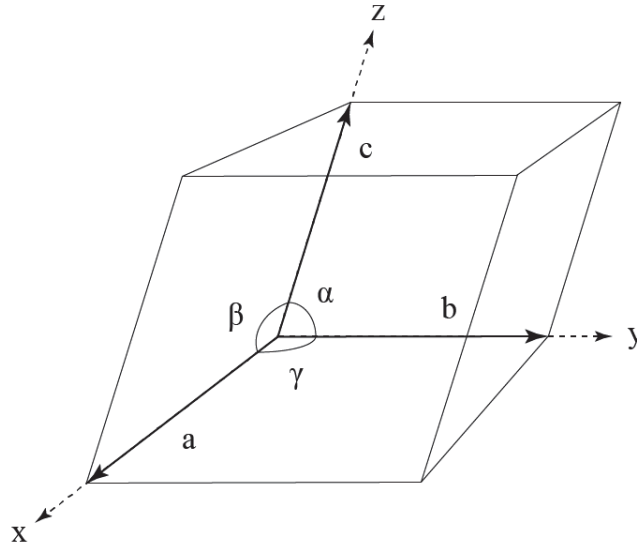


Figure 5 – Coordinate System for Crystal Structures

In addition to hexagonal close-packed and face-centered cubic twelve other types of crystal structures exist. All fourteen structures are called space lattices or Bravais lattices. Each space lattice (Figure 5) has specific characteristics that could be extensively discussed, but for the purpose of this work it is sufficient to know that crystal structure gives rise to many different material properties. For example, the packing of atoms sometimes results in large gaps that can be filled by smaller impurity or alloying atoms, called interstitial sites. These impurities can be more readily attacked by a reactive, invasive species.

An important parameter for discussing crystal structures is the lattice parameter, the length of a face edge. Lattice parameters are the simple result of basic geometry. As an example, the lattice parameter for FCC structures is :

$$a = \frac{4r}{\sqrt{2}} \quad (7)$$

Bond radii vary with the type of bond, so bond radii are usually given as a covalent radius, an ionic radius, or a metallic radius. Unit cells are defined in terms of cell coordinates, which can be combined to create a vector called cell direction (Figure 5). If two points have the

same fractional portions of their coordinates they are considered equivalent. In cell coordinate notation, a negative is denoted by an overbar. The cell volume can then be determined in terms of the lattice parameters and interaxial angles :

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos\alpha\cos\beta\cos\gamma)^{\frac{1}{2}} \quad (8)$$

The cell volume and lattice parameters are useful for finding the theoretical size of crystal structures and determining theoretical densities of materials.

Another important parameter in crystal structure is a description of crystal planes. An arbitrary plane can be defined relative to the lattice parameters with :

$$\frac{1}{A} \frac{x}{a} + \frac{1}{B} \frac{y}{b} + \frac{1}{C} \frac{z}{c} = 1 \quad (9)$$

Where A , B , and C are the intercepts of the plane. The most common way of representing crystal planes is using a system introduced by Miller in 1839, and now known as Miller indices, where the reciprocal of the intercepts is taken and is written in parentheses : ^[6]

$$\left(\frac{1}{A} \frac{1}{B} \frac{1}{C}\right) = (hkl) \quad (10)$$

Planes with common factors are parallel, for example (222) and (111) are parallel. The planar density, the density of atoms on a plane, is given by :

$$PD = \frac{A_c}{A_p} \quad (11)$$

Where A_c is the area taken up by atoms and A_p is the area of the plane. Since actual crystal lattices are made up of an array of unit cells, many parallel crystal planes and the interplanar spacing can be calculated with :

$$d = V[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta) + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma) + 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha)] \quad (12)$$

Actual materials do not follow a perfect repetition of their unit cell to infinity without any variation. Variations in the lattice structure are referred to as defects or imperfections and are categorized as point defects, line defects, or planar defects. Point defects occur when an atom is added, removed, or displaced in the lattice structure.

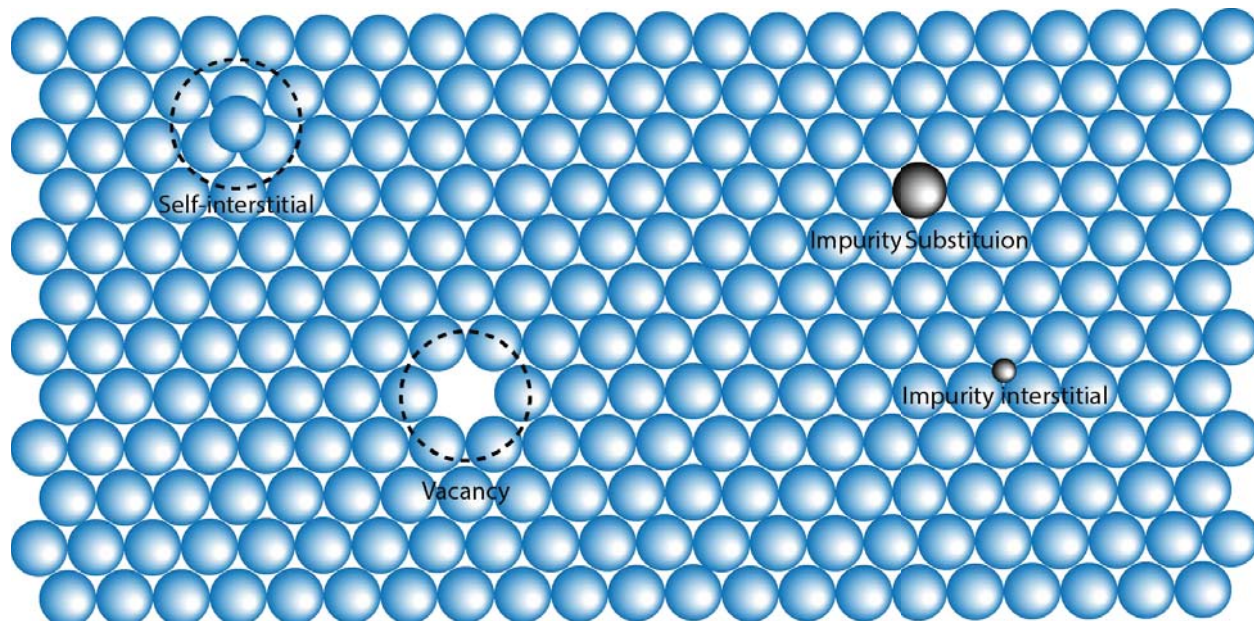


Figure 6 – Vacancy and self-interstitial defects (left), and impurity interstitial and substitutional defects (right)

Self-interstitial defects create significant strain on the lattice since the plane must distort to fit the atom. At the surface of a material, or crystal, the opposite of vacancy called an adatom can occur. An adatom is an atom that fits into the crystal structure, but it is on a higher plane and not surrounded by other atoms. Cases where a vacancy and self-interstitial occur at the same time are called Frenkel defects. Impurity atoms aren't always a problem and can lead to desirable properties through the formation of an alloy. In other cases, impurity atoms can be a reactive species and lead to further lattice defects. A cation and anion vacancy pair are called a Schottky defect. Schottky defects occur to maintain charge neutrality. Atoms leaving an ionic lattice typically occur at lattice boundaries.

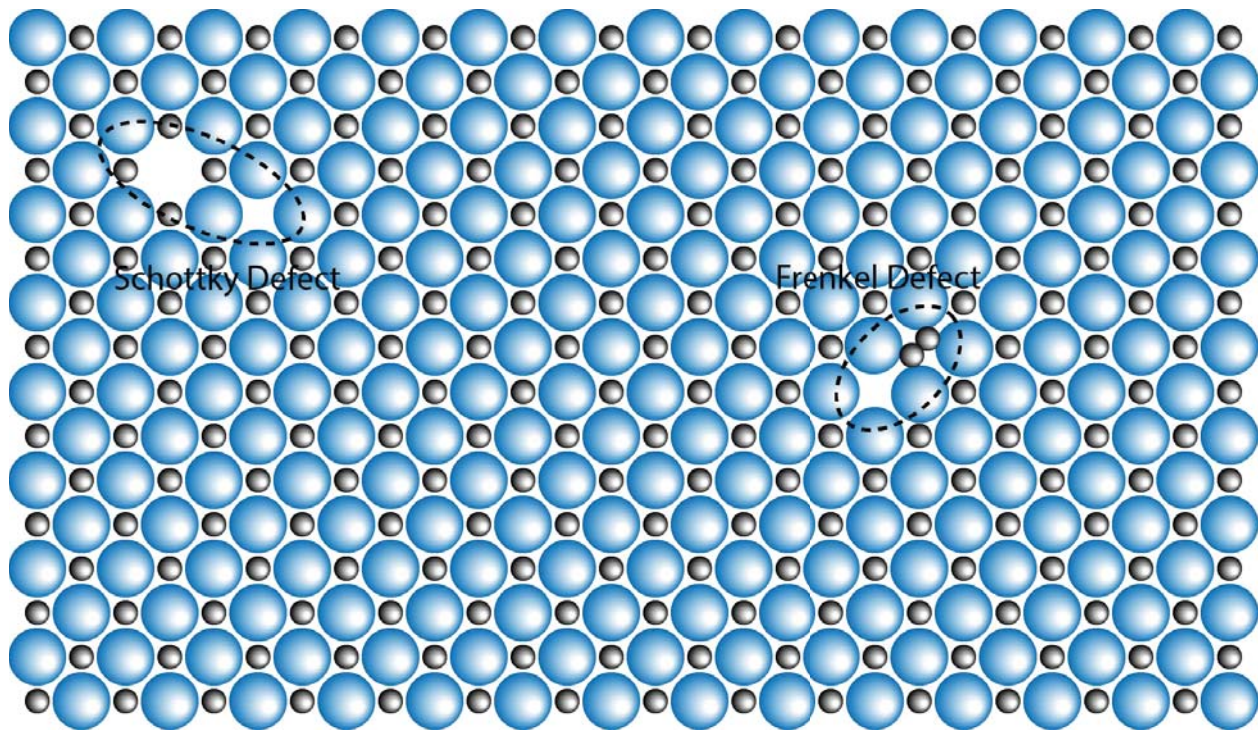


Figure 7 – Frenkel and Schottky defects

Line defects occur when a linear group of atoms are displaced from their expected location and are comprised of three types: edge dislocation, screw dislocations, and mixed dislocations. Edge dislocations occur when an atomic plane does not continue through the entire lattice. Screw dislocations occur when part of an atomic plane shift with respect to another part. Mixed dislocation are a combination of edge and screw dislocations.

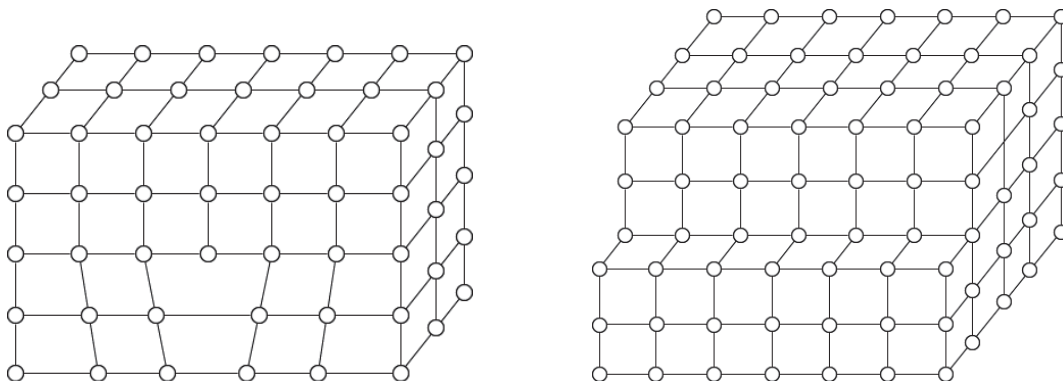


Figure 8 – Edge (left) and Screw Dislocations (right)

The final type of defect is planar defects. Planar defects are two-dimensional defects and are split into stacking faults and grain boundaries. Stacking faults occur when planes of atoms incorrectly stack, for example in an HCP structure when ABCAB|ABC occurs instead of ABCABC stacking. If a plane is missing it is called an intrinsic stacking fault, an extrinsic stacking fault if an extra plane is introduced, and a twinning fault when the pattern mirrors itself. An example of a twinning fault would be $ABCABC\underline{C}BACBA$, where the under-barred C is the mirror plane about which the sequence reverses.

Grain boundaries occur at the boundary between different crystals. Most materials are polycrystalline, meaning they are a single bulk material made up of various smaller crystals, referred to as grains. The grain boundary is then the intersection between the adjacent grains regardless of individual grain orientation. Grain boundaries are classified as tilt boundaries and twist boundaries. A tilt boundary is a collection of edge dislocations and a twist boundary is a collection of screw dislocations. Grain boundaries have a direct impact on the properties of a material in the sense that they are flaws and create mechanical failure points, regions of increased material diffusion (impurities or otherwise) and change the interactions between atoms (can change thermal conductivity).

2.2.2 Metal Thermodynamics

2.2.3 Kinetic Processes in Metals

Kinetics describes the rate at which chemical reactions and ionization processes take place. Kinetics can be divided into three different processes: formation rate, decomposition rate, and transformation rate. Formation processes are usually chemical and describe how materials

form. Decomposition processes are usually chemical and are the reverse of formation processes. Transformation processes are typically physical like phase change.

The most basic description of kinetic processes starts with a reaction of some sort:



According the Law of Mass Action the rate of reaction at a given temperature is proportional to product of the reactants. So, the forward and backward reaction rates can be given by :

$$r_f = k_f[A]^a[B]^b \quad (14)$$

$$r_b = k_b[C]^c[D]^d \quad (15)$$

If reactions are not elementary (single-step), the reaction orders are not always equal to the stoichiometric coefficients and are instead based on the reaction mechanism. At equilibrium, the forward and backward reaction rates are equal, and a general equilibrium rate constant can be found with :

$$\frac{k_f}{k_b} = K_p = \frac{[A]^a[B]^b}{[C]^c[D]^d} \quad (16)$$

K_p is the equilibrium rate constant. Kinetics helps describe the relationship between standard free energy changes, species concentrations and thermodynamic state properties.

$$\Delta G^0 = -RT \ln \left\{ \frac{[A]^a[B]^b}{[C]^c[D]^d} \right\} = -RT \ln K_p \quad (17)$$

Rearranging gives a result for the equilibrium constant in terms of the standard free energy change and temperature at equilibrium:

$$K_p = \exp \left(-\frac{\Delta G^0}{RT} \right) \quad (18)$$

The above relation is useful if the reaction is at equilibrium but isn't particularly helpful if the system is in a transient state. If instead of the standard free energy a different general energy term is used an expression for the rate constants can be found with :

$$k = k_0 e^{-\frac{E_a}{RT}} \quad (19)$$

k_0 is a proportionality constant called the preexponential factor and E_a is the activation energy as defined by gas dynamics and statistical mechanics (Boltzmann distribution). The activation energy is the minimum energy required to reach an activated state and react.

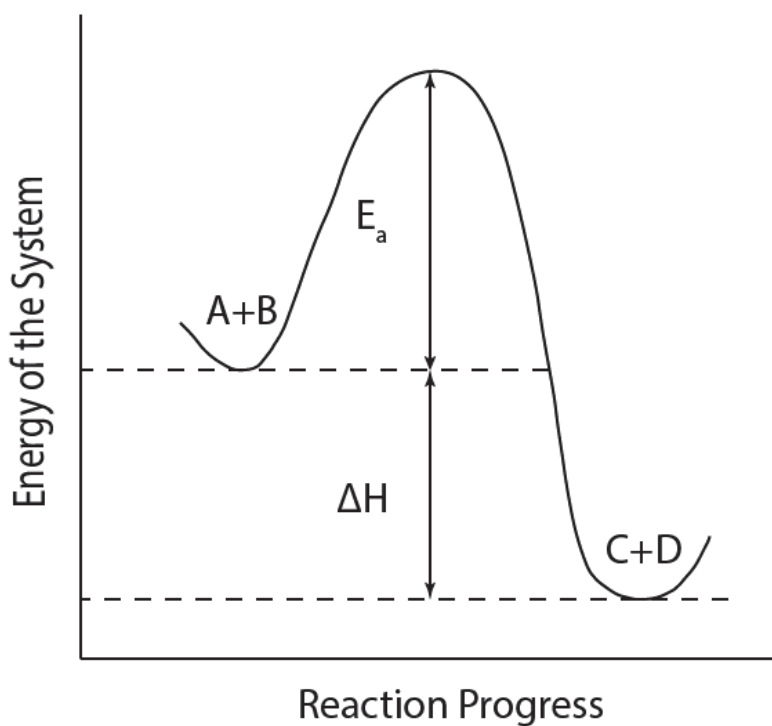


Figure 9 – Activation Energy Barrier

In *Figure 9*, ΔH is the heat of reaction and can either be positive (endothermic) or negative (exothermic) depending on whether energy is absorbed or released during the reaction. Activation energy can be calculated by measuring the reaction rate with respect to temperature or vice versa.

2.2.3.1 Phase Transformation

Phase transformations can be divided into either physical state changes (e.g. solid to liquid), crystal type transformation, or reordering. In the context of transformation, reordering means the change from a disordered state to a more ordered crystalline state.

The rate at which an amorphous material, at a sufficiently high fixed temperature, transforms into a crystalline material is :

$$\frac{dx}{dt} = nk(1 - x)t^{n-1} \quad (20)$$

Solving the above equation gives the Johnson-Mehl-Avrami equation: ^[7,8,9]

$$x = 1 - e^{-kt^n} \quad (21)$$

Plotting the above equation for various temperatures, from empirical data, allows for the determination of the reaction order and the activation energy of the process.

2.2.4 Transport Properties

Transport properties of materials describe how various fundamental quantities move through a material. For solid materials, the transport property most people are probably most familiar with is heat transport, or how thermal energy moves through an object. From a fundamental perspective, transport is the rate of flow per unit area of some quantity. That rate of flow per unit area, flux, is then proportional to a driving force. The level of proportionality is based on the material. The three fundamental transport processes are momentum, heat, and mass transport.

In heat transport the driving force is described best by a temperature gradient. The proportionality constant is thermal conductivity. Fourier's Law of heat transfer in one dimension is :

$$q = -k \frac{dT}{dx} \quad (22)$$

In momentum transport the driving force is a velocity gradient and the proportionality constant is viscosity. Newton's Law of viscosity in one dimension is :

$$\tau_{yx} = -\mu \frac{dv_x}{dy} \quad (23)$$

In mass transport the driving force is a concentration gradient and the proportionality constant is molecular diffusivity. Fick's Law is :

$$J_{Ay}^* = -D_{AB} \frac{dc_A}{dy} \quad (24)$$

2.2.4.1 Momentum Transport in Metals

Momentum transport in all materials is defined in terms of viscosity. The origin of viscosity comes from kinetic theory of gases, which starts with the interaction of atoms or molecules with one another. Atoms or molecules very close together repel one another, Pauli repulsion. At a sufficiently large distance they begin to experience an attractive force, which reaches a maximum and then decreases back to zero with increasing distance. The potential energy function of the interaction between two particles can be modeled with the relatively simple Lennard-Jones potential:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (25)$$

The potential function with respect to radius reaches a minimum, potential well, where the atoms or molecules typically remain. The previous quantities have been extensively studied for numerous materials and can be approximated for the rest based on fluid critical properties. So, for low density gases a relatively simple expression can be derived for viscosity:

$$\mu = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega} \quad (26)$$

M is the molecular weight and Ω is a dimensionless number related to the dimensionless temperature $k_b T / \varepsilon$. It is somewhat difficult to correlate the above viscosity with the viscosity seen in liquids but assuming nonattracting hard spheres in a dense liquid the following relation can be made:

$$\mu = 3.8 \times 10^{-8} \frac{\sqrt{MT}}{V^{\frac{2}{3}}} \left[\frac{PF^{\frac{4}{3}} \left(1 - \frac{PF}{2}\right)}{(1 - PF)^3} \right] \quad (27)$$

V is the molar volume and PF is the packing fraction, which can be related to the collision diameter with :

$$PF = \frac{\pi n_0 \sigma^3}{6} \quad (28)$$

n_0 is the average number density. Other methods exist for determining theoretical viscosity predominantly based on statistical mechanics but currently no method applies broadly across all system. In practice it is far more useful to use empirical or semi-empirical relationships. The previously mentioned Arrhenius relation can be used to make a empirical relationship for viscosity:

$$\mu = A \exp\left(\frac{H_\mu}{RT}\right) \quad (29)$$

A and H_μ are constants usually found with respect to the melting point for metals. The composition of alloys has significant impact on viscosity and is always determined with empirical relationships because theoretical methods have to create a realistic model. Even empirical relationships are typically limited to binary mixtures with very specific compositions.

For this work materials are not being tested at conditions where any significant liquid formation will occur and basic understanding of the gas phase should be sufficient to understand the results.

2.2.4.2 Heat Transport

Heat transport occurs through three different forms: conduction, convection, and radiation. In conduction atoms transfer energy through collisions, with “free electrons” also contributing to the energy transfer in metallic solids. In convection, energy is transferred through the movement of macroscopic fluid elements. In radiation, energy is transferred through the emission, propagation, and absorption of electromagnetic waves. In solid materials conduction dominates and as such will be discussed below.

Similar to Eq. 26, the thermal conductivity of gas can be derived from the Lennard-Jones potential to get the following for low density atomic gases:

$$k = 8.32 \times 10^2 \frac{\sqrt{T/M}}{\sigma^2 \Omega} \quad (30)$$

As the gas gets more complicated, so too does the method of determining thermal conductivity. For polyatomic gases the thermal conductivity becomes:

$$k = \frac{15R\mu}{4M} \left(\frac{4C_v}{15R} + \frac{3}{5} \right) \quad (31)$$

In metallic solids, the “free electrons” can act as thermal energy carriers and contribute an electronic heat capacity to a material given by :

$$C_{ve} = \frac{\pi^2 n k_b^2 T}{2E_F} \quad (32)$$

n is the valence electrons per unit volume, k_B is Boltzmann’s constant, and E_F is the energy of the Fermi level. The electronic heat capacity is typically quite small but becomes significant at very low temperatures (<4K). Pure metals have electrons with a mean free path

significantly higher than the heat carrier in the lattice, which results in the electrons dominating the thermal conductivity at low temperatures.

2.2.4.3 Mass Transport

In order for reactions to take place, which will be discussed in more detail in a later section, reactants need to move from one point to another. Mass transport describes the motion of molecules or atoms through a material and explains how reactants in a solid can move from one point to another. As with heat and momentum transport, a relationship for the molecular diffusivity can be found from the Lennard-Jones potential in a low-density gas:

$$D = 2.6380 \times 10^{-7} \frac{\sqrt{T^3/M}}{P\sigma^2\Omega} \quad (33)$$

Where P is the pressure. The above relation is for self-diffusion of an atom or molecule through a gas composed of the atom or molecules. The diffusion coefficient for a gas of two species is :

$$D_{AB} = 2.6280 \times 10^{-7} \frac{\sqrt{T^3(M_A + M_B)/2M_A M_B}}{P\sigma_{AB}^2\Omega_{AB}} \quad (34)$$

In solids diffusion takes place through random walk motion caused by atomic vibrations in solids. Diffusion in solids can be modeled with another Arrhenius-type relationship :

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (35)$$

D_0 is a preexponential factor called the frequency factor. Three different mechanisms for diffusion in solids have been identified: interchange, vacancy, and interstitial mechanisms.

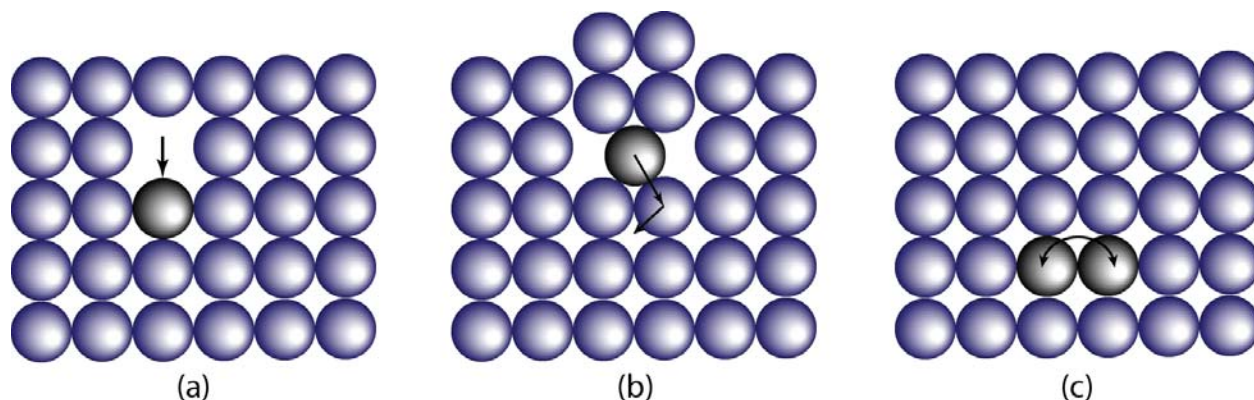


Figure 10 – Diffusion Mechanisms in Solids (a) vacancy, (b) interstitial, and (c) interchange

The diffusion can be ranked by their likelihood of occurrence based on activation energy. In pure metals, the vacancy mechanism requires the lowest energy, followed by interstitial, and the interchange mechanism requires the highest energy. In alloys, the solute atoms are frequently small enough that the activation energy for interstitial mechanisms is low and dominates. If the alloy has solute atoms closer in size, diffusion behavior follows a similar to self-diffusion in pure metals.

Diffusion processes exist in metals other than random walk diffusion and can be caused by pressure and temperature gradients or be driven by structural processes (dislocation diffusion, surface diffusion, and grain-boundary diffusion). Faults or boundaries in a crystal structure create a path of easier diffusion through a material.

2.3 Iodine Properties

Iodine is the heaviest stable halogen and has an atomic number of 53. At standard conditions, pure iodine exists as a diatom and appears as a lustrous dark purple to black crystalline solid. Iodine is classified as a reactive non-metal and is in group 17 (halogens) on the periodic table. Iodine has an electron configuration of $[\text{Kr}]4d^{10}5s^25p^5$ and is missing one electron from a full octet in its valence shell.¹⁰ The lack of one electron in its valence shell makes iodine

a strong oxidizing agent like the other halogens. Among the stable halogens, iodine is the weakest oxidizing agent and has the lowest electronegativity as is expected from periodic table trends. Iodine forms a diatom to form a complete octet in its valence shell, which at high temperatures dissociates to iodine atoms.¹⁰

Iodine forms a violet gas when heated. The violet color of iodine gas comes from the electron transition between the highest occupied antibonding π_g molecular orbital and the lowest vacant antibonding σ_u molecular orbital.^[10]

Table 1 – Physical Properties of Iodine at Standard Atmosphere^[10]

Melting Point	K	386.85
Boiling Point	K	458.2
Density	g/cm ³	4.933
Triple Point	K	386.65
Critical Point	K	819
Heat of Vaporization	kJ/mol	15.52
Heat of Fusion	kJ/mol	41.57
Molar Heat Capacity	K/(mol K)	54.44
Temperature for 1% dissociation	K	848

Table 2 – Atomic Properties of Iodine^[10]

Atomic Number	53
Number of Stable Isotopes	1
Atomic Weight	126.90447(3)
Electronic Configuration	[Kr]4d105s25p5
First Ionization Potential (eV) [11]	10.45126
Second Ionization Potential (eV) [11]	19.1313
Third Ionization Potential (eV) [11]	33
Electron Affinity (eV) [12]	3.0590463(38)
Ionic Radius (I ⁻)	220
van der Waals radius (pm)	215
Bond Length of Diatom I-I (pm)	266

As previously mentioned, one of the attractive aspects of iodine is the ease with which it can be stored as a solid and consequently vaporized. In vacuum conditions iodine requires even less energy to vaporize and directly sublimates as can be seen in the phase diagram below:

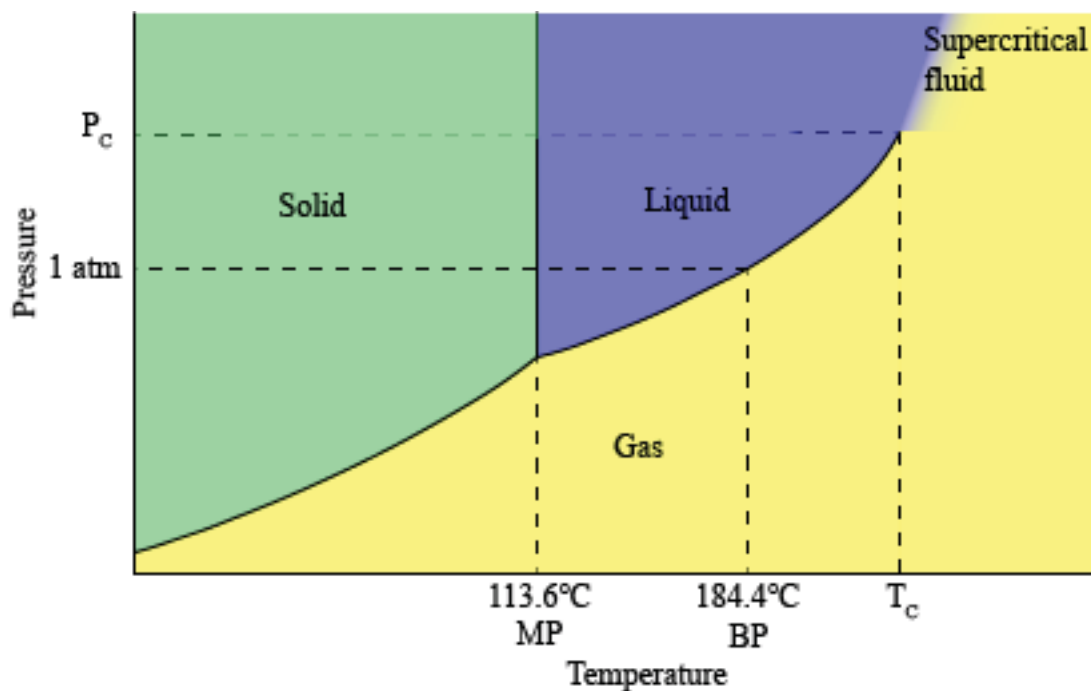


Figure 11 – Iodine Phase Diagram

The National Institute of Standards and Technology (NIST) provides a useful relationship (Antoine equation) for the vapor pressure of iodine above 1.0 torr as can be seen below: ¹³

$$\log_{10} P = 3.36429 - \left(\frac{1039.159}{T - 146.589} \right) \quad (36)$$

Pressure is in bar and temperature is in kelvin. For pressures below 1.0 torr, empirical data from Honig was plotted and fit to an Antoine equation: ¹⁴

$$\log_{10} P = 10 - \frac{3060}{T - 7.5} \quad (37)$$

Pressure is in torr and temperature is in kelvin. The above equation matches relatively well but is off by a few degrees at some pressures, so the data taken from Honig's graph is attached in *Appendix A*.

2.4 Iodine Chemical Reactivity

As a halogen, iodine is highly reactive and can cause extensive corrosion of metals. This corrosivity was what led to the initial discovery of iodine. Copper vessels holding soda ash, with iodine as an impurity, began to corrode unexpectedly.¹⁵ The general mechanisms of halogen attack is influenced by the presence of oxygen and water, producing significant variation in corrosion rates.

The primary goal in examining the mechanisms of halogenation is to determine the expected reactions. Using the standard free energies of formation, and any additional variations from standard conditions, the thermodynamic stability of any condensed phase (solid or liquid) relative to a chemical reaction can be determined. The formation reaction of the lowest halide can be written as :^[16]



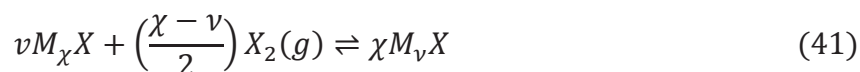
M is the metal, X is the halogen, and $M_\chi X$ is the lowest halide product. The Gibbs free energy of the reaction is given by :¹⁶

$$\Delta G_1 = \Delta G_{M_\chi X}^0 + RT \ln \frac{a_{M_\chi X}}{a_M^\chi P_{X_2}^{\frac{1}{2}}} \quad (39)$$

Using the Gibbs free energy, the critical halogen partial pressure required for the formation of the halide is given by :¹⁶

$$P_{X_2}^* = \exp\left(\frac{2\Delta G_{M_\chi X}^0}{RT}\right) \quad (40)$$

Additional formation of a higher halide gives the following reaction and critical halogen pressure:



$$P_{X_2}^* = \exp\left[\frac{2\left(\chi\Delta G_{M_\nu X}^0 - \nu\Delta G_{M_\chi X}^0\right)}{(\chi - \nu)RT}\right] \quad (42)$$

The standard Gibbs energy of formations for the previous equation is required in units of energy per mole of condensed phase or per molecular formula for the gaseous species.¹⁶

The melting temperatures for iodides of the primary iodides of interest are compiled below in *Table 3 – Melting Point of Iodide Phases*. It is important to note that in the case of multiple halides forming simultaneously or coexisting the minimum liquidus temperature can be dramatically different, and the appropriate phase diagram should be referred to. Liquid phases can provide some degree of passivation, but more frequently the liquid product dissolves other reactants and can accelerate the reaction.

Table 3 – Melting Point of Iodide Phases

Element	Melting Temperature (K)	Iodide Melting Point (K)	Di-Iodide Melting Point (K)	Tri-Iodide Melting Point (K)	Tetra-Iodide Melting Point (K)	Penta-Iodide Melting Point (K)
Molybdenum [10,17,18,19]	2895	No Data	Product of MoI ₃ in I ₂ gas	1200	Decomposes at 373	No Data
Tantalum [10,20,18,21,22]	3290	No Data	Ta ₆ I ₁₄ melts at > 925	Product of Ta + TaI ₅ gas at 803-858	Decomposes @673 into Ta ₆ I ₁₄	769

Tungsten [10,17,18]	3695	No Data	Decomposes at 1073	Unstable, Decomposes @ 298	Decompose s @ 900 into solid WI ₂ and I ₂	No Data
Rhenium [10,17]	3732	Decompose s in vacuum	No Data	See ReI ₄	Unstable at room temp and vacuum, decomposes into ReI ₃ at 623	No Data
Iron [10,17]	1811	No Data	860-867	Forms in vapor phase only, with FeI ₂ in I ₂ gas	No Data	No Data
Nickel [10,17 ,23]	1728	No Data	1070-1073	No Data	No Data	No Data
Chromium [10,17 ,18]	2180	No Data	1129-1140	Decomposes at 700K	No Data - Probably Exists	No Data

Due to the lack of available information on the diffusion rates of halides, a basic relationship between the melting point and the diffusion rates is sometimes useful. At temperatures below half the melting point of the halide, diffusion of metal ions and halogen ions will be very slow. Above half the melting point, diffusion can be significantly higher. For example, the diffusion coefficient of silver ions through silver bromide is on the order of 10^{-11} cm²/sec at 0.5MP. At 0.75MP the diffusion coefficient is on the order of 10^{-7} cm²/sec, a factor of 10,000 ²⁴

Some of the iodide phases form as solids and will likely produce a scale (*Table 3 – Melting Point of Iodide Phases*). The formation of a scale can result in a physical separation between the two reactants, iodine and metal, and may provide a degree of protection similar to an aluminum oxide on aluminum. If, however, the scale is porous or cracks, the iodine can still

access the metal either through diffusion or flow through cracks like rust on iron. The main takeaway is that in addition to the actual reactivity of the metal the state in which the product forms has a significant impact on the resulting erosion rate. A product that forms as a dense uniform and well-bonded coating on the metal will dramatically reduce the erosion rate or even potentially stop the reaction. A product that forms a low density and cracking product will provide a small degree of protection. Finally, a product that forms as a gaseous component will provide very little protection and likely lead to rapid erosion rates.

Very little information on the formation of halogen scales is available, and in an effort to better understand the formation and properties of potential iodide scale, oxide scales are included here for comparison.

2.4.1 Scale Formation

If most ionic defects in the scale are cation vacancies or cation interstitials, scaling occurs at the scale/gas interface. The scaling occurs through diffusion of cations with a counterflow of vacancies/interstitials and positive holes/electrons. If diffusion of interstitial cations and electrons predominate, scale also forms at the scale/gas interface. Conversely, if most ionic defects are anion interstitials or anion vacancies, scale growth occurs at the metal/scale interface.

Scale growth is limited by the diffusion of ions and electrons through a material. It follows that the growth rate is limited by the transport of the ions and electrons, and growth rate can be found as function of the activity of the reactants, the mobility of the ions/electrons, and properties of the scale. Wagner formulated a mathematical model for the diffusion-controlled growth of a dense one-phase scale on a pure metal: ²⁵

$$\frac{dn}{dt} = \frac{1}{\xi} \frac{RT}{2FF'Z_X^2} \int_{P_{X_2}^i}^{P_{X_2}^0} t_e(t_M + t_X) \sigma d \ln P_{X_2} \quad (43)$$

If a product with a high ionic conductivity, but a low electronic conductivity, is added to another phase with high electronic conductivity, corrosion may take place at a higher than expected rate. In addition, the reverse, low ionic conductivity, high electronic conductivity, and an addition of another phase with high ionic conductivity, can also lead to more rapid corrosion. For example, Ilschner-Gench and Wagner reacted a silver specimen with iodine vapor at 174°C and noticed a significant overgrowth of silver iodide onto the tantalum specimen holder. ²⁶

Compared to oxides, halides exhibit relatively high vapor pressures, which can lead to a simultaneous loss of the scale to a gas and scale growth from diffusional transport. ^[16] The thickening of the scale for a short initial period can be expressed in terms of scale growth and loss :

$$\frac{d\xi}{dt} = \frac{k_p}{\xi} - k_v \quad (44)$$

As the scale continues to get thicker the rate of growth and loss approach each other and the scale thickness reaches an equilibrium point, where scale thickness is equal to k_p/k_v . In addition to the growth and loss of the scale, the metal is also changing. The loss of metal can be written as : ^[16]

$$\frac{dy}{dt} = \frac{V_M}{V_{MX_v}} \left(\frac{d\xi}{dt} \right) + \frac{V_M}{V_{MX_v}} k_v = \frac{V_M}{V_{MX_v}} \left(\frac{k_p}{\xi} \right) \quad (45)$$

The mass change of the metal and scale can be written : ¹⁶

$$\frac{d\left(\frac{\Delta m}{A}\right)}{dt} = \rho_{MX} \frac{d\xi}{dt} - \rho_M \frac{dy}{dt} \quad (46)$$

Combining the three-previous equation gives a more general equation for the mass gain or loss of the material: ^[16]

$$\frac{d\left(\frac{\Delta m}{A}\right)}{dt} = \frac{vN_X}{V_{MX_v}}\left(\frac{k_p}{\xi}\right) - \rho_{MX_v}k_p \quad (47)$$

N_X is the atomic weight of the halogen. Once steady state scale thickness is achieved the rate of metal loss and scale growth is only dependent on the linear evaporation rate. ¹⁶ Reaction rate and the evaporation rate of the resulting product are the most important factors in erosion rates. The vaporization rate of materials is a function of when the molecules or atoms have enough kinetic energy to overcome the intermolecular forces at the gas/material barrier. The maximum possible evaporation rate assumes no condensation occurs and is given by the Hertz-Langmuir equation:

$$J_i = \frac{P_i}{\sqrt{2\pi m_i kT}} \quad (48)$$

The vapor pressure is a representation of the tendency of the particle to overcome the intermolecular forces. A more useful equation for the actual evaporation rate is :

$$G_i = \frac{\alpha_i P_i}{2.256 \times 10^{-2}} \left(\frac{M_i}{T}\right)^{\frac{1}{2}} \quad (49)$$

The degree of vaporization is the fraction of the maximum achievable vaporization that occurs at a specific set of conditions (pressure, temperature, etc..). Combining Eq. 9 and 12 gives a relation for the loss of metal:

$$\frac{dy}{dt} = \frac{\alpha_i V_{MX_v} P_i}{2.256 \times 10^{-2}} \left(\frac{M_i}{T}\right)^{\frac{1}{2}} \quad (50)$$

The degree of vaporization strongly depends on the pressure and temperature, and at low pressures, it may approach maximum evaporation. So, depending on the scale in question, if the

pressure is sufficiently low the limiting factor on erosion rate may be the transport of the reactive species through the boundary layer of vaporized products and reactive species. In the case where the flux of reactive species is significantly higher than the evaporation rate, the scale is expected to reach a partial chemical equilibrium with the partial pressure of halogen.¹⁶ The boundary layer thickness is given by :

$$\delta = 1.5LSc^{-\frac{1}{3}}Re^{-\frac{1}{2}} \quad (51)$$

The boundary layer is found with respect to a characteristic length of the system, material surface properties, and fluid properties. In the case where the diffusion of the halogen is too low for diffusion-limited vaporization of the scale, the scale will be completely consumed, and the vaporization rate will just be equivalent to the rate of arrival of the halogen.

In scale where the majority of ionic defects are cation vacancies, the layer grows via outward diffusion of cations as mentioned previously. The scale becomes more resistant to plastic deformation as it thickens and can lead to collections of vacancies and the formation of voids. The formation of voids results in a porous area at the metal/scale interface. The resulting material has compact columnar grains through most of the scale but with a porous area at the metal/scale interface. This morphology is most likely to form when the plasticity is low (low temperatures), impure metals with more reactive solutes, impure metals with impurities that react to form volatile products with the halogen, and at corners or edges where plastic deformation is limited due to geometry. The primary concern for the formation of a porous zone is the reduced scale/metal bond strength, which can lead to reduced protection from the scale through cracking or flaking. If the scale is broken in any way, the porous zone is unlikely to impact the rate of scaling or erosion unless material transport through the voids is especially fast.¹⁶

In the case where the main source of ionic defects is anion vacancies or anion interstitials, the layer grows via inward diffusion of anions. This process results in the scale growing at the metal/scale interface instead of at the scale/gas interface. The products typically take up a larger volume than the metal reactant, which results in the scale being forced to deform to make room for the new material forming at the metal/scale interface. As previously mentioned, as the scale thickens the ability to plastically deform reduces, which results in the scale cracking to make room for new material. The resulting cracking creates a significantly more porous scale that allows the reactants to more easily reach the metal and reduces the effectiveness of any potential protective scaling.¹⁶

The mechanisms for scaling are predominately understood through research of oxidation of alloys. The scaling of alloys is best understood by investigating the differing reaction rates of the components based on their thermodynamic stability.

2.5 Gas/Plasma and Solid Surface Interactions

A plasma introduces additional complexity to the problem of material interactions by adding charged particles. When an object is placed into a plasma, a sheath forms around it (sheaths and why they are formed are discussed in greater detail in the plasma basics section of this work). The result is an area where the ions in the plasma that reach the plasma-sheath boundary are accelerated towards the material of interest. An iodine plasma contains a combination of ions, electrons, photons, atomic iodine, diatomic iodine, excited states, and metastables that may be present at any given point.

Plasmas introduce a variety of impacts on materials primarily through bombardment by high energy ions but also introduce other effects as well. Dissociated iodine no longer has its

valence shell filled via the bond with another iodine and becomes even more reactive. Ionized iodine has even less electrons and lead to an increased reaction rate at the material surface. Excited states, and ions, introduce an additional source of energy that may provide enough energy to more easily overcome the activation energy of a reaction. In addition, a combination of phenomena can result in the reaction or erosion rate being varied what it is expected and ultimately can make it challenging to determine what the variation is due to. The figure below summarizes the primary interactions of a solid surface with a plasma.

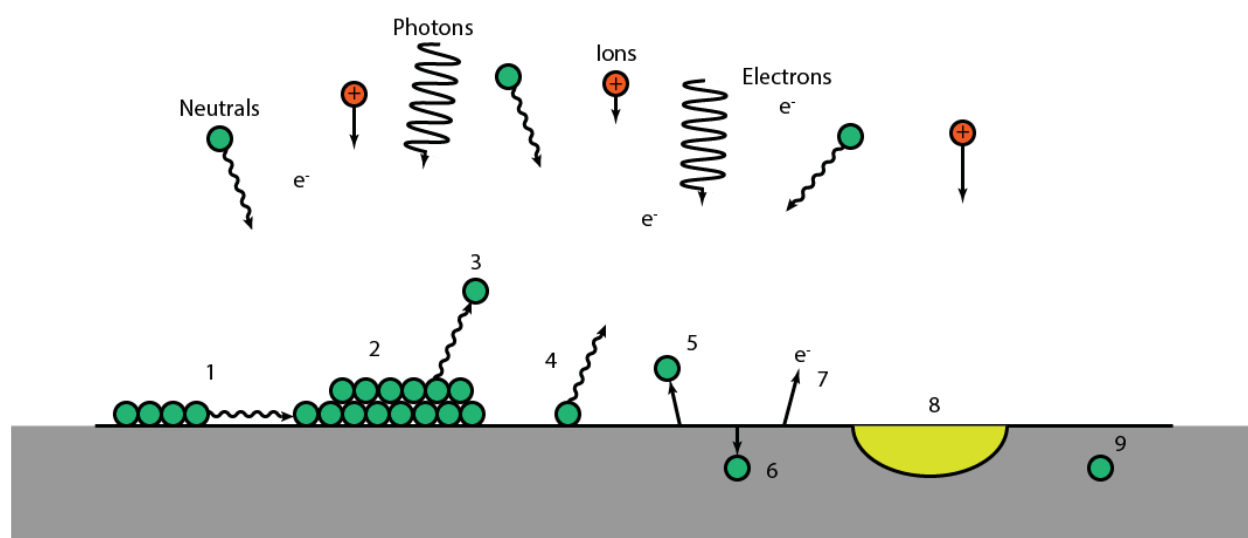


Figure 12 – Summary of Plasma-Material Interactions

In *Figure 12*, straight arrows indicate highly directional effects and wavy arrows indicate diffusion phenomena. Neutrals are primarily controlled via diffusion but in the event of recombination event after ion acceleration a neutral can also be directional.

Table 4 – Summary of Plasma-Material Interactions

Number	Interaction
1	Surface diffusion
2,3	Nucleation and growth
4	Adsorption, reaction, desorption, and reflection
5	Sputtering
6	Implantation
7	Secondary electron emission

8	Surface and near-surface damage
9	Trapped Species

The relatively high energy speed of the ions bombarding the materials surface results in a significant momentum transfer that can result in the formation of defects, heating, and phonon interactions in the surface and near surface region.²⁷ Energy transfer to the surface can lead to increased surface diffusion and defect mobility (particularly adatoms). As a result, materials can maintain more uniform surface properties than expected at lower temperatures, could provide increased transport mechanisms for reaction, or modify the surface crystal structure.

High energy particles that collide with the material surface are either incorporated by the material or reflected. If a particle is incorporated all the energy is transferred to the material surface or in the case of reflection only some of the energy is transferred. If the energy is higher than a few electron volts chemical bonds can be broken. If the energy is even higher ionization can occur. As a result, at the site of particle collision, chemical reaction rates can be increased, physisorbed and/or chemisorbed species can be removed, and nucleation or adsorption sites can form.²⁷ Particles that have been accelerated chemisorb more strongly than particles with only thermal-energy.²⁸ It is extremely difficult to separate the impact of reaction enhancement due to high energy particle bombardment, adsorption, and desorption due to apparent synergistic effects between them. For example, Coburn and Winters exposed a silicon sample to XeF₂ and an argon plasma together and separately.²⁹ Xenon difluoride by itself resulted in a pure chemical etch rate of about 0.5 nm/min, and the argon plasma by itself resulted in a pure sputtering rate of about 0.2 nm/min. When the two beams were combined, an etch rate of about 5.5 nm/min was measured. Clearly a synergistic effect between chemical reactions and energetic particles, which is believed to be due to ion-enhanced gas-surface chemistry.²⁹

When particles have even higher energies ($\geq 30\text{eV}$, almost always ions), the momentum transfer can result in ejection of particles from the surface instead of just a transfer of energy.³⁰ When ions collide with a surface, they set off a cascade of collision processes in the material. Once the cascade returns to the surface, any atoms with energies higher than the surface binding energy is ejected. So, the sputter rate or sputter yield, the average number of atoms ejected per incident ion, is a function of the incidence angle, momentum of the incident ion, the surface binding energy, and mass of the surface atom.

As previously stated, sometimes energetic particles are incorporated, called implantation, into the material instead of reflecting off the surface. The depth of implantation varies based on properties of the incident particles and the material (mass, energy, incidence angle, etc..). Implantation can result in what is called collisional mixing, which can be mixing of the implanted particle into the material or mixing of surface material. Collisional mixing can result in variations in surface properties due to defect creation or bond rearrangement.

According to theoretical studies, almost all the incident ions are neutralized very rapidly in the surface (a few atomic radii). It is hypothesized that due to Auger emission where the surface relaxes by emitting secondary electrons.^{30,31} Secondary electrons can also be produced from collisions with the surface layer. The secondary electrons are then accelerated into the bulk plasma and can impact the plasma parameters in sufficiently high quantities.

Weakly bound atoms or molecules can be trapped in a material surface when said species is covered by a different process taking place above it, from defects trapping ions usually mobile, or the formation of volatile species under the surface. A common form of trapping occurs when deposition happens on top of a weakly bound species.²⁷ Volatile species may form from a variety of the previously discussed phenomena energizing reaction below the surface.

2.6 Properties of Specific Metals and Associated Iodides

The next section aims to investigate the known iodides and erosion rates associated with the refractory metals of this study and an additional selection of metals commonly used in spacecraft. The primary refractory metals identified for this study are tungsten, tantalum, rhenium, and molybdenum. Stainless steel is prevalent in spacecraft construction and test setups and is added to the detailed study as a material for testing the experimental setup and to provide information to future researchers looking to design test setups (vacuum chambers, feed systems, etc.).

2.6.1 Stainless Steel

2.6.1.1 Iron

Iron forms two known iodide compounds: FeI_2 and FeI_3 . [10, 17] Iron (III) iodide forms as a gaseous compound only and leads to very rapid erosion. At standard conditions, iron reacts to form only one iodide, iron (II) iodide, which has either the CdI_2 - or $\text{Cd}(\text{OH})_2$ -type crystal structure. Iron (II) iodide is stable up to at least 1000°C in one atmosphere of iodine but melts at 590°C and maintains a vapor pressure of 10^{-4} atm at 475°C .³² The vapor phase of iron and iodine can contain FeI_3 , Fe_2I_6 , and FeI_2 .³²

Stainless steel has a significantly increased resistance to iodine, over carbon steels which are not particularly resistant to iodine at room temperatures. [33, 34] The erosion rate of various stainless-steel alloys from published data can be seen below.

Table 5 – Stainless Steel Alloy Erosion Rates³⁵

Stainless Steel Alloy	Corrosion Rate (mm/yr) @ 450°C
304	3.2
310	1.8
316	2.1

347	2.1
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2.6.1.2 Chromium

Chromium forms two known iodide compounds: CrI_2 and CrI_3 .^[10,17,18] At high temperatures, on the order of 2000°C, chromium reacts readily with iodine vapor.¹⁷

2.6.1.3 Nickel and Nickel Alloys

Nickel has been extensively tested with a fluorine, chlorine, and bromine but minimal testing has been performed with iodine. Previous work with the other three halogens has shown nickel to be relatively resistant to halogen attack.¹⁶ The previous work with the other halogens suggests nickel should be resistant to iodine attack.

Nickel forms one known iodide compound: NiI_2 , which has a relatively high melting point (800°C) and a low vapor pressure saturation point.^[17,16] Nickel (II) iodide sublimes in high vacuum at 500-600°C.^[17] This results in very minimal expected erosion rates at low temperatures, but the protection provided by the scale probably reduces once the NiI_2 begins to evaporate. Published corrosion rates for nickel include 0.27 mm/year at 300°C and 1.2 mm/year at 450°C at an iodine gauge pressure of 400 torr.^[36] Based on qualitative data from Mott and Arbellot, Hastelloy B and C are likely suitable for dry and moist iodine vapor at room temperatures and pressures.^[34,37]

2.6.2 Tungsten

Tungsten has been used in metal iodide transport apparatuses as hot filament materials for decomposition of metal iodide compounds and is commonly used as a filament in halogen lamps. The filaments were operated at a temperature in excess of 1400°C. Iodine forms three known iodides WI_2 , WI_3 , and WI_4 . Tungsten triiodide is very unstable and rapidly decomposes

after formation. Tungsten diiodide can be prepared by reacting iodine vapor with tungsten heated to 727°C, but tungsten diiodide and tetraiodide are only stable solids at standard atmosphere up to 227°C and 137°C respectively. ^[17]

Published corrosion rates for tungsten in iodine vapor include 0 mm/year at 300 °C and 0.008 mm/year at 450 °C at an iodine pressure of 400 Torr. ^[36] The relatively low erosion rates, and high temperature characteristics, make tungsten a common material for high temperature filaments. In halogen lamps filled with iodine, the iodine reacts with tungsten deposited on the lamp walls to form tungsten diiodide. The tungsten diiodide then transport to the hot filament and decomposes and redeposits tungsten on the filament. ^[38] The result is that in sealed systems the presence of iodine gas reduces the loss of tungsten on the filament due to a transport mechanism back to the filament, but in a non-sealed system tungsten can be transported away with the flow or towards a different hot surface.

2.6.3 Molybdenum

Molybdenum has been used in metal iodide transport apparatuses as hot filament materials for decomposition of metal iodide compounds. ^[39,40 ,41]

The molybdenum filaments were operated at a temperature in excess of 1400°C. Molybdenum forms three known iodides: MoI₂(s), MoI₃(s), and MoI₄(v). ^[42] Published corrosion rates for molybdenum in iodine vapor include 0.003 mm/year at 300 °C and 0.033 mm/year at 450 °C. ^[36]

2.6.4 Tantalum

Tantalum forms four known iodide compounds: Ta₆I₁₄, TaI₃, TaI₄, and TaI₅. ^[10,20,17,18,21,22] Ta₆I₁₄ is the most stable of the tantalum iodides. Ta₃ only forms when solid tantalum is in contact

with the TaI_5 gas. TaI_4 decomposes into Ta_6I_{14} at 450°C . TaI_5 has the lowest melting point, at 496°C , and is the most likely provides the highest vapor transport mechanism. Tantalum has a similar interaction with higher vapor pressures as titanium and has a dramatically higher erosion rate at high vapor pressures.

2.6.5 Rhenium

Rhenium forms three known iodides: ReI , ReI_3 , and ReI_4 with ReI_3 being the most stable. ^[17] None of the rhenium iodides are particularly easy to form and when rhenium and iodine are placed in a sealed tube at an elevated temperature no reaction occurs. ¹⁷ Minimal information on the reaction kinetics of rhenium is available, but several of the low valence iodides are thermodynamically stable around room temperature. ^[16]

2.6.6 Miscellaneous

Element	Melting Temperature (K)	Iodide Melting Point (K)	Di-Iodide Melting Point (K)	Tri-Iodide Melting Point (K)	Tetra-Iodide Melting Point (K)	Penta-Iodide Melting Point (K)
Aluminum [¹⁰ , ¹⁷]	933	Product of liquid Al + AlI ₃ at 1273K	Unstable	Al ₂ I ₆ ~ 464K	No Data	No Data
Cobalt [¹⁰ , ¹⁷]	1768	No Data	758-793	No Data	No Data	No Data
Copper [10,17,43,44]	1358	861-879	Not Stable Decomposes to form CuI	No Data	No Data	No Data
Gold [10,17]	1337	Decomposes from 323-463 in vacuum	No Data	Unstable and decomposes at 293	No Data	No Data
Iodine [10]	387	N/A	N/A	N/A	N/A	N/A
Iridium [10,17]	2992	Decomposes at 800K	Disproportionates	Decomposes at 700K	No Data	No Data
Iron [10,17]	1811	No Data	860-867	Forms in vapor phase only, with FeI ₂ in I ₂ gas	No Data	No Data
Niobium [10,17,18,45]	2750	Does not exist	Nb ₂ I ₃ melts at > 1000	Sublimes in vacuum @673 Decomposes to Nb ₂ I ₈ @ 799	776	673
Platinum [10,17]	2041	No Data	Decomposes at 598	No Data	Decomposes @ 403	No Data
Silver [10,17]	1235	931	No Data	No Data	No Data	No Data
Titanium [10,17,46]	1943	No Data	873	Decomposes into solid TiI ₂ & TiI ₄ in I ₂	429	No Data
Zinc [10,17]	693	Decomposition product of ZnI ₂	719	No Data	No Data	No Data
Zirconium [10,17,35]	2127	No Data	1100	1000	772	No Data

2.6.6.1 Aluminum and Aluminum Alloys

Aluminum forms three known iodide compounds: AlI, AlI₂, and AlI₃. [¹⁰,¹⁷] Aluminum iodide only forms when AlI₃ comes into contact with liquid aluminum. Aluminum di-iodide is unstable and won't form readily in the expected conditions. In aluminum alloys, AlI₃ is the only

compound of concern. The melting point of AlI_3 (189.4°C) is lower than the expected 200°C , so aluminum is expected to readily erode in testing. Aluminum has a published corrosion rate of greater than 1.3mm/year at room temperature. ^[47]

2.6.6.2 Carbon and Carbon Composites

Carbon forms four known iodide compounds: C_2I_2 , C_2I_4 , C_2I_5 , and CI_4 . These compounds have the following melting points: C_2I_2 (82°C), C_2I_4 (192°C), C_2I_5 (377°C), and CI_4 (-129°C). ^[17] Carbon fiber should theoretically react to the iodine and then shrink due to erosion.

2.6.6.3 Titanium and Titanium Alloys

Titanium forms three known iodide compounds: TiI_2 , TiI_3 , and TiI_4 . The titanium iodides having the following melting points: TiI_2 (600°C), TiI_3 (156°C), and TiI_4 (156°C). ^[10,17,46] The melting point of TiI_3 is lower than AlI_3 so titanium is expected to erode faster than aluminum. Similar to aluminum titanium forms an oxide layer that protects the material until it is eroded away. At higher vapor pressures the formation of gaseous titanium iodides should rapidly erode the material and as such, it not likely to be useful in feed systems. The protective oxide layer of the titanium will minimize the effects of iodine plume interactions and should be acceptable for use in structural components.

2.6.6.4 Copper and Copper Alloys

Copper forms two known iodide compounds: CuI and CuI_2 . CuI_2 is unstable and rapidly decomposes into CuI . ^[10,17,43,44] Zinc, typically found in copper alloys, forms two known iodide compounds: ZnI and ZnI_2 . ^[10,17] Copper and copper alloys readily react and erode, and neither should be suitable for iodine contact.

2.6.6.5 Silver, Gold, Platinum

Silver forms one known iodide compound: AgI, which has a melting point of 558°C.

^[10,17] No corrosion rates for silver have been published. Gold forms two iodide compounds but both decompose at low temperatures. ^[10,17] Gold has two published corrosion rates in 0.53 atm of iodine vapor: <0.μ36m/year at 300°C and 0.024mm/year at 450°C. ^[36] Gold has been used as seals to prevent the escape of iodine and metal iodide vapors in a metal iodide transport apparatus as patented by Z.M. Shapiro. ^[39] Platinum has two known metal iodide compounds that decompose at higher temperatures than gold iodides. ^[10,17] Platinum has two published erosion rates in iodine vapor: 0mm/year at 300°C and 0.006mm/year at 450°C. ^[17] The relatively low erosion rates indicate that platinum could be used as a seal material where gold begins to soften due to heating.

2.6.6.6 Lanthanum and Cerium

Lanthanum and cerium are of interest for use in hollow cathode inserts as LaB₆ and CeB₆. Lanthanum forms only one known iodide: LaI₃ and has a melting point of 761°C. Lanthanum triiodide has been produced with a reaction of La₂O₃, I₂, and Al. ^[17] Cerium has one known iodide: CeI₃ and has a melting point of 752±2°C. Cerium Triiodide can be formed by heating cerium and gaseous iodine at red heat in vacuum. ^[17] Cerium is expected to react more readily with iodine and would most likely not be suitable as lanthanum for exposure to iodine.

2.6.6.7 Iridium

Iridium forms three known iodides: IrI₃, IrI₂, and IrI. Iridium and iodine do not react at 80-100°C. ^[17]

2.7 Characterization Devices

2.7.1 Scanning Electron Microscopy

The main objective of microscopy is to resolve visual features that otherwise impossible to view without any assistance. The naked eye can resolve a minimum feature size of around 0.1mm. Microscopy is divided into three major categories: optical, electron, and scanning probe. Optical and electron microscopy both rely on the same operating principle of a source beam diffracted, reflected, or refracted by a specimen and then collected to form an image. The difference lies in the type of beam used. In optical microscopy electromagnetic radiation is used, but in electron microscopy an electron beam is used. Scanning probe microscopy uses a probe in physical contact with the specimen and actuates a sensor as it moves.

Optical microscopy uses visible light and can produce an accurate color representation of the sample of interest but reaches a resolution limit due to the diffraction properties of light. Electron microscopy has a much higher resolution limit due to electrons have a much lower wavelength than visible light, which means the diffraction effects become a problem at significantly smaller feature sizes.

Table 6 – Selected Differences between Electron and Optical Microscopy ⁴⁸

	Electron	Optical
Beam Type	Accelerated electron (20-100+kV)	Electromagnetic Radiation
Lens Type	Magnetic or Electrostatic	Optical lens
Beam Wavelength	0.037-0.859 Å	2000-7500Å
Operating envelope	Vacuum	Atmosphere
Magnification	90-800,000x	10-2000x
Resolution	1.4Å – Lattice 3Å - Point to Point	3000Å – visible light 1000Å – UV light

Table 1 clearly demonstrates how electron microscopy can resolve features significantly smaller than what optical microscopy can do. For materials characterization, electron microscopy can provide significantly more information on the specimen of interest than optical microscopy.

Electron microscopy is further split into two different categories based on how the electron beam interacts with the specimen: transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM looks at electrons transmitted through the sample, and SEM looks at backscattered electrons emitted from the surface of the specimen. TEM requires much higher accelerating voltage ($>100\text{kV}$) and very thin samples ($<100\text{nm}$) to transmit the electrons through the sample but provides information about the internal composition of the material such as morphology, crystallization, stresses, and magnetic domains.⁴⁸ SEM, on the other hand, only requires accelerating voltages on the order of $10\text{-}40\text{kV}$ and thickness of the sample is only limited by the physical size of the device. As a result of collecting emitted electrons, SEM only provides information about the surface of the sample but is an excellent tool for surface characterization. TEM has a significantly higher resolution than SEM, but SEM has a higher depth of field.

The primary interest is the surface changes due to exposure to a plasma. SEM is the preferred tool. The limiting factor in optical and electron microscopy is the diffraction effects on their respective sources. The criterion of interest is the resolution, which can be described more accurately as the resolvable distance between two objects. The resolvable distance is the distance two objects need to be apart in order for them to be easily recognized as two different objects. Due to diffraction, the smallest objects will appear as Airy discs, a small spot surrounded by halos. When the maximum of one Airy disc intersects with the first minimum of the other disc the images are overlapping but can still be distinguished as two different objects. The resolution

limit is found at the point where the overlap forms a blur that can no longer be distinguished as two different objects. This limit is known as the Rayleigh criterion, which states that two points can be resolved if maximum of the first disc intersects with the minimum of the other disc.⁴⁹ The result is that the minimum resolvable separation can be found as a function of the wavelength, refractive index, and angle the sample is viewed at.

$$d_0 = \frac{0.66\lambda}{n \sin \alpha} \quad (52)$$

From the above equation, it is clear that decreasing the wavelength will decrease the size of the minimum resolvable separation.

In SEM, electrons are generated and focused into a narrow beam used to scan across the specimen surface. These primary electrons from the beam hit the surface of the specimen and interact with the atomic electrons by imparting energy. The imparted energy is then remitted through a variety of processes. The volume that the primary electrons are scattered through in the material is known as the interaction volume, which is dependent on the atomic number, density of atoms, and primary electron energy. Materials with atomic number and/or atom concentration reduce scattering and high electron energy increases scattering. Inside this interaction volume the primary electrons interact with the atoms (nuclei and electrons) due to Coulomb interaction and produce secondary electrons, backscattered electrons, x-ray, and visible light (cathodoluminescence) and are collected by various instruments.

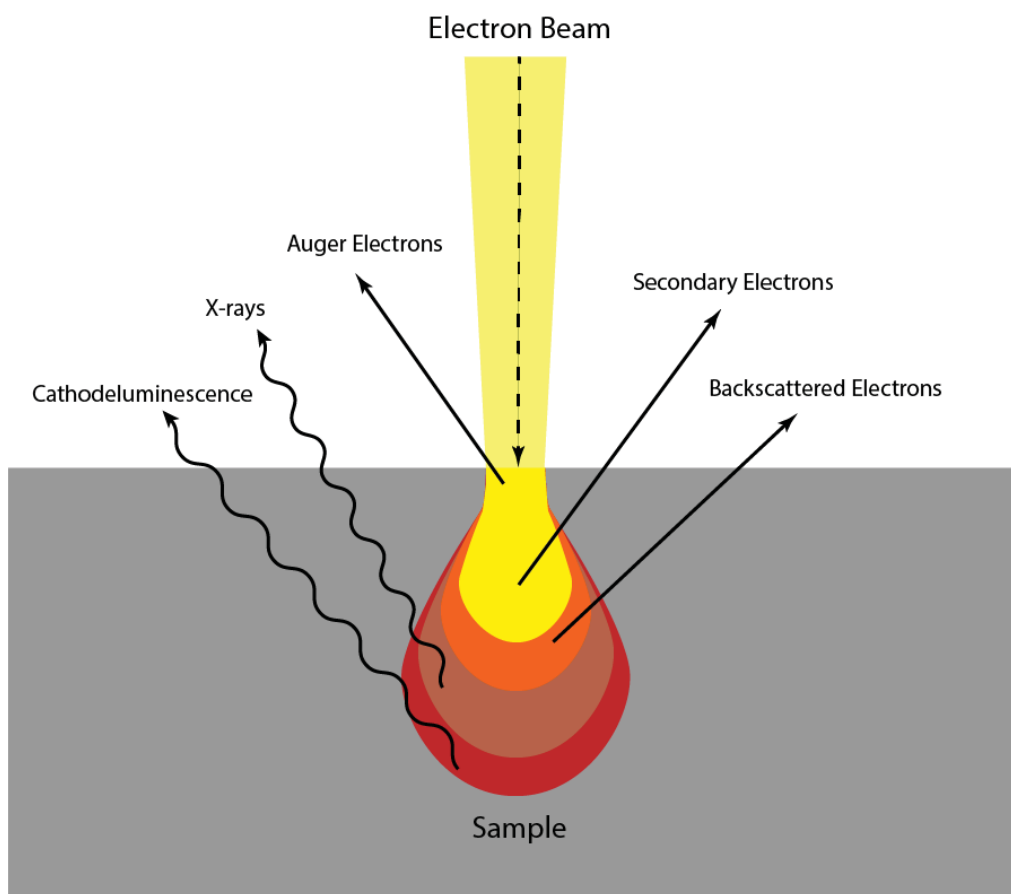


Figure 13 – Electron Beam Interaction with Sample

Secondary electrons are produced from collisions of the primary electrons and weakly bonded outer electrons and are relatively low energy ($<50\text{eV}$). Due to their low energy, secondary electrons have a very low escape depth and are produced near the surface, which provides information on the topography and surface morphology. Backscattered electrons are primary electrons reflected by the atoms and have a relatively high energy. The number of backscattered electrons increases with higher atomic number, which means that backscattered electrons can be used to determine surface composition. X-rays are generated through inelastic interactions of the primary electrons with the electrons in orbitals. Depending on the orbital the

generated X-rays are different, and the combination of these X-rays provides a unique “fingerprint” for each element, which can be used to determine elemental composition.

2.7.2 X-ray Diffractometry

An important aspect of the behavior of materials is based on the crystal structure and how defects impact that structure. Fortunately, a result of the crystal structure is that electromagnetic radiation scatters when it interacts with the atoms of the crystal structure in a very specific way. An object struck by a wave will create a secondary wave with a spherical form, and an array of similarly spaced objects will create an array of spherical waves. The end result is an array of waves that cancel out in most directions through deconstructive interference, but combine constructively in a few directions which can be represented mathematically by Bragg’s law:

$$2d\sin\theta = n\lambda \quad (53)$$

Ideally to create significant diffraction, the spacing between the objects causing the scattering needs to be of a similar magnitude as the wave being scattered. So, in order to investigate the crystal structure of a material, an electromagnetic radiation source needs to be chosen with a wavelength compared to the spacing of the crystal planes, such as X-rays.

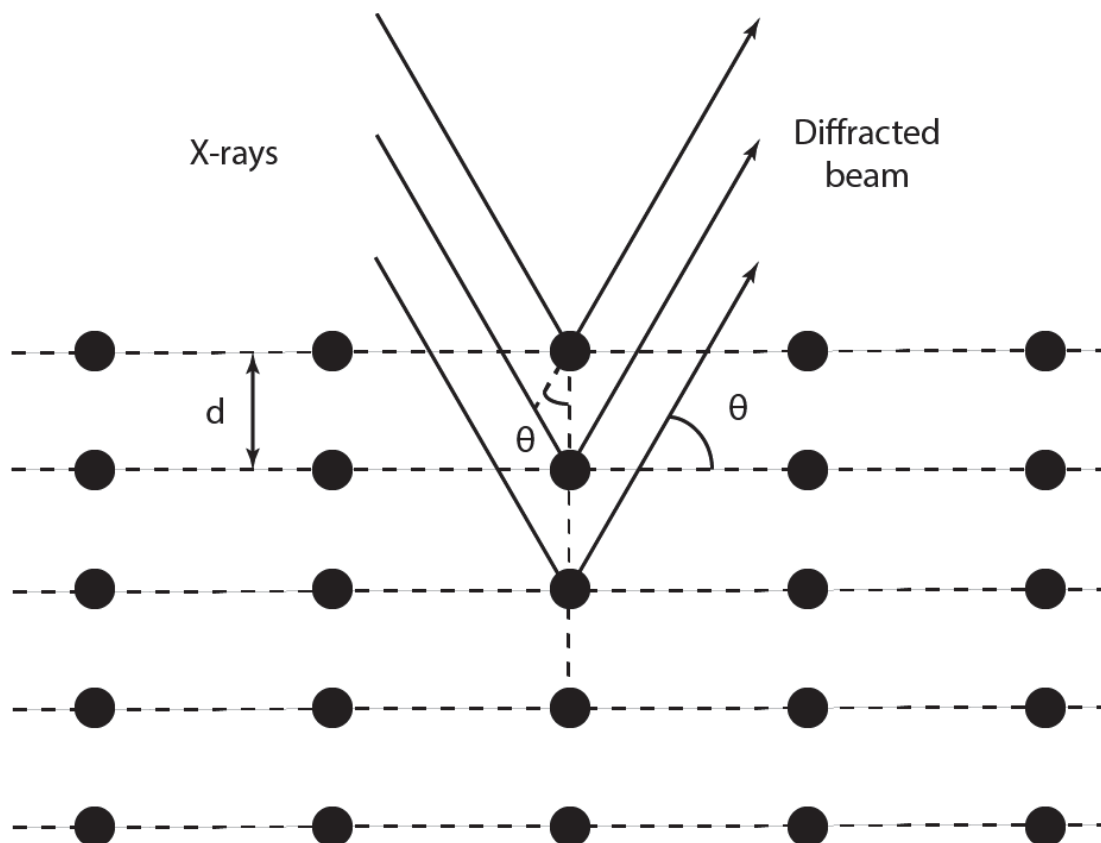


Figure 14 – X-Ray diffraction

It is easiest to imagine the diffraction in a crystal structure as X-rays colliding and being diffracted by hard spheres, but in reality, the X-rays are interacting with the electrons of each atom. The result is that an X-ray source can be scanned across a material at varying incidence angles and the intensity of the diffracted X-rays can be measured to give a so-called diffraction pattern. An example diffraction pattern for tungsten is shown below.

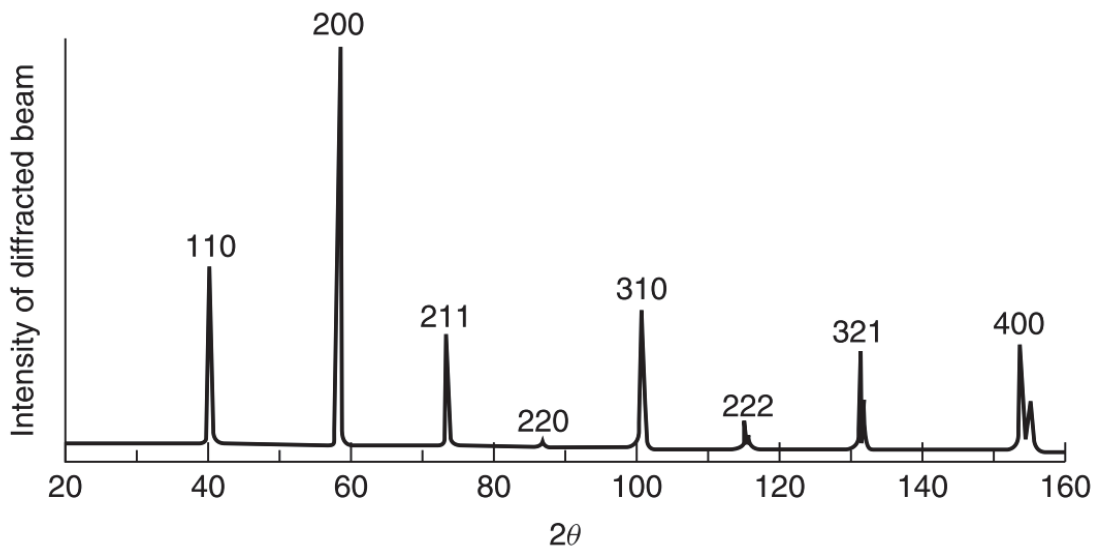


Figure 15 – Example X-Ray diffraction pattern for tungsten

In *Figure 15*, the x-axis is given in terms of 2θ which is done as a convention due to the instrumentation used. It is important to note that the Miller indices (numbers above peaks) increase with increasing 2θ and that different planes (seen as peaks) have different intensities. Using the incidence angle the interplanar spacing can easily be determined using Bragg's law.

Identification of crystal structure in an experimental setting is usually done via matching a material's diffraction pattern to existing diffraction patterns for well characterized materials.

2.7.3 X-ray Photoelectron Spectroscopy

Scanning electron microscopy and X-ray diffractometry can both provide information about the state of the material being investigated but are limited in compositional studies. With the use of EDS (EDX) techniques, SEM can provide a useful qualitative measure of the elemental composition of the material. X-ray diffractometry provides a relatively simple and fast method of investigating the crystallography of the material. Neither techniques provide particularly detailed information about the chemical composition. A more complete picture of a

material is attained by combining multiple different techniques. In order to get more information about the chemical composition spectroscopic techniques can be used by looking at the state of the atoms or molecules of the material. In spectroscopic methods, the material of interest is excited with an energy source and the material either absorbs or emits light or electrons based on unique transitions of the electronic states.

Spectroscopic techniques for material analysis can take a variety of approaches based on the energy used for excitation and whether absorption or emission is being measured. For this work, primarily photoelectron emission spectroscopy (PES) will be investigated, where electrons are emitted after being excited by an energy source.

When a material is illuminated with electromagnetic radiation of a sufficiently high energy, electrons from a specific energy level are ejected from the source atoms with a specific kinetic energy. The goal of PES is to measure the energy of the ejected electrons to determine the energy level (or orbital shell) it was ejected from. The energy of the emitted electrons is given by the Einstein equation for the photoelectric effect:

$$E = h\nu - h\nu_0 - \phi \quad (54)$$

ν_0 is the threshold frequency and ϕ is the work function of the material. The threshold frequency is based on the specific orbital the electron is ejected from. So, the energy of an electron describes the state it was ejected from and the number of electrons at a given energy level describes the density of said states.

In PES, the photoelectron current is the result of the characteristics of the excitation photons and the ejected electrons. The photons and electrons are described by their direction and polarization. So, the photoelectron current can be written as a function of this characteristics:⁵⁰

$$I = F(E_{ph}, \theta_{ph}, \varphi_{ph}, p_{ph}; E_{el}, \theta_{el}, \varphi_{el}, p_{el}) \quad (55)$$

E is the energy, θ is the polar angle, φ is the azimuthal angle, and p is the polarization. The methods of sorting the components of the photoelectron current vary depending on the type of device. Three common techniques are energy-dispersive curve (EDC), angle-resolved (ARPES), and spin resolved photoelectron spectroscopy (SRPES). In EDC, the photoelectrons are measured as a function of energy and the other parameters are kept fixed. In ARPES, the electron azimuthal and polar angles are resolved in addition to the energy. In SRPES, the electron spin is also resolved in addition to the parameters normally resolved in ARPES.⁵⁰

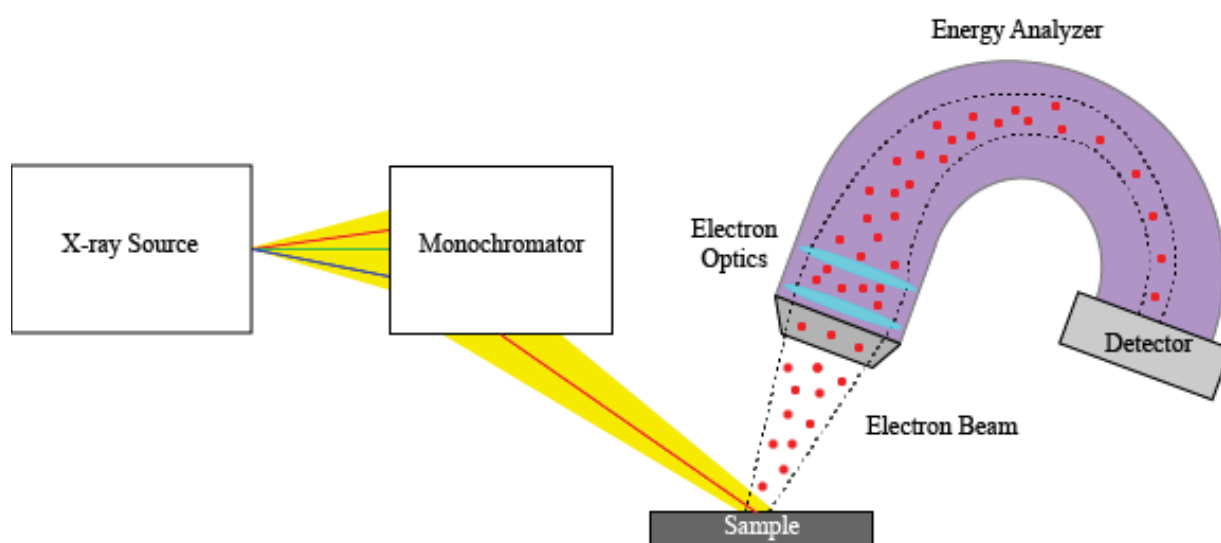


Figure 16 – Basic block diagram of how a photoelectron spectroscopy works

The electron optics guide the electrons into an electron energy analyzer, which splits electrons into different groupings based on their energy level. The electron detector then measures the number of electrons in each respective energy level grouping.

The radiation source for sample excitation is important because different electron states require different energy sources to cause ejection. To study the core states (from 200 to 2000eV), X-ray sources are typically used due to their high frequency. To study valence and conduction band states typically ultraviolet sources are used.

3 Inductively Coupled Plasma Sources

3.1 Plasma Physics Basics

The primary focus of this work is on the interaction between an iodine plasma and various spacecraft materials and as such a brief overview of plasma generation and properties are given in the next section. This section provides a brief overview of plasma physics. Special attention is devoted to inductively coupled sources. Chen defines a plasma : “A *plasma is a quasineutral gas of charged and neutral particles which exhibits collective behavior*”. ^[51] As a rough overview, to be plasma a substance needs to meet three major criteria:

1. the physical length scale of the system must be significantly larger than the Debye length

$$\frac{L}{\lambda_D} \gg 1 \quad (56)$$

2. A significant number of charge particles must exist within the Debye sphere

$$N_D \gg 1 \quad (57)$$

3. The electron plasma frequency must be faster than the gaseous collisional timescale

$$\frac{\omega_{pe}}{\nu_c} \gg 1 \quad (58)$$

3.1.1 Ionization

On a surface level ionization occurs when an atom is provided with sufficient energy to eject an electron. For the purpose of this discussion, an atom is composed of a very small nucleus composed of protons and neutrons with a total dimension of around 10^{-12} cm and is surrounded by a much larger area (about 10^{-18}) filled with electrons diffusely spread out in specific areas (orbitals). This electron cloud has a base specific energy distribution based on the internal energy and internal angular momentum of the atom. From this base state (ground state)

the atom can only absorb energy in specific discrete quantities (quanta), which raises the electrons to higher energy configurations. These higher energy configurations are progressively farther and farther away from the nucleus. Once an electron moves far enough away from the nucleus it detaches and creates a positively charged ion and a free electron. The sum of the quanta required to release an electron is known as the ionization potential.

An atom can reach its ionization potential through one event or a sum of smaller events. These events can take any one of the following forms:

- Inelastic collision: an atom undergoes an inelastic collision with a sufficiently high energy particle.



- Photoionization: an atom absorbs a sufficiently high frequency photon



- Field ionization: a strong electric field removes an electron from the atom



- Charge-exchange ionization: a strong valence interaction results in an electron being transferred from one atom to the other



The ionization of molecules adds the additional facet of internal rotation and vibrations modes that can interact with the electronic mode. In addition, the occasional reaction results in an ion and electron pair, which is known as chemical ionization. While the above ionization processes are going on, electrons are being recaptured by atoms in recombination processes. The recombination events can take any of the following forms:

- Radiative Recombination



- Three-body Recombination



- Dissociative Recombination



- Dielectronic Recombination



- Electron-attachment (negative ionization)



- Negative ion recombination



In the case of a pure and atomic gas, the above recombination and ionization processes can be simplified into one reaction:



ε_i is the energy required for ionization. By introducing a rate constant in terms of the internal and translational partition functions, an equation can be derived for the degree of ionization as shown by Meg Nah Saha in the now famous Saha equation:

$$\frac{\alpha^2}{1 - \alpha^2} = \frac{2(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{ph^3} \left(\frac{f_+^i}{f_A^i} \right) e^{-(\varepsilon_i/kT)} \quad (71)$$

3.1.2 Quasi-neutrality and the Debye Length

Ionization results in a collection of positively and negatively charged particles affected by external electric and magnetic fields but also can produce electric fields and magnetic fields through the motion of said charge particles. The resulting internal and external electric and magnetic fields interact with one and another and create a complex situation that obeys Maxwell's equations but needs to be solved self-consistently with the particle motions and electromagnetic fields.

As mentioned in the introduction, the physical length scale of the system needs to be significantly larger than the Debye length. In simple terms the Debye length is a measure of how far a charge group's electrostatic effect persists. An equation for the Debye length can be derived starting with Poisson's equation:

$$\nabla \cdot \mathbf{D} = \nabla \cdot \epsilon \mathbf{E} = e(n_i - n_e) \quad (72)$$

Where D is the electric displacement field, E is the electric field, ϵ is the permittivity, e is the charge of an electron, n_i is the ion number density, and n_e is the electron number density. The electric field is a result of a potential, V , :

$$\mathbf{E} = -\nabla V \quad (73)$$

Substituting Eq. 16 into Eq. 15, results in :

$$\nabla^2 \phi = \frac{e}{\epsilon_0} (n_e - n_i) \quad (74)$$

Defining the system in one dimension simplifies the analysis without ignoring the physical processes. Take a plane with a fixed potential at the origin and assume that the inertia of the ions is large enough to prevent them from moving. In this one-dimensional system Poisson's equation can be written :

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\varepsilon} (n_i - n_e) \quad (75)$$

The number density far away, n_∞ , so at far away points:

$$n_i = n_\infty \quad (76)$$

Assuming a potential energy of $q\phi$, the electron distribution function is :

$$f(u) = A \exp \left[-\frac{\left(\frac{1}{2} mu^2 + q\phi \right)}{kT_e} \right] \quad (77)$$

The charge can then be set equal to $-e$ and the electron distribution function can be integrated over u .

$$n_e = n_\infty \exp \left(\frac{e\phi}{kT_e} \right) \quad (78)$$

Where the electron density is assumed to equal the number density at far away points as the potential approaches zero. Combining Eq. 18 and 20 results in :

$$\varepsilon_0 \frac{d^2\phi}{dx^2} = en_\infty \left[e^{\frac{e\phi}{kT_e}} - 1 \right] \quad (79)$$

Expanding the exponential in a Taylor series where $|e\phi/kT_e| \ll 1$ and only keeping the linear terms gives :

$$\varepsilon_0 \frac{d^2\phi}{dx^2} = \frac{n_\infty e^2}{kT_e} \phi \quad (80)$$

Introducing and solving for a length scale that the potential varies across gives the following result:

$$\lambda_D = \left(\frac{\varepsilon_0 kT_e}{n_\infty e^2} \right)^{\frac{1}{2}} \quad (81)$$

The natural length scale, λ_D , is called the Debye length. This Debye length is where the electrostatic no longer persists and results in a shielding effect where charges struggle to overcome the potential energy resulting from the potential. It is important to note that since electrons are significantly more mobile than the ions they are the source of the shielding, and the equation represents this phenomenon by using electron temperature.

When the physical length scale of system is significantly larger than the Debye length, external fields and charge concentrations create small areas of shielding and most of the plasma experiences minimal electric potentials. Since the plasma is relatively free fields and potentials, the expected number densities of electrons and ions will be very close to equal and is called “quasineutral”.

The final two considerations for a gas to be considered a plasma require the charged particle densities to be sufficiently high to exhibit “collective behavior” and for particle collisions to take place frequently enough for electromagnetic forces to have a significant impact. The previously discussed Debye shielding requires non-negligible number of particles for it to be a statistical valid concept. The number of particles contained inside the sphere that the Debye length forms can be found with :

$$N_D = \frac{4}{3} n \pi \lambda_D^3 \quad (82)$$

The “collective behavior” requirement is satisfied when the number of particles inside the Debye sphere is significantly greater than one and the Debye length is significantly smaller than the characteristic length. The particle collisions criterion is satisfied when the plasma oscillation frequency is significantly higher than the collisional timescale.

3.1.3 Sheath Formation

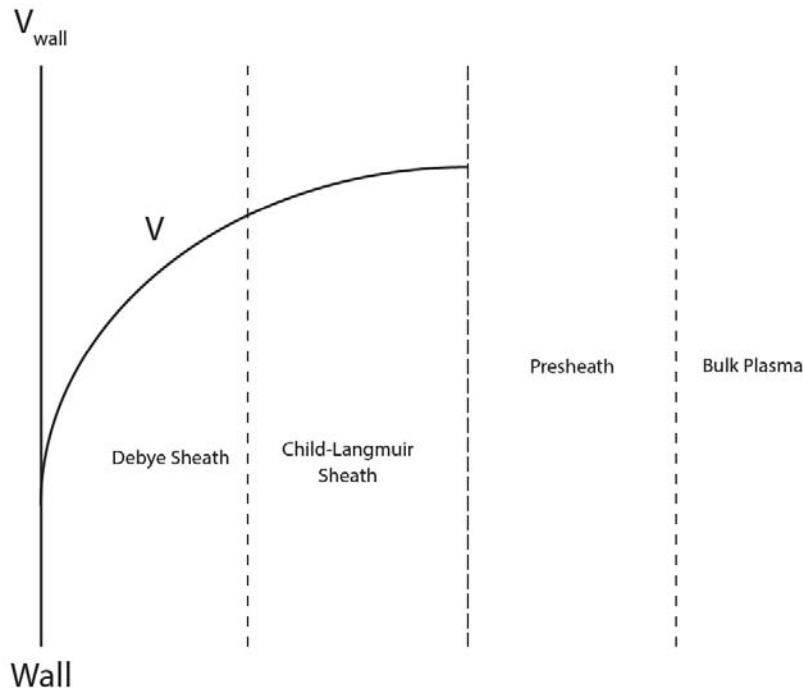


Figure 17 – Planar Sheath

Since electrons are significantly more mobile than ions, objects in a plasma experience a significantly greater flux of electrons and typically charge negatively with respect to the plasma potential. The transition region between the negative potential, with respect to the plasma, and the plasma is called the plasma sheath. In discussion, the sheath is typically split into several different components based on their characteristics: the Child-Langmuir sheath, the Debye sheath, and then the presheath. In the Child-Langmuir sheath the electron density is a negligible value. In the Debye sheath the electron density drops exponential with respect to the voltage. At the edge of the sheath the electron distribution is isotropic, and the ion distribution is unidirectional, due to the probe absorbing the incoming ions. In order to have a unidirectional ion direction, an electric field at the sheath edge accelerates ions which results in the Bohm current:

$$I_B = \alpha neAc_s \quad (83)$$

$$c_s = \left(\frac{kT_e}{m_i} \right)^{\frac{1}{2}} \quad (84)$$

I_B is the Bohm current, m_i is the ion mass, c_s is the terminal ion velocity in the sheath or the Bohm velocity, A is sheath area, and α is a constant. This region with an electric field is known as the presheath and meets the plasma which is neutral and electric field free.

The solution for the combined Debye and Child-Langmuir sheath, in a plane, can be found from Poisson's equation:

$$\frac{d^2V}{dx^2} = \frac{e}{\epsilon_0} (n_e - n_i) \quad (85)$$

In order to solve Poisson's equation a boundary for the sheath must be chosen, otherwise the density at infinity would have to be infinite to give an ion velocity of zero and a finite ion flux. A significant dispute in literature over where the sheath edge should be defined. [52,53,54,55] For this work, the sheath edge will be defined at the edge of the Debye sheath where the Bohm formula is valid. At the sheath edge the voltage is set to zero. For Maxwellian electrons the number density is :

$$n_e = n_s e^{\frac{eV}{kT_e}} \quad (86)$$

According to energy conservation the ions:

$$\frac{1}{2} m_i v_i^2 = \frac{1}{2} m_i c_s^2 - eV \quad (87)$$

And continuity of the ion flux is given by :

$$n_i v_i = n_s c_s \quad (88)$$

Which gives the following relation for the ion number density:

$$n_i = n_s \left(1 - \frac{2eV}{m_i c_s^2} \right)^{-\frac{1}{2}} \quad (89)$$

Substituting the electron and ion number densities into Poisson' equation gives :

$$\frac{d^2 V}{dx^2} = \frac{e}{\epsilon_0} n_s \left[e^{\frac{eV}{kT_e}} - \left(1 - 2 \frac{eV}{kT_e} \right)^{-\frac{1}{2}} \right] = - \frac{kT_e}{e} \frac{d^2 \left(\frac{eV}{kT_e} \right)}{dx^2} \quad (90)$$

The above equation does not have an explicit solution and requires initial boundary conditions at the sheath edge. Finding boundary conditions at the sheath edge requires matching to the presheath, which are complicated, vary based on the discharge, and may not be possible. For the purpose of this work it is far important to understand that ions are accelerated towards an object whether it has a potential on it or not.

3.2 Inductively Coupled Plasma Source

3.2.1 Introduction

An inductively coupled plasma (ICP) source is a type of plasma source that supplies energy to a gas through electromagnetic induction. ICP's are a form of electrodeless discharge. Electrodeless discharges are discharges where the plasma is not in contact with the source of the electric field. The first electrodeless discharge was demonstrated by Hittorf in 1884. ^[56] Electrodeless discharges were later categorized by Babat in the 1940's as H-type (inductive) and E-type (capacitive) discharges. ^[57]

H-type discharges are excited by an applied radio frequency electric field, so the conduction current in the plasma is closed. The sheath voltages in H-type discharges are on the order of the mean energy of the electrons, which is low and comparable to dc discharges. ^[58] E-type discharges are excited primarily by the applied electrostatic field and do not have a closed

conduction current. The resulting sheath voltages are relatively high due to most of the voltage drop occurring near the electrodes. Due to the fact that ICP's do not have the high electrostatic fields that CCP's have, ICP's experience lower ion losses to walls and can more efficiently produce high density discharges.

Inductively coupled plasma sources have two primary benefits: they do not require internal electrodes and do not require an external magnetic field.

In an ICP, electromagnetic induction produces electric currents through a time-varying magnetic field produced by a time-varying electric current, typically in the radio frequency range. The resulting time-varying magnetic field has the following flux:

$$\Phi = \iint_{\Sigma(t)} \mathbf{B}(\mathbf{r}, t) \cdot d\mathbf{A} = \pi r^2 H_0 \cos \omega t \quad (91)$$

This flux results in an azimuthal electromotive force according to Faraday's Law of Induction.

$$\mathcal{E} = -\frac{d\Phi}{dt} \quad (92)$$

The electromotive force corresponds to an electric field strength found by :

$$E = \frac{\mathcal{E}}{2\pi r} = \frac{\omega r H_0}{2} \sin \omega t \quad (93)$$

The induced electric field drives a current of charged particles and results in figure-eight electron trajectories, which at sufficient energy levels generate plasma.

$$\bar{J} = \sigma \bar{E} \quad (94)$$

3.2.2 Applications of Inductively Coupled Plasma Sources

The simplicity of inductively coupled plasma sources make them an incredibly attractive solution for many research and industrial applications.

The semiconductor industry makes extensive use of plasma for etching and deposition of various substrates. ICP's have several characteristics that make them attractive to semiconductor manufacturing. They can produce high plasma densities, which provide high ion fluxes to the surface and faster deposition and etching rates. Substrates can be independently biased, which enables the separate control of both plasma density and ion flux. The ability to build external electrodes also eliminates exposure to the plasma and the commonly used corrosive gases, which greatly increases tool lifetime.

Optical emission spectroscopy and mass spectroscopy techniques frequently make use of inductively plasma sources for their ability to produce high density plasmas that can ionize a significant fraction of the elements, up to a 90% ionization fraction for over 60 elements. ^[59] In optical (atomic) emission spectroscopy the species in the plasma are investigated and sorted based on their spectral emission lines. In mass spectroscopy the species are sorted based on their mass-charge ratio. Both methods are frequently used in chemistry and biology to identify mixtures and find traces elements.

Inductively coupled plasma sources can relatively easily be scaled up for generation of high density positive or negative beams in fusion devices. ^[60,61] Inductively coupled plasma sources provide one of the simplest and most efficient methods of generating metastable noble gas ion beams. ^[62]

Electrostatic gridded ion thrusters accelerate plasma by use of closely spaced charged metals grids. Ion thrusters use a variety of ionization techniques but inductively coupled plasma

sources provide a unique method that eliminates internal electrodes and can lead to longer lifespans, especially with corrosive propellants.

3.2.1 Model

The most basic method of investigating the behavior of inductively coupled plasma discharges is to treat system as a basic RF circuit where the antenna and plasma form a transformer. ^[63] In the transformer model the antenna is the primary and the plasma is the secondary. The discharge can be treated as a one turn secondary because the antenna induces an electric field that drives a closed current. The resulting circuit can be analyzed to estimate the discharge impedance.

The plasma impedance has three components: inductance of the plasma, resistance, and the electron inertia inductance. The resistance and the electron inertia inductance are the results of the real and imaginary components of the plasma conductivity. The plasma conductivity σ is given by :

$$\sigma = \frac{n_e e^2}{m_e} \frac{1}{(\nu + i\omega)} \quad (95)$$

n_e is the electron number density, m_e is the mass of an electron, ν is the electron collision frequency, and ω the frequency of the applied electric field. The plasma conductivity is broken into the previously mentioned components. The real component is from the plasma current in phase with the induced electric field and the imaginary component is from the current 90° out of phase. The real component of the conductivity is inversely related to the plasma resistance. The imaginary component of the conductivity is inversely related to the plasma inductance, which is called the electron inertia inductance and is given by :

$$L_{ele} = \frac{R_{plasma}}{\nu} \quad (96)$$

The final component of the plasma impedance is due to the path taken by the plasma current. The path of the plasma current results in an inductance and is referred to as the inductance of the plasma. The plasma inductance is directly coupled to the inductance of the antenna. The mutual inductance of the antenna and the plasma inductance is given by the following Neumann equation:

$$M_{ab} = \frac{\mu_0}{4\pi} \oint_a \oint_b \frac{d\mathbf{I}_a \cdot d\mathbf{I}_b}{r} \quad (97)$$

r is the distance between the elements. The above can be simplified with the use of a coupling coefficient and the self-inductance of the elements.

$$M = k\sqrt{L_{ant}L_{plasma}} \quad (98)$$

k is the coupling coefficient. In an ideal transformer the coupling coefficient is equal to unity. ^[64] The coupling coefficient of any antenna and plasma will be less than one.

With the above in kind, the circuit of an inductively coupled plasma source can be constructed. The circuit can be represented by the circuit below.

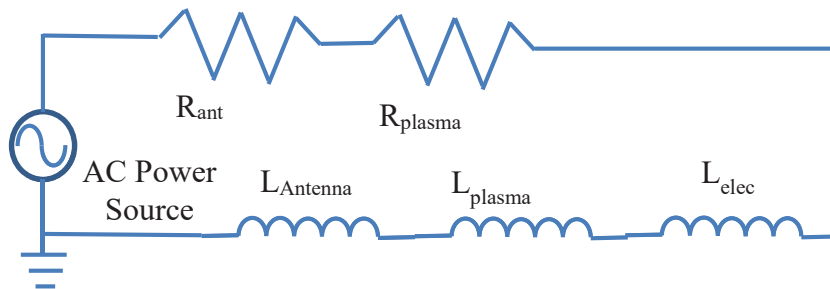


Figure 18 – Equivalent Circuit for ICP

From Figure 18, the impedance at the input node of the antenna can be found with the two equations below:

$$R_{input} = R_{ant} + \omega^2 M^2 \frac{R_{plasma}}{Z_{plasma}^2} \quad (99)$$

$$L_{input} = L_{ant} - \omega M^2 \frac{(\omega L_{plasma} + \omega L_{ele})}{Z_{plasma}^2} \quad (100)$$

Z_{plasma} is the impedance of the plasma. The most important takeaway from these equations is that there is an increase in resistance and a decrease in inductance while a plasma is present. From a conceptual standpoint, the magnetic field induced by the plasma current opposes the magnetic field induced by the antenna, which reduces the total inductance.

3.2.2 Plasma Heating

As with any plasma source, the ionization rate must be balanced by the rate of plasma loss. In most ICP's, the predominant source of plasma loss is to the walls and requires a constant source of energy to the gas. ICP's have two separate mechanisms for energy transfer to the discharge based on the pressure. At pressures where the plasma is collisional, the plasma is Ohmically heated. At pressures below the above threshold, the plasma becomes collisionless and is non-Ohmically heated. [65]

A discharge is considered to be Ohmically heated when the electron collision frequency is greater than the RF frequency. The induced current in the discharge is near the antenna-plasma interface and penetrates around one skin depth into the plasma. The electrons in the current collide with particles in the plasma and transfer energy.

Another important condition of ICP's is the plasma initiation phase before collisional or collisionless heating develop. At low power levels, the azimuthal electric field, E_θ , is too weak to

provide a balance of losses and ionization, and the electric field between turns of the coil, E_z , capacitively couple and form a low-density plasma next to the wall. The ratio between the longitudinal and azimuthal fields is constant when no space charges are present. ^[66] Once a space charge develops the electrons oscillate in a manner that results in an intensification of the longitudinal field strength and space charge density at the ends of the coil and a reduction in the middle region. ^[67] As additional power is added, increase in antenna current, the space charge density further increases near the ends of the coil, which results in an increase of the azimuthal electric field in the middle of the coil and eventually a switch to a predominately inductively coupled mode. The impacts of capacitive coupling can be eliminated by placing an electrostatic shield, a slotted conductor, between the coils and the discharge, which only allows the azimuthal electric field to interact with the plasma.

3.2.3 Radio Frequency Impedance Matching

The use of alternating current sources introduces an additional facet to design in the form of reactance, as compared to direct current sources. In DC circuits the impedance is equivalent to the resistance because the frequency is low (zero). AC circuits frequently have non-negligible frequencies where the reactive components significantly contribute to the overall impedance. The total impedance is a complex number, where the resistance is the real component and the reactance is the imaginary part. If the source and load do not have proper “matched” impedances signal reflection or reduced power transmission can occur.

To maximize power transmission to the load, the impedance of the source and the load need to be complex conjugates of each other. If minimum power reflection is desired the impedance of the source and load should be equivalent. In the case where the source has an

entirely real impedance, maximum power transmission is found in the same condition as minimum reflected power.

The circuits designed to match the impedance of the source and load are typically referred to as matching networks. Matching networks use a combination of transformers, resistors, inductors, capacitors, and transmission lines to bring the effective impedance that the source sees to a matched value. Resistive networks are relatively easy to design but bring unavoidable power losses and are typically avoided in high power systems.

Filter based matching networks are frequently used due to the ability to make a “lossless” network with only reactive components. Filter networks use a combination of inductors and capacitors to vary the impedance and can be grouped into L-networks, Pi-networks, and T-networks based on their geometry.

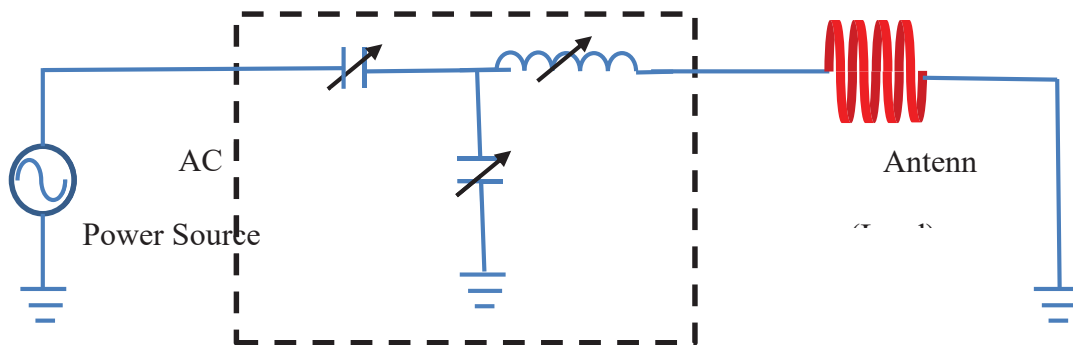


Figure 19: T-matching network

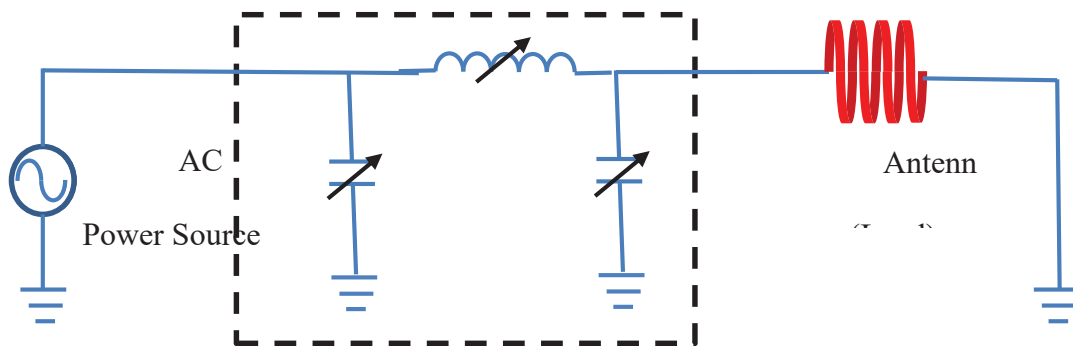


Figure 20: Pi-matching Network

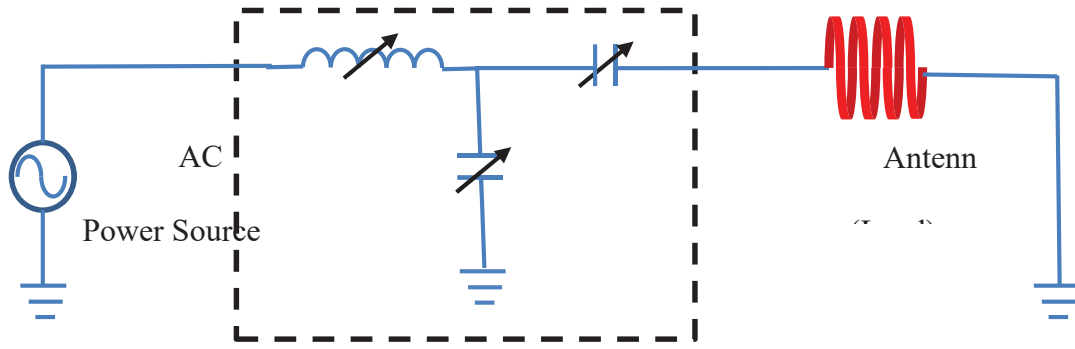


Figure 21: L-Matching Network

In the above configurations the placement of the capacitors and inductors can vary depending on the type of filter being created. The capacitors are indicated as variable capacitors and the inductors are fixed. Variable capacitors are used due to ease of manufacturing low ESR components.

An important consideration for the design of matching networks is what is known as the skin depth effect. RF frequencies cause a magnetic field to develop in the center of a conductor, due to moving charges, which restricts the flow of current in the region of magnetic field. This current restriction results in a larger percentage of the current flowing through the outer regions of the conductor. As the frequency increases the magnetic field becomes stronger pushing the current into an increasingly small area around the perimeter. The distance from the perimeter inwards where the current falls to $1/e$ of the surface current. The skin depth is given by :

$$\delta = \sqrt{\frac{2\rho}{\omega\mu}} \sqrt{(1 + (\rho\omega\epsilon)^2)^{\frac{1}{2}} + \rho\omega\epsilon} \quad (101)$$

ρ is the resistivity, μ is the permeability of the material, and ϵ is the permittivity of the material. The above equation can be simplified when the frequency is significantly below $\frac{1}{\rho\epsilon}$ to :

$$\delta = \sqrt{\frac{2\rho}{\omega\mu}} \quad (102)$$

The resistance is then :

$$R_{rf} = R \frac{r^2}{2\delta r - \delta^2} \quad (103)$$

r is the radius of the conductor. The result is that at RF frequencies conductors have resistances significantly higher than what is measured with a multimeter due to a reduced effective cross section.

3.3 Hollow Cathodes

In order for Hall Effect thrusters to function properly, a sufficient quantity of electrons must be generated for the neutralization of the plasma and the ionization process.

Cathodes are electron emitting devices used in a variety of applications wherever a stream of electrons is needed. For this work, the primary application of interest is in electric propulsion devices. Electrons are generated by an electrode through thermionic emission, where the electrode material is heated until electron emission occurs. At emissive temperatures, the electrode produces an electron current density based on its temperature and material work function, which is described by the Richardson-Dushman relation. ^[68]

$$j = A_G T^2 e^{-\frac{e\phi}{kT}} \quad (104)$$

The constant A_G is defined by :

$$A_G = \frac{4\pi m_e q k^2}{h^3} \quad (105)$$

m_e is the mass of an electron, q is the charge of an electron, k is Boltzmann's constant, and h is Planck's constant.

The easiest to build cathode is a simple tungsten filament heated with a large current source. Tungsten has a work function of 4.5 eV and requires a temperature of 2500°C to reach current densities of 5 A/cm², which requires hundreds of watts of power to achieve. The plasma environment created by electric propulsion systems also leads to ion sputtering and evaporation of tungsten, which coupled with the relative thinness of tungsten filaments results in rapid erosion and an upper limit on operation of hundreds of hours.

The most direct route to increasing the lifespan of cathodes is to reduce the operating temperature required to obtain the desired emission current density. Higher temperatures lead to increased chemical reactivity and evaporation of emitter material. To reduce emitter temperatures, a variety of different emitter materials and configurations have been extensively tested. The most commonly used emitter materials used in electric propulsion are currently barium oxide and lanthanum hexaboride. In addition to different emitter materials the hollow cathode is the predominate configuration.

Hollow cathodes can produce an order of magnitude higher current and breakdown at lower voltages than glow discharges with the same parameters. Friedrich Paschen first recognized the hollow cathode effect in 1916. ^[69] Hollow cathodes have the electron emitting surface on the inside of a tube. The prevailing theory for hollow cathode's operating efficiency is the combination of several processes: the pendulum effect, photoionization, stepwise ionization, and sputtering. ^[70] The pendulum effect is where electrons oscillate inside the tube and produce additional secondary electrons. The enclosed nature of hollow cathodes results in more of the produced photons being absorbed and causing photoionization. Sputtered particles from the emitter surface can be ionized. Stepwise ionization occurs when ionization is not a single step but is rather a collection of events that provide sufficient energy for ionization. ^[71]

Hollow cathodes are the most commonly used source for electrons in HETs due to their ability to produce very high beam currents with low mass flow rates and cathode sizes. Iodine functions as a relatively straightforward drop-in replacement for xenon in HETs with minor changes to construction materials, but the high operating temperatures of cathodes results in rapid erosion of some commonly used materials.

Hollow cathodes are designed to generate a cold, low-pressure, and high-density plasma. The plasma provides sufficient heat to maintain the emission temperature and eliminates space-charge effects between the cathode and anode.

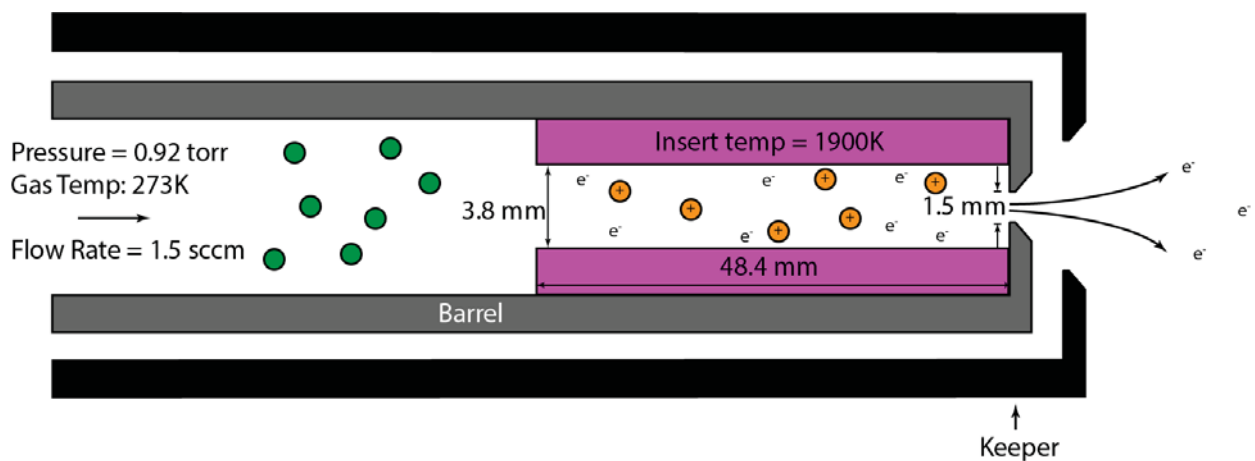


Figure 22 – Cathode Diagram

Figure 22 shows a cross section of a typical hollow cathode. The refractory metal barrel holds the insert with use of carbon spacer tubes against an orifice. The carbon spacer in between the insert and the insert is there to minimize insert diffusion into the barrel and modifying its material properties. The keeper is frequently made out graphite and is charged to create a plasma discharge in the inert region. The electrons are accelerated towards an anode.

3.3.1 Hollow Cathode Operating Conditions

Hollow cathode inserts are typically contained inside a tube made of a refractory metal, commonly molybdenum or tantalum. To identify appropriate test conditions the internal temperature and pressure of a hollow cathode is important. Depending on desired emission current and configuration the internal pressure can vary by more than a magnitude.

The pressure inside a hollow cathode can be approximated as a function of propellant flow rate and cathode temperature. The method shown below can approximate to around 10-20% of the actual pressure. ^[72] The pressure inside of a cylindrical tube is governed by Poiseuille flow and the flow rate of a compressible gas through a tube is given by:

$$N_m = \frac{\pi}{16\zeta} \frac{a^4}{l} \frac{P_1^2 - P_2^2}{R_0 T} \quad (106)$$

N_m is the molar flow rate, ζ is the viscosity, a is the tube radius, l is the tube length, P_1 is the pressure upstream, and P_2 is the downstream pressure. The viscosity of xenon is given by:

$$\zeta = 2.3 \times 10^{-4} T_r^{0.965} \quad T_r < 1 \quad (107)$$

$$\zeta = 2.3 \times 10^{-4} T_r^{(0.71 + \frac{0.29}{T_r})} \quad T_r < 1 \quad (108)$$

T_r is the reduced gas temperature ($T_r = T/T_m$), T_m is the input gas temperature, and T is the cathode temperature. The cathode wall temperature can be used to determine the gas temperature with:

$$T = T_{wall} + \frac{M}{k} [(f v_r)^2 + v_0^2] \quad (109)$$

To simplify, the gas temperature can be approximated as three times the wall temperature. ^[73] Substituting in the ideal gas law and rewriting the flow rate in terms of more useful units, the pressure inside the cathode is : ^[72]

$$P = \left(0.78 Q \zeta T_r \left(\frac{l_{orifice}}{d_{orifice}^4} + \frac{l_{insert}}{d_{insert}^2} \right) \right)^{\frac{1}{2}} \quad (110)$$

Where Q is the flow rate in sccm, ζ is the viscosity in poises, and d is the diameter of the orifice or insert in cm, and l is the length of the orifice or insert in cm (pressure in units of torr).

Once the pressure is determined, the neutral and ion number density can be found with: ^[72,73]

$$n_0 = 9.65 \times 10^{24} * \frac{P}{T} \quad (111)$$

$$n_e = \frac{R I_e^2 - \left(\frac{5}{2} T_{ev} - \phi_s \right) I_e}{(f_n T_{ev} \sqrt{\frac{e T_{ev}}{\pi m}} e A e^{-\frac{\phi_s}{T_{ev}}} + n_0 e (\sigma_i v_e) V (U^+ + \phi_s))} \quad (112)$$

The results for a lanthanum hexaboride cathode tested in the Space Propulsion and Observation Laboratory are shown below.

Table 7 – Operating Conditions of LaB₆ Cathode

Orifice Diameter (mm)	d _{orifice}	1.5
Orifice Plate Thickness (mm)	l _{orifice}	0.35
Current (A)	I	6
Flow Rate – Xe (sccm)	Q	1.5
Insert Length (mm)	l _{insert}	48.4
Insert Inner Diameter (mm)	d _{insert}	3.8
Pressure (torr)	P	0.92
Neutral Density (#/m ³)	n₀	8.03x10 ²¹
Electron Temperature (eV)	T _e	2-4
Measured wall temperature (K)	T	1100
Plasma Density (#/m ³)	n _e	3.2x10 ²⁰

3.4 Plasma Characterization

3.4.1 Langmuir Probe

Langmuir probes are one of the most widely used plasma diagnostic tools due to their low cost and ease of construction. A Langmuir probe can be used to determine the electron and

ion density, the electron temperature, plasma potential, floating potential, and electron energy distribution function. The primary issue with Langmuir probes is interpreting the measurements can be challenging.

3.4.1.1 Probe Operation Theory

The most basic description of a Langmuir is that it is a conductor placed in plasma. The conductor is then biased with respect to the discharge chamber and the conductor draws a current. As the bias voltage is changed the current also changes. The relationship between the bias potential and current drawn can then be used to determine the plasma density, the electron temperature, and the plasma potential.

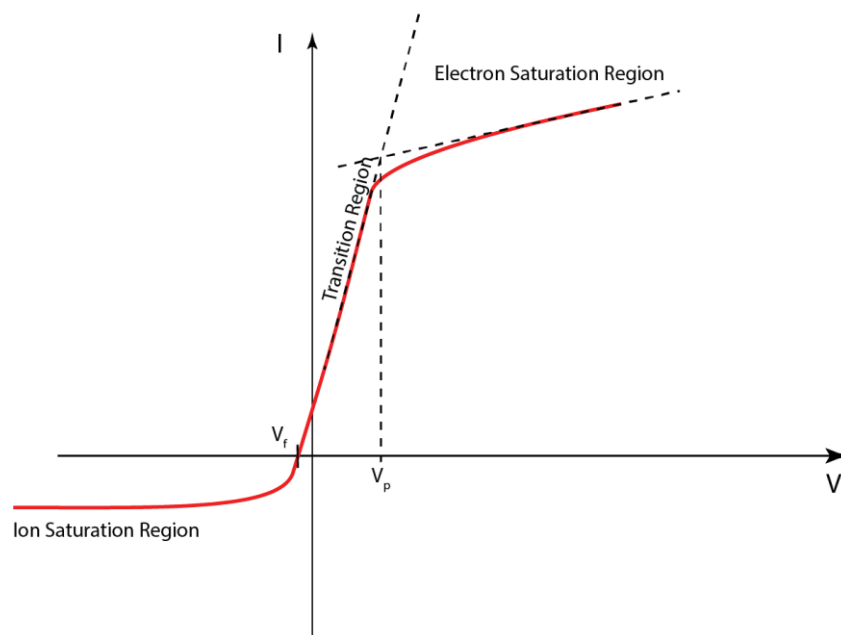


Figure 23 – Idealized I-V Curve

In Figure 23 the electron current is positive, and the ion current is negative, but the actual measured current will be negative. The plasma potential is at the intersection of the transition region and the electron saturation region. The ion saturation current occurs when the bias voltage is high enough to repel all the electrons. The electron saturation region is where the sheath

begins to expand slows the electron current growth. In the transition region the electrons are partially repelled by the bias voltage. The transition region is exponential in a Maxwellian plasma.

3.4.1.2 Langmuir Probe Plasma Parameters

If the transition region is plotted semi-logarithmically, it should become linear. If the electrons are Maxwellian the electron current should follow the below relationship with respect to probe voltage:

$$I_e = I_{es} \exp \left[\frac{e(V_p - V_s)}{kT_e} \right] \quad (113)$$

$$I_{es} = \frac{eAn_e\bar{v}}{4} = en_eA \left(\frac{kT_e}{2\pi m} \right)^{\frac{1}{2}} \quad (114)$$

Taking the natural logarithm of Eq. 63, gives the following relation:

$$\frac{d \ln I_e}{dV} = \frac{e}{kT_e} \quad (115)$$

Conveniently, the slope of the $(\ln I - V_p)$ curve is $1/T_{eV}$, and consequently electron temperature is the easiest value to calculate with Langmuir probes.

The plasma potential can be estimated from finding the maximum in the first derivative of the I-V characteristic.

$$\frac{dI}{dV_{max}} = V_p \quad (116)$$

The derivative can sometimes have its maximum below electron saturation voltage point, and a more accurate solution can be found by using current and voltage at the maximum derivative.

$$I_{derivmax} = I_0 \exp\left(\frac{V_{derivmax} - V_p}{kT_e}\right) \quad (117)$$

I_0 is the ion saturation current. Using the current and voltage at the maximum derivative results in the following plasma potential:

$$V_p = V_{derivmax} + kT_e \ln\left(\frac{I_0}{I_{derivmax}}\right) \quad (118)$$

The above equations only work Using the found electron saturation current and electron temperature, the electron density can be found with :

$$n_e = \frac{4I_0}{ev_e S} = \frac{4I_0}{eS} \left(\frac{\pi m_e}{8kT_e}\right)^{\frac{1}{2}} \quad (119)$$

The electron density can also be estimated based on the electron saturation current, but unless the plasma is low density and low pressure the current collected by the probe is so significant that it changes the equilibrium properties of the plasma.

3.4.1.3 Langmuir Probe Theories

As previously stated measuring the plasma density can either be done with the electron saturation current or the ion saturation current, but both present problems. The electron saturation current region frequently does not occur in a well-defined fashion and often forms a very indistinct “knee” in the I-V curve. The ion saturation current is a much smaller and safer current but is difficult to calculate. For a cylindrical probe three predominant theories exist that describe ion collection: orbital motion limit theory, Allen-Boyd-Reynolds theory, and Bernstein-Rabinowitz-Laframboise theory.

3.4.1.4 Orbital Motion Limited Theory

The simplest of the three theories is the orbital motion limited theory presented by Langmuir and his associates. ^[74] Orbital motion limited theory presents a relatively simple solution for finding the ion current, but it assumes the sheath thickness is infinite and there is no so called “absorption radius” where the E-field prevents the escape of ions. Theoretically OML theory only applies in very low-density plasmas where the sheath is significantly larger than the probe, but sometimes can give acceptable results for higher density plasmas.

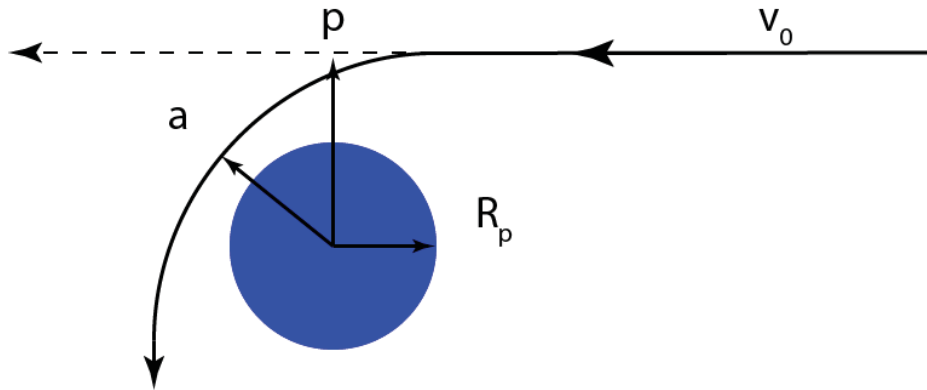


Figure 24 – OML Theory

The ions are attracted to the negatively biased probe at a velocity, v_0 , and have impact parameters of p . Assuming the plasma potential is zero at infinity and becomes negative gradually as it approaches the probe, at potential V_0 . From conservation of energy and angular momentum:

$$\frac{1}{2}mv_0^2 = -eV_0 \quad (120)$$

$$pv_0 = av_a \quad (121)$$

The above equations can be rewritten :

$$\frac{1}{2}mv_a^2 = \frac{1}{2}mv_0^2 \left(1 + \frac{V_a}{V_0}\right) \quad (122)$$

$$p = a \frac{v_a}{v_0} = a \left(1 + \frac{V_a}{V_0} \right)^{\frac{1}{2}} \quad (123)$$

If the distance of closest approach is less than or equal to the probe radius then the ion will be collected, which results in the effective probe radius being the probe radius times the collision parameter. The resulting monoenergetic ion flux to the probe is :

$$\Gamma = 2\pi r_p L \left(1 + \frac{V_a}{V_0} \right)^{\frac{1}{2}} \Gamma_r \quad (124)$$

This result was then expanded to Maxwellian energy distributions at a large distance from the probe, defined as the “sheath edge”, $r = s$.^[74] The resulting random flux is :

$$\Gamma_r = n \left(\frac{kT_i}{2\pi m_i} \right)^{\frac{1}{2}} \quad (125)$$

Integrating across all velocities results in :

$$\Gamma = A_p \Gamma_r \left\{ \frac{s}{a} \operatorname{erf} \left(\Phi^{\frac{1}{2}} \right) + e^{\chi} \left[1 - \operatorname{erf}(\chi + \Phi)^{\frac{1}{2}} \right] \right\} \quad (126)$$

$$\chi \equiv -\frac{eV_p}{kT_i}, \quad \Phi \equiv \left(\frac{a^2}{s^2 - a^2} \right) \chi, \quad a = R_p \quad (127)$$

Since Langmuir assumed the sheath edge is far away, $s \gg a$, $\Phi \ll \chi$ and when the ion temperature goes to zero $1/\chi \ll 1$. By expanding in a Taylor series and simplifying a limiting value of the current is found with :

$$I \xrightarrow{T_i \rightarrow 0} A_p n e \frac{\sqrt{2}}{\pi} \left(\frac{|eV_p|}{m_i} \right)^{\frac{1}{2}} \quad (128)$$

3.4.1.5 Allen-Boyd-Reynolds Theory

Orbital motion limited theory provides a relatively simple solution for ion current but makes some assumptions that make it not particularly useful for a variety of plasmas. A more

complete solution requires the solution of Poisson's equation of the potential from the probe surface to infinity, which is somewhat complicated. Allen, Boyd, and Reynolds came up with a simpler problem by assuming from the beginning that the ion temperature is zero, which eliminates orbital motion and all the ions are attracted radially. ^[75] The original theory was only solved for spherical probes, but Chen solved for cylindrical geometries. ^[76] Poisson's equation in cylindrical coordinates is :

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial V}{\partial r} \right) = \frac{e}{\epsilon_0} (n_e - n_i) \quad (129)$$

The probe center is placed at $r = 0$ and the ions start at a distance where $r = \infty$ and the potential is equal to zero. According to continuity:

$$\Gamma = n_i v_i = \frac{I}{2\pi r} \quad (130)$$

$$v_i = \left(-\frac{2eV}{m_i} \right)^{-\frac{1}{2}} \quad (131)$$

So, the ion number density is :

$$n_i = \frac{I}{2\pi r} \left(-\frac{2eV}{m_i} \right)^{-\frac{1}{2}} \quad (132)$$

For Maxwellian electrons the electron number density is :

$$n_e = n_0 e^{\frac{eV}{kT_e}} \quad (133)$$

Substituting Eq. 90 and 91 into Poisson's equation results in the follows:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial V}{\partial r} \right) = -\frac{e}{\epsilon_0} \left[\frac{I}{2\pi r} \left(-\frac{2eV}{m_i} \right)^{-\frac{1}{2}} - n_0 e^{\frac{eV}{kT_e}} \right] \quad (134)$$

To simplify the expressions the following variables are introduced:

$$\eta = -\frac{eV}{kT_e} \quad (135)$$

$$v_B = \left(\frac{kT_e}{m_i}\right)^{\frac{1}{2}} \quad (136)$$

Rewriting Eq. 92 with the above variables:

$$-\frac{\varepsilon_0 kT_e}{n_0 e^2} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \eta}{\partial r} \right) = \frac{I}{2\pi r} \frac{(2\eta)^{-\frac{1}{2}}}{n_0 v_B} - e^{-\eta} \quad (137)$$

The natural length scale appears on the right side of the equation, and normalizing r with the Debye length results in the following new variable:

$$\xi = \frac{r}{\lambda_D} \quad (138)$$

Introducing the new normalized length gives :

$$\frac{\partial}{\partial \xi} \left(\xi \frac{\partial \eta}{\partial \xi} \right) = \frac{I \xi}{2\pi r} \frac{1}{n_0 v_B} (2\eta)^{-\frac{1}{2}} - \xi e^{-\eta} = \frac{eI}{2\pi kT_e} \left(\frac{m_i}{2\varepsilon_0 n_0} \right)^{\frac{1}{2}} \eta^{-\frac{1}{2}} - \xi e^{-\eta} \quad (139)$$

Normalizing the probe current:

$$J \equiv \frac{eI}{2\pi kT_e} \left(\frac{m_i}{2\varepsilon_0 n_0} \right)^{\frac{1}{2}} \quad (140)$$

Inserting the above results in the ABR equation for cylindrical geometries:

$$\frac{\partial}{\partial \xi} \left(\xi \frac{\partial \eta}{\partial \xi} \right) = J \eta^{-\frac{1}{2}} - \xi e^{-\eta} \quad (141)$$

Eq. 99 can then be integrated from infinity to some small value of ξ for an assumed value of J . The resulting curve can then be investigated to find the probe potential, η_p , which is at the point where $\xi = \xi_p$. A curve of normalized current versus probe potential can then be found by cross-plotting a variety of curves for different values of J . The resulting curve can be used to find the value for probe current at different probe potentials.

3.4.1.6 Bernstein-Rabinowitz-Laframboise Theory

Allen-Boyd-Reynolds theory presents a solution that applies to a greater number of plasmas than orbital motion limited theory, but it ignores orbital motion and only looks at sheath formation. Bernstein and Rabinowitz came up with the first solution that included both orbital motion and sheath formation by assuming an isotropic distribution of ions with a single value of energy.⁷⁷ Laframboise refined Bernstein and Rabinowitz's theory by applying the calculations to a Maxwellian distribution.⁷⁸ Since in ABR theory all of the ions hit the probe, the flux depends on the conditions at infinity and not the probe radius. In BRL theory, the ions collected by the probe contribute to the ion density once, but the orbiting ions contribute twice. The result is that BRL theory requires the ion density to be known before a solution can be found. The solution was found by Bernstein by writing the ion distribution in terms of energy and angular instead of the more typical radial and tangential velocities.⁷⁷ To solve BRL for cylindrical probes the following equation needs to be solved:

$$\frac{1}{\xi} \frac{d}{d\xi} \left(\xi \frac{d\eta}{d\xi} \right) = 1 - \frac{1}{\pi} \sin^{-1} \left(\frac{\frac{\iota}{\xi^2}}{1 + \frac{\eta}{\beta}} \right)^{\frac{1}{2}} \quad \xi > \xi_0 \quad (142)$$

$$\frac{1}{\xi} \frac{d}{d\xi} \left(\xi \frac{d\eta}{d\xi} \right) = \frac{1}{\pi} \sin^{-1} \left(\frac{\frac{\iota}{\xi^2}}{1 + \frac{\eta}{\beta}} \right)^{\frac{1}{2}} \quad \xi < \xi_0 \quad (143)$$

β is the ion energy divided by kT_e , ι is the non-dimensional probe current per unit length, and everything else carries over from ABR theory. The resulting computation required for solution is somewhat complicated. The results for BRL theory compare favorable to experimental results in fully ionized plasmas.⁷⁹

3.4.1.7 Radio Frequency Compensation

The radio frequencies used to generate the plasma discharge in inductively and capacitively coupled plasma sources creates a significant potential for distortion of the I-V characteristic curve due to pick of the RF signal by the probe. In a DC discharge plasma, the plasma potential is constant with respect to time at steady state conditions. In a RF plasma the plasma potential is varying with respect to time. The current on a probe in a RF plasma is : ⁸⁰

$$I = I_i - I_e(t) \quad (144)$$

The ion current should not be affected by the RF due its frequency being less than the driving frequency of the RF source.

$$\omega > \left(\frac{ne^2}{m_i \epsilon_0} \right)^{\frac{1}{2}} \quad (145)$$

The RF source has a sinusoidal shape and is expected to induce a sinusoidal shape into the plasma potential :

$$V_p(t) = V_{DC} + V_{RF} \sin(\omega t) \quad (146)$$

Substituting Eq. 104 into Eq. 102 results in :

$$I(t) = -I_0 \exp(e(V - V_{DC} - V_{RF})) + I_i \quad (147)$$

The time averaged probe current is :

$$I = -AI_{DC} + I_i \quad (148)$$

A is a constant that takes into account the RF distortion. The result is that the electron saturation region has a less well define “knee” and a lower total current. Since the ions are not impacted by the RF, the floating potential will occur at a lower voltage than in a comparable DC plasma.

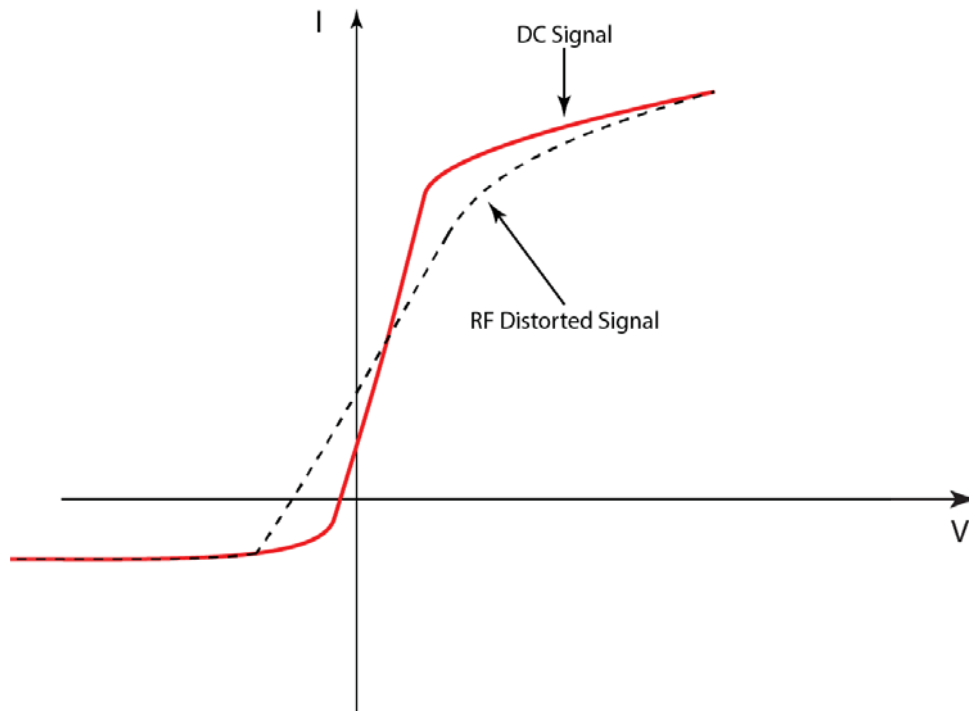


Figure 25 – Comparison of RF and DC I-V Characteristic Curve

Since the DC component of the plasma potential is the component of interest, the best solution is to simply remove the RF component of the plasma potential. A few different approaches to filtering out the RF component exist: time resolving the probe output, superimpose a RF signal on the probe, measure the time varying component with a capacitive probe and subtracting the distortion from the signal, or using a filtering circuit to remove the RF signal. Time resolving the probe output requires very measurement times, significantly greater than one RF cycle, and the sheath cannot fully develop in less than one RF cycle.⁸¹ Superimposing a RF signal would require a signal that matches the harmonics in the RF plasma, which is very difficult in practice.⁸² A capacitive probe requires complicated numerical methods in order to remove the RF distortion from a distorted signal and requires an additional probe.⁸³ Using a filtering circuit to remove the RF signal is the simplest and cheapest method.

In order to minimize distortion of the signal, the sheath potential needs to be less than the electron temperature. The probe sheath impedance can be approximated as a cylindrical capacitor :

$$C_{sheath} = 2\pi\epsilon_0 \frac{1}{\ln\left(\frac{r_{sheath} + r_p}{r_p}\right)} \quad (149)$$

The sheath thickness can be estimated with :

$$r_{sheath} = \lambda_D \left(1 + \frac{V}{kT_e}\right)^{\frac{1}{2}} \quad (150)$$

The goal is then to reduce the probe impedance to less than the stray impedance to the chamber by adding a capacitance in parallel with the sheath, which will reduce the RF fluctuations to the probe. A band-stop or low pass filter can then be added to remove the remaining RF signal on the probe. The resulting should have only the DC component of the plasma potential and an undistorted I-V characteristic curve.

3.4.2 Spectroscopy

Spectroscopy is a technique of splitting electromagnetic radiation into its constituent wavelengths to study matter. Due to the quantization of electron energy levels in atoms and molecules, electromagnetic radiation is only absorbed and emitted at specific wavelengths. When electrons undergo an energy level transition, photons are either emitted or absorbed at a specific wavelength. For simplicity the following section will describe the fundamentals in terms of the hydrogen atom.

3.4.2.1 Development of Quantum Numbers from Schrödinger's Equation

The hydrogen atom is a one-electron system, meaning it as a nucleus with a positive charge of one and single electron with a negative charge. For simplicity, an atom with stationary states can be described by the time independent Schrödinger equation: ⁸⁴

$$H\psi(r) = E\psi(r) \quad (151)$$

H is the Hamilton energy operator, ψ is the state vector, r is the position vector, and E is the total energy of the system. The Eigen functions, or wave functions ψ , must be single valued, continuous and finite. The Hamiltonian is given by :

$$H = \frac{p^2}{2\mu} + V \quad (152)$$

The linear momentum can be written as the following using a simple quantum-mechanical substitution:

$$p \rightarrow -i\hbar\nabla \quad (153)$$

The Coulomb potential energy is :

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (154)$$

Substituting Eq. 64, 65, and 66 into Eq. 63 results in :

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right) \psi(r) = E\psi(r) \quad (155)$$

Writing the Laplacian in spherical coordinates, makes the above equation separable and can be written as:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad (156)$$

$$-\frac{r}{R(r)} \frac{d^2}{dr^2} [rR(r)] + \alpha = \frac{2\mu r^2}{\hbar^2} [E - V(r)] \quad (157)$$

$$\left[\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = -\alpha Y(\theta, \phi) \quad (158)$$

α is the separation constant. $Y(\theta, \phi)$ can be further separated into $\Theta(\theta)\Phi(\phi)$:

$$\left[-\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\frac{\sin \theta}{d\theta} \right) + \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = \alpha \Theta(\theta) \quad (159)$$

$$\frac{d^2 \Phi(\phi)}{d\phi^2} = -m^2 \Phi(\phi) \quad (160)$$

m^2 is the separation constant. The solution to Eq. 72 involves a function of $e^{im\phi}$, which only meets the previously discussed requirement of being single valued if $m=0, \pm 1, \pm 2, \pm 3, \dots$ and gives rise to the quantum number, m . The solution for $\Theta(\theta)$ results in another quantum number l . In order for the solution to fit the criteria of being finite in the range of $0 \leq \theta \leq \pi$ means $\alpha = l(l+1)$, $l=0, 1, 2, 3, \dots$ and $l \geq |m|$. Inserting $\alpha = l(l+1)$ into the radial equation, Eq. 68, results in the principal quantum number, n . The important takeaway from above is the existence of the spatial quantum numbers: n , l , and m , which can be used to describe the energy state of electrons.

In addition to the three spatial quantum numbers, a quantum number associated with spin of the electron also exists. There are a total of four quantum numbers, which are :

1. The principal quantum number: n
 - a. Describes the most probable distance of electrons from the nucleus
 - b. A non-zero positive integer
2. Orbital angular momentum quantum number: l
 - a. Describes the angular distribution of electrons and thus the shape of the orbitals
 - b. Can be any positive integer (including zero) under one less than the principal quantum number

- c. The quantum numbers $l = 1, 2, 3, 4$ are historically written as s, p, d, f, g
3. Magnetic quantum number: m_l
- a. Describes the number and orientation of orbitals
 - b. Dependent on the orbital angular momentum
 - c. An integer in the interval of $-l$ to $+l$
4. Electron spin quantum number: m_s
- a. Describes the electron spin direction and is not dependent on the other quantum numbers
 - b. Typically described as either spin up ($+1/2$) or spin down ($-1/2$)

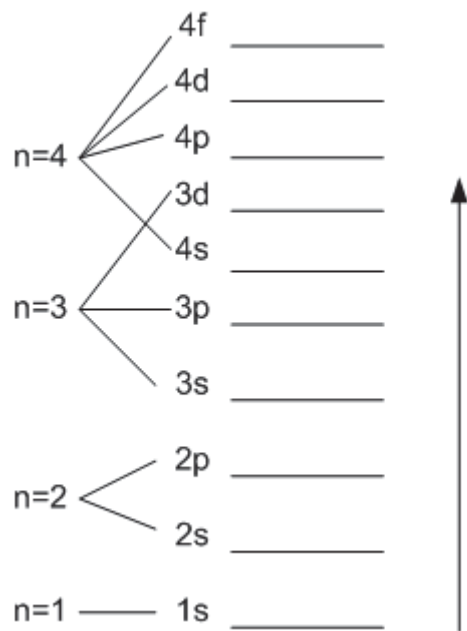


Figure 26 – Energy Level Diagram

The energy eigenvalues, energy levels, are given by :

$$E_n = \frac{\frac{1}{2} e^4 \mu}{(4\pi\epsilon_0)^2 \hbar^2} \frac{Z^2}{n^2} = -R_M \frac{Z^2}{n^2} \quad (161)$$

R_M is the Rydberg constant, which is 13.606eV for hydrogen. The energy levels for one electron systems can be simply calculated since they only depend on the principal quantum number. The difference in energy between two states results in a discrete amount of energy either being absorbed or emitting for the transition to occur. The photon emitting transitions can be used to determine what transitions are taking place. For one electron systems, sometimes called hydrogenic systems, the wavelength of the resulting energy change is given by:

$$\lambda = \frac{hc}{Z^2 I_H \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)} \quad (162)$$

n and n' are the principal quantum numbers of the upper and lower states respectively. In plasmas, two primary variations result in spectral emissions lines not being perfect lines. Motion in plasma relative to the observation point will result in a shift of the central wavelength called Doppler shift, which is given by :

$$\Delta\lambda = \lambda_0 \left(\sqrt{\frac{1 + \frac{v}{c}}{1 - \frac{v}{c}}} - 1 \right) \quad (163)$$

Every plasma will have some degree of random thermal motion that causes some of the photons to be red shifted and some to be blue shifted, resulting in a broadening in the measured line. The resulting Doppler width is given by :

$$\lambda_D = \left(\frac{2kT}{mc^2} \right)^{\frac{1}{2}} \lambda_0 \quad (164)$$

T is the ion temperature and m is the ion mass. If a sufficiently high-resolution spectrometer is available, the line width can be used to determine the ion temperature in a plasma.

For the purpose of this work, the primary interest from the emission spectra is the composition of the plasma, i.e. what plasma species are present. At a given state there are a number of possible conditions that the electrons can be in, so to differentiate atoms condition will be written with : configuration, term, level, and state. In order to define the previous conditions, it is helpful to define the total spin angular momentum and total orbital angular momentum. The total orbital angular momentum follows the triangle inequality and is given by :

$$|l_1 - l_2| \leq L \leq l_1 + l_2 \quad (165)$$

L is the total orbital angular momentum. The total spin angular momentum also follows the triangle inequality :

$$|s_1 - s_2| \leq S \leq s_1 + s_2 \quad (166)$$

S is the total spin angular momentum. The total angular momentum is then :

$$|L - S| \leq J \leq L + S \quad (167)$$

J is the total angular momentum. The result is that configuration is just the n and l quantum numbers specified for each electron. The term is total spin and orbital angular momentums specified. The level is the total angular momentum specified. The state is the azimuthal angular momentum quantum number specified. The summation of the total angular momentums to get L , S , and J is called “LS-coupling” and can be conveniently written in Russel-Saunders notation.

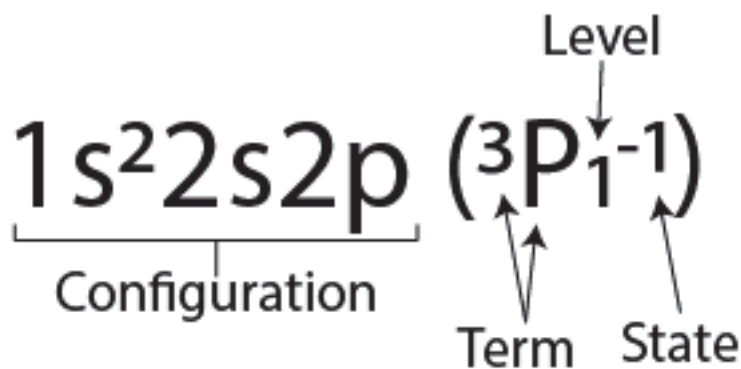


Figure 27 – Russel-Saunders Notation

In Russel-Saunders notation, the L value is given by a capital letter preceded by the value of $2S+1$ as a superscript and the total J value given by a subscript. Russel-Saunders notation is frequently used to describe the transitions taking place. The below table lists several direct emission lines from singly ionized atomic iodine.

Table 8 – Example Iodine Emission Lines ⁸⁵

Observed Wavelength (nm)	Ritz Wavelength (nm)	E_i (cm ⁻¹)	E_k (cm ⁻¹)	Lower Level			Upper Level		
				Config.	Term	J	Config.	Term	J
562.569	84842.87	102613.52	102613.52	$5s^25p^3(^4S^o)6s$	$^3S^o$	1	$5s^25p^3(^4S^o)6p$	^3P	2
533.822	533.820	93691.35	112419.04	$5s^25p^3(^2D^o)6s$	$^3D^o$	2	$5s^25p^3(^2D^o)6p$	^3F	3

The NIST spectral database can be used to match up observed emission lines with the specific transition that takes place. From a spectroscopy standpoint, iodine is not particularly well characterized outside of the realm of absorption spectroscopy for iodine vapor. Part of the goal of this work will be to produce spectral data for ionized iodine at several different plasma conditions.

4 Experimental Setup

My two experimental setups recommended for testing iodine material interactions are the iodine cathode testing chamber and the high-temperature material testing chamber. The iodine exposure testing was performed in the Space Propulsion Observation and Testing (SPOT) Laboratory. The facility features two large vacuum chambers, one of which has been designated for use with iodine.

4.1 Material Exposure Apparatus.

The material exposure apparatus is constructed beneath a fume hood to minimize incidental contact while handling iodine. A cylindrical quartz tube serves as the plasma confinement tube and is inserted into a Mellen NACCI tube furnace. A coil (RF antenna) is placed around the quartz tube on one end. The tube is sealed by a vacuum flange assembly. To provide RF shielding, a cylindrical frame of a metal box was constructed and placed over the antenna end of the tube. The other end of the quartz tube was connected via a vacuum sealing flange assembly to stainless steel tubing. This line was connected to a liquid nitrogen cooled cold trap to prevent iodine vapor from escaping and damaging the vacuum pump. In addition, a ISO25 nipple tube is filled with activated charcoal, and a sintered metal foam filter is between it and the vacuum pump to hold the charcoal in in the tube and prevent any charcoal from reaching the pump. The vacuum pump exhaust is then plumbed into the fume hood.

The gas feed system has a metal iodine flask connected to a shutoff valve. The iodine flask is a gold-plated stainless-steel tube capped with DN40 Conflat flanges. The shutoff valve is then connected to a MKS 1150C heated mass flow controller, which is then fed into the 50 mm OD quartz glass tube. Two valves are placed before and after the shutoff valve that allow for

argon or nitrogen to feed into the system. All of the tubing exposed to iodine is heated to prevent condensation of iodine. The tubing before the mass flow controller is heated to 120°C and the tubing after is heated to 140°C.

An Inficon SKY CDG100D 100 torr capacitance manometer is used for pressure measurement. The capacitance manometer is heated to 100°C to minimize iodine condensation and has an alumina ceramic diaphragm for corrosion resistance. The 100-torr sensor has a measurement range from 0.01 to 100 torr and a resolution of 0.003 torr.

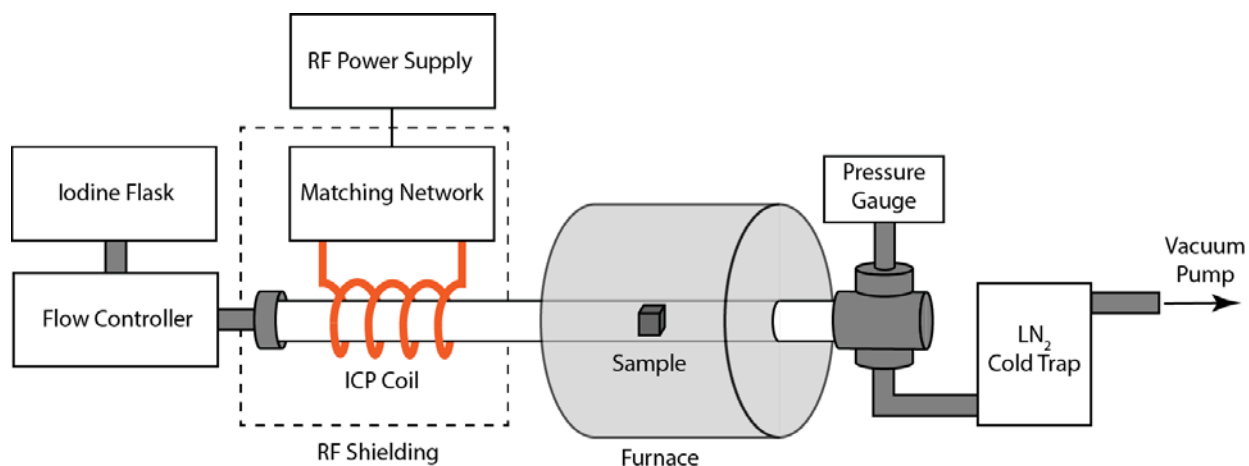


Figure 28: Material Exposure Experimental Setup



Figure 29: Material exposure experimental setup, without heaters.

4.1.1 Radio Frequency Inductively Coupled Plasma Source

In this experimental setup a six-turn helical hollow copper coil is used as the load. The resistance is relatively low, and the load is primarily reactive (25.1Ω reactance and 0.16Ω resistance). The coil is connected to a Radio Frequency Power Products RF10 power supply with an output impedance of 50Ω (purely resistive). In between the load and the source is a T-matching network made from components from a Seren AT-10 matching network. The Seren matching network was designed for 13.56MHz so it was reconfigured to be used for 2.0MHz.

The plasma source underwent multiple iterations as modifications were made to the matching network. The initial coil design was a three-turn coil, which was changed to a five and half turn coil, closely surrounded by a faraday cage. In the initial design the matching network was connected to the coil via a ten-foot coaxial cable. The faraday cage was made out of steel

and drew too much of the RF power, which prevented plasma ignition. After modification of the faraday cage (larger not made of ferrous materials), plasma operation was limited due to the capacitors in the matching network overheating and the coaxial cable eventually failing due to melting of the insulation and grounding. The matching network was moved to directly under the coil with short approximately four-inch copper bars connecting the coil in and out. After the modification, plasma ignition occurred at significantly lower power levels (<150W at 1 torr).

The matching network was then modified to add a large inductive element in series with the plasma antenna. This change was necessitated by the loss of inductance of the antenna during plasma discharge operation. Adding an inductive element with a much larger (2-3x) inductance than the load stabilizes the matching network frequency as the impedance varies with the plasma.

⁸⁶ A two-turn coil was initially used as the antenna to minimize inductance loss but required high RF power (>250W) to run and had to be ignited with a small DC discharge. The antenna was replaced with a six-turn coil and plasma ignition occurred without the DC discharge and at much lower forward power (<150W) and had a higher intensity plasma. The larger coil also operated at a wider pressure range with the same power input. Both the antenna coil and the additional inductive element are water-cooled to minimize variation in coil shape due to thermal expansion.

4.1.2 Langmuir Probe

The Langmuir probe is designed and built as a radio frequency compensated single wire probe. The filter is a band pass filter designed to remove the 2MHz power supply signal and the 4MHz harmonic frequency.

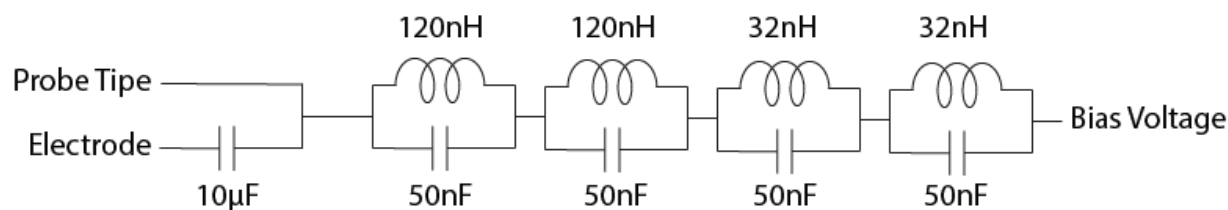


Figure 30 – Langmuir probe RF filter

The first segment with the 120nH and 50nF inductors and capacitors filters out the 2.0MHz signal and the second segment filters out the 4.0MHz harmonic. The components are doubled to increase the Q-factor of the filter.

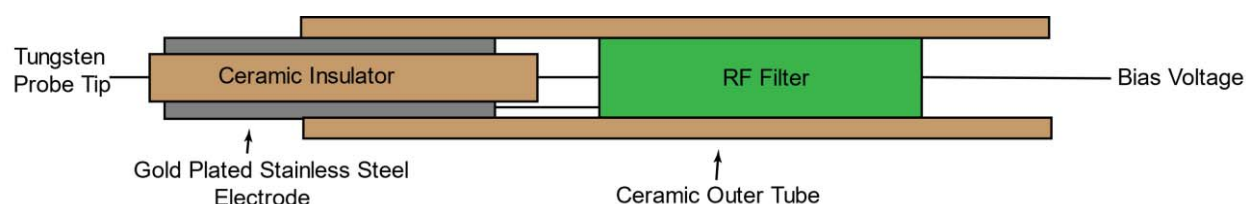


Figure 31 – Langmuir probe construction

The Langmuir probe consists of a 0.5mm tungsten wire probe tip held in a ceramic tube surrounded by a gold-plated stainless-steel electrode and enclosed in a 0.25in ceramic outer tube.

4.1.3 Spectral Measurements

The spectral measurements will be performed with two different spectroscopy setups: a Stellernet low resolution spectrometer for survey spectroscopy and a Horiba microHR scanning monochromator for higher resolution measurements.

The Horiba microHR monochromator is used in conjunction with a photomultiplier tube to measure the relative intensity of emission lines. The monochromator has 630nm and 750nm blaze gratings which can be swapped depending on the desired the wavelength range and accuracy. The 1800 blaze grating has a wavelength range of 450-850nm and provides a typical array solution of $\leq 0.2nm$. The 750nm blaze grating has 1200 lines/mm and wavelength range of 400-1200nm and provides a typical array resolution of $\leq 0.3nm$.

Stellernet BLACK-Comet has a built in CCD camera for measurements and returns intensity in terms of photon counts. The spectrometer has a 590 lines/mm grating and a 50 μ m slit size, which results in a resolution of approximately 1.5nm and wavelength range of 280-900nm

4.1.4 Resistance Measurement

The high temperature and plasma environment adds significant complication to erosion rate measurements. Several methods were considered including but not limited to: quartz crystal microbalances, SEM cross section measurements, resistance variation, and surface profilometry.

Quartz crystal microbalances are commonly used in deposition and etch systems to determine film thickness and can provide high accuracies (1 ng causes a frequency change of 1 Hz with a 9 MHz crystal).⁸⁷ The primary issue with quartz crystal microbalances is their construction. Cathode operating conditions are high enough that the quartz will either melt or severely deform, quartz crystals have a melting point of 1670°C or 1713°C depending on the phases.⁸⁸

Surface profilometry provides a relatively straight forward method of measuring the change in thickness of thin film before and after exposure but requires the film to be on a non-varying substrate. For iodine vapor, a high temperature ceramic, like boron nitride, will most likely experience minimal erosion and could potentially be used as a base material to compare the film to. In iodine plasma however, high temperature ceramics are expected to have some degree of erosion due to a combination of interactions from high energy particles. Since surface profilometry techniques are usually relative, if both the substrate and the sample of interest erode the resulting measurement will not be accurate.

SEM cross section measurements can provide relative high accuracy cross section measurements and information about scale formation but requires careful preparation. The primary issues for using SEM for cross section measurements are a combination of field of view and magnification. In theory SEM images can have resolutions on the order of nanometers but the field of view is going to be dramatically reduced. So, a very thin sample would have used to get high resolution erosion data, which presents challenges with preparation and transfer of the sample.

Another approach is to measure the resistance of the material as it is being eroded and relating the corresponding change in resistance with erosion rate based on its geometry. The resistance of a material is given by :

$$R = \frac{\rho L}{A} \quad (168)$$

ρ is the resistivity of the material. So, to measure a larger change in resistance it is desirable to increase the total area eroded away. The figures below show examples of how the material can be patterned onto a non-reactive substrate.

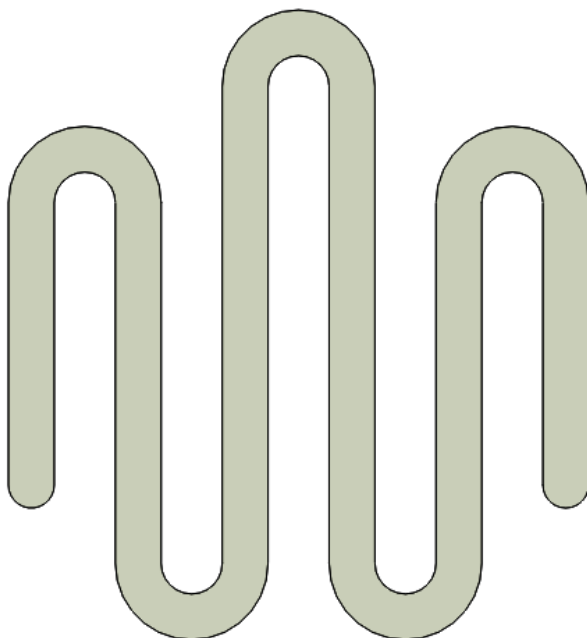


Figure 32 – Example geometry of metal film for resistance change measurement

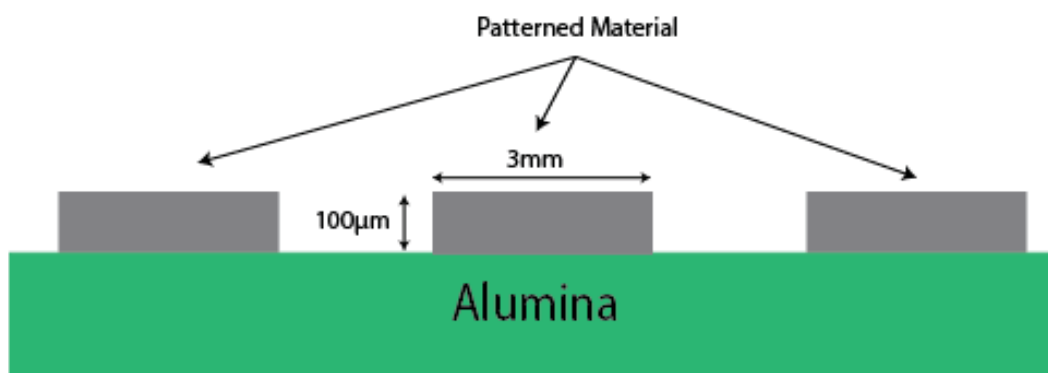


Figure 33 – Example cross-section of patterned material



Figure 34 – Stainless steel test sample

In iodine vapor flow, the flow regime should result in a relatively even erosion rate on all exposed sides. *Figure 33* has a pattern taller than it is wide due to the fact that maintenance of the total area keeps the total resistance the same but increasing the surface area of the sides increases the total erosion, and therefore the change in resistance. In iodine plasma, the iodine incidence is significantly more directional and may result in a distortion of the erosion rate calculation with respect to the change in resistance. So, verification with surface profilometry and SEM measurements will be more important.

The table below illustrates how the resistance changes in materials of interest with respect to erosion.

Table 9 – Resistance change of the geometry pictured in *Figure 33*

Material	Resistivity at 1750°C ($\mu\Omega \cdot cm$)	Length (mm)	Resistance Change $\frac{m\Omega}{\mu m}$
Tungsten ⁸⁹	57	150	3.07
Tantalum ⁸⁹	80	150	4.31

Molybdenum ⁹⁰	53	150	2.86
Rhenium ⁹¹	105	150	2.86
Graphite ⁹²	32.4	150	1.75

In addition to providing a way to measure the erosion in-situ, creating a resistive element out of the materials of interest provides a method for heating the samples above maximum temperature of the tube furnace (1250°C).

The erosion rate of each material will be measured at several different temperatures, but constant pressure. The resulting erosion rates will then be fitted to an Arrhenius relationship.

$$k = k_0 \exp\left(\frac{E_a}{RT}\right) \quad (169)$$

The resulting equation can then be used as a tool to estimate the erosion rate in the tested temperature range.

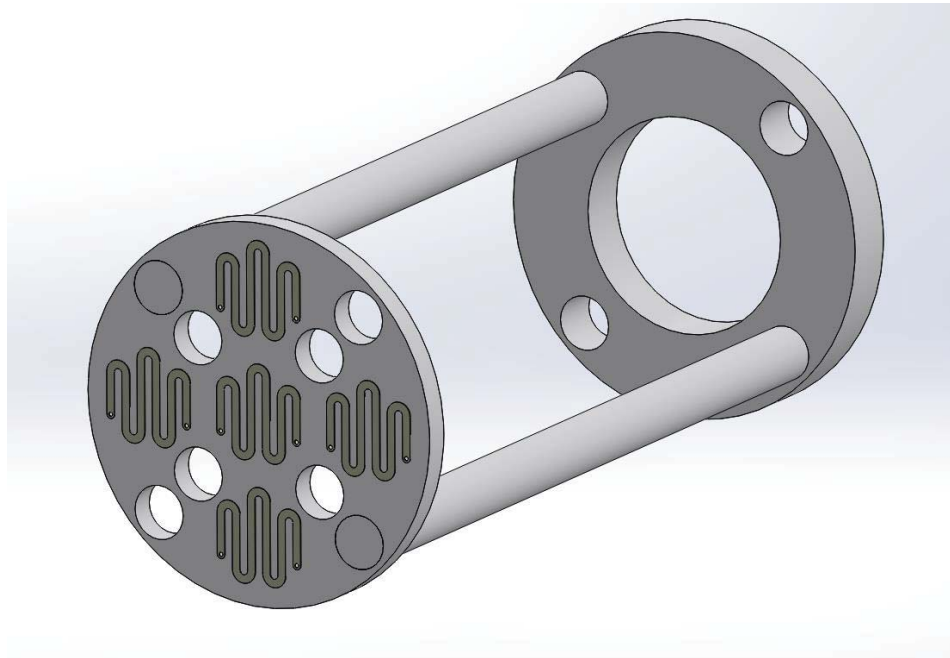


Figure 35 – Multiple Sample Material Holder

4.2 Cathode Testing Chamber

The cathode testing was performed inside of 1.5-meter diameter by 2.3-meter long cylindrical stainless-steel vacuum chamber. The vacuum chamber has six large flanges and six KF25 flanges. Currently the chamber has eleven vacuum feedthroughs installed. The vacuum chamber uses a mechanical pump (Leybold D65BCS) with a nominal pumping speed of 75 cfm to rough down the chamber to 100 mtorr. Then a Varian diffusion pump with a pumping speed of 17500 l/s on air can pump down the chamber to the base pressure of 10^{-6} torr.

In order to minimize iodine exposure to the mechanical pumps, a liquid nitrogen cold trap was placed between diffusion pump and the mechanical pump. The cold trap is filled with liquid nitrogen before the pump down procedure is initiated, and the liquid nitrogen supply is shutoff after the chamber is vented to a minimum of 150 torr. After chamber venting, a gate valve attached to the top of the chamber, above the diffusion pump, is opened and a small ducted fan is turned on that vents the chamber into a fume hood.

4.2.1 Cathode Setup and Gas Feed System

The cathode assembly is made of two parts: the argon and iodine supplies with mass flow control on the outside of the chamber and the cathode on the inside of the chamber. The figure below shows the layout of the feed system.

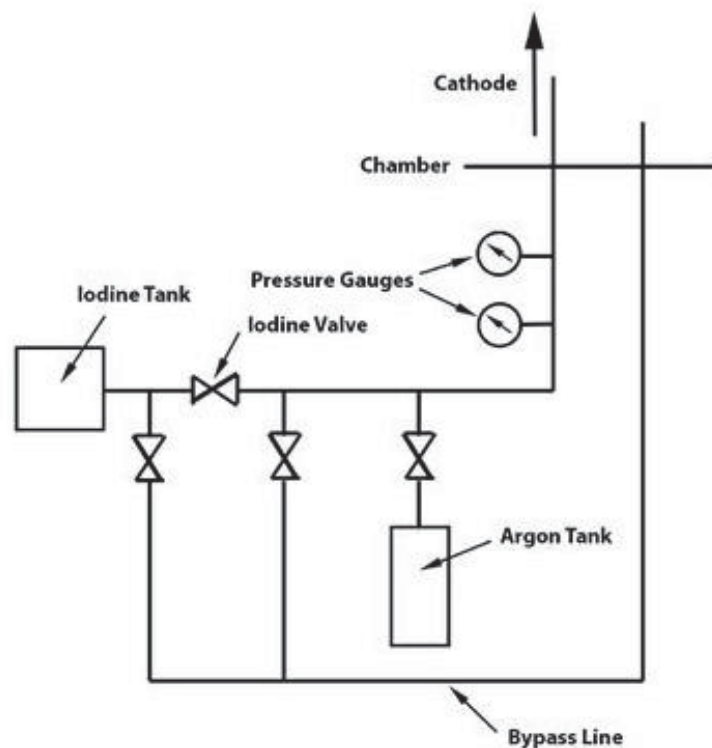


Figure 36: Cathode testing gas feed system

The exterior of the chamber has one main ½" gold plated stainless steel line with two thermocouple pressure gauges for mass flow measurement. A bypass line is connected before and after the iodine shutoff valve to allow the line and iodine tank to independent vented. The bypass line after the iodine line is used to pump down the feed lines faster than would occur through the cathode orifice. The iodine source bypass valve allows the tank to be removed after pump down to refill or measure the iodine and then evacuate the air while minimizing oxygen exposure to the cathode. The argon tank is connected to a mass flow controller and then connected to the feed system with valve so that the argon can be shutoff and lines protected from iodine.

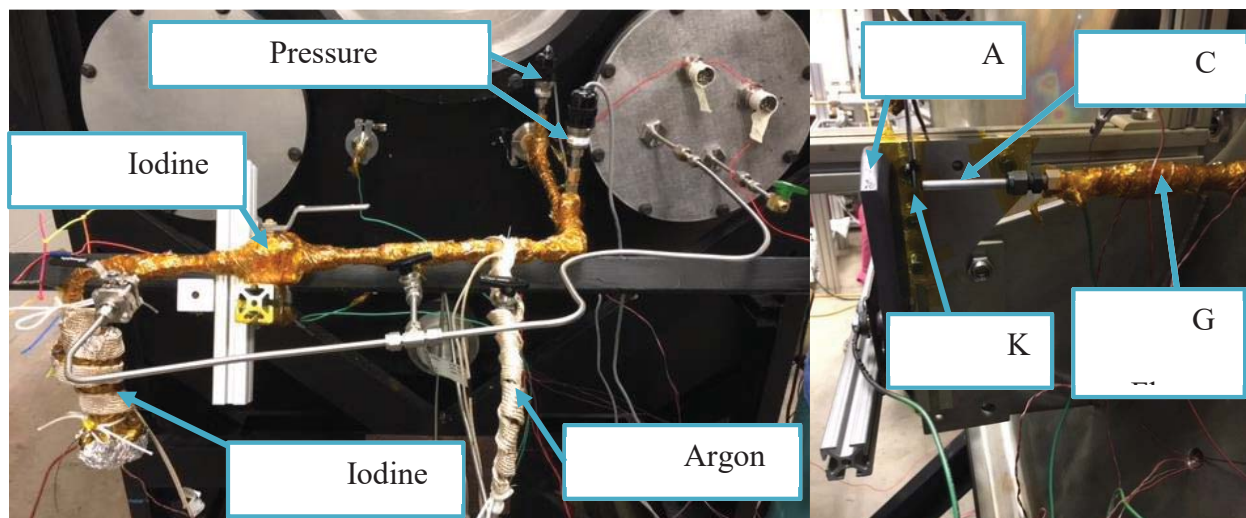


Figure 37: Cathode testing setup

4.2.2 Electrical Setup

The experimental test stand inside of the chamber consists of a cathode tube, keeper, and an anode. The cathode tube and the keeper were provided by Plasma Controls. An electron emitting material shaped like a cylinder is in the inside of cathode tube which supports the emission of electrons.

A graphite disc was used with an orifice of approximately 2 mm. An anode was placed around 30mm downstream to act as beam for the electrons. Two high voltage power supplies (total of 650V and 1.313A each) were placed in series, with diodes for protection, were connected to a series ballast resistor to ionize the gas between the keeper and the cathode. The anode was connected to a 60V and 20A power supply to create the electron beam.

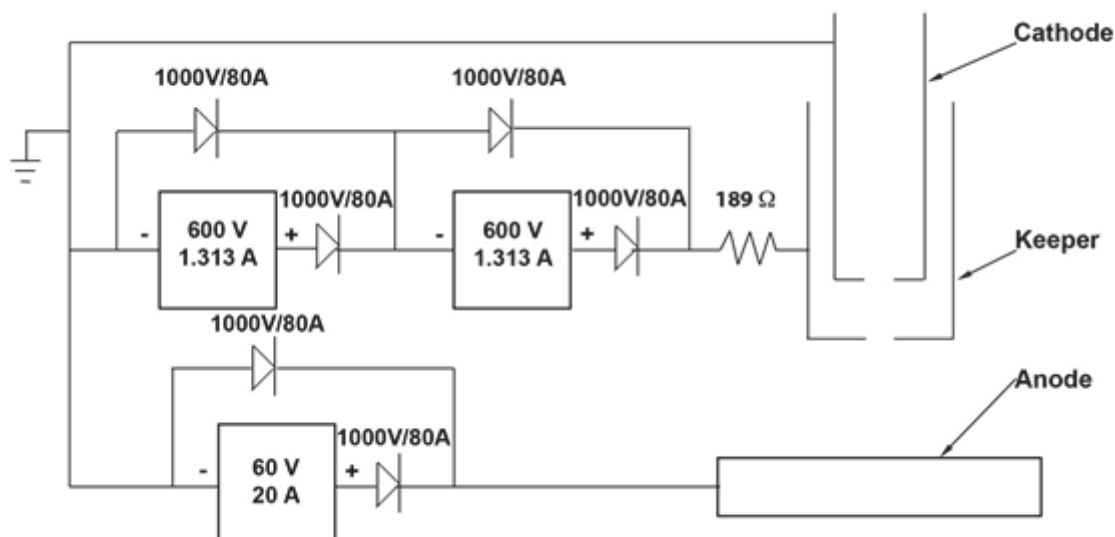


Figure 38: Cathode Electric Diagram

4.2.3 Test Procedure

Due to cathode not having an external heater, it was determined that running the cathode on another gas (argon in this case) before iodine operation was necessary to minimize condensation and eventually clogging in the cathode tube.

1. Fill the iodine tank and measure weight of the iodine.
2. Heat up the iodine tank to around 80°C to melt the loose crystals, wait for 30 minutes, and allow the tank to cool down. This melting creates a more consistent block of iodine at the bottom of the tank.
3. Open the argon tank.
4. Set argon gas flow rate to 50 sccm.
5. Turn on the high voltage power supplies (1300V, 1.313A) to ionize the between cathode and keeper.

6. Turn on the discharge power supply (60V, 8A) to create an electron beam from the cathode/insert to the anode.
7. Decrease argon gas flow rate to 20 sccm.
8. While the cathode and the keeper are warming up, turn on the heaters for the iodine gas feed lines to around 100°C. Wait approximately 30 minutes until thermal equilibrium is reached
9. Heat up the bottom of the iodine source to 70°C and wait 15-30 minutes until tank reaches equilibrium.
10. Open valve to the iodine source.
11. Wait approximately 10 minutes to reach a steady gas flow rate of the iodine/argon combination. A light blue/green plasma should be visible near the keeper orifice.
12. Start decreasing argon gas flow by 5 sccm steps in 5 minutes interval. Until argon flow can be shutoff.
13. Record data at desired time intervals.
14. After the run, shut iodine valve and reopen argon line. Run on argon for 30-60 minutes to clean cathode.
15. Measure the remaining mass of the iodine in the source tank to determine the mass flow rate relative to the run time.
16. Keep the heaters on while flowing argon to remove iodine residue in the lines and in the chamber for at least 12 hours, if possible.

4.2.4 Cathode Configurations

Several different iterations of cathode were tested using iodine as the propellant. Initially the cathodes were tested inside a stainless-steel tube that held the cathode tube and keeper in place with the desired spacing. This configuration functioned acceptably when tested on xenon and argon, but when tested with iodine the ceramic spacers got plated with a conductive material and grounded the cathode. The stainless-steel enclosure can be seen below:

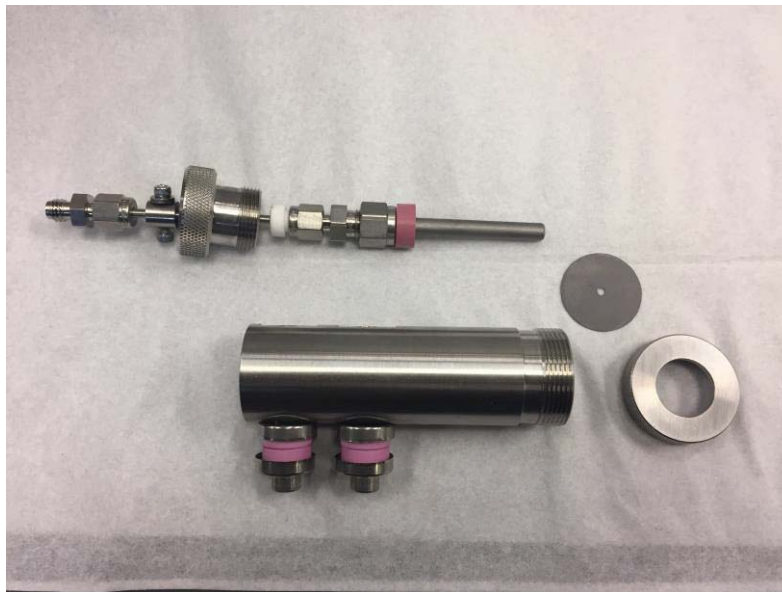


Figure 39: Plasma Controls cathode assembly.

To alleviate this grounding, the cathode was instead assembled in an open configuration as seen in Figure 37: Cathode testing setup. Initially a gold plated stainless steel anode was used, but when running with iodine a black buildup slowly reduced the surface conductivity and eventually made it too difficult to continue operation. The anode was replaced with a graphite plate to fix this issue. Three cathodes were tested for appreciable times on iodine:

1. Molybdenum hollow cathode tube (PC-I3)
2. Tantalum hollow cathode tube (PC-I4)
3. Tantalum hollow cathode tube with a graphite tube liner (PC-I20)

5 Test Plan

5.1 Introduction

The experiment is divided into two primary categories to measure the differences between the chemical erosion and the erosion due to plasma interactions. The first phase is characterizing the material erosion process, the second phase is exposing material samples to iodine vapor, and the third and final phase is exposing material samples to an iodine plasma. In the first phase the test setup will be characterized and adjusted to meet the desired operating conditions and stainless steel will be used as test material. In the second phase the five refractory materials of interest will be exposed to iodine vapor and characterized before and after exposure. The final phase will be similar to the second phase but with the addition of plasma.

5.2 Characterization Phase

The first step in characterizing the process will be to better understand the plasma being generated with a Langmuir probe and spectral measurements. The Langmuir probe will be used to determine electron temperature and plasma density at various power levels. The intention is to determine what input parameters are required to simulate the previously outlined hollow cathode operating conditions.

The spectral measurements will be used to accomplish two goals: to identify the plasma species present in the plasma and to identify if a significant quantity of erosion is occurring upstream in the feed system. The direct emission spectra will correspond to what transitions are taking place and can be used to identify the dominate species, expected to be excited state atomic iodine and singly ionized atomic iodine. The presence and relative intensity of gold or iron

emission lines will help to determine if the feed system experiences an unacceptable level of erosion.

Stainless steel will be used as a test material due to having a significantly higher expected erosion rate than the refractory materials of interest, which will make it easier to identify changes. The initial testing will be performed by characterizing the material with XRD, SEM, and a surface profiler, then exposing the material, then characterizing the material again with previously stated devices. During iodine exposure erosion is expected to occur on the substrate and the surface profiler will not provide useful erosion rate information and may not be used depending on the results. Resistance measurements will be taken throughout testing and compared to measurements from the SEM and surface profiler. Due to the vapor pressure of the expected halides and the testing pressure, it is unlikely that significant formation of iodides occurs and XPS may be not be used if the EDS analysis suggests negligible surface iodine.

Phase identification will be performed with X-Ray Diffraction (XRD) using a Bruker Discovery D8 diffractometer. The operating parameters are summarized below:

- Cobalt- $k\alpha$ radiation – 45 keV and 20 mA
- Scan speed 0.1 degrees/second
- 10-130 degrees 2Θ
- ICDD databases for peak matching

Imaging will be primarily performed with scanning electron microscopy (SEM) using a JEOL FESEM 7000F. The operating parameters are summarized below.

- 10 – 30 keV beam voltage
- As close to 10 mm working distance as possible for EDS (ideal distance for available EDS hardware)

- Secondary Electron (SE) and Back-Scattered Electron (BSE) modes will be used.

Secondary electron mode provides high resolution topographical sensitive micrographs. Back-scattered electron mode provides atomic number contrast micrographs and another topographic image.

- Energy dispersive x-ray spectroscopy (EDS) will be used to obtain chemical maps

SEM imaging will be used to identify the majority of the structural changes. Both surface imaging and cross-sectional imaging will be done. Surface imaging will be done to determine variations in bulk topographical changes (i.e. surface roughness), grain structure changes, and compositional analysis with EDS. Specific focus will be devoted to determining if specific features result in increased erosion rates, for example does erosion occur more readily at grain boundaries. Cross-sectional imaging will be done to investigate any scale formation that occurs and/or if the surface undergoes changes in porosity or experiences cracking.

XRD will be used to determine the phase composition of the material sample surface. The primary goal will be used in conjunction with EDS to determine if any significant iodide formation occurs. Of the primary materials of interest only carbon and graphite form in different phases and XRD will primarily provide information on if/how the exposure affects phase.

If in EDS imaging significant iodine concentrations are found on the surface and XRD proves to not provide a useful metric for determining what iodides are present, XPS will also be used. Most iodide are expected to have relatively high vapor pressures and will not form in any appreciable concentrations at the test conditions.

Resistance measurements will provide the primary form of erosion rate measurements, and will be backed up with surface profilometry and SEM. For the resistance measurements a

minimum of 30 data points at each test point will be taken to ensure that the average effectively fits a standard deviation.

5.3 Testing

The first material test after stainless steel has been tested and the system appropriately calibrated will be used to determine test length. Since the erosion rate of materials in iodine and iodine plasma has not been well tested, the first step will be determining the length of testing required to make a measurable erosion. The chemical and plasma testing phases should be performed for the same length of time for a defensible comparison to be made. The first material will first be exposed to an 8-hour test and examined for changes. If 8 hours is insufficient, new tests will be performed starting at 12 hours, then 24 hours, 48 hours, 72 hours, or until a sufficient erosion is measured.

The actual test will consist of a minimum of a two-hour pump-down time with a small flow rate of argon, after the ultimate pressure has been reached. After the ultimate pressure is reached the feed system heaters will be turned on. The furnace will then be turned on and the heat ramped up over a period of 30-60 minutes, and then the sample heater will be ramped to the final temperature over a period of 30-60 minutes. Once the sample is at the appropriate temperature, the iodine flow will be started and slowly increased until the desired operating pressure is reached. The plasma can then be started at previously determined appropriate plasma conditions from Langmuir probe measurements.

Once the desired test length has been reached, the plasma and iodine will be turned off and replaced with an argon flow and the sample temperature slowly reduced. After the sample has fully cooled off, the vacuum pumps will be turned off and the system brought back to

ambient conditions with argon. The sample will then be removed from the system and immediately vacuum bagged for storage and transport to characterization devices.

In the interest of minimizing the number of tests that need to be performed, sample geometry will be modified as is suitable to the minimum feasible size and multiple different materials can be tested simultaneously. The below table shows an example testing matrix, with the assumption of all five test materials being run simultaneously. The goal will be to test each temperature condition at least twice.

Table 10 – Material Sample Testing Matrix

Series #	Temperature (K)	Pressure (torr)	Plasma Density (m^3)	Material (# samples)	Electron Temperature (eV)
1	1600	1	3.2×10^{20}	5	3
2	1700	1	3.2×10^{20}	5	3
3	1800	1	3.2×10^{20}	5	3
4	1900	1	3.2×10^{20}	5	3
5	2000	1	3.2×10^{20}	5	3

5.3.1 Startup Procedure

1. Plug in roughing pump
2. Open liquid nitrogen line
3. Open upstream and downstream cold trap valves
4. Once pressure reaches 0.5 torr open water valve and turn on diffusion pump
5. Wait until ultimate pressure is reached
6. Turn on feed system heaters
7. Close argon bypass valve and set argon mass flow rate to 10 sccm
8. Fill the iodine tank and measure weight of the iodine.
9. Slowly open iodine shutoff valve, making sure pressure does not rise above 1 torr
10. Once pressure begins dropping again close iodine valve

11. Heat up the iodine tank to around 80°C to melt the loose crystals, wait for 30 minutes, and allow the tank to cool down. This melting creates a more consistent block of iodine at the bottom of the tank.
12. Turn on furnace and set to 200°C
13. Allow material sample to bake under argon flow for >2 hours
14. Ramp up furnace to 1250°C
15. Ramp up sample heater to 1750°C
16. Heat up the bottom of the iodine source to 70°C and wait 15-30 minutes until tank reaches equilibrium.
17. Open valve to the iodine source.
18. Close argon valve
19. Turn on RF power supply and set to desired power level

5.3.2 Shut-down Procedure

1. Shut-off RF power supply
2. Close iodine shutoff valve
3. Turn off iodine source heater
4. Open argon valve and set to 10 sccm
5. Ramp down sample heater
6. Ramp down furnace
7. Fully open all cold trap valves and run argon at 10 sccm for 2 hours
8. Close cold trap valves
9. Wait argon has refilled chamber

10. Carefully remove sample
11. Quickly transfer sample to vacuum bag
12. Carefully reopen cold trap valves, pump down chamber to under 5 torr
13. Shut cold trap valves
14. Unplug diffusion pump
15. Wait for cooldown then shut water valve
16. Leave roughing pump on and leave chamber under vacuum
17. Close liquid nitrogen line

5.4 Statistical Significance

To ensure accuracy of measurements, each characterization technique needs to be carefully performed. For SEM and XRD measurements, multiple different sites on the sample will be investigated to look for uniformity. For the resistance measurements, the samples will be measured at various temperatures, as they are being heated, to see if they follow the expected resistance variation. In addition, at each measurement point the samples numerous data points (>25) will be taken to in an effort to characterize the random drift of the multimeter's measurement accuracy. The resulting total erosion rate of the material samples measured via the resistance will then be compared with measurements using SEM and surface profilometry.

6 Results

6.1 Preliminary Results

The following results are primarily qualitative and were derived from testing cathodes and the material testing apparatus.

6.2 Feed Lines and Vacuum Chamber

Initial testing was performed with non-coated or plated stainless-steel tubing in the feed system for some of the components. The unprotected stainless-steel quickly developed a significant amount of rust after being exposed atmosphere. This rust led to increased clogs in areas with small orifices and was ruled out as a non-viable setup. Ideally, when not pumped down, the feed system should be filled with an inert gas to prevent iodine or oxygen attack. Literature and theory suggest that the primary erosion expected at standard conditions is due to the formation of hydroiodic acid due to moisture exposure and oxygen to a lesser extent. All future steel components were plated in gold to protect from iodine attack. The gold plating process requires care not to get oils onto the piece to be plated between electro-cleaning and plating or the gold will not properly adhere. The places where the gold rubbed off form areas for rust formation and then expansion into the rest of the tubing. Gold plated nickel tubing or thoroughly PTFE coated stainless steel might provide a better solution for long-term testing.

The first cathode testing was performed without a cold trap between the diffusion pump and the roughing pump, which eventually led to a mechanical pump seizing and no longer pumping. The iodine from testing mixes with the mechanical pump oil and attacks the metal components slowly building up rust and eventually causes the pump to fail. Future iodine testing should always be performed with a cold trap protecting the mechanical pumps.

Two different pressure gauges were initially used in testing: a Leybold Pennivac PTR90 and an Inficon PCG554. The PTR90 was used for the measuring chamber pressure and stopped measuring pressure accurately after minimal iodine exposure. The PCG554 was used for measuring the iodine source pressure, due to its ceramic sensor, but was unable to withstand higher pressures of iodine. An iridium coated filament ionization pressure gauge was then used for measuring the chamber pressure, due to iridium's apparent lack of reactivity to iodine. The ionization gauge has proven to very resistant iodine and shows no signs visible signs of erosion or change in pressure measurement. The PCG554 was switched out for Varian 531 equivalent thermocouple gauges due to their wetted materials (nickel, glass, and Platinel®) and relatively disposable nature. The thermocouple gauges proved to survive iodine attack for an extended period of time but provided limited useful information due to the lack of a proper pressure correction curve for iodine. The primary information provided by the thermocouple gauges was to show the pressure rise over time during iodine cathode operation presumably due to orifice clogging. As mentioned in the experimental section, a Inficon Sky CDG100D heated manometer is now being used on the material characterization apparatus, which provides gas independent pressure measurement and an effectively corrosion proof ceramic sensor.

6.3 Cathode

The high pressure and temperature environment of hollow cathodes present unique challenges for material interaction investigations. The very high temperatures make it difficult to reach without either building a cathode or large capital investments into very high-temperature furnaces. The cathodes tested provided very promising results for future long-lasting cathodes, but some challenges to overcome were discovered. The erosion of the insert material during

initial operation results in the cathode eventually clogging with a very hard metallic material. This metallic material does not behave like stainless steel or iron oxides, no rust developed in atmospheric conditions and it required a diamond burr to drill out. XRD analysis revealed that the insert material consisted of almost entirely tungsten. EDS analysis of the keeper plates showed heavy deposition tungsten onto the surface. The combination of orifice clogging and tungsten deposition on the keeper plate suggests a significant erosion and transport of tungsten away from the insert occurs.

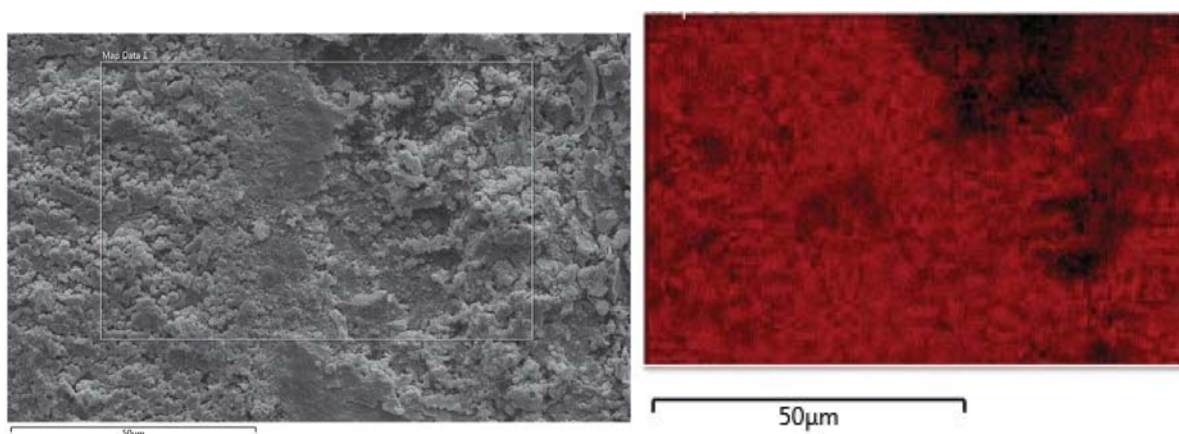


Figure 40 – Secondary electron image at 1000x and 20kV (left), Tungsten EDS map (right)

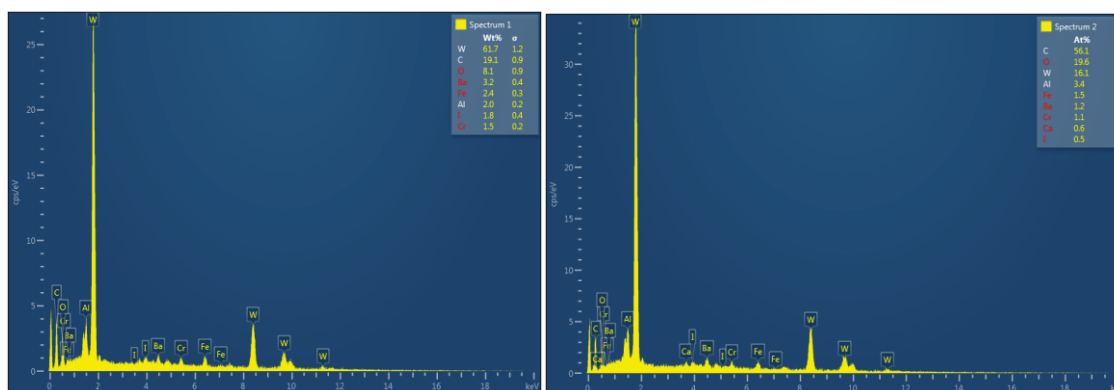


Figure 41 –EDS atomic composition by wt% (left) and at% (right)

The initial anode was made of gold-plated stainless steel, but the gold was quickly eroded off and the anode was coated with a black substance that eventually caused to the discharge to

shut off. Replacing the anode with graphite eliminated this conductivity issue. Until a superior material is found graphite is the recommended material for future testing.

6.4 PC-I3 and PC-I4

The following table describes the results of testing the PC-I3 and PC-I4 cathodes with iodine.

Table 11: Summary of PC-I3 and PC-I4 cathodes with iodine

Date	Cathode	Argon [hours]	$\dot{m}$ [sccm]	Iodine [hours]	AR + I2 [hours]	Comment
11/14/2017	PC-I3	3	20	0	0	Inside heater shorted.
11/16/2017	PC-I3	2	20	0	1.5	Clogged cathode.
11/21/2017	PC-14	2.5	30	0	1.67	Clogged cathode.
11/23/2017	PC-14	1.5	20	0	0	Clogged feed line.
11/30/2017	PC-14	1	20	0.3	0.5	Hole in side of tantalum tube.
12/01/2017	PC-I3	1	40	0	0.75	Intermittent, I ₂ seemed to turn off discharge.

PC-I3 and PC-I4 both encountered issues with iodine interactions. The molybdenum cathode (PC-I3) would not maintain a consistent discharge without argon flow. The orifice of both systems clogged during the first four hours of running, which was due to insufficient gold plating of the gas lines and what is believed to be insert erosion (see PC-I20 testing results). In addition, material built up between the cathode and keeper (see Figure 42) which resulted in shorting both parts. Increasing the distance between the cathode and keeper to approximately

4mm eliminated the shorting issue. The tantalum cathode ran very stably until the iodide eroded a hole through the tube right before insert (see Figure 43).

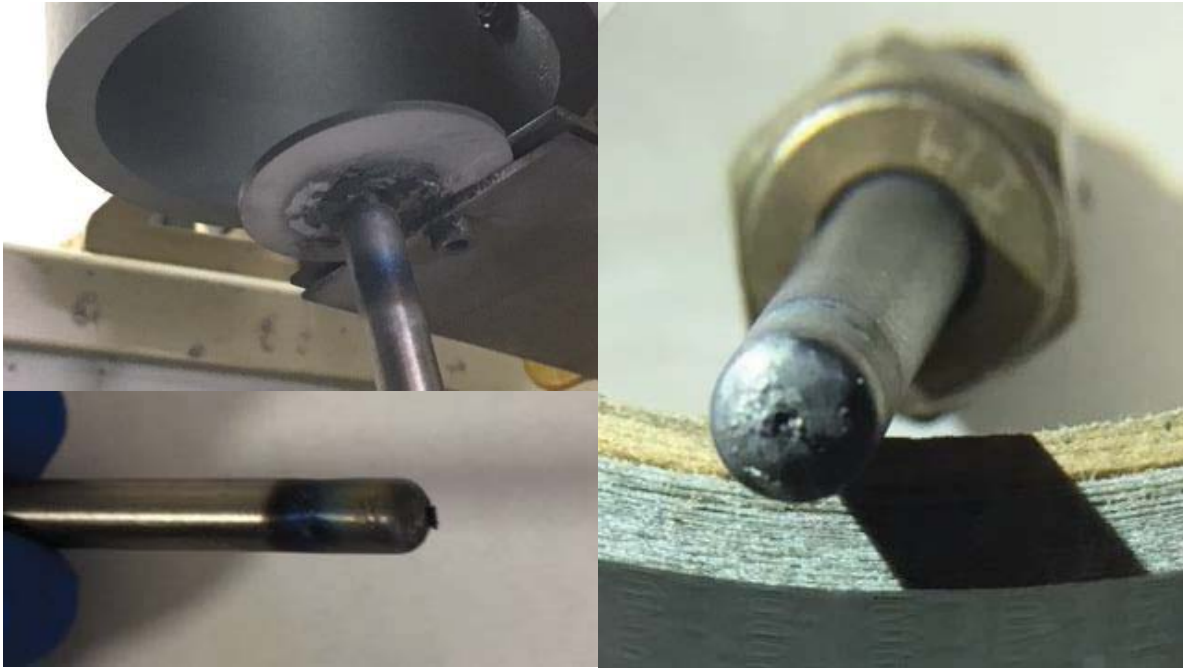


Figure 42: Clogged orifice and material build up on the cathode tip.

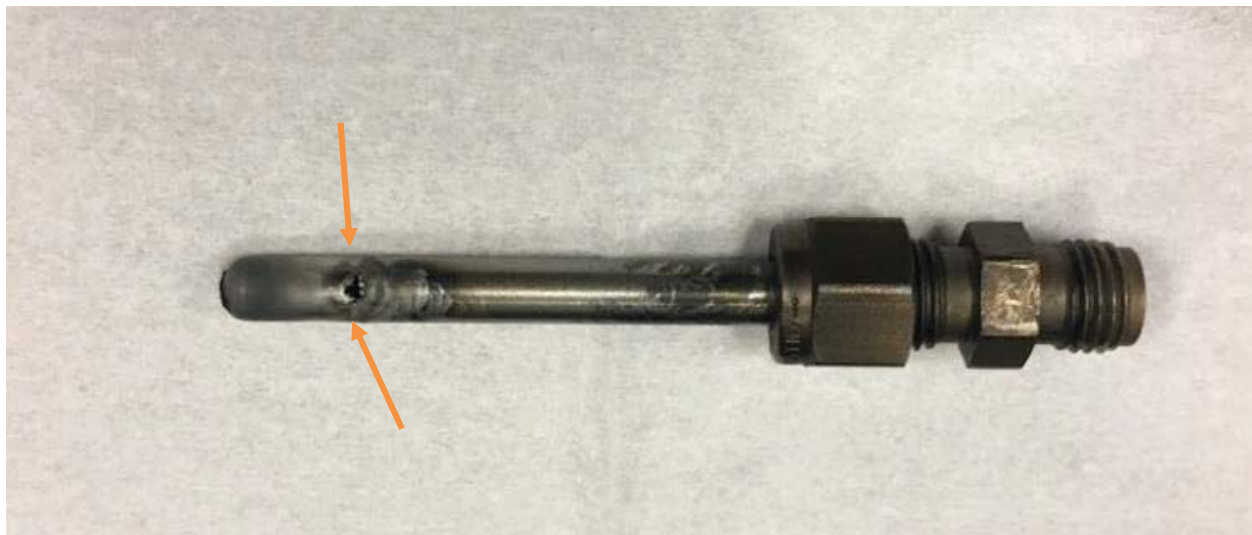


Figure 43: PC-I3 cathode after iodine erosion created a hole in the tantalum tube.

6.5 PC-120

After the erosion of the tantalum tube in the PC-I3 testing, the cathode design was updated with a carbon tube inside the tantalum tube as a liner. The cathode to keeper spacing was

kept the same as the previous test at approximately 4mm, and the keeper to anode spacing was approximately 30mm. The PC-120 was tested for a total of 44 hours in two runs: first run for 13 hours and the second run for 30 hours. In both runs mass transport of the insert in the cathode eventually resulted in a metallic material clogging the orifice.

The first run was performed with an orifice diameter of approximately 2.5mm. The cathode was first ignited at an argon flow rate of 50 sccm and was run for around eight minutes at a discharge current and voltage of 8A and 30.3V respectively. The argon flow rate was then steadily decreased to 20sccm, at which the discharge voltage was 29.9V. The gas feed lines were then heated to 120-130°C. The iodine shutoff valve was then opened with a source temperature of 45.3°C. The discharge initially spiked to 49.1V and then steadily decreased to 25.2V. The keeper voltage varied around $\pm 3V$ during this period. The iodine source was then heated from 45.3°C to 70.5°C. The argon flow rate was then steadily decreased until 4sccm and then shut off. During the first five hours of operation the source temperature was varied slightly to keep an optimal discharge voltage of 35V. The cathode was then run at discharge conditions of approximately 35V and a constant 8A and keeper conditions of approximately 22V and a constant 1.313A for 12 hours and 40 minutes. At the 12 hours and 40-minute mark the discharge and plasma ionization turned off. The cathode was then successfully restarted with a mix of argon and iodine, and then the argon was turned off. After reignition, the discharge voltage was varying between 50-60V. After 50 minutes of an inconsistent discharge voltage the cathode began to clog, as evidenced by an increase in pressure in the feed lines, and eventually stopped and could not be reignited. Further information regarding the discharge and keeper voltage can be seen below:

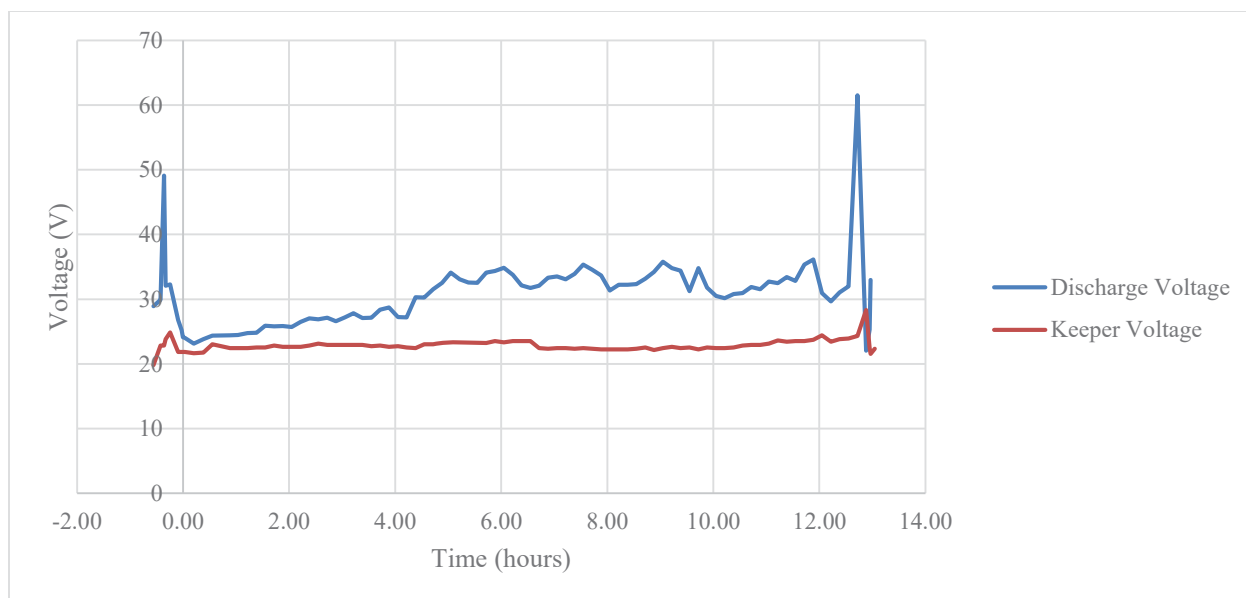


Figure 44: Keeper and discharge voltage information for the 13-hour run of the PC-120 cathode. Time zero is the point when the argon flow was shutoff.

After the clog in the cathode was removed with a diamond burr, the cathode was reignited using argon. Iodine was slowly introduced into the cathode with a procedure the same as the previous run and run on an argon/iodine mix for 1 hour and 48 minutes. The argon flow was then shutoff, and the cathode began operation of only iodine. The cathode then ran for approximately 30 hours with an average keeper voltage of 25V, a constant keeper current of 1.313A, an average discharge voltage of 33V, and a constant discharge current of 8A. In the last 30 minutes of operation the discharge voltage slowly increased to 60V and then the discharge current slowly decreased to zero. During this 30-minute period, the pressure in the gas feed line slowly increased until the cathode completely clogged and could not be reignited. Further information regarding the discharge and keeper voltage can be seen below:

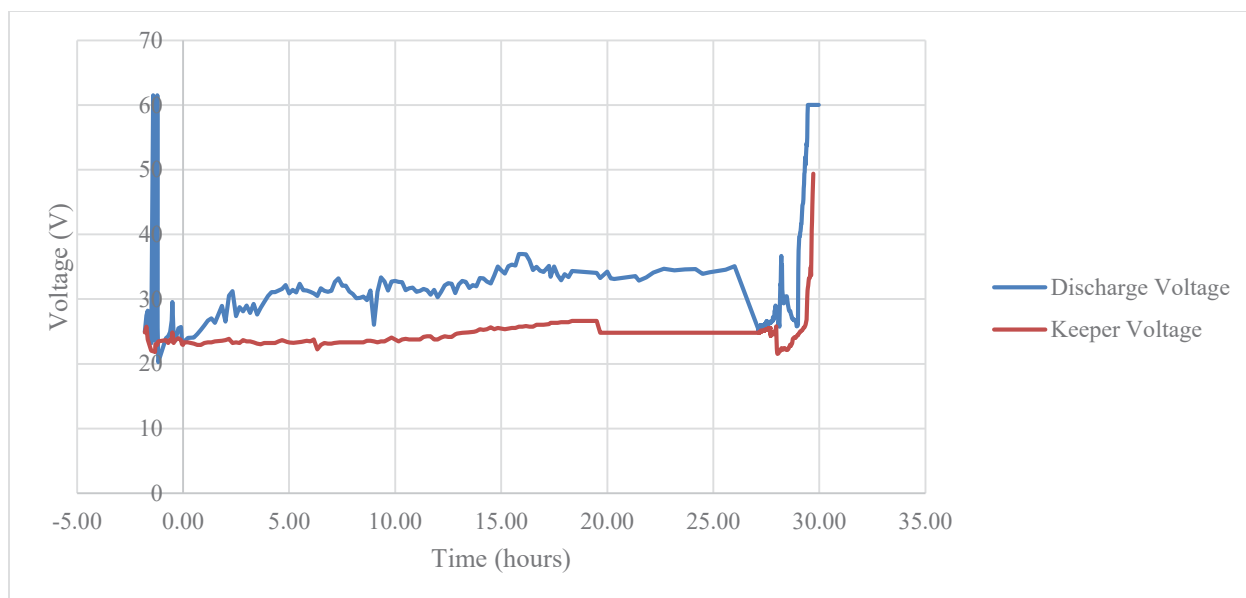


Figure 45: Keeper and discharge voltage information for the 30-hour run of the PC-120 cathode. Time zero is the point when the argon flow was shutoff.

Table 12: PC-I20 cathode run mass flow rates.

<i>Cathode run</i>	<i>Date</i>	<i>Initial Iodine Mass (g)</i>	<i>Final Iodine Mass (g)</i>	<i>Estimated Mass Flow Rate (mg/s)</i>
<i>PC-I20 – 13 hours</i>	12/05/2018	217.6	142.6	1.52
<i>PC-I20 – 26 hours</i>	12/06/2018	142.6	35.52	0.99



Figure 46: Material removed from clogged cathode orifice (left), clogged cathode orifice (right).

In all cathode testing scenarios, a high mass flow rate of iodine resulted in a yellow plume and a low mass flow rate resulted in green plume.



Figure 47: Cathode running with a low iodine flow rate (left), and with a high iodine flow rate (right)

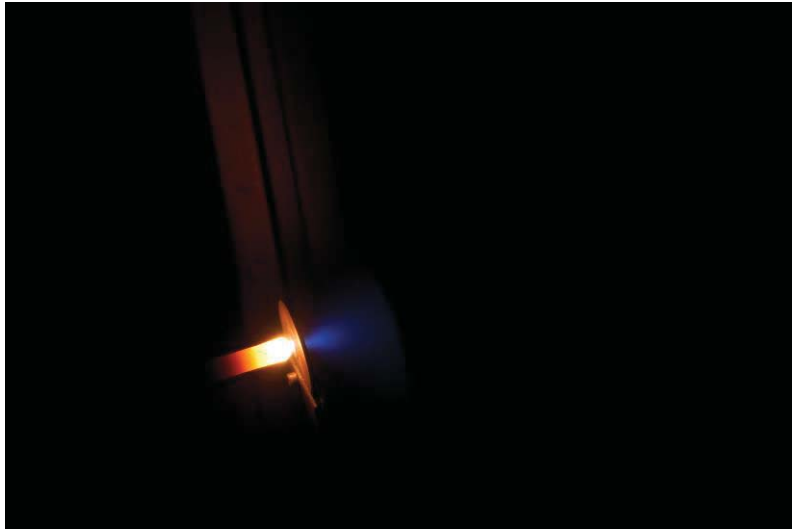


Figure 48: Cathode running on argon only

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Appendix B: List of Symbols

χ	Electronegativity
n	Number of valence electrons
c	Formal valence charge
r	Covalent radius
Δ_{A-B}	Excess binding energy
DE_{ij}	Bond dissociation energy
r_0	Ionic bond radius
b	Unit cell edge
a	Unit cell edge
c	Unit cell edge
α	Interaxial angle
β	Interaxial angle
γ	Interaxial angle
ϵ_0	Permittivity of free space
U_0	Equilibrium potential energy
ΔE_{ions}	Energy required to form an ion
U_L	Equilibrium potential energy in a lattice
α_M	Madelung constant
a	Lattice parameter
r	Atomic radius
r_f	Forward reaction rate
r_b	Backward reaction rate
k_f	Forward rate constant
k_b	Backward rate constant
K_p	Equilibrium rate constant
ΔG^0	Change in Gibbs free energy
R	Ideal gas constant
T	Temperature
k_0	Proportionality constant
E_a	Activation energy
n	Reaction order
k	Rate constant
q	Heat flux
k	Thermal conductivity
τ_{yx}	Momentum flux
μ	Viscosity
J_{Ay}^*	Mass flux
D_{AB}	Molecular diffusivity
ϵ	Maximum energy of attraction
σ	Collision diameter
M	Molecular weight

Ω	Dimensionless temperature
V	Molar volume
PF	Packing fraction
n_0	Average number density
C_v	Heat capacity
C_{ve}	Electronic heat capacity
k_B	Boltzmann's constant
E_F	Energy of the Fermi level
P	Pressure
D_0	Frequency factor
ΔG	Gibbs free energy
ΔG^0	Gibbs standard free energy of formation
P^*	Partial pressure
$\frac{dn}{dt}$	Growth rate
ξ	Scale thickness
F	Faraday's constant
F'	Faraday's constant
z_x	Anion valence
t_M	Electrical transference number for cations
t_X	Electrical transference number for anions
t_e	Electrical transference number for electrons
σ	Electrical conductivity of scale
$P_{X_2}^i$	Nonmetal activity at metal/scale interface
$P_{X_2}^0$	Nonmetal activity at gas/scale interface
k_p	Parabolic rate constant for scale growth from diffusion
k_v	Linear rate constant for scale loss due to vaporization
y	Metal loss
V_M	Molar volume of the metal
V_{MX_v}	Molar volume of the scale
ρ_{MX}	Bulk density of the scale
ρ_M	Bulk density of the metal
N_X	Atomic weight of the halogen
J_i	Vaporization rate (molecules/cm ² -sec)
P_i	Vapor pressure
m_i	Mass of evaporating molecule
k	Boltzmann's constant
G_i	Vaporization rate (g/cm ² -sec)
α_i	Degree of vaporization
M_i	Molecular weight of vapor species
δ	Boundary layer thickness
L	Characteristic length
Sc	Schmidt number
Re	Reynolds number

d_0	Minimum resolvable separation
λ	Wavelength
n	Refractive index
α	Semi-angle of sample
d	Inter-planar spacing
θ	Diffraction angle
n	Path difference (integer value)
ν_0	Threshold frequency
ϕ	Work function
E	Energy
θ	Polar angle
φ	Azimuthal angle
p	Polarization
λ_D	Debye length
N_D	Number of particles inside Debye length
ω_{pe}	Electron plasma frequency
ν_e	Gaseous collisional timescale
ε_i	Ionization energy
α	Degree of ionization
h	Planck's constant
f_+^i	Total partition function for ions
f_A^i	Total partition function for neutral atoms
∇	Laplace operator
D	Electrical displacement field
E	Electric field
ε	Permittivity
e	Charge of an electron
n_i	Ion number density
n_e	Electron number density
ϕ	Potential
n_∞	Number density at infinity
u	Velocity
T_e	Electron temperature
I_B	Bohm current
m_i	Ion mass
c_s	Terminal ion velocity
A	Sheath area
α	Constant
v_i	Ion velocity
n_s	Ion number density at terminal velocity
Φ	Magnetic flux
B	Magnetic field
H_0	Magnetic field strength
ω	Angular frequency

$\mathcal{E}$	Electromotive force
J	Current
σ	Plasma conductivity
L_{ele}	Electron inertia inductance
R_{plasma}	Plasma resistance
M_{ab}	Mutual inductance
M	Coupling coefficient
R_{input}	Resistance at input node of antenna
R_{ant}	Antenna resistance
Z_{plasma}	Plasma impedance
L_{input}	Inductance at input node of antenna
L_{plasma}	Plasma inductance
δ	Skin depth
ρ	Resistivity
μ	Permeability
R_{rf}	Effective resistance in conductor
r	Conductor radius
q	Charge
N_m	Molar flow rate
ζ	Viscosity
a	Tube radius
l	Tube length
P	Pressure
T_r	Reduced gas temperature
T_m	Input gas temperature
T_{wall}	Wall temperature
Q	Flow rate
d	Diameter
I_e	Electron current
I_{es}	Electron saturation current
V_p	Probe voltage
V_s	Sheath voltage
A	Probe surface area
I_0	Ion saturation current
S	Probe collecting area
a	Radius of closest approach
r_p	Probe radius
L	Probe length
Γ_r	Random ion flux
Γ	Ion Flux
r_{sheath}	Sheath radius
H	Hamiltonian energy operator
ψ	State vector

r	Position vector
E	Total energy in the system
p	Linear momentum
μ	Reduced mass of the electron
V	Potential energy
R_M	Rydberg constant

Appendix C: List of Abbreviations

AFIT	Air Force Institute of Technology
ICP	Inductively Coupled Plasma
SEM	Scanning Electron Microscope
SE	Secondary Electron
BSE	Backscatter Electron
EDS	Energy Dispersive Spectroscopy
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy
HET	Hall Effect Thruster
AC	Alternating Current
DC	Direct Current
RF	Radio Frequency
ICDD	International Centre for Diffraction Data
NIST	National Institute of Standards and Technology

Appendix D: Iodine Vapor Pressure ¹⁴

Table 13: Iodine Vapor Pressure

Pressure (torr)	Temperature (K)	Temperature (°C)
1.00E-08	177.5	-95.5
5.00E-08	185	-88
1.00E-07	187.5	-85.5
5.00E-07	195	-78
1.00E-06	198.75	-74.25
5.00E-06	207.5	-65.5
1.00E-05	212.5	-60.5
5.00E-05	220	-53
1.00E-04	225	-48
5.00E-04	237.5	-35.5
1.00E-03	242.5	-30.5
5.00E-03	255	-18
1.00E-02	262.5	-10.5
5.00E-02	275	2
1.00E-01	285	12
5.00E-01	300	27

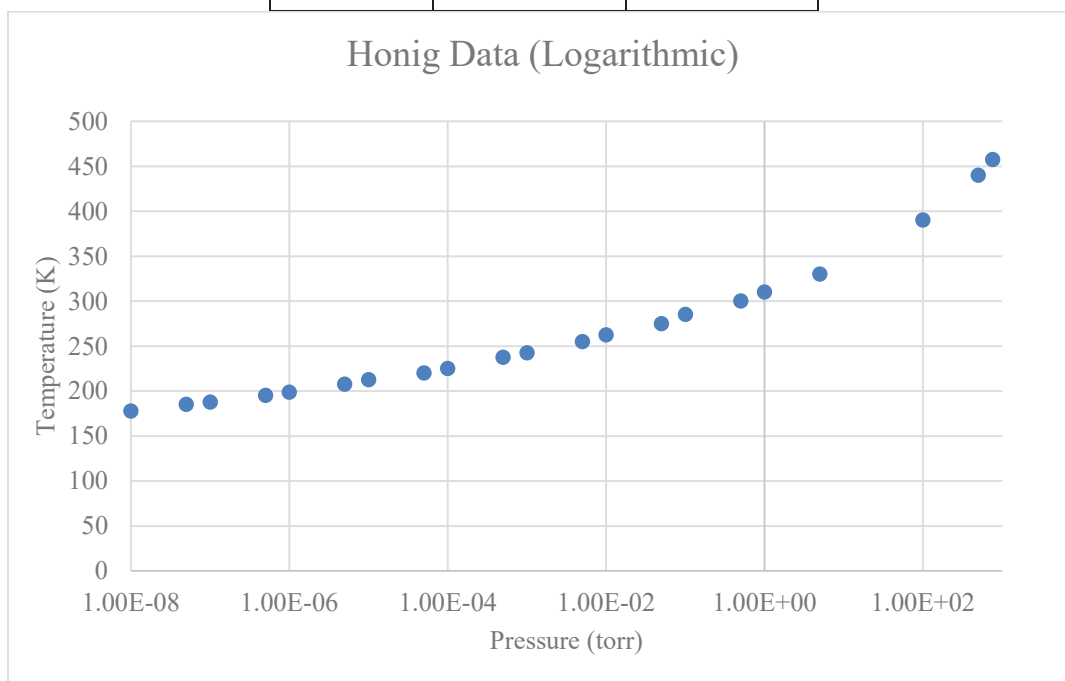


Figure 49: Honig Data

Appendix E: Selected Iodine Spectral Lines

Excited State atomic iodine ^[93,94]

Observed Wavelength (nm)	Ritz Wavelength (nm)	E _i (cm ⁻¹)	E _k (cm ⁻¹)	Lower Level			Upper Level		
				Config	Term	J	Config	Term	J
130.0335	130.033484	0.000	76903.269	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (³ P ₂)6d	² [2]	5/2
142.5490	142.549234	0.000	70151.201	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (³ P ₂)5d	² [2]	5/2
145.7389	145.739168	0.000	68615.734	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (³ P ₂)5d	² [0]	1/2
145.7981	145.798399	0.000	68587.859	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (¹ D ₂)6s	² [2]	5/2
150.7041	150.704333	0.000	66355.093	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (³ P ₂)5d	² [1]	3/2
151.4682	151.468176	0.000	66020.469	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (³ P ₂)5d	² [3]	5/2
151.8048	151.802970	7602.970	73477.834	5s ² 5p ⁵	² P ^o	1/2	5s ² 5p ⁴ (¹ D ₂)5d	² [0]	1/2
159.3582	159.357816	7602.970	70354.834	5s ² 5p ⁵	² P ^o	1/2	5s ² 5p ⁴ (³ P ₂)5d	² [2]	3/2
161.7606	161.760527	0.000	61819.779	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (³ P ₁)6s	² [1]	3/2
178.2757	178.27572	0.000	56092.881	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (³ P ₂)6s	² [2]	3/2
179.9092	179.90873	7602.970	63186.758	5s ² 5p ⁵	² P ^o	1/2	5s ² 5p ⁴ (³ P ₁)6s	² [1]	1/2
183.0380	183.038014	0.000	54633.460	5s ² 5p ⁵	² P ^o	3/2	5s ² 5p ⁴ (³ P ₂)6s	² [2]	5/2
184.4453	184.444643	7602.970	61819.779	5s ² 5p ⁵	² P ^o	1/2	5s ² 5p ⁴ (³ P ₁)6s	² [1]	3/2
206.1633	206.16255	7602.970	56092.881	5s ² 5p ⁵	² P ^o	1/2	5s ² 5p ⁴ (³ P ₂)6s	² [2]	3/2
804.374	804.3701	54633.46	67062.130	5s ² 5p ⁴ (³ P ₂)6s	² [2]	5/2	5s ² 5p ⁴ (³ P ₂)6p	² [1]	3/2

Singly ionized atomic iodine ^[85]

Observed Wavelength (nm)	Ritz Wavelength (nm)	E _i (cm ⁻¹)	E _k (cm ⁻¹)	Lower Level			Upper Level		
				Config	Term	J	Config	Term	J
71.9546	71.9539	0.0	138 977.84	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (² D ^o)6d	12 ^o	1
72.2980	72.2980	0.0	138 316.49	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (² D ^o)6d	10 ^o	2
79.8158	79.8159	0.0	125 288.29	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (⁴ S ^o)6d	³ D ^o	3
83.4095	83.4106	0.0	119 888.77	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (⁴ S ^o)7s	³ S ^o	1
84.7796	84.7795	7 086.888	125 040.?	5s ² 5p ⁴	³ P	1	5s ² 5p ³ (² P ^o)5d	³ P ^o	0
87.3489	87.3495	0.0	114 482.59	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (² D ^o)5d	³ P ^o	2
87.5941	87.5940	13 727.2	127 890.23	5s ² 5p ⁴	¹ D	2	5s ² 5p ³ (² P ^o)5d	¹ P ^o	1
87.9844	87.9847	0.0	113 656.16	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (² P ^o)5d	³ D ^o	3
88.1881	88.1889	0.0	113 392.94	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (² D ^o)5d	¹ F ^o	3
89.0995	89.0994	7 086.888	119 321.09	5s ² 5p ⁴	³ P	1	5s ² 5p ³ (² P ^o)5d	³ D ^o	2
89.3167	89.3164	0.0	111 961.58	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (² P ^o)6s	¹ P ^o	1
100.0572	100.0569	0.0	99 943.10	5s ² 5p ⁴	³ P	2	5s ² 5p ³ (² D ^o)5d	³ F ^o	3

100.3350	100.3354	13 727.2	113 392.94	$5s^25p^4$	^1D	2	$5s^25p^3(^2D^\circ)5d$	$^1F^\circ$	3
101.8583	101.8581	0.0	98 175.75	$5s^25p^4$	^3P	2	$5s^25p^3(^2D^\circ)5d$	$^3D^\circ$	3
103.4655	103.4655	0.0	96 650.55	$5s^25p^4$	^3P	2	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	3
105.4742	105.4738	13 727.2	108 537.50	$5s^25p^4$	^1D	2	$5s^25p^3(^2D^\circ)5d$	$^1D^\circ$	2
106.7341	106.7334	0.0	93 691.35	$5s^25p^4$	^3P	2	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	2
107.5210	107.5200	0.0	93 005.95	$5s^25p^4$	^3P	2	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	3
110.5000	110.4993	0.0	90 498.31	$5s^25p^4$	^3P	2	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	2
111.1165	111.1155	7 086.888	97 083.30	$5s^25p^4$	^3P	1	$5s^25p^3(^2D^\circ)5d$	$^3D^\circ$	2
111.7219	111.7219	6 447.9	95 955.85	$5s^25p^4$	^3P	0	$5s5p^5$	$^1P^\circ$	1
112.5251	112.5252	7 086.888	95 955.85	$5s^25p^4$	^3P	1	$5s5p^5$	$^1P^\circ$	1
113.1504	113.1511	6 447.9	94 825.33	$5s^25p^4$	^3P	0	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	1
113.9752	113.9751	7 086.888	94 825.33	$5s^25p^4$	^3P	1	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	1
113.9805	113.9808	0.0	87 734.06	$5s^25p^4$	^3P	2	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	1
115.4668	115.4675	7 086.888	93 691.35	$5s^25p^4$	^3P	1	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	2
115.9871	115.9879	13 727.2	99 943.10	$5s^25p^4$	^1D	2	$5s^25p^3(^2D^\circ)5d$	$^3F^\circ$	3
116.0562	116.0566	0.0	86 164.86	$5s^25p^4$	^3P	2	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	2
116.6482	116.6480	0.0	85 727.98	$5s^25p^4$	^3P	2	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	3
116.7054	116.7069	6 447.9	92 132.61	$5s^25p^4$	^3P	0	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	1
117.5841	117.5838	7 086.888	92 132.61	$5s^25p^4$	^3P	1	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	1
117.8650	117.8649	0.0	84 842.87	$5s^25p^4$	^3P	2	$5s^25p^3(^4S^\circ)6s$	$^3S^\circ$	1
118.7338	118.7336	0.0	84 222.19	$5s^25p^4$	^3P	2	$5s5p^5$	$^3P^\circ$	1
119.0853	119.0850	13 727.2	97 700.81	$5s^25p^4$	^1D	2	$5s^25p^3(^2D^\circ)6s$	$^1D^\circ$	2
119.8884	119.8877	7 086.888	90 498.31	$5s^25p^4$	^3P	1	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	2
120.0223	120.0220	7 086.888	90 404.95	$5s^25p^4$	^3P	1	$5s5p^5$	$^3P^\circ$	0
122.0887	122.0884	0.0	81 907.83	$5s^25p^4$	^3P	2	$5s5p^5$	$^3P^\circ$	2
123.4063	123.4070	0.0	81 032.70	$5s^25p^4$	^3P	2	$5s^25p^3(^4S^\circ)6s$	$^5S^\circ$	2
133.6517	133.6524	7 086.888	81 907.83	$5s^25p^4$	^3P	1	$5s5p^5$	$^3P^\circ$	2
240.8008	240.8006	98 175.75	139 691.25	$5s^25p^3(^2D^\circ)5d$	$^3D^\circ$	3	$5s^25p^3(^2D^\circ)4f$	^3G	3
241.9176	241.9177	98 175.75	139 499.57	$5s^25p^3(^2D^\circ)5d$	$^3D^\circ$	3	$5s^25p^3(^2D^\circ)4f$	^3F	4
249.4738	249.4741	99 377.47	139 449.71	$5s^25p^3(^2D^\circ)5d$	$^3F^\circ$	4	$5s^25p^3(^2D^\circ)4f$	^3G	5
253.3605	253.3603	85 384.15	124 841.77	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	0	$5s^25p^3(^4S^\circ)4f$	^5F	1
253.4272	253.4273	86 036.32	125 483.51	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	4	$5s^25p^3(^4S^\circ)7p$	^5P	3
256.6242	256.6242	85 727.98	124 683.79	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	3	$5s^25p^3(^4S^\circ)4f$	^5F	4
258.2794	258.2794	86 036.32	124 742.50	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	4	$5s^25p^3(^4S^\circ)4f$	^5F	5
259.3458	259.3455	86 164.86	124 711.93	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	2	$5s^25p^3(^4S^\circ)4f$	^5F	3
273.0124	273.0123	103 101.57	139 719.12	$5s^25p^3(^2D^\circ)5d$	$^1G^\circ$	4	$5s^25p^3(^2D^\circ)4f$	^1G	4
276.5149	276.5153	99 943.10	136 096.79	$5s^25p^3(^2D^\circ)5d$	$^3F^\circ$	3	$5s^25p^3(^2D^\circ)4f$	^3F	3
280.8594	280.8590	101 157.79	136 752.36	$5s^25p^3(^2D^\circ)5d$	$^3G^\circ$	4	$5s^25p^3(^2D^\circ)4f$	^3H	5
287.8632	287.8626	90 498.31	125 226.92	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	2	$5s^25p^3(^4S^\circ)4f$	^3F	3
299.3866	299.3861	92 132.61	125 524.56	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	1	$5s^25p^3(^4S^\circ)4f$	^3F	2

307.8754	307.8764	93 005.95	125 477.08	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	3	$5s^25p^3(^4S^\circ)4f$	^3F	4
316.1027	316.1027	108 537.50	140 163.63	$5s^25p^3(^2D^\circ)5d$	$^1D^\circ$	2	$5s^25p^3(^2D^\circ)7p$	^1F	3
317.5066	317.5070	84 222.19	115 708.45	$5s5p^5$	$^3P^\circ$	1	$5s^25p^3(^2D^\circ)6p$	^3P	2
335.5531	335.5534	84 842.87	114 635.82	$5s^25p^3(^4S^\circ)6s$	$^3S^\circ$	1	$5s^25p^3(^2D^\circ)6p$	^3P	0
342.4993	342.4989	107 511.77	136 700.57	$5s^25p^3(^2D^\circ)5d$	$^3F^\circ$	2	$5s^25p^3(^4S^\circ)8p$	^3P	2
349.7406	349.7402	90 498.31	119 082.78	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^1D	2
352.6904	352.6891	109 295.45	137 640.93	$5s^25p^3(^2D^\circ)5d$	$^3S^\circ$	1	$5s^25p^3(^2D^\circ)4f$	^3P	2
374.2138	374.2135	113 392.94	140 108.06	$5s^25p^3(^2D^\circ)5d$	$^1F^\circ$	3	$5s^25p^3(^2D^\circ)7p$	^3F	4
445.2858	445.2855	99 327.14	121 778.34	$5s^25p^3(^4S^\circ)6p$	^5P	2	$5s^25p^3(^4S^\circ)6d$	$^5D^\circ$	3
463.2446	463.2447	81 032.70	102 613.52	$5s^25p^3(^4S^\circ)6s$	$^5S^\circ$	2	$5s^25p^3(^4S^\circ)6p$	^3P	2
466.6484	466.6485	100 402.68	121 826.09	$5s^25p^3(^4S^\circ)6p$	^5P	3	$5s^25p^3(^4S^\circ)6d$	$^5D^\circ$	4
467.5530	467.5529	97 700.81	119 082.78	$5s^25p^3(^2D^\circ)6s$	$^1D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^1D	2
498.6922	498.6916	92 132.61	112 179.49	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	1	$5s^25p^3(^2D^\circ)6p$	^3D	2
506.537	506.537	81 907.83	101 644.21	$5s5p^5$	$^3P^\circ$	2	$5s^25p^3(^4S^\circ)6p$	^3P	1
514.973	514.973	93 005.95	112 419.04	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	3	$5s^25p^3(^2D^\circ)6p$	^3F	3
516.120	516.119	81 032.70	100 402.68	$5s^25p^3(^4S^\circ)6s$	$^5S^\circ$	2	$5s^25p^3(^4S^\circ)6p$	^5P	3
517.619	517.620	110 458.93	129 772.76	$5s^25p^3(^2P^\circ)6s$	$^3P^\circ$	2	$5s^25p^3(^2P^\circ)6p$	^3P	2
521.627	521.626	92 132.61	111 298.09	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	1	$5s^25p^3(^2D^\circ)6p$	^3F	2
522.897	522.897	106 103.28	125 222.20	$5s^25p^3(^2P^\circ)6s$	$^3P^\circ$	1	$5s^25p^3(^2P^\circ)6p$	^3D	2
524.571	524.571	96 650.55	115 708.45	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	3	$5s^25p^3(^2D^\circ)6p$	^3P	2
526.936	526.936	110 458.93	129 431.27	$5s^25p^3(^2P^\circ)6s$	$^3P^\circ$	2	$5s^25p^3(^2P^\circ)6p$	^3D	3
529.978	529.979	111 961.58	130 824.99	$5s^25p^3(^2P^\circ)6s$	$^1P^\circ$	1	$5s^25p^3(^2P^\circ)6p$	^1P	1
532.280	532.281	84 222.19	103 004.04	$5s5p^5$	$^3P^\circ$	1	$5s^25p^3(^4S^\circ)6p$	^3P	0
533.822	533.820	93691.35	112419.04	$5s25p3(^2D^\circ)6s$	$^3D^\circ$	2	$5s25p3(^2D^\circ)6p$	^3F	3
534.515	534.514	96 650.55	115 353.94	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	3	$5s^25p^3(^2D^\circ)6p$	^3F	4
536.986	536.986	96 650.55	115 267.82	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	3	$5s^25p^3(^2D^\circ)6p$	^3D	3
540.542	540.541	81 907.83	100 402.68	$5s5p^5$	$^3P^\circ$	2	$5s^25p^3(^4S^\circ)6p$	^5P	3
540.736	540.737	93 691.35	112 179.49	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^3D	2
543.583	543.583	84 222.19	102 613.52	$5s5p^5$	$^3P^\circ$	1	$5s^25p^3(^4S^\circ)6p$	^3P	2
543.800	543.799	97 700.81	116 084.84	$5s^25p^3(^2D^\circ)6s$	$^1D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^3P	1
546.462	546.462	81 032.70	99 327.14	$5s^25p^3(^4S^\circ)6s$	$^5S^\circ$	2	$5s^25p^3(^4S^\circ)6p$	^5P	2
549.150	549.151	100 402.68	118 607.56	$5s^25p^3(^4S^\circ)6p$	^5P	3	$5s^25p^3(^4S^\circ)7s$	$^5S^\circ$	2
549.694	549.693	81 032.70	99 219.61	$5s^25p^3(^4S^\circ)6s$	$^5S^\circ$	2	$5s^25p^3(^4S^\circ)6p$	^5P	1
550.472	550.472	84 842.87	103 004.04	$5s^25p^3(^4S^\circ)6s$	$^3S^\circ$	1	$5s^25p^3(^4S^\circ)6p$	^3P	0
552.206	552.204	110 458.93	128 563.14	$5s^25p^3(^2P^\circ)6s$	$^3P^\circ$	2	$5s^25p^3(^2P^\circ)6p$	^3S	1
559.852	559.851	95 955.85	113 812.79	$5s5p^5$	$^1P^\circ$	1	$5s^25p^3(^2D^\circ)6p$	^1P	1
560.032	560.031	107 625.89	125 477.08	$5s^25p^3(^2D^\circ)5d$	$^3G^\circ$	3	$5s^25p^3(^4S^\circ)4f$	^3F	4
561.289	561.289	111 961.58	129 772.76	$5s^25p^3(^2P^\circ)6s$	$^1P^\circ$	1	$5s^25p^3(^2P^\circ)6p$	^3P	2
562.569	562.569	84 842.87	102 613.52	$5s25p3(^4S^\circ)6s$	$^3S^\circ$	1	$5s25p3(^4S^\circ)6p$	^3P	2
567.808	567.807	93 691.35	111 298.09	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^3F	2

569.091	569.091	97 700.81	115 267.82	$5s^25p^3(^2D^\circ)6s$	$^1D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^3D	3
570.205	570.204	100 402.68	117 935.41	$5s^25p^3(^4S^\circ)6p$	^5P	3	$5s^25p^3(^2P^\circ)5d$	$^3P^\circ$	2
570.205	570.205	98 175.75	115 708.45	$5s^25p^3(^2D^\circ)5d$	$^3D^\circ$	3	$5s^25p^3(^2D^\circ)6p$	^3P	2
571.053	571.053	96 650.55	114 157.21	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	3	$5s^25p^3(^2D^\circ)6p$	^1F	3
573.827	573.827	84 222.19	101 644.21	$5s5p^5$	$^3P^\circ$	1	$5s^25p^3(^4S^\circ)6p$	^3P	1
576.072	576.071	94 825.33	112 179.49	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	1	$5s^25p^3(^2D^\circ)6p$	^3D	2
577.483	577.481	81 907.83	99 219.61	$5s5p^5$	$^3P^\circ$	2	$5s^25p^3(^4S^\circ)6p$	^5P	1
578.702	578.702	102 613.52	119 888.77	$5s^25p^3(^4S^\circ)6p$	^3P	2	$5s^25p^3(^4S^\circ)7s$	$^3S^\circ$	1
595.025	595.026	84 842.87	101 644.21	$5s^25p^3(^4S^\circ)6s$	$^3S^\circ$	1	$5s^25p^3(^4S^\circ)6p$	^3P	1
606.893	606.895	94 825.33	111 298.09	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	1	$5s^25p^3(^2D^\circ)6p$	^3F	2
607.498	607.498	97 700.81	114 157.21	$5s^25p^3(^2D^\circ)6s$	$^1D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^1F	3
612.749	612.750	93 691.35	110 006.71	$5s^25p^3(^2D^\circ)6s$	$^3D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^3D	1
620.486	620.485	97 700.81	113 812.79	$5s^25p^3(^2D^\circ)6s$	$^1D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^1P	1
625.749	625.747	99 377.47	115 353.94	$5s^25p^3(^2D^\circ)5d$	$^3F^\circ$	4	$5s^25p^3(^2D^\circ)6p$	^3F	4
666.596	666.597	84 222.19	99 219.61	$5s5p^5$	$^3P^\circ$	1	$5s^25p^3(^4S^\circ)6p$	^5P	1
671.883	671.882	87 734.06	102 613.52	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	1	$5s^25p^3(^4S^\circ)6p$	^3P	2
681.257	681.257	85 727.98	100 402.68	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	3	$5s^25p^3(^4S^\circ)6p$	^5P	3
695.878	695.879	86 036.32	100 402.68	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	4	$5s^25p^3(^4S^\circ)6p$	^5P	3
708.521	708.520	101 157.79	115 267.82	$5s^25p^3(^2D^\circ)5d$	$^3G^\circ$	4	$5s^25p^3(^2D^\circ)6p$	^3D	3
735.135	735.137	85 727.98	99 327.14	$5s^25p^3(^4S^\circ)5d$	$^5D^\circ$	3	$5s^25p^3(^4S^\circ)6p$	^5P	2
841.460	841.460	124 742.50	136 623.34	$5s^25p^3(^4S^\circ)4f$	^5F	5	$5s^25p^3(^4S^\circ)5g$	$^5G^\circ$	6
919.587	919.590	92 132.61	103 004.04	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	1	$5s^25p^3(^4S^\circ)6p$	^3P	0
948.033	948.031	108 537.50	119 082.78	$5s^25p^3(^2D^\circ)5d$	$^1D^\circ$	2	$5s^25p^3(^2D^\circ)6p$	^1D	2
1 040.549	1 040.561	93 005.95	102 613.52	$5s^25p^3(^4S^\circ)5d$	$^3D^\circ$	3	$5s^25p^3(^4S^\circ)6p$	^3P	2
1 108.468	1 108.482	125 483.51	134 502.39	$5s^25p^3(^4S^\circ)7p$	^5P	3	$5s^25p^3(^4S^\circ)7d$	$^5D^\circ$	4