THE EFFECT OF A DC VOLTAGE ON THE CATALYTIC COMBUSTION OF NATURAL GAS IN AIR OVER PLATINUM
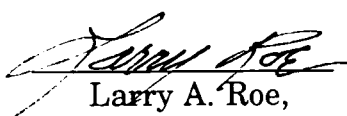
by

ANDREW C. HALSEY

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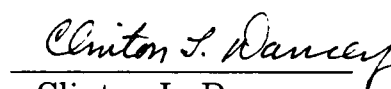
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Approved:

Larry A. Roe,
Chairman

David F. Cox   Clinton L. Dancey

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Andrew C. Halsey
Committee Chairman: Dr. Larry A. Roe
Mechanical Engineering

(ABSTRACT)

The effects of a DC voltage on the catalytic combustion rate of natural gas in air over a platinum wire in various configurations is examined. In most cases a high applied voltage reduces and quenches the catalytic reaction. These effects are dependant on the catalyst surface charge density but not on the direction of the field. Greater effects were also observed when the field was applied on the upstream rather than the downstream side of the catalyst. Although the mechanism of this quenching effect is unknown, it is suggested that it involves the generation and diffusion of charged gas-phase species and their interaction with the catalyst surface. Possible quantum effects are also discussed. Further work to verify or refute the mechanisms presented here is suggested.

Acknowledgements

I would like to thank Dr. Larry Roe for helping me get started; and for his guidance and many helpful suggestions throughout the research. I also would like to thank him for allowing me to work at my own pace, pursuing an interesting problem somewhat removed from the field of mechanical engineering. His assistance in putting together this final text was invaluable.

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1. Introduction

1.1 Background and Motivation

Recently much attention has been given to the field of catalytic combustion. In catalytic combustion a fuel is oxidized over the surface of a catalyst rather than in a flame. This allows the fuel's chemical energy to be released, but at a much lower temperature. Because the reaction temperature is lower, much less NO_x is formed, drastically improving emissions performance.

The catalyst used in these types of combustors is often platinum dispersed over some type of honeycomb support material. Platinum is chosen because of its high reactivity as well as its resistance to high operating temperatures. While many workers, such as Yoshine et al. [1] and Kitajima et al. [2], are addressing the problems of combustion stability and catalyst deterioration over time, fundamental knowledge of the platinum surface reaction mechanism is lacking.

In addition to catalytic combustion, platinum catalysts are used in a wide variety of industrial applications ranging from automotive catalytic converters (NO_x removal) to cooking oil and margarine production (hydrogenation and dehydrogenation) [3]. Platinum catalysts are also used extensively in

electrocatalysis and fuel cells [4]. Although the chemical reactions involved in these processes may be very different from those involved in catalytic combustion, information regarding surface mechanisms on platinum catalysts would be potentially useful in any of these fields.

Because platinum has so many uses as a catalyst, especially in the combustion field, the question of using electric fields to change the catalytic combustion reaction rate was posed. Strong fields will both create and propel electrons and ionized molecules in the gas phase. In addition, fields will affect the electronic surface characteristics of a metal. Since these effects will vary depending on both field strength and configuration, it is possible that the resulting effects on the catalytic combustion reaction occurring on a platinum surface subjected to these fields would vary as well.

The motivation for this thesis was to examine the effect of an applied DC electrostatic field on a catalytic combustion reaction and determine if any practical benefit could be realized. In addition, it was hoped that applying fields in various configurations would help elucidate possible reaction mechanisms.

1.2 Scope of Thesis

This thesis examines the effects of an applied DC electrostatic field on a catalytic combustion reaction. In addition, a consistent explanation for the

observed field effects is discussed. Organization of this material is described in the following paragraph.

Chapter 2 provides general background material concerning catalysis, chemical bonding, and the electronic structure of metal surfaces. While rigorous treatment of this topic would involve a thorough treatment of Schrödinger's equation, none will be attempted here. Rather, solutions to this equation and the corresponding consequences for chemical bonding are qualitatively discussed. In Chapter 3 relevant literature concerning platinum surface reactions is reviewed, including some studies of electric field effects on chemical adsorption. Chapter 4 details the experimental apparatus, electronic configurations, and experimental procedure used. Results are presented and discussed in Chapter 5. Chapter 6 summarizes this thesis and suggests additional work in this area.

2. Background Fundamentals

This section provides an introductory background to the field of surface catalysis. Most of the information presented in this chapter is available in any text or reference work dealing with this subject. Particularly useful were texts by Szabó and Kalló [5], Gates [3], Bockris and Conway [6], [7], [8], and Morrison [9]. Other references are noted where appropriate.

2.1 Basic Catalysis Concepts

A catalyst is a substance that can increase the rate of a chemical reaction. Although the catalyst chemically interacts with the reactants, it is not (in the ideal case) altered or consumed in the overall reaction. In general, this is accomplished by allowing the reaction to proceed by a different reaction pathway than would normally be utilized. This alternate reaction mechanism tends to be more complex than the normal mechanism; however, the net energy barrier (activation energy) is significantly lower. Hence the overall reaction proceeds at an accelerated rate. It should be noted that a catalyst cannot cause a thermodynamically unfavorable reaction ($\Delta G > 0$) to proceed.

As stated above, a catalyst must chemically combine with reactant species in order to enhance a reaction. In surface (or heterogeneous) catalysis,

this requires that the reactants chemically adsorb (chemisorb) onto the catalyst surface. It is not sufficient that reactant gas phase species be held close to the catalyst surface by van der Waals forces. Species in this state are said to be physically adsorbed (physisorbed) on the surface. While this state may be a precursor to chemisorption, catalysis cannot occur while reactant molecules are physisorbed since catalysis initially requires the breaking of chemical bonds in the reactant species.

Species may be adsorbed in one of three ways. If the adsorbate donates (on average) an electron to the surface, it acquires a net positive charge. This is called cationic adsorption. Anionic adsorption occurs when the adsorbate gains (on average) an electron from the metal surface and acquires a net negative charge. Cationic and anionic adsorption are types of ionic bonding. If the bonding electrons are equally distributed between the surface and the adsorbate, a covalent bond is formed (adsorbate has no net charge).

While most metals will chemisorb various gas phase molecules, it is vital that this bond be only temporary if the metal is to serve as a catalyst. If the adsorbed species is held too strongly, it will not be able to escape from the surface and complete the reaction. In extreme cases, the adsorbed species will be permanently attached to the catalyst and will deactivate the surface for further adsorption. This is known as "poisoning" of the catalyst. In the opposite extreme the bond between the adsorbed species and the catalyst is too weak, and adsorbed species will desorb before they have a chance to react with

other adsorbed species. This requirement that the bond strength be within a relatively narrow range is known as the Volcano Principle (because a plot of catalytic activity vs bond strength is cone shaped) and dictates which substances will be good catalysts for a given reaction.

All surface catalytic processes consists of five fundamental steps, illustrated in Fig. 1. In step one, gas phase species diffuse close enough to the catalyst surface to allow chemical bonding to occur. Step two involves reactant chemisorption onto the catalyst surface. This state may be preceded by physisorption. Next the adsorbed species undergoes a series of chemical interactions including breaking of species bonds and interaction with other adsorbed species. After completing the chemical conversions in step three, the new product species must desorb from the catalyst surface. Finally the gas phase product must diffuse away from the catalyst.

This series of reaction steps gives a clear qualitative picture of surface catalysis. The first quantitative work done in this field was by Langmuir [10] who in 1915 proposed an expression for surface coverage of a catalyst resulting from chemisorption as the dynamic equilibrium of adsorbing and desorbing species. Langmuir assumed that each molecule of the catalyst could adsorb (only) one molecule from the gas phase. When every site was occupied, the resulting monolayer would prevent any further chemisorption. As a result, Langmuir proposed an equation for surface coverage (at a constant temperature) in terms of the rate constants for adsorption and desorption, and the

Five Steps in Surface Catalysis

1. Diffusion of Reactants
   to the Surface

5. Diffusion of Products
   from the Surface

2. Adsorption

3. Surface Reactions

4. Desorption

Catalytic Surface
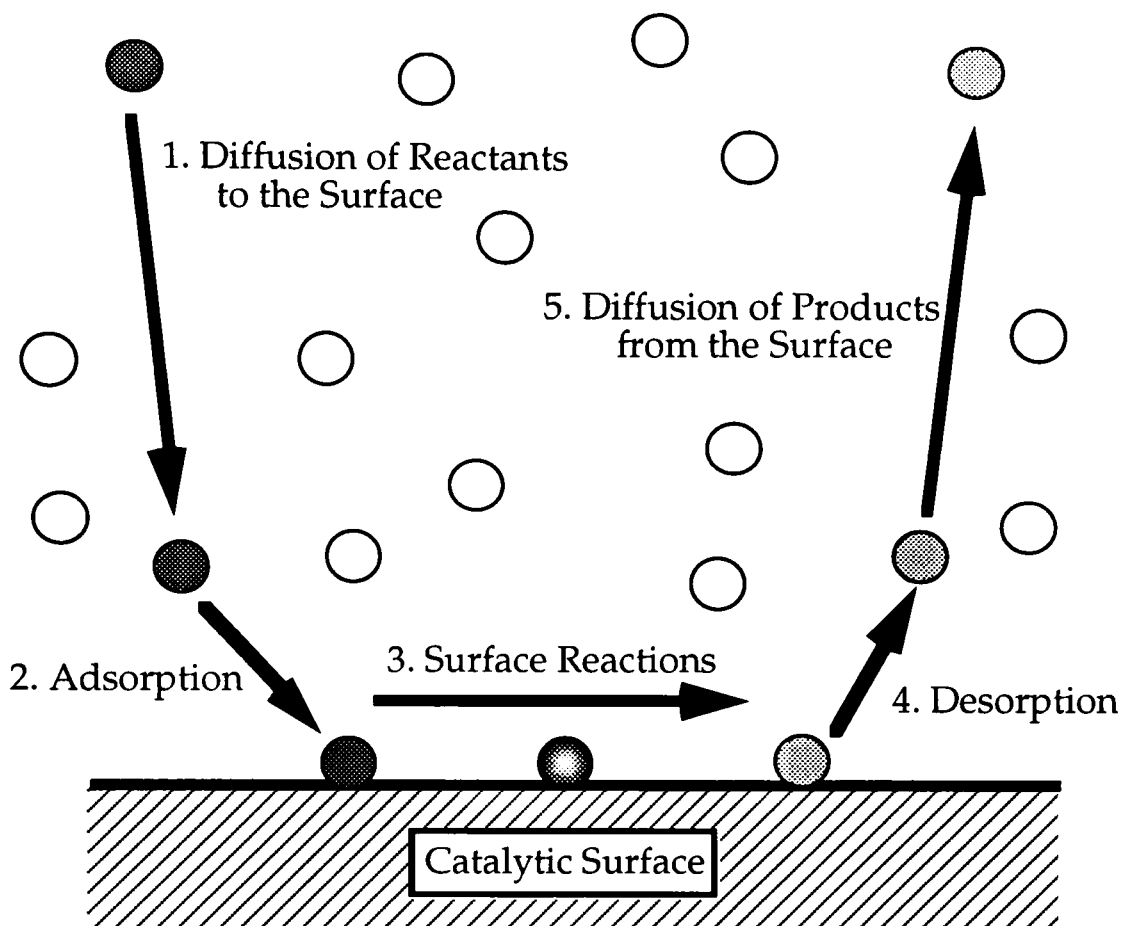
Figure 1 - Five Fundamental Steps in Surface Catalysis

pressure above the catalyst. This is the Langmuir isotherm for adsorption. Since then a number of other more complex isotherms describing surface coverage have been proposed by various workers.

In 1923, Taylor [11] proposed a modification to this basic scheme. Rather than allowing every available surface molecule of the catalyst to participate in surface reactions, he proposed that only certain "active centres" or active sites were involved. Most of the surface area of the catalyst therefore was inert to catalytic reactions. This theory was quickly confirmed by Armstrong and Hilditch [12], who found that the amount of poison needed to deactivate a catalytic surface was significantly less that the amount required to cover the entire surface with a monolayer. Later work revealed that different adsorbates were processed on different active sites, and that active sites were often reaction specific.

While the concept of the active site has become fundamental to studies of catalysis, no general consensus has been reached regarding the exact nature of an active site. It is generally thought that the activity of these sites involves both the physical geometry of the catalytic surface as well as its electronic configuration. The concept of the active site, specifically active sites on transition metal catalysts, is discussed in section 2.3.

While specific studies of reaction mechanisms will be discussed in Chapter 3, a distinction between two general types of surface reactions is appropriate at this time. Once reactant species have been adsorbed on the

catalytic surface, the ensuing chemical reactions can proceed via two general mechanisms. The first, the Langmuir-Hinshelwood scheme, involves a reaction between two adsorbed species. The other general mechanism is the Eley-Rideal scheme. Reactions of this type involve the combination of one adsorbed reactant and one gas phase reactant.

While both Langmuir-Hinshelwood and Eley-Rideal mechanisms are thought to be important in surface catalysis systems, it is not always clear which mechanism is at work. Several examples are given in Chapter 3 that illustrate how the same products can be formed by either mechanism. While experimental verification of a particular reaction step is difficult, a calculation of the activation energy for the Langmuir-Hinshelwood and the Eley-Rideal mechanisms may suggest which is the preferred route.

2.2 Properties of Platinum Metal Surfaces

2.2.1 Electronic and Surface Structure of Platinum

Chemical reactions in catalysis, as in all fields of chemistry, arise from the interaction of reactant species' electron shells to form or sever chemical bonds. Calculation of properties and interactions of these electron shells or orbitals arise from solutions to Schrödinger's equation (1). In this equation E is the energy and ψ is the wave function of an electron. The wave function is

$$\mathcal{H}\psi = E\psi \qquad (1)$$

related to the electron's probability density function. $\mathcal{H}$ is the Hamiltonian operator.

Although beyond the scope of this work, calculation of electron orbitals for simple atoms (such as hydrogen) is fairly well understood. The mathematics involved in determining the electron structures of larger atoms and molecules, however, becomes very difficult. Ideally, Schrödinger's equation should be applied to determine the electronic structure and interaction of a catalyst surface and any impinging gas phase molecules. This type of calculation could lead to a formal, quantitative "electronic" theory of catalysis. Unfortunately the mathematics involved in solving for the electronic structure of this species-catalyst interface in three dimensions are intractable.

Although this approach does not allow quantitative calculations for catalytic systems, some qualitative applications can be observed. First consider an isolated platinum atom. Platinum is a transition metal with half-filled 6s and (one) 5d electron shells. It is believed that these 5d electron vacancies are primarily responsible for the high reactivity of platinum. Gold, which is in the same row of the periodic table as platinum but has completely filled 5d shells, is unreactive. If not completely filled, this d orbital can match up with a bonding orbital of an impinging molecule to form a chemical bond. The outer s orbitals could also form bonds of this type; however, in a metal

catalyst these s orbital electrons become part of a non-localized "band" state. The band theory of metal surfaces is discussed in section 2.2.2.

The importance of the d electrons in catalytic activity was demonstrated by Dilke et al. [13], who measured the variation of magnetic properties of palladium with surface poisoning. Since the magnetic properties of metals are dependent on vacancies in the outer d orbitals, Dilke observed that as the catalyst poison gradually contaminated the surface (by bonding to these d electrons), the magnetic susceptibility also decreased.

Because of the complexities of completely modeling a catalyst system, several workers have attempted to generalize these observations to small groups of platinum atoms and isolated crystal geometries with moderate success. In both cases, systems of atoms have been selected for which the calculation of the wave functions of the (outermost) electrons can be computed from Schrödinger's equation. Although still overly simplified, these studies attempt to account for the electric potential field on each electron orbital caused by the surrounding electron orbitals and the charge in the bulk lattice.

Balazs and Johnson [14] modeled isolated groups of 5, 6, and 10 platinum atoms. Their calculations predict that the field caused by the electron repulsion between orbitals will direct some d orbitals perpendicularly away from the platinum atoms into the vacuum. It is assumed that these "dangling orbitals" are associated with the catalytic activity of platinum. Experimental UV photoelectron spectroscopy of a platinum surface by Helms,

Bonzel, and Kelemen [15] confirms the existence of a peak in the appropriate energy range that could correspond to these "dangling bonds". This peak is greatly diminished during chemisorption of H_2 and O_2, which indicates that electrons in this orbital are involved in this process.

Tsang and Falicov [16], [17] have modeled the electric field effect caused by irregularities such as kinks, steps, and corners on the platinum surface (see Fig. 2) in an attempt to explain the experimentally observed enhanced catalytic activity at such sites. By solving for the orbital wave functions, they found that certain d orbitals would be directed perpendicularly away from the surface at these irregularities. Activation energy for C-C, C-H, and H-H bond severing was calculated to be lower at these surface irregularities than at flat plane sites. This result agrees with experimental evidence that corners, steps, and kinks on the platinum surface are more catalytically active than plane sites.

2.2.2 Band Theory of Metal Surfaces

As an alternative to modeling the activity of catalysts in terms of surface geometry and isolated "dangling" d orbitals, models based on the band structure of a metal or semi-conductor surface are also frequently used. Both approaches have their advantages and drawbacks. Although band theory models tend to be more useful in describing interactions on a semi-conductor surface, the general concepts are presented in this section. Rigorous
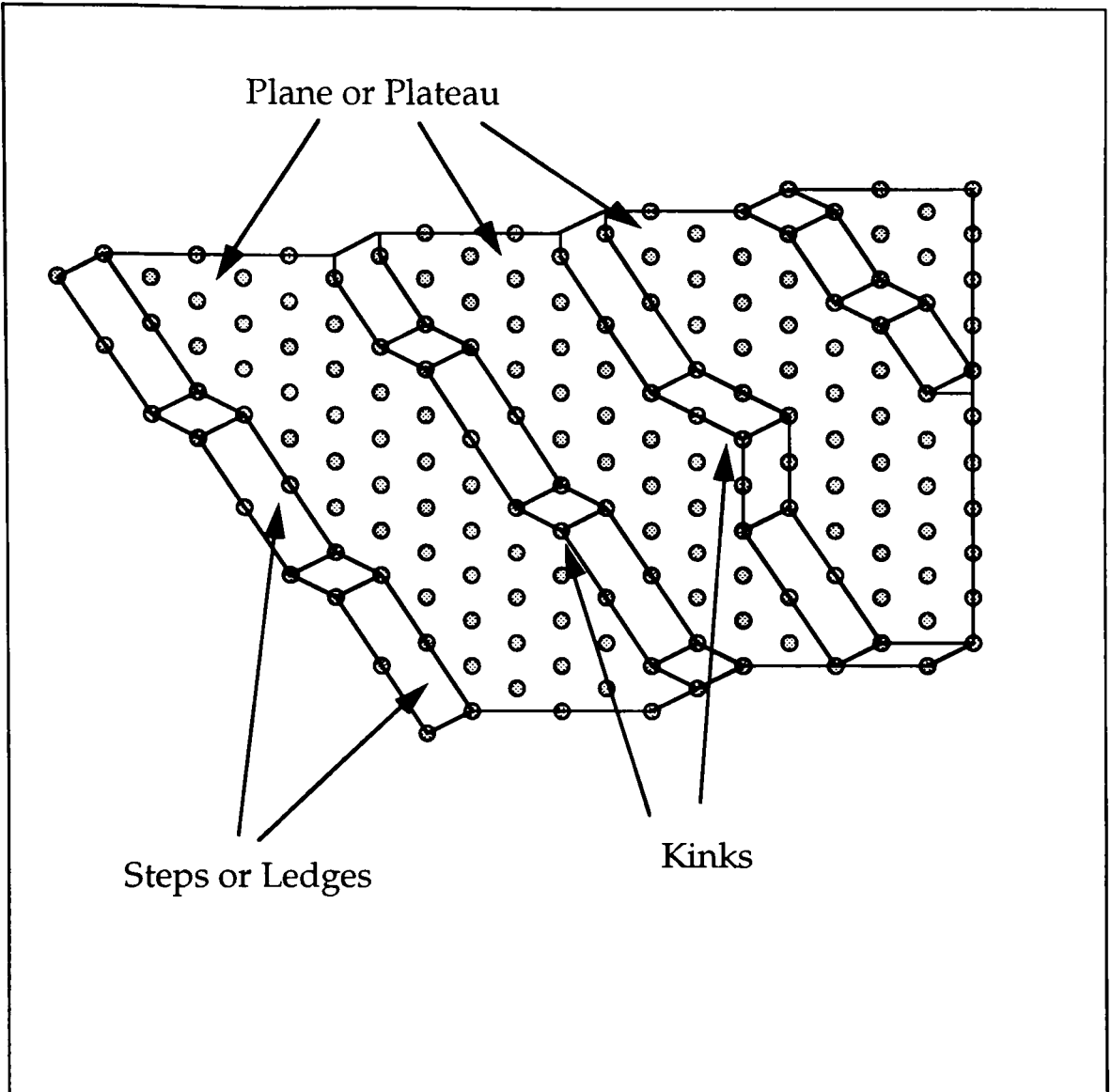
Figure 2 - Surface Irregularities on a Platinum Crystal

calculation and analysis of the energy bands of metal surfaces is well beyond the scope of this work. This section explains this theory qualitatively, so that the possible effects of an externally applied potential on the band structure may be discussed and its possible effect on surface catalysis examined.

While the models discussed in section 2.2.1 show good agreement with experimental data, they make two simplifying assumptions. First, it is assumed that the conduction band of the platinum is made up of only s orbital electrons, and that the d electrons responsible for bonding are localized on particular atoms. Second, the calculation of the interaction of electrons from other orbitals is (necessarily) limited. It is also assumed that localized (valence) and nonlocalized (conduction) electrons do not interact.

In an actual metal, far more electron interactions occur than can be quantitatively discussed. Because the energy separation of the various s, p, and d orbitals of an atom is small for the transition metals, these orbitals may overlap, resulting in hybridization or mixing. This results in new atomic orbitals which must be considered. In addition to hybridization, orbitals both on the surface and in the bulk of the metal crystal lattice interact in such a way as to form energy bands. Electrons in these bands are not localized at a particular atom, but are allowed to exist anywhere in the metal lattice.

2.2.2.1 Band Structure in Infinite Crystals

In an infinite crystal, the valence electrons of the individual metal atoms will become non-localized and travel freely through the lattice. This does not imply that the electrons are randomly distributed; instead their wave functions (defined by Schrödinger's equation) coalesce into discrete energy levels or bands analogous to atomic orbitals. These energy bands are quasi-continuous and overlap for metals, and are separated by "forbidden" gaps (band gaps) in semi-conductors (see Fig. 3).

The characteristics of these bands will depend on the atomic orbitals from which they were formed. For example, the more valence electrons available (d electrons) per atom, the greater the number of energy bands formed. If there are vacancies in the valence shells of the individual atoms, there will also be vacancies in the corresponding energy band.

Two general types of bands exist. Throughout the metal lattice various valence bands occur which bond the atoms of the lattice together. A conduction band is also formed of free (non-bonding) electrons that is responsible for the conduction of electric current.

All electrons in the metal atoms do not form these non-localized energy bands. If the attraction between an electron and its atomic nucleus is strong
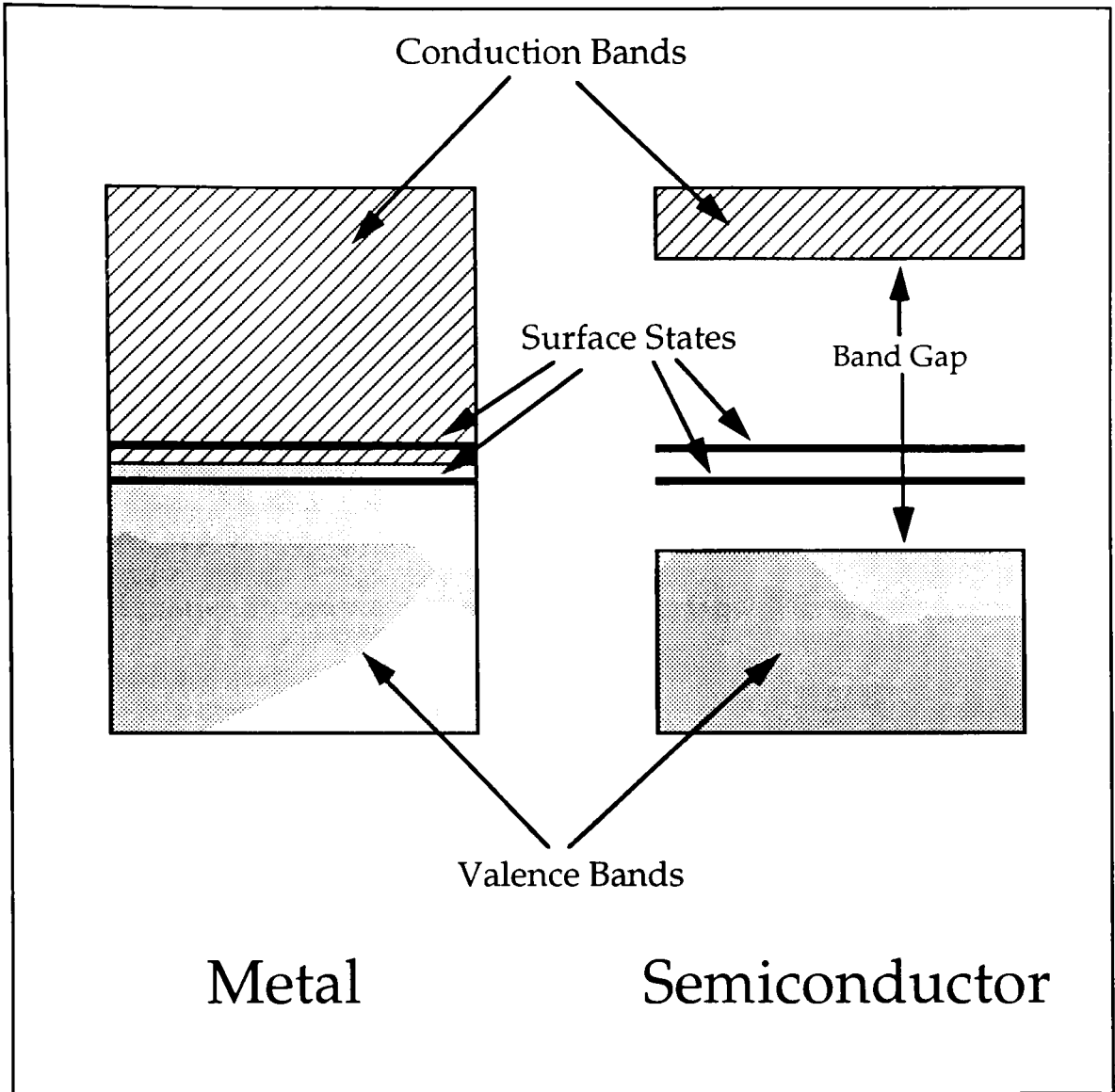
Figure 3 - Band Structure of Metals and Semiconductors

enough, the wave function of the electron will (on average) be unaffected by the other electron wave functions, and it will remain localized at the metal atom. These localized electrons are said to occupy "core" levels.

2.2.2.2 Surface States

The introduction of a free surface to a metal crystal changes the boundary conditions of Schrödinger's equation. This results in new solutions to the equation in the vicinity of the metal surface. These new solutions are called surface states.

Surface states are narrow energy bands that only exist within a few Angstroms of the metal surface. They are localized at a lattice point (metal atom) and occur between the normal energy bands in the forbidden energy region (see Fig. 3). The existence of these surface states allows for the formation of localized covalent bonding between the surface and an adsorbate. In addition, surface states determine which adsorbed species will remain stable on the catalyst surface.

2.2.2.3 The Fermi Level

One final concept concerning the band structure of metals and semi-conductors requires attention before proceeding to a discussion of externally
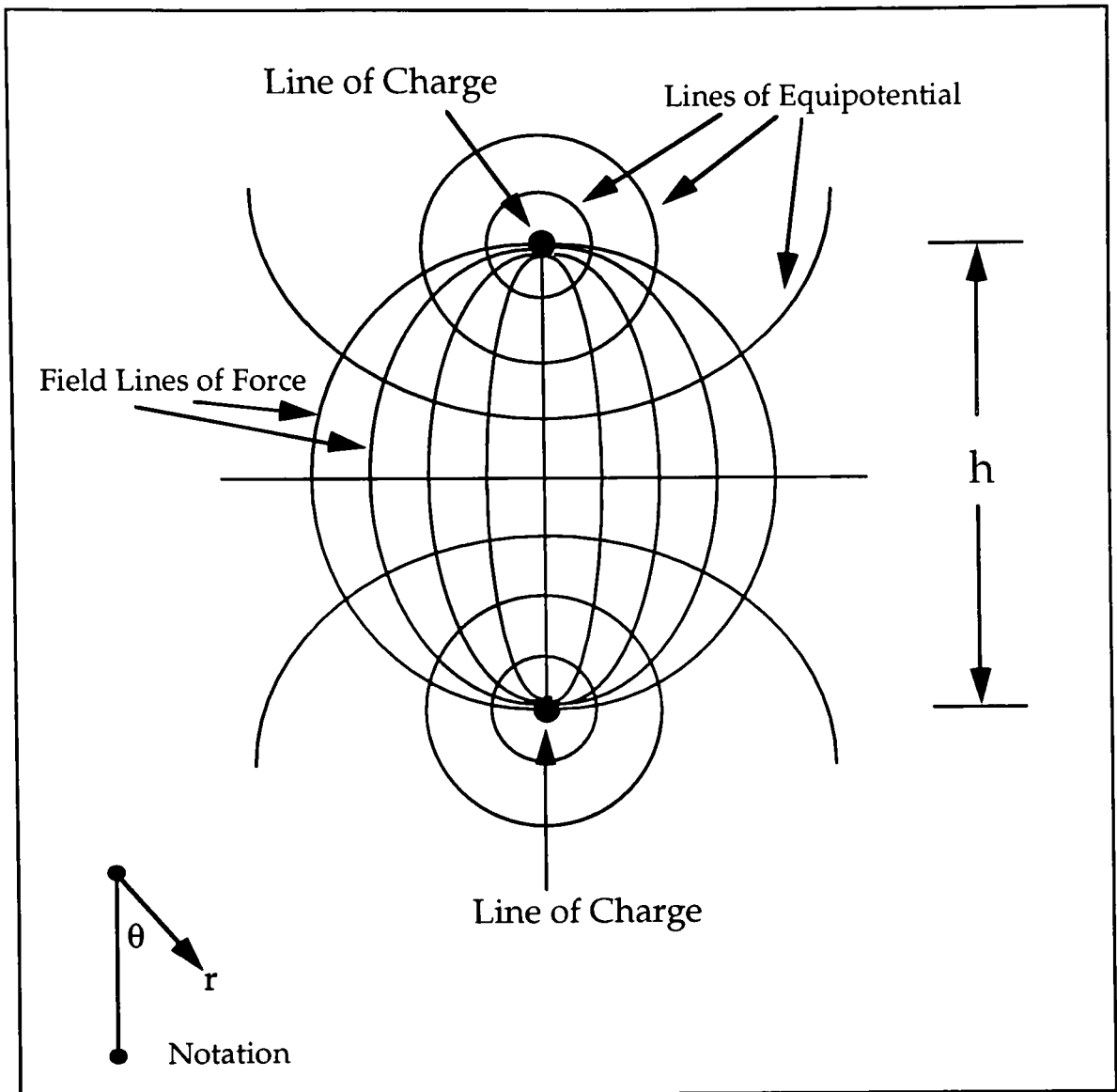
Figure 4 - Electric Field Resulting From 2 Infinite Lines of Charge

illustrated in Fig. 4. A voltage applied between the two wires will cause a surface charge density of +λ on one wire and -λ on the other. In this study, one of the wires was grounded and thus had a surface charge distribution of zero. Since the applied voltage will still cause the same difference in λ, the non-grounded wire will attain a surface charge distribution of 2λ.

The electric field strength as a function of surface charge density and the radial distance (r) from the wire for this configuration is then computed

$$E(\lambda) = \frac{4\lambda}{r}\cos\theta \qquad (2)$$

from (2). Since the surface charge density is not generally known, it is desired to compute the electric field strength as a function of applied voltage. This can be found by integrating (3) across the electrode gap, h. For θ=0, this simplifies

$$V = \int E(\lambda)\, dr \qquad (3)$$

$$V = 4\lambda \ln(h) \qquad (4)$$

$$E(V) = \frac{V\cos\theta}{r\ln(h)} \qquad (5)$$

to (4). This expression for charge density in terms of voltage can then be substituted back into (2) to give an expression for the electric field strength as a function of voltage (5).

2.3.1.2 Field Between an Infinite Line of Charge and an Infinite Conducting Plane

The field in the case of an infinite charged wire and an infinite, grounded conducting plane is solved in a very similar way. This configuration is solved by the method of image charges. If the separation between the line and plane is h, then an oppositely charged infinite line of charge is assumed to exist a distance h below the surface of the plane. This is illustrated in Fig. 5. The resulting separation between the real and "image" lines of charge is then 2h. By doing the same analysis as in section 2.3.1.1, the field strength as a function of applied voltage and radial distance from the wire is obtained.

$$E(V) = \frac{V \cos \theta}{r \ln(2h)} \tag{6}$$

Two things can be observed from equations (5) and (6). First as the radial distance to the wire decreases, the field strength becomes very large. Although the surface charge distribution λ is twice as large for the two wire case, the electric field strength close to the wire is expected to be similar because of the $1/r$ dependence.

At larger distances, however, the fields will be quite different. Since the effective "h" that is used to calculate the charge density is twice as large for a plane-line configuration than for the two line configuration, the field resulting from two lines of charge (2 wires) is larger than that resulting from an infinite line of charge and a conducting plane (wire and burner exit) for the
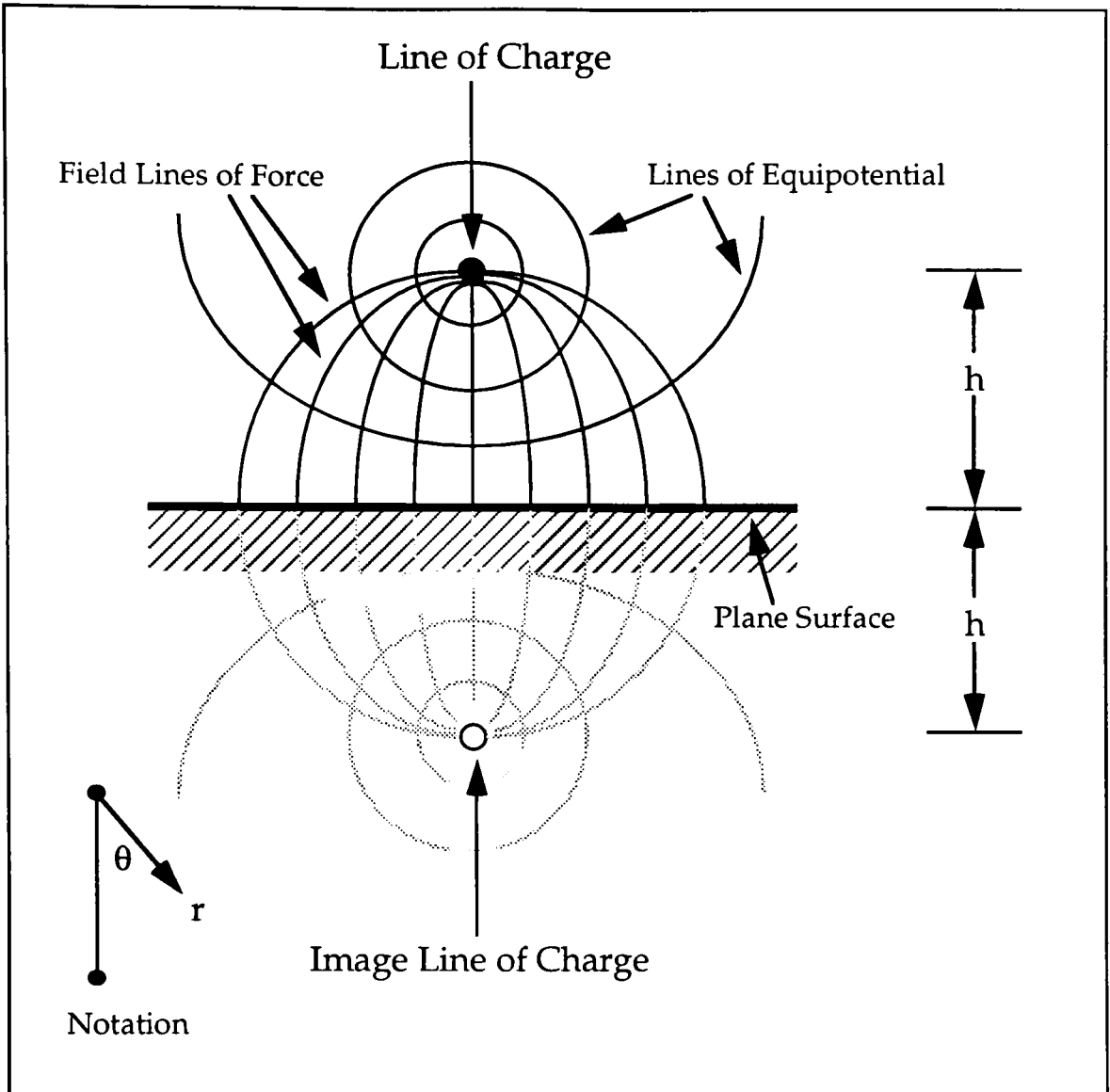
Figure 5 - Electric Field Resulting from an Infinite Line of Charge and an Infinite Conducting Plane

same applied voltage and separation distance h. The field strength ratio for the two wire and the wire-plane configurations is a function of separation distance, h, and is given in equation (7).

$$\frac{E_{Two\ wires}}{E_{Wire\text{-}plane}} = \frac{\ln(2h)}{\ln(h)} \tag{7}$$

The magnitude of these field strengths will be the same regardless of whether the wire or the plane is charged or grounded.

2.3.2 Effects on the Surface Band Structure

Much of the literature concerning electrocatalysis is specific to a solid-electrolyte (liquid) interface [4], [6], [7], [22]. Although there are obvious differences between this and the solid-gas phase interface discussed here, it is expected that the electronic effects of an applied field on the surface itself will be very similar.

The surface band structure of a semi-conductor can be altered by external conditions. Although the Fermi level of the bulk is not affected, the valence and conduction bands near the surface of a semi-conductor can be bent by the electric field created by the adsorption of foreign species. Likewise, an applied field can also cause the bending of these energy bands. If the surface is cathodically polarized (lower potential), the bands are bent up. In this case,

case, the electrons making up the bands are "pulled" further away from the semi-conductor surface into higher energy levels. The bands are bent down when the semi-conductor is anodically polarized (higher potential), as the electron levels are drawn down closer to the atomic nuclei in the bulk lattice. These effects are illustrated in Fig. 6.

This band bending occurs for semiconductors because the conduction band is mostly empty. These effects are not significant for metal surfaces because there are many free electrons in the metal's conduction band that can redistribute to compensate for the effects of an applied field.

2.3.3 Grimley's Virtual Level Model

Grimley [19], [20], [21] has suggested that the interactions between adsorbed species on metal surfaces play a role in determining what adsorbed species will be stable and which will be desorbed. These adsorbed species will interact because they presumably share conduction band electrons. As a gas phase molecule approaches the metal band structure, its discrete molecular orbitals are split into two virtual energy levels as defined by the solution to the wave equation. One of these levels will be a bonding level ("orbital") and the other will be an anti-bonding level. Electrons are then transferred between the adsorbate and the metal surface state, and a chemical bond is formed. If the energy of these virtual levels is near the Fermi level of the metal, the
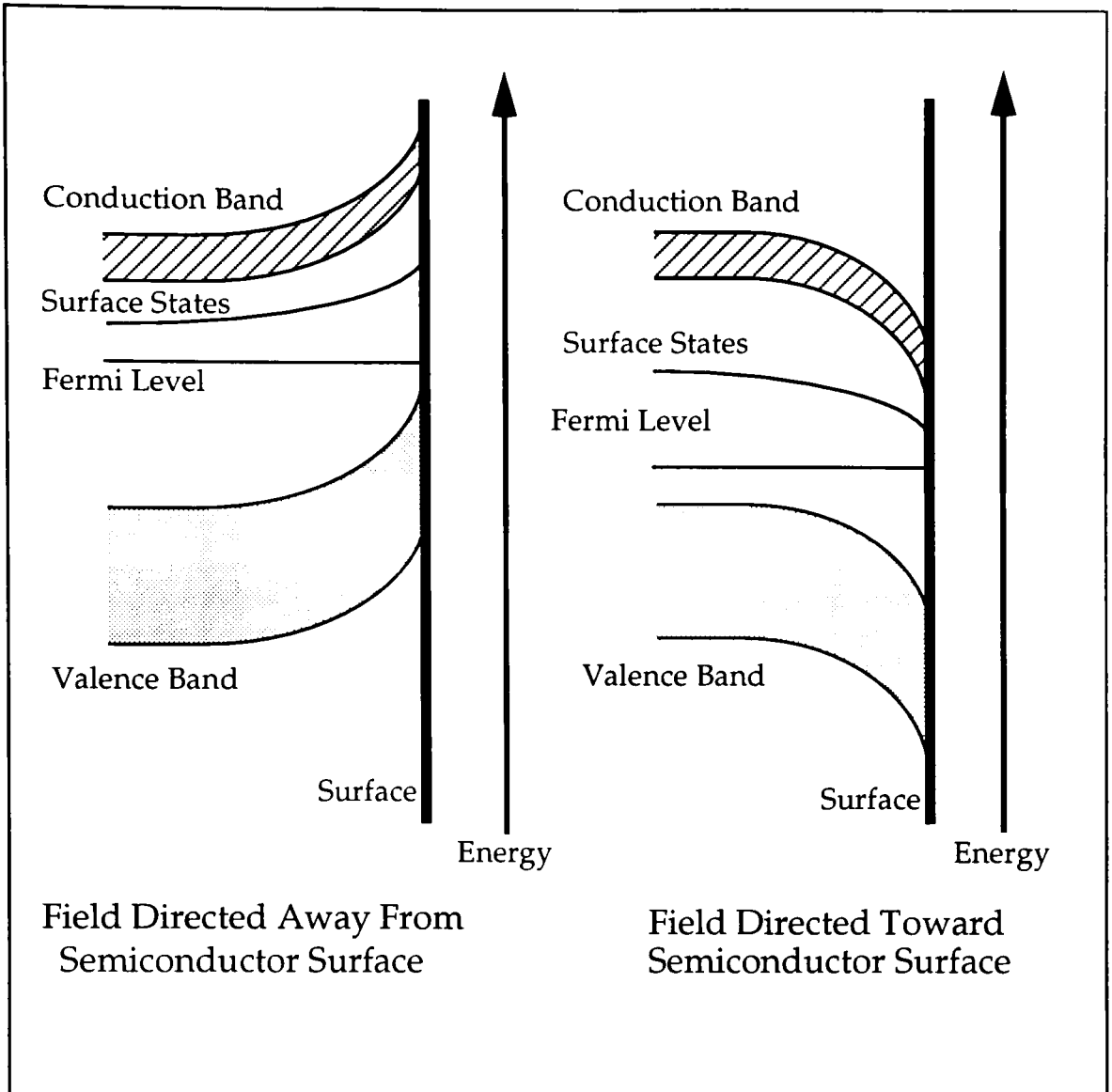
Figure 6 - Band Bending in a Semiconductor Caused by an Electric Field

populations of the virtual levels will be sensitive to the interaction between the two adsorbed species. Since the stability of the adsorbate is dependent on the populations of these virtual levels, Grimley suggests that the interactions between adsorbed species can, for certain adsorbates and surfaces, affect adsorption characteristics.

For this to occur, the energy of the virtual levels must be near the Fermi level of the metal. This is so electrons can travel from one adsorbate to the other via the conduction band. Grimley has suggested that these conditions are met for alkali metal atoms on tungsten and nickel and also for hydrogen. Although alkali metals are not present in the current study, adsorbed atomic hydrogen is clearly an important reaction intermediate. A review of relevant surface reaction mechanisms is done in Chapter 3.

Blyholder [22] has suggested that the application of an applied potential may affect the populations of the virtual levels described by Grimley, thereby effecting adsorbate stability. Depending on the bias of the potential, this could either force electrons out of the bonding virtual level (potential lowered), or force the electrons into the higher energy anti-bonding virtual level (potential raised). Either shift would destabilize the metal-adsorbate bond, eventually resulting in desorption.

2.3.4 Effects on Surface Molecular Orbitals

If the band structure of a metal surface is ignored (as it often is) in modeling catalytic activity, another interesting possible effect of applied potentials can be discussed. Several studies discussed in section 2.2.1 [14, 15, 16, 17] suggest that the catalytic activity of surfaces is due to "dangling" bonding orbitals directed away from the catalyst surface. The directions of these dangling orbitals may be influenced by the local field resulting from the repulsive charge of neighboring electrons. The studies presented in Chapter 3 suggest that the enhanced activity of surface irregularities (kinks, steps, corners) is a result of the local field at these sites causing a dangling orbital to be directed perpendicularly away from the surface.

Although the local field strength associated with electron repulsion is very strong, it is conceivable that a sufficiently high applied voltage could create a field that is effecting the shape of these highly reactive dangling bonding orbitals. Since the field strength increases as distance from the surface decreases, it is possible that at atomic distances, the applied field could compete with the local electron repulsive field in shaping the bonding orbitals.

2.3.5 Electron Generation

The work function of a metal is a measure of the amount of energy needed to remove an electron from the highest occupied energy level (the Fermi level) to infinity. A sufficiently strong applied potential can cause electrons to be emitted from a metal surface by supplying the energy to overcome this work function. This is called field (cold) emission and in this study could originate from a non-reacting metal surface (burner mesh or quenched wire).

The reacting wire surface is also heated to approximately $1000°$ C by the catalytic combustion reaction. This heat energy excites the electrons of the metal, making emission more likely. This thermal effect coupled with the outwardly directed electric field discussed above greatly reduces the effective work function, allowing lower energy electron emission from the surface. This process is known as thermionic emission [23]. When the field is directed toward the wire, the effective work function is increased, and it is harder for conduction band electrons to escape.

2.3.6 Ion Generation and Transport

The applied field can also ionize neutral gas phase species. Although intense electric fields can form ions in a variety of ways, only several will be presented below. Like the work function of a metal, the ionization energy describes the amount of energy needed to strip an outer shell electron from a gas phase molecule. Ionization energies of relevant species are given in Table 1. As this table shows, the ionization energies are similar for these species. Therefore it is expected that ions of these species will be formed in the same ratio as their mole fraction in the gas phase.

One way neutral species can become ionized is through electron collisions. These electrons could be emitted from an electrode surface, or may just be statistically present in the gas phase. If an electron (driven by the applied field) collides with a neutral molecule with enough energy (energy greater than the ionization energy), it may knock out one of the molecule's outer shell electrons. This process not only ionizes the molecule (forming a positive species), but increases the number of free electrons in the gas phase. This rapid increase in the number of free electrons in the gas phase can lead to electric breakdown.

Electron bombardment can also result in the formation of negative ions. In some cases, the impacting electron will be absorbed by the neutral species, which then acquires a negative charge. Molecular oxygen is an example of a

Table 1 - Ionization Energies of Several Species [24]

Ion	Formed From	Ionization Energy (eV)
CH_4^+	CH_4	12.5 - 13.0
O_2^+	O_2	12.0 - 24.6
O^+	O_2	17.2 - 17.5
N_2^+	N_2	15.5 - 18.8
N^+	N_2	24.3
H_2O^+	H_2O	12.6
CH_4^{2+}	CH_4	40.7
O_2^{2+}	O_2	26.0 - 37.4
N_2^{2+}	N_2	42.7 - 44.2
H_2O^{2+}	H_2O	39.2

molecule that can form a negative species (O_2^-) as a result of electron bombardment [25].

Molecules can also be ionized by high temperature. Although species near the reacting platinum wire may experience temperatures of up to 1000°C, this temperature alone is much too low to liberate an electron from a gas phase molecule. The combined effects of intense electric field and temperature, however, might provide enough energy to accomplish this.

It is also possible that the platinum wire catalyst could be desorbing charged species. A study discussed in Chapter 3 has found hydroxyl species desorbing from the surface of platinum [26]. These OH radicals or other charged species could be significant in gas phase or surface processes.

Finally, it is possible that ionized species could be generated by the intense local electric fields associated with surface irregularities such as kinks and steps. This phenomena is the basis for field ion microscopy, a technique used to image the surface details of some metals [38]. Distortion of the local field and generation of ions at these locations might be especially interesting, since these surface irregularities are often considered the "active sites" of the catalyst surface.

The charged species generated in the above (and other) processes will tend to move along the electric lines of force, which are directed from the cathode to the anode for negatively charged species. As they migrate to either the cathode or the anode, however, ionized species will collide with neutral

molecules. This collision process will slow their progress. The net velocity an ionized species attains between acceleration by the field and collisions with neutral species is called the drift velocity. Because of their very low mass and small collision cross section, the drift velocity of electrons is considered very large compared to the bulk gas flow velocity.

This may not be the case for larger, positively or negatively charged species. If the ions' drift velocity is on the order of the bulk gas flow velocity, the positive ions will not be able to travel against the bulk flow and thus would not be able to reach the cathode. Information in von Engel [25] was used to estimate the drift velocity of ions formed from air at the conditions in this study. This drift velocity was estimated to be approximately 6000 cm/s, well in excess of the calculated bulk flow velocity (160 cm/s). Thus electrons and positive ions under the conditions of this study move relatively unimpeded toward the anode and cathode, respectively.

2.3.7 Electric Breakdown

As the field strength increases, the population of free electrons in the gas phase also increases. The migration of these free electrons toward the anode is observed as leakage current. At some field strength, this leakage current rapidly increases, and electric breakdown or sparking will occur. This is a very complex statistical phenomena, complete discussion of which is

beyond the scope of this thesis. It is mentioned here because breakdown phenomena occurred in many preliminary test runs, and the experimental apparatus had to be modified in order to minimize the probability of breakdown occurring [25].

2.4 Effects of Electric Charge versus Electric Field

In many tests conducted in this work, the catalyst surface is subjected to an applied electric field. Because the catalyst does not acquire an electric charge in all test cases (i.e. when the catalyst is grounded), it is necessary to qualitatively distinguish between the different physical effects on the metal surface under these two conditions.

When a voltage is applied across a charged and grounded electrode, an electric field will result as discussed in section 2.3.1. Although there is no charge density on the grounded surface, the electric lines of force still terminate on the surface as shown in Figs. 4 and 5. As these figures show, trajectories followed by charged species in an applied field should be identical whether they terminate on a charged or a grounded surface. By definition, there is no net charge density on the grounded surface. In addition to generating ions and propelling them along the electric lines of force, the field may also disrupt the "dangling" orbitals on the grounded metal surface.

A charge density, however, does change the overall electron population density. When the metal surface acquires a negative charge, an excess of electrons are present in the energy bands near the surface (primarily the conduction band). At positive bias, the opposite is true. Although not clearly understood, this surface charge density could have some effect on the adsorption properties of the surface in addition to the ion transport properties discussed above.

3. Literature Review

Mechanisms for catalytic reactions over platinum have been studied by many workers. Experimental work is frustrated by the fact that the reaction intermediates on the platinum surface are present in low concentrations and are hard to detect. Theoretical work in reaction mechanisms, particularly surface mechanisms, is difficult because of the complexities of the platinum surface. In general the surface will not only have a varied geometry (kinks, steps, and corners), but also will be non-uniformly covered with adsorbates and contaminants. These non-uniformities truly define the state of the surface and hence the catalytic activity; however, the ability to model these complexities tends to be (necessarily) restricted [26].

One simplification commonly made in studies of this type is that nitrogen gas does not adsorb onto the platinum surface [27]. While some small amount of N_2 does probably adsorb, the other gas phase species present (O_2, CH_4, etc.) are much more readily adsorbed on platinum. It will be assumed throughout this work that the amount of N_2 adsorbed on the platinum surface is negligible compared to other adsorbates.

This Chapter will review experimental and theoretical studies in three broad categories deemed relevant to this work: surface mechanisms, gas phase effects, and gas phase electrocatalysis. In the chemical equations that appear

throughout this and ensuing sections, a "*" refers to an active site on the catalyst surface, and a "starred" species is adsorbed on the catalyst surface. All other reactants are in the gas phase.

3.1 Surface Mechanisms

3.1.1 Hydrogen Oxidation

The hydrogen-oxygen system is the most commonly studied oxidation reaction over platinum. Although the amount of gaseous hydrogen present in this study is expected to be relatively small, the interaction of adsorbed hydrogen and oxygen is important. In addition, discussion of possible mechanisms involved with this system will give insight into the (more relevant) mechanisms for hydrocarbon oxidation discussed in section 3.1.2.

Tevault et al. [28] and Zhdanov [29] have proposed the following mechanism for the catalytic oxidation of hydrogen gas over platinum:

$$H_2 + 2* \rightarrow 2H* \tag{8}$$

$$O_2 + 2* \rightarrow 2O* \tag{9}$$

$$H* + O* \rightarrow OH* + * \tag{10}$$

$$H* + OH* \rightarrow H_2O + 2* \tag{11}$$

$$OH^* \rightarrow OH + * \qquad (12)$$

$$O^* + OH^* \rightarrow HO_2 + 2^* \qquad (13)$$

These workers find the adsorption of H_2 (8) and O_2 (9) to be the rate limiting steps. Note that in addition to water, this mechanism allows for the release of OH and HO_2 into the gas phase. The presence of OH desorbing from a platinum catalyst has been experimentally confirmed by Talley et al. [26]. It should be noted that the breakdown of reactant water vapor can proceed by the reverse of (11). This is important since a small amount of water vapor is expected to be present in the reactants of the present study. The reverse of (12) allows for the re-adsorption of desorbed OH.

Another possibility is that H_2 is oxidized by an Eley-Rideal mechanism rather than a combination of two adsorbed species. A study by Weinberg and Merrill [30] compared the theoretical activation energy of a Langmuir-Hinshelwood (14) versus an Eley-Rideal (15) hydrogen oxidation.

$$O^* + H_2 \rightarrow H_2O + * \qquad (14)$$

$$O^* + 2H^* \rightarrow H_2O + 3^* \qquad (15)$$

The Eley-Rideal mechanism was found to have a lower activation energy and thus was suggested as the preferred mechanism. Unfortunately other Langmuir-Hinshelwood reactions (such as Tevault's equations 8-11) were not specifically examined.

3.1.2 Methane Oxidation

The fuel used in this study was natural gas, which is mostly methane. Although small amounts of other hydrocarbons and other species are present, only processes involving methane are considered here.

The presence of carbon species greatly increases the number of possible oxidation mechanisms. An experimental study by Cullis and Willatt [31] found that the catalytic oxidation of methane over platinum was first order in methane concentration and zero order in (gaseous) oxygen concentration. This indicates that this process is strongly dependent on adsorbed oxygen. This work also indicated that methane oxidation was strongly dependent on temperature.

While no detailed mechanisms have been experimentally verified, there is general agreement in the literature concerning the adsorption of methane on platinum. Methane, like all of the alkanes, must chemisorb dissociatively on the platinum surface (16) [5]. This is because one of the C-H bonds must
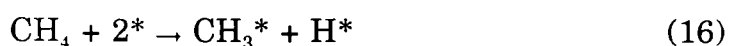
$$CH_4 + 2* \rightarrow CH_3* + H* \qquad (16)$$

be severed to form the bond with the catalyst. Species with multiple bonds, such as CO, can chemisorb this way or retain their molecular character.

At high surface temperatures (above 700°K), the remaining C-H bonds in CH_3* are severed, leaving adsorbed atomic hydrogen (H*) and a graphite-

like adsorbed carbon (C*) layer. At these temperatures, the C-C skeletal bonds of the more complex alkanes are also severed. Although they are reaction intermediates, C* and H* impede further chemisorption of methane, which requires two adjacent active sites.

A simple mechanism for the oxidation of methane that does not account for possible C-H intermediate species reactions could proceed as follows:

$$CH_4 + 2* \rightarrow CH_3* + H* \tag{16}$$

$$O_2 + 2* \rightarrow 2O* \tag{8}$$

$$H* + O* \rightarrow OH* + * \tag{10}$$

$$H* + OH* \rightarrow H_2O + 2* \tag{11}$$

$$CH_3* + 3* \rightarrow C* + 3H* \tag{17}$$

$$C* + O* \rightarrow CO* + * \tag{18}$$

$$CO* + O* \rightarrow CO_2 + 2* \tag{19}$$

After dissociative chemisorption of methane and oxygen (16) and (8), CO* and OH* are formed as reaction intermediaries. These species then go on to form CO_2* and H_2O*, which then desorb. In general, adsorbed species will desorb when it is energetically favorable for them to do so. This means that the bonds holding the adsorbate molecule together are strong compared to the bonds holding the adsorbate to the surface. The breaking of these adsorbate-surface bonds allows the electrons of the adsorbed molecule to enter lower energy states.

In addition to overlooking C-H intermediate species, this mechanism does not account for possible Eley-Rideal or gas phase reactions. An Eley-Rideal mechanism for the oxidation of CO is discussed below, and possible gas phase reactions are discussed in section 3.2.

Weinberg and Merrill [30] have also computed the activation energies of a Langmuir-Hinshelwood and an Eley-Rideal mechanism for CO oxidation. As in their study of hydrogen oxidation, the Eley-Rideal mechanism had a lower computed activation energy and was proposed as the favored mechanism. As before, only one possible mechanism of each type was examined. In reality it is likely that both types of mechanisms can be involved in catalytic oxidation reactions.

3.2 Gas Phase Reactions

In addition to Langmuir-Hinshelwood and Eley-Rideal reaction steps, Berlowitz et al. [32] have suggested that intermediate OH species may be desorbed from the platinum surface and react with other species in the gas phase. Various workers [26], [33], [34] have observed elevated OH concentrations immediately downstream of a platinum catalyst.

Talley et al. [26] used laser-induced fluorescence to observe the formation of OH when passing H_2 and O_2 over platinum. Bruno et al. [33] observed elevated OH levels when using a CO, O_2, N_2 mixture. Fujimoto et al.

[34] used H_2 and O_2 and observed a decrease of the OH species up to a catalyst temperature of 900°K, above which the OH levels drastically increased.

These studies indicate that some of the OH* present on the catalyst surface will desorb into the gas phase and quickly react with other gas phase species. It is possible that the overall mechanism of methane oxidation over platinum includes gas phase reaction steps. It is also possible that these gas phase reactions are secondary, and that most of the methane is oxidized either by Langmuir-Hinshelwood or Eley-Rideal mechanisms.

The study by Berlowitz et al. [32] also examined the possibility of methyl radicals (CH_3) desorbing from the platinum surface. Up to catalyst temperatures of 900°C no methyl groups were observed. This is because the Pt-C bond is relatively strong compared to the C-H bonds of the methyl group. This results in a long residence time, during which the methyl radical is decomposed.

The lack of observable methyl radicals is significant because it also eliminates two possible reaction steps. The Eley-Rideal dehydrogenation reaction (20) is not allowed, nor is the gas phase reaction between OH and

$$CH_4 + * \rightarrow CH_3 + H* \qquad (20)$$

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (21)$$
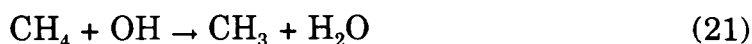
methane (21) likely to proceed. Both of these reactions would produce methyl radicals that conceivably should have been observed by Berlowitz et al. [32].

3.3 Electrocatalysis in the Gas Phase

As previously stated, much of the work in electrocatalysis is specific to electrodes in liquid solution. Because there is no electrolyte solution in gas phase electrocatalysis, and the temperatures and field strengths involved are significantly different, much of this material is not relevant. However, several studies of the effects of electrostatic fields on gas phase catalysis were found and are reviewed below.

Hoenig and Lane [35] studied the effect of a DC field on chemisorption of oxygen on a zinc oxide surface. They found that chemisorption was enhanced when the field was directed to attract electrons to the ZnO surface, and impeded when the field was reversed.

Hoenig and Lane's work, however, differs from the current study in a number of ways. First, ZnO is a semi-conductor and has a different electronic structure that platinum. Also, Hoenig and Lane do not use the ZnO surface as one of their electrodes; rather it is configured between two metallic electrodes. Finally, their study is done at room temperature and significantly lower applied voltages (800 V) than the current work.

Lincoln and Olinger [36] studied the influence of an AC field on the adsorption of ethylene and hydrogen on nickel, and on the hydrogenolysis of ethylene over nickel. They found that at low pressures (on the order of 0.05 atm), chemisorption of ethylene could be enhanced by the field, but chemisorp-

tion of hydrogen could not. No field effects on chemisorption were observed at higher pressures. They also found that the field had no effect on the catalytic hydrogenolysis reaction. The authors propose that the applied field changes the mechanism of chemisorption at low pressures, but offer no theoretical explanation for this.

The main difficulty in applying these results to the current study is that Lincoln and Olinger only observe a field effect at low pressures. Also, an AC rather than a DC voltage is used, and the temperatures and applied voltages are once again much lower that those of the current work (100°C, 4kV, respectively).

Kristyan and Timmons [37] studied the DC field effects on hydrogenolysis of ethylene and ethane over a nickel wire. They observe dramatic increases in CH_4 production when either a positive or a negative potential is applied to the wire. They also observe that when the wire is negatively biased, the increased activity persists in subsequent (no applied voltage) tests. The authors propose that this subsequent increase in activity is the result of leakage current somehow removing carbon deposits on the surface, thereby regenerating the catalyst.

Although the Kristyan and Timmons' study differs from the current work, there is an interesting similarity. The field strengths used and the leakage currents reported by these authors are similar to the values observed in the current work. Although Kristyan and Timmons studied a hydrogeno-

lysis (rather than an oxidation) reaction, it is possible that a similar mechanism could account for both observed field effects.

In Kristyan and Timmons' work, free carbon on the surface acts as a catalyst poison, occupying active sites needed for reactant adsorption. In the current work, similar surface carbon deposits (C*) may be an important intermediate species in the oxidation reaction (see section 3.1.2, equation 19, for example). In the former case, removal of these carbon deposits would increase the rate of formation of CH_4. In the latter case, removal of this species may interfere with the oxidation reaction.

4. Experimental Apparatus and Procedure

4.1 Experimental Apparatus

4.1.1 Gas Flow System

In order to examine the effects of a high voltage DC field on catalytic combustion of natural gas, the apparatus described in this section was constructed. The main elements consisted of a premix burner to supply gas flow, a high voltage DC power supply, an optical pyrometer, and two platinum wires. A schematic of the overall system is given in Fig. 7; the gas flow, electronic configurations, and optical measurement systems are described in detail below. Dimensions of the reaction zones for the different geometries are given in Figs. 8 and 9.

Natural gas and compressed air were drawn from lab lines. Pressure in the air line slowly drifted up and down, while the gas pressure cycled between two relatively stable values. These pressure variations caused the effective flow rates of the gas and air to vary substantially. Although an inconvenience, constant gas and air flow rates were maintained by manual adjustment to the corresponding gas (Aaborg Instruments) and air (Brooks Instruments model 1112CH11FE2AA) flow meters. These flow meters were
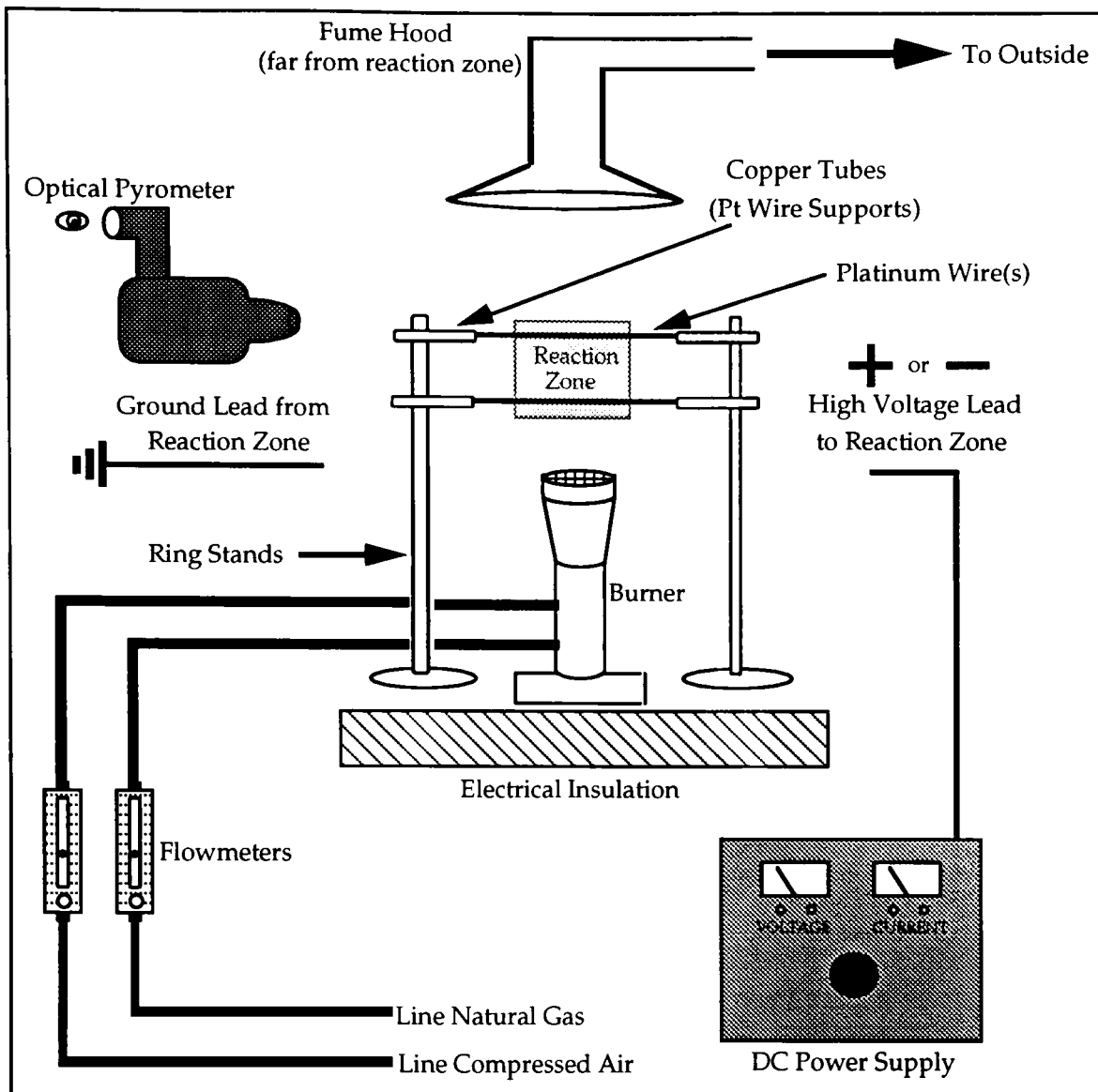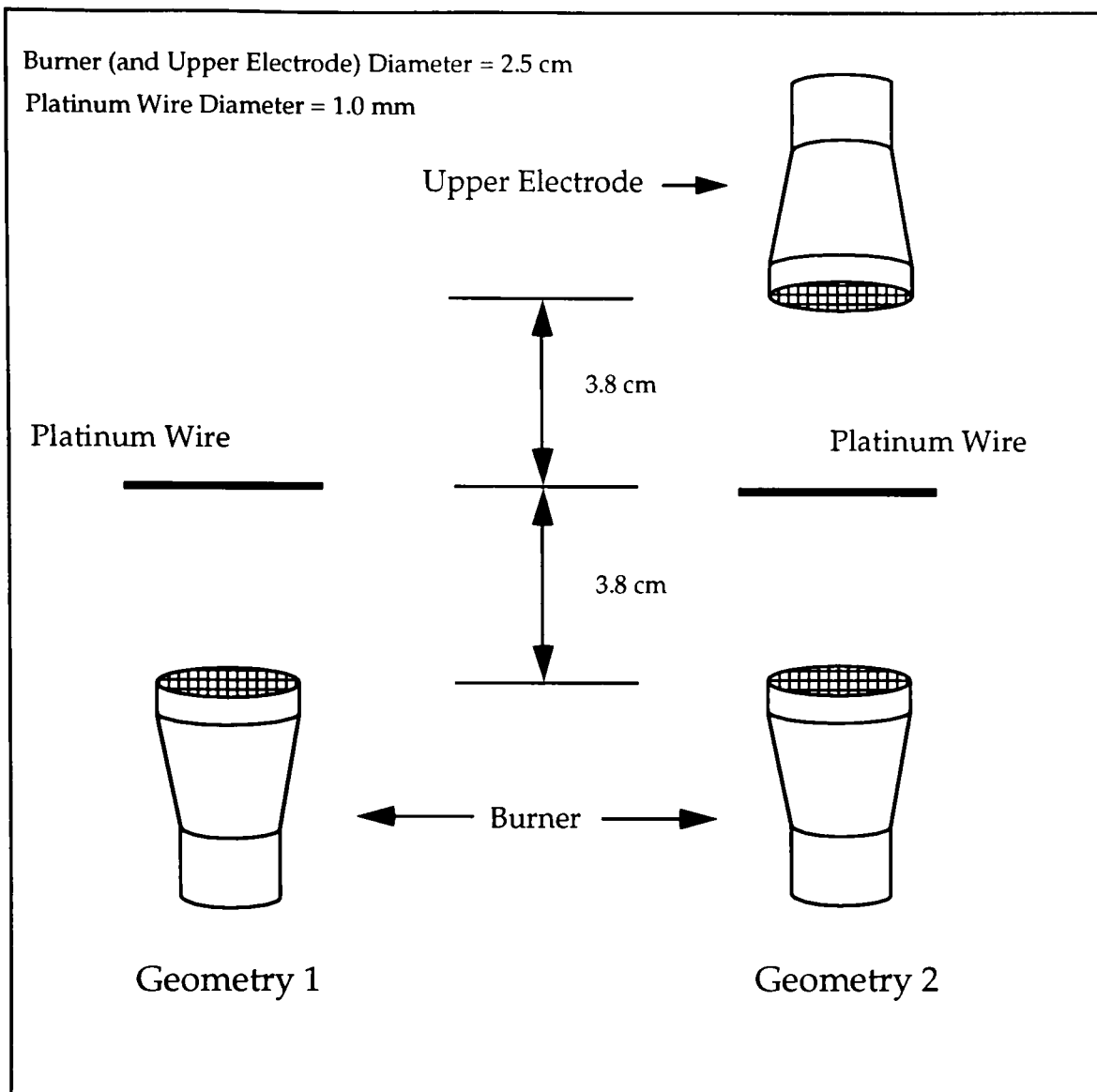
Figure 7 - Experimental Set-up

Burner (and Upper Electrode) Diameter = 2.5 cm
Platinum Wire Diameter = 1.0 mm

Upper Electrode →

3.8 cm

Platinum Wire   Platinum Wire

3.8 cm

← Burner →

Geometry 1   Geometry 2

Figure 8 - Reaction Zone Specifics: Geometries 1 and 2

Burner Exit Diameter = 2.5 cm
Platinum Wire Diameter = 1.0 mm

Upper Pt Wire

3.3 cm

3.8 cm

0.5 cm

Lower Pt Wire

Burner

Front View

Side View
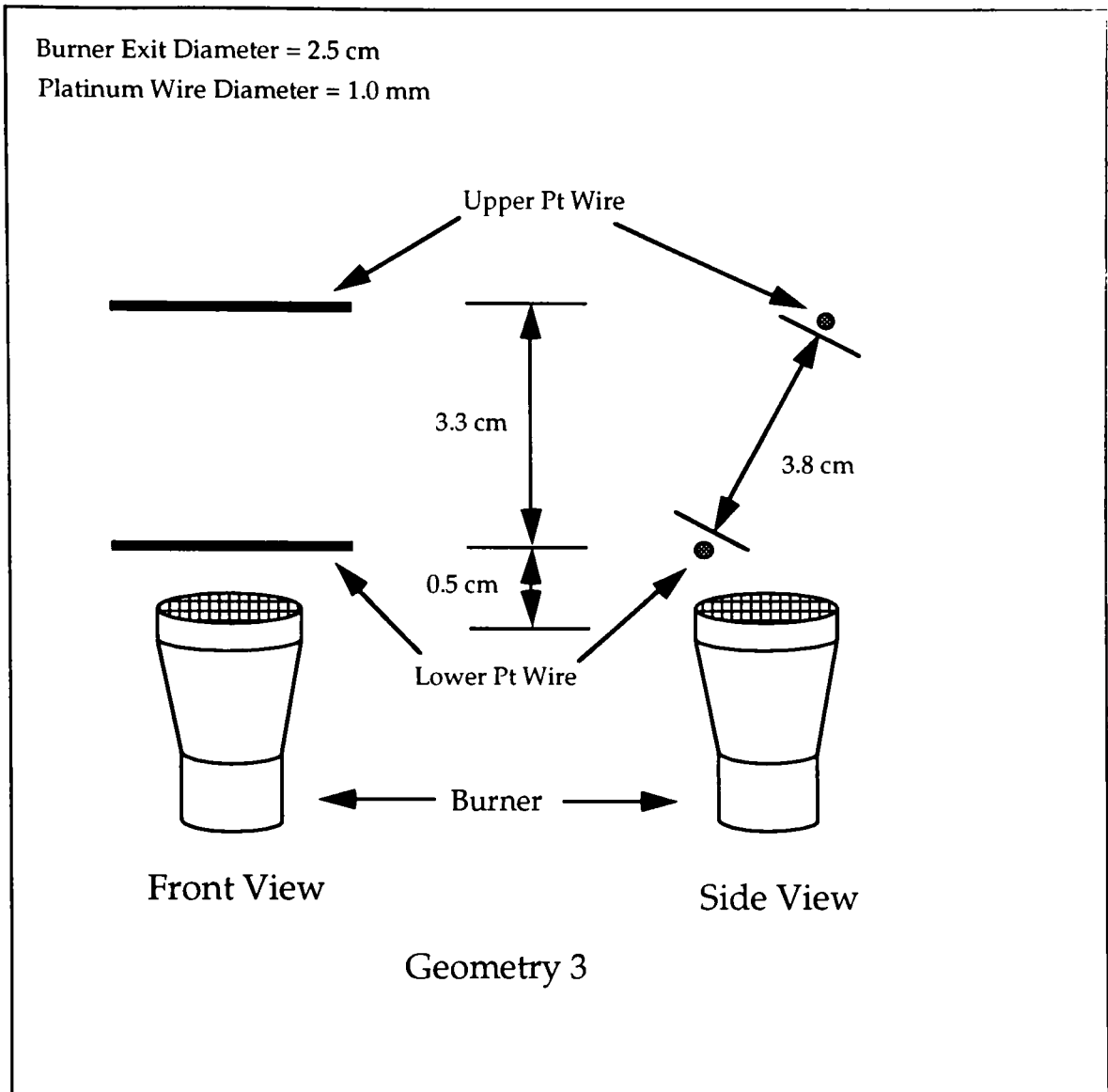
Geometry 3

Figure 9 - Reaction Zone Specifics: Geometry 3

calibrated using a Singer model DTM-115 dry gas meter.

Gas and air then flowed through a premix burner and entered the reaction zone. The flow velocity was approximately 1.6 m/s, resulting in a Reynolds number per unit length of 110000 m^{-1}. If the 1 mm wire diameter is used as the characteristic length, the corresponding Reynolds number is about 110.

Above the burner the gas mixture passed over 1 mm diameter platinum wire(s) (Fisher Scientific # 13-766-3A). These wire(s) were supported by metal ring stands in various geometries detailed in section 4.1.2. After leaving the reaction zone, the gas mixture was ventilated to the outside by a fume hood.

4.1.2 Electronic Configurations

The DC electrostatic field was provided by a Hipotronics model 830B high voltage power supply. Voltage on the Hipotronics could be varied between 0 and 36 kilovolts (positive or negative bias). In addition, the power supply also had a current meter which measured currents as low as 5 μA.

The reaction zone was configured using four different physical geometries. In the first three of these geometries, the platinum wire was used as one of the electrodes; in the fourth geometry, the wire was located between two electrodes. For each of these four physical geometries, there were four corresponding electronic configurations consisting of various combinations of

positive, negative, and ground potential. These combinations of physical geometry and electronic configuration provided 16 different test cases. These cases are detailed below.

Geometry 1 used the burner as one electrode and a single platinum wire as the other. The platinum wire was supported 3.8 cm above the burner. The burner exit was circular (2.5 cm diameter). Since this opening was filled with a metallic flame holder mesh, it is assumed that the burner exit approximates a plane surface. Geometry 1 is shown in Fig. 8, and the four electronic arrangements (A, B, C, and D) for this Geometry are shown in Figs. 10 and 11.

Geometry 2 used the platinum wire as one electrode. This wire was supported 3.8 cm above the burner. The other electrode was an identical burner fixture supported 3.8 cm above the wire. Geometry 2 is shown in Fig. 8, and the corresponding electronic arrangements are shown in Figs. 12 and 13.

Geometry 3 used platinum wires for both electrodes. These wires were staggered in the gas flow because this arrangement was less prone to electric breakdown. The lower wire was 0.5 cm above the burner. The upper wire was staggered so that the distance between the upper wire and the burner was 3.8 cm. The separation between the two wire was also 3.8 cm. This geometry is shown in Fig. 9, and the corresponding electronic arrangements are shown in Figs. 14 and 15.
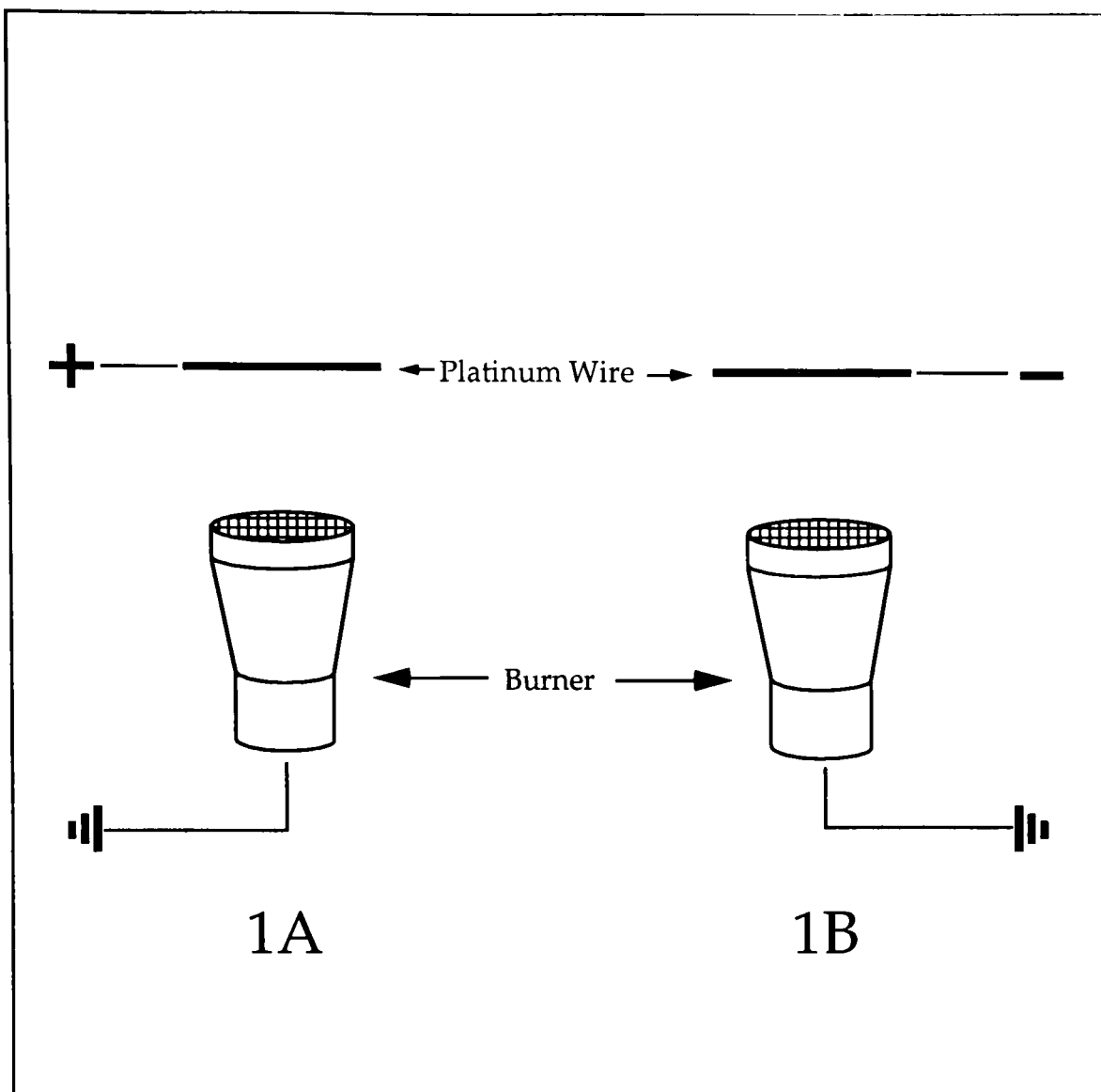
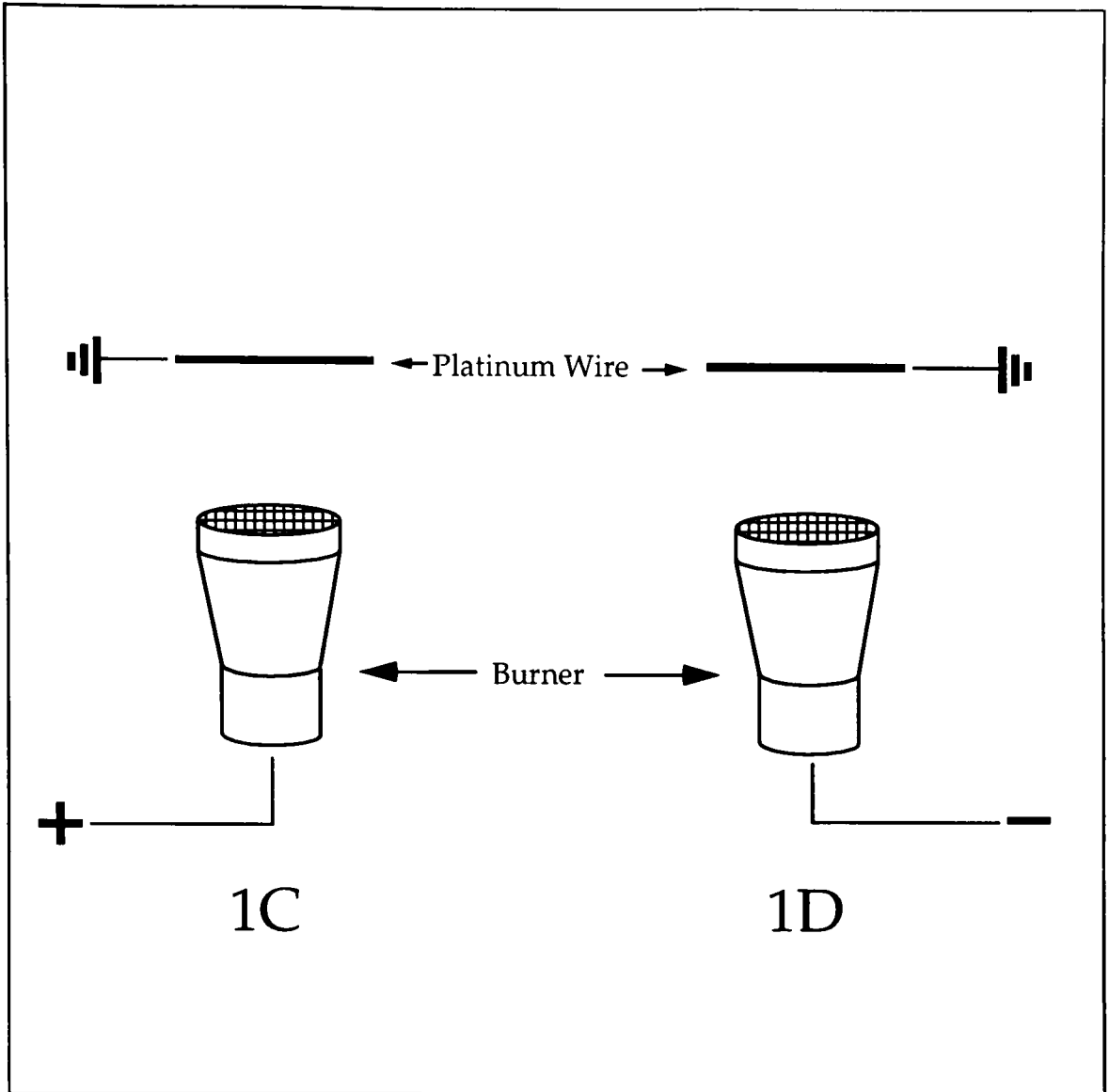Figure 10 - Electronic Configurations A and B, Geometry 1

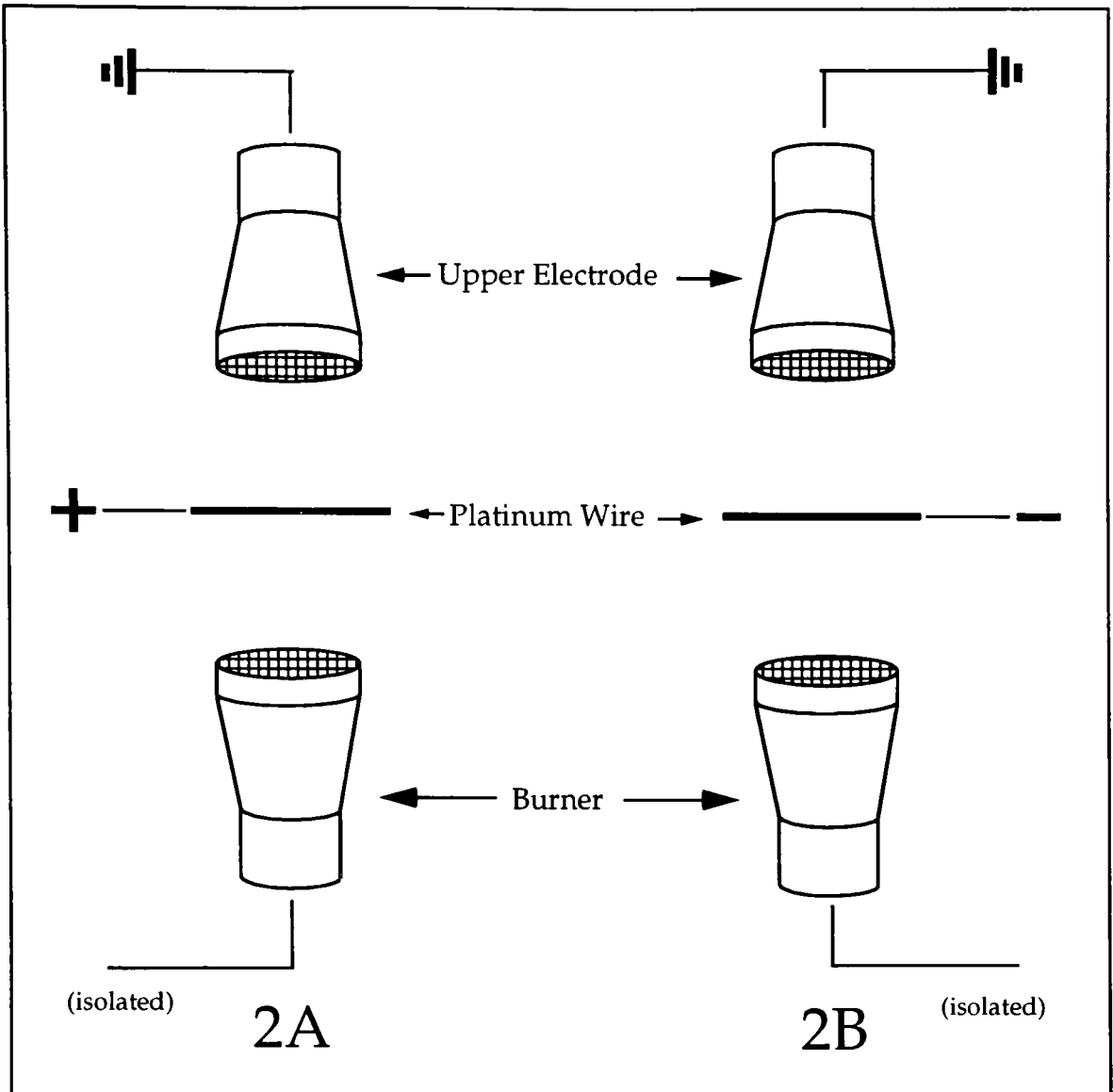Figure 11 - Electronic Configurations C and D, Geometry 1

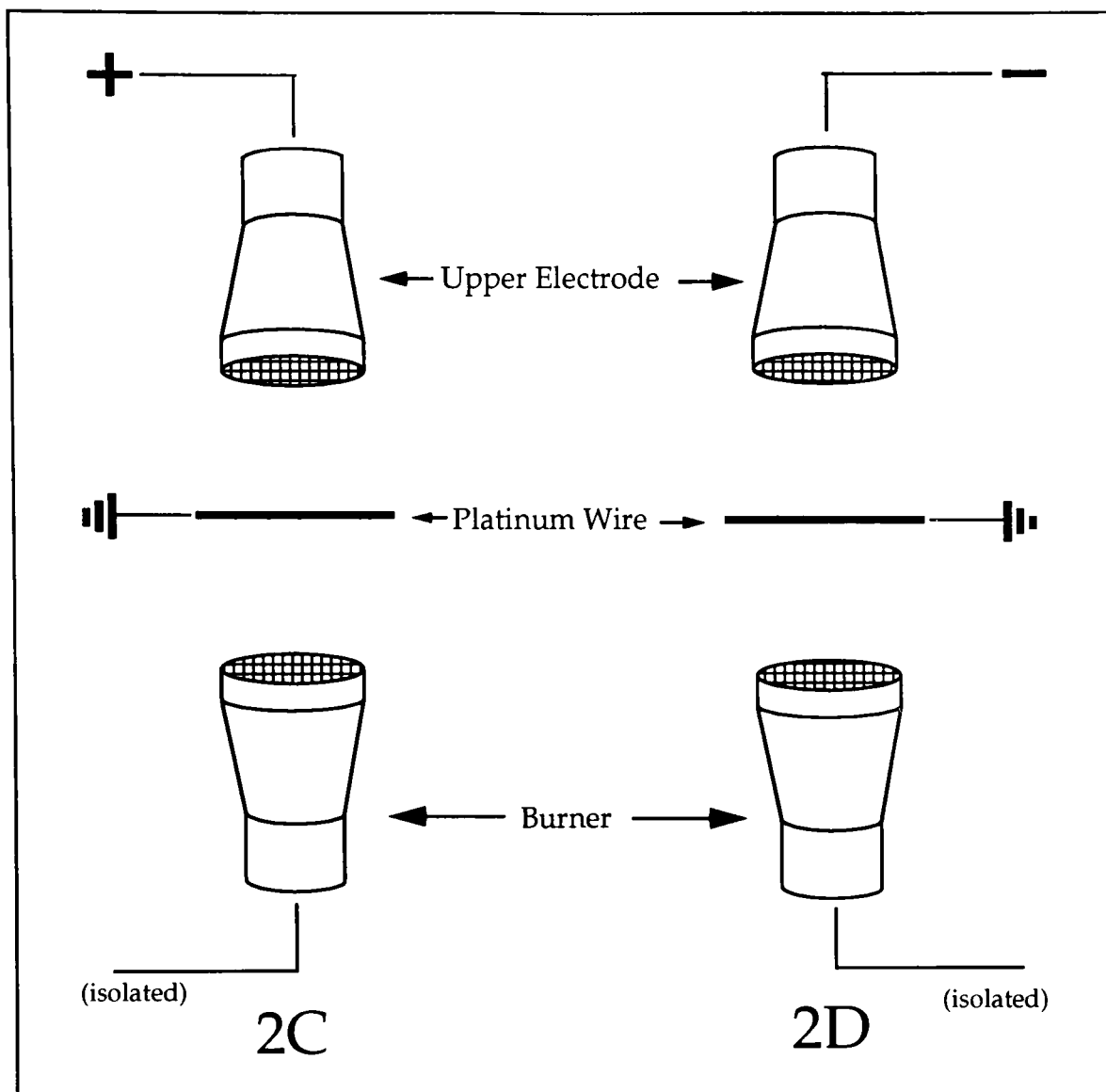Figure 12 - Electronic Configurations A and B, Geometry 2

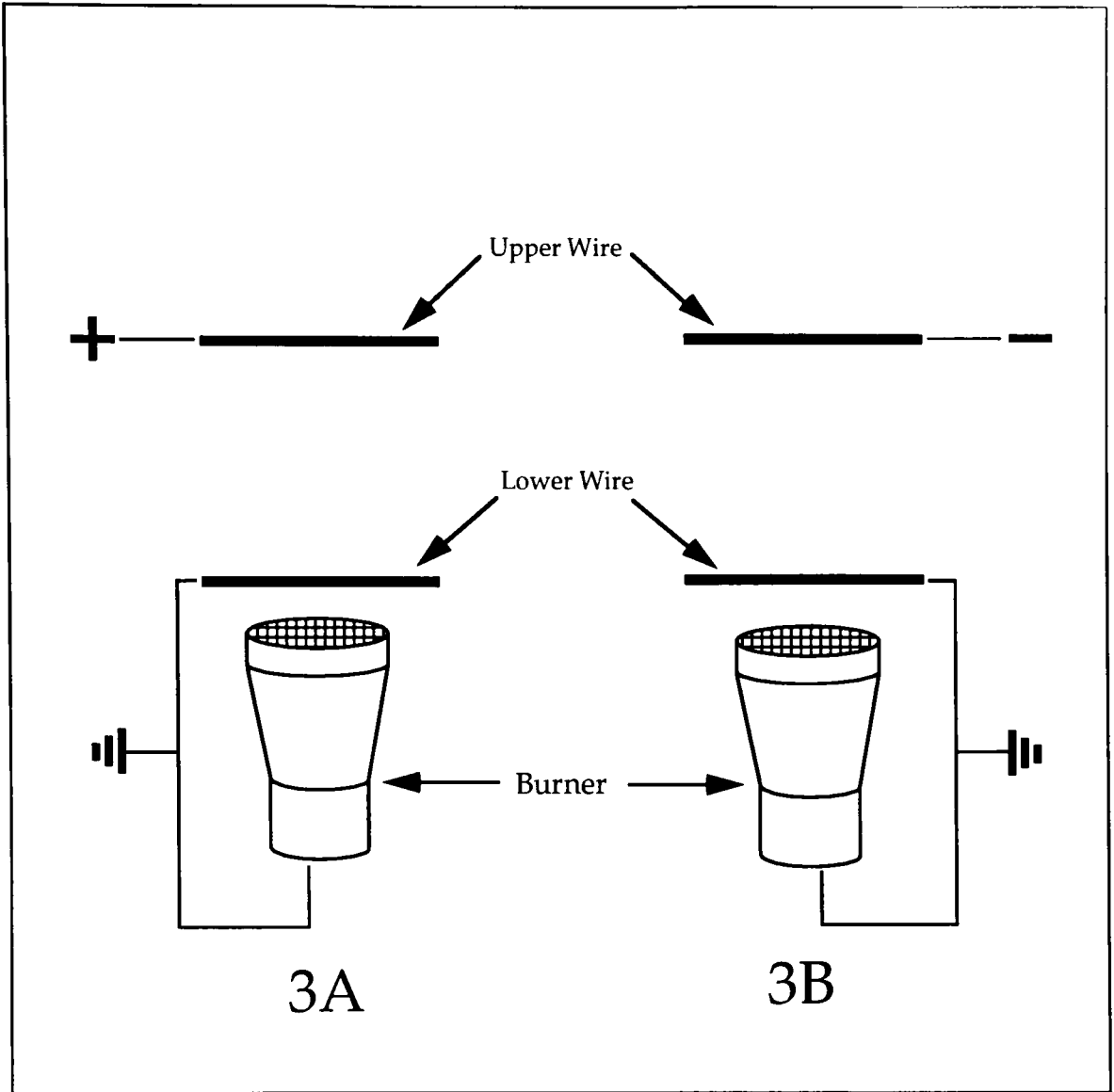Figure 13 - Electronic Configurations C and D, Geometry 2

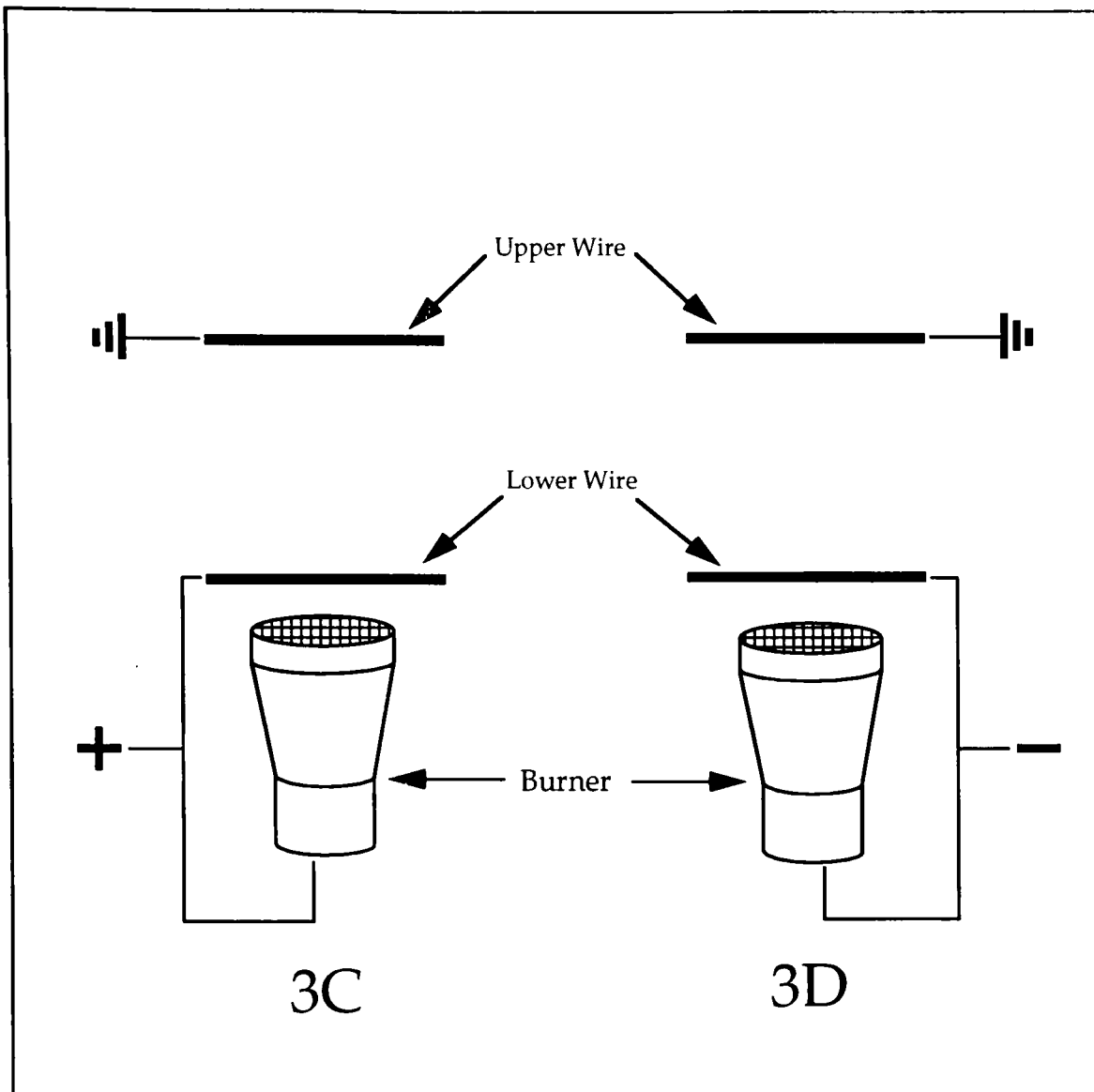Figure 14 - Electronic Configurations A and B, Geometry 3

Figure 15 - Electronic Configurations C and D, Geometry 3

Geometry 4 used the burner as one electrode, and the identical burner fixture as the other. The platinum wire was then supported midway between the two (approximately) flat plate electrodes. The two electrodes were spaced 3.8 cm apart. Electronic configurations for Geometry 4 are shown in Figs. 16 and 17.

4.1.3 Optical Measurements

The catalytic combustion reaction temperature was measured manually with a Leeds and Northrop 8632-C optical pyrometer. The lower operating range limit of this instrument was 850°C, which was below the lowest stable temperature observed. The uncertainty of temperature measurements made with this pyrometer was judged to be ±10°C, based on repeated observations. This uncertainty corresponds to the error bars indicated on all temperature data plots. Measurements of the wire surface temperature were taken as a measure of the catalytic combustion reaction rate.
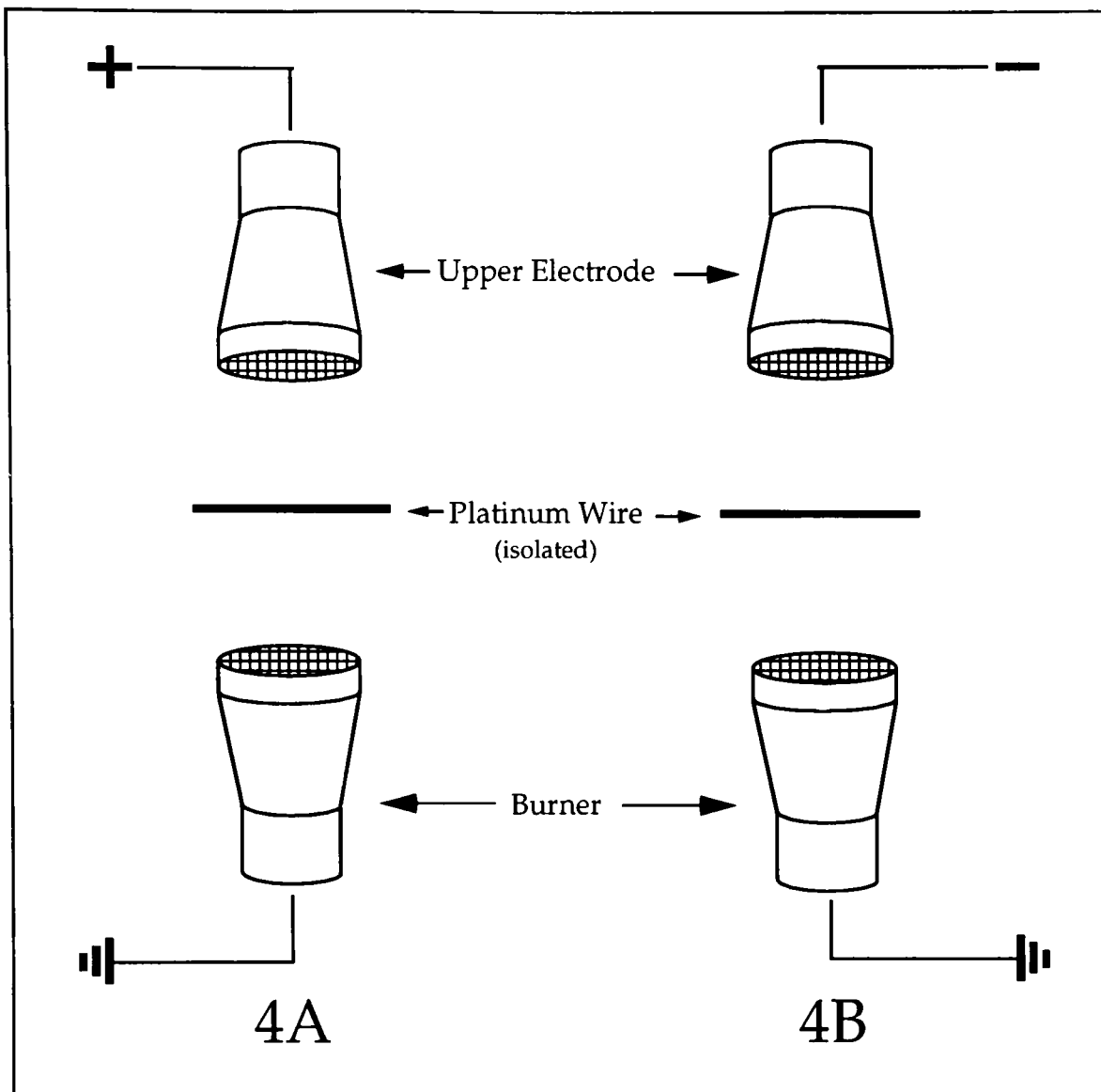
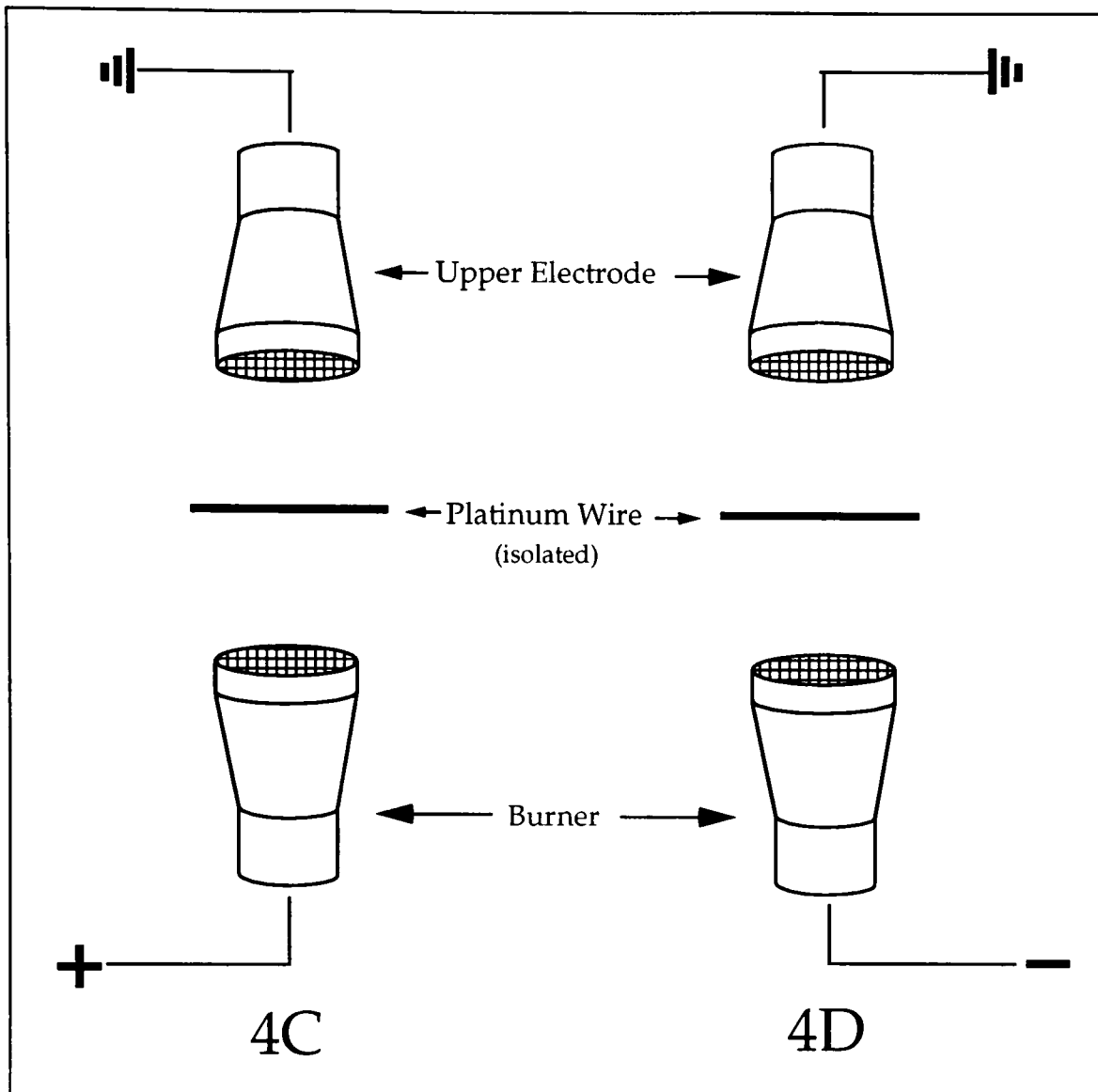Figure 16 - Electronic Configurations A and B, Geometry 4

Figure 17 - Electronic Configurations C and D, Geometry 4

4.2 Experimental Procedure

4.2.1 Air to Fuel Ratio Determination

Many different air-fuel ratios supported stable catalytic combustion on the platinum wire surface. This operating range for a 3.8 cm spacing is given in Fig. 18. A molar mixture ratio of 14.7:1 (air:fuel) was chosen for this study because it gave one of the highest nominal temperatures and thus a very strong and easily read optical signal. Slightly leaner mixtures tended to be less stable; that is, wire surface temperature was not constant, varied considerably with time. This mixture ratio was fixed for all tests, and corresponds to a bulk equivalence ratio of $\phi \approx 0.65$.

A potential problem with accurately determining the mixture ratio was air entrainment. Because the reaction zone was open to the room, air could mix with the flow leaving the premix burner, diluting the mixture. A plot illustrating the effect of air entrainment on nominal reaction temperature is given in Fig. 19. As seen in this plot, at the 3.8 cm distance used throughout this study, these effects were minimal. For this reason, any change in fuel-air mixture caused by air entrainment was ignored.
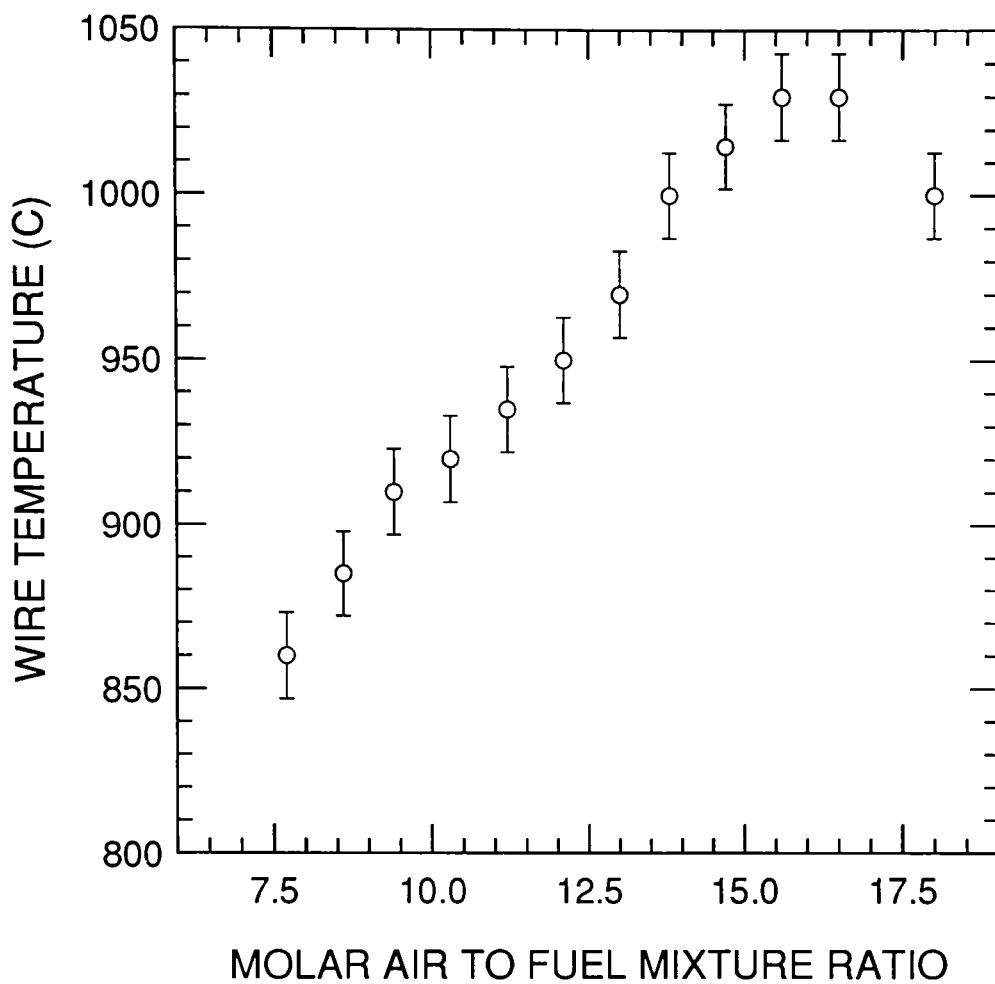
Figure 18 - Effect of Molar Air-Fuel Ratio on Reaction Temperature

4.2.2 Gap Size Determination

Although relative field strengths were estimated in section 2.3.1, the spacing or gap, h, between the electrodes was experimentally set. The gap between the electrodes was chosen to be 3.8 cm for most tests because it was small enough to produce a high enough field strength (given the limits on the Hipotronics supply) to allow the quenching effect (i.e. a reduction in wire surface temperature with applied voltage) to be observed in most configurations, while remaining fairly resistant to electric breakdown. Larger gap sizes required higher voltages to produce the same observed effects. In some cases the voltage required to produce a field of sufficient strength to cause these effects apparently exceeded the Hipotronics limit of 36 kV. Gap sizes smaller that 3.8 cm were more prone to electric breakdown.

4.2.3 Catalyst Preparation

Once the mixture ratio and gap size parameters were fixed, data collection could begin. Prior to each test run, however, the platinum wire catalyst was "cleaned" in a natural gas / air flame for at least ten minutes. This had the effect of removing any contaminants from the surface.

When the catalyst is first placed in the flame, a bright orange flame originating on the catalyst surface is visible. After several seconds this orange
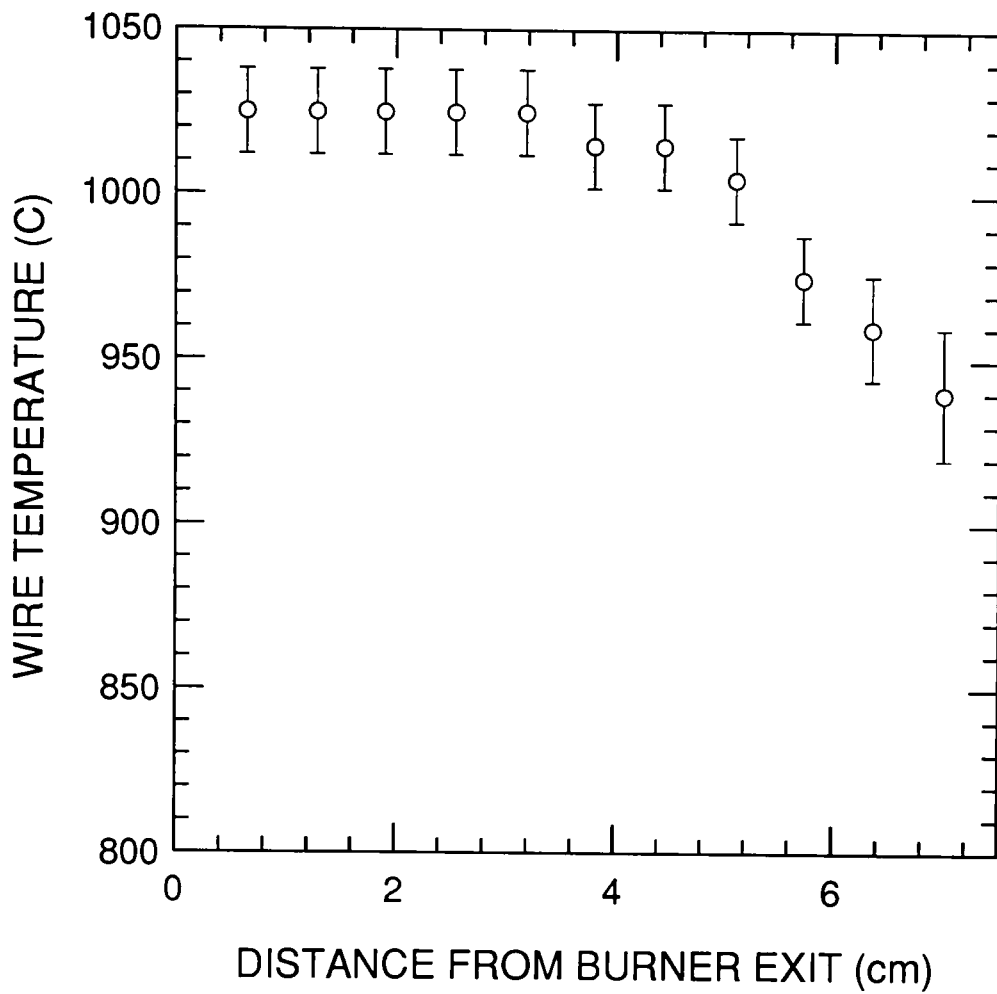
Figure 19 - Effect of Air Entrainment on Reaction Temperature

region disappears. This orange region is presumably caused by contaminants burning off the catalyst surface. This effect is especially apparent after the catalyst has been handled, or has not been used for a while. If the catalyst is not pre-treated in this way, it is very difficult to set up a self-sustaining reaction on the surface.

This cleaning process also preheats the catalyst to a temperature necessary to sustain the catalytic reaction without the natural gas flame.

4.2.4 Data Collection

After the catalyst surface has been cleaned, the gas-phase flame is extinguished. The platinum wire continues to glow because of the catalytic reaction. The wire is then allowed to "cool" to its equilibrium reaction temperature. This process takes about one minute.

Once the reaction has attained its nominal temperature, voltages can be applied and the corresponding effects on wire temperature measured. At each data point, temperature data is taken with the pyrometer and current data is read from the power supply. Flow rates are carefully monitored at this stage, since wire temperature is a sensitive function of mixture ratio. Data for each test were taken both starting from zero voltage and also starting from the highest stable reacting voltage. Results measured both ways were consistent within the established uncertainty of $\pm 10°C$.

This procedure was performed for each of the 16 test cases described above. The only variation was in running the tests from Geometry 2. In this case the upper electrode (identical burner fixture) was not put into position until after the cleaning/preheat flame was extinguished. This was done to minimize the heat loading on the upper electrode.

5. Results and Discussion

This Chapter will present and discussed the results of tests using the four different geometric configurations detailed in Chapter 4. Tests which gave similar results are presented and discussed together in separate sections. The basis for these divisions (primarily the applied voltage at which reaction quenching occurs) is given in Table 2. Several additional tests were also done to clarify the "no reaction" leakage currents (section 5.1), and to determine the field strength necessary to quench the reaction occurring on the lower platinum wire in Geometry 3 (section 5.7).

In most test cases where the catalyst was one of the electrodes, the presence of a sufficiently high electric field extinguished the surface reaction. The voltage required to extinguish the reaction varied with the physical and electrical configuration. This Chapter will also propose an explanation for these variations.

Before discussing the specific cases, one general observation applicable to all of the data should be noted. The data points indicated on the figures presented in this chapter are stable operating points. For a given applied voltage and mixture, the wire temperature and current remains constant. If the field is reduced, the reaction temperature returns to the nominal value, or the temperature indicated for the new voltage. Likewise the current returns

Table 2 - Summary of Experimental Data

TEST CASE	QUENCHING VOLTAGE (kV)	MAXIMUM CURRENT (μA)	FIGURE
1A	14 ± 1	20 ± 5	24
1B	13.5	20	25
3A	15	120	26
3B	14	60	27
1C	16	(0)*	28
1D	18	(0)*	29
3C	11	40	30
3D	12	40	31
2C	28	85	32
2D	29	60	33
2A	21	150	36
2B	27	85	35

* Within Current Meter Sensitivity

to its nominal value. This indicates that more ions are formed when the wire is reacting. In some cases, a reaction was briefly sustained above the highest indicated voltage. These points were not considered.

As explained in section 4.1.3, the uncertainty in temperature was determined by the resolution of the pyrometer. There was some uncertainty as to the location of the highest stable data point. In all cases the quenching voltages presented (i.e. the highest stable data points) were repeatable to within ±1 kV.

Note that the surface temperatures corresponding to the last data point on each plot is between 910 and 950 °C. Since the location of this final data point represents a reaction stability limit, its position is not known precisely. This, combined with the ±10°C error bars on all temperature measurements, suggests that the surface reaction is quenched at essentially the same temperature in each case.
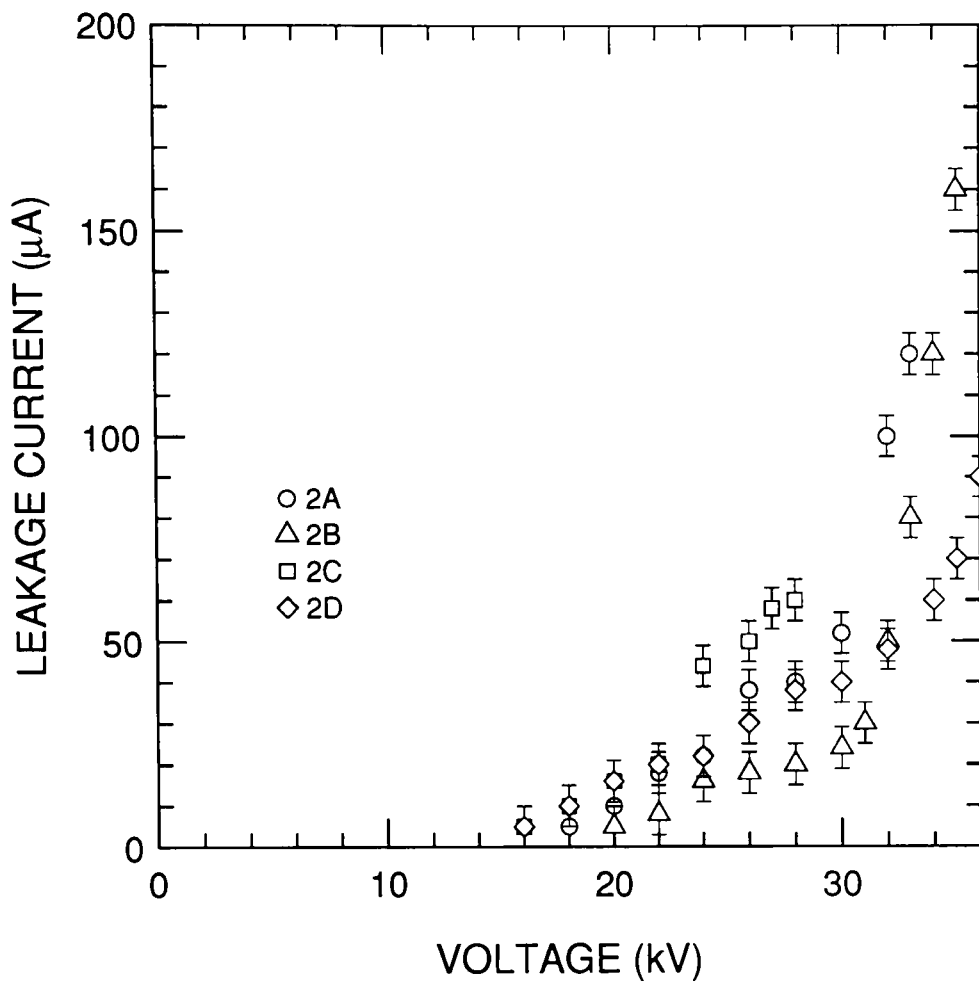
5.1 Nominal Leakage Current Data

In order to illustrate the formation of ions and free electrons independent of catalytic reactions, nominal leakage current data is presented in Figs. 20 through 23. As in all test cases, the measured current was taken as an indication of the amount of flow ionization (i.e. formation of positively and negatively charged gas-phase species) resulting from the applied field. This
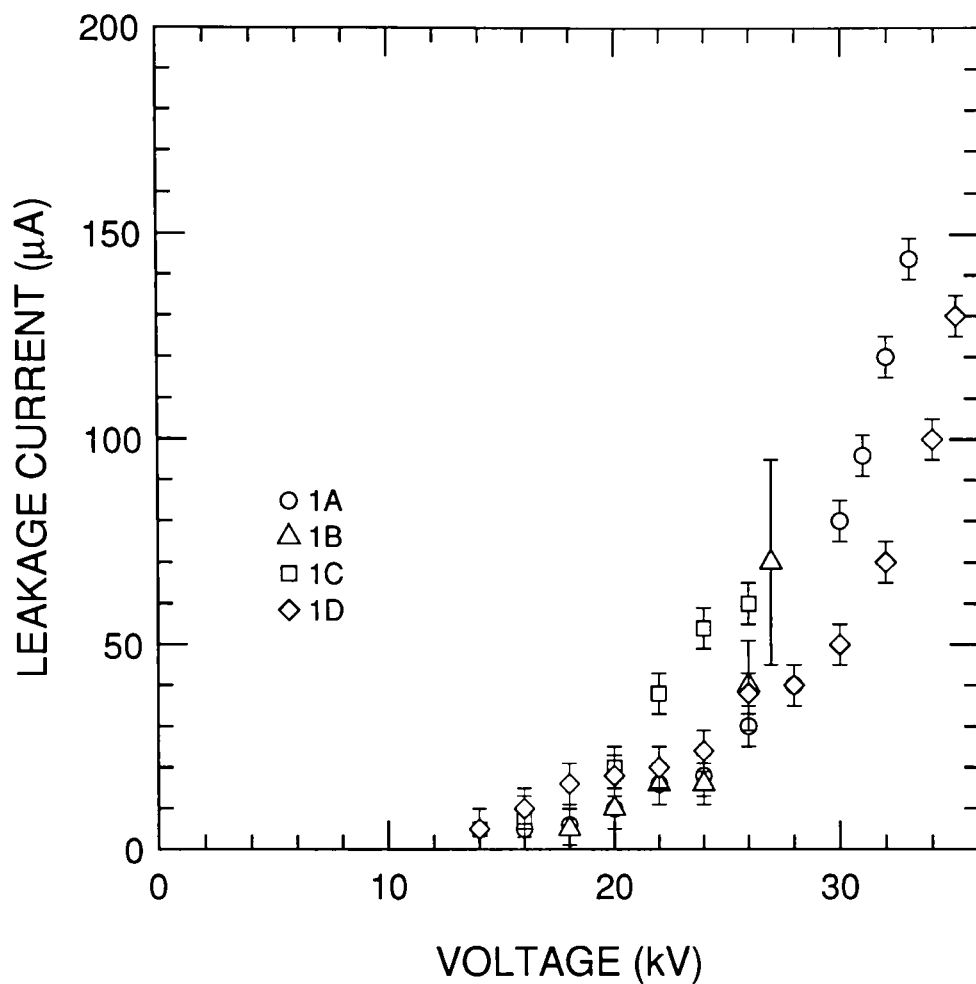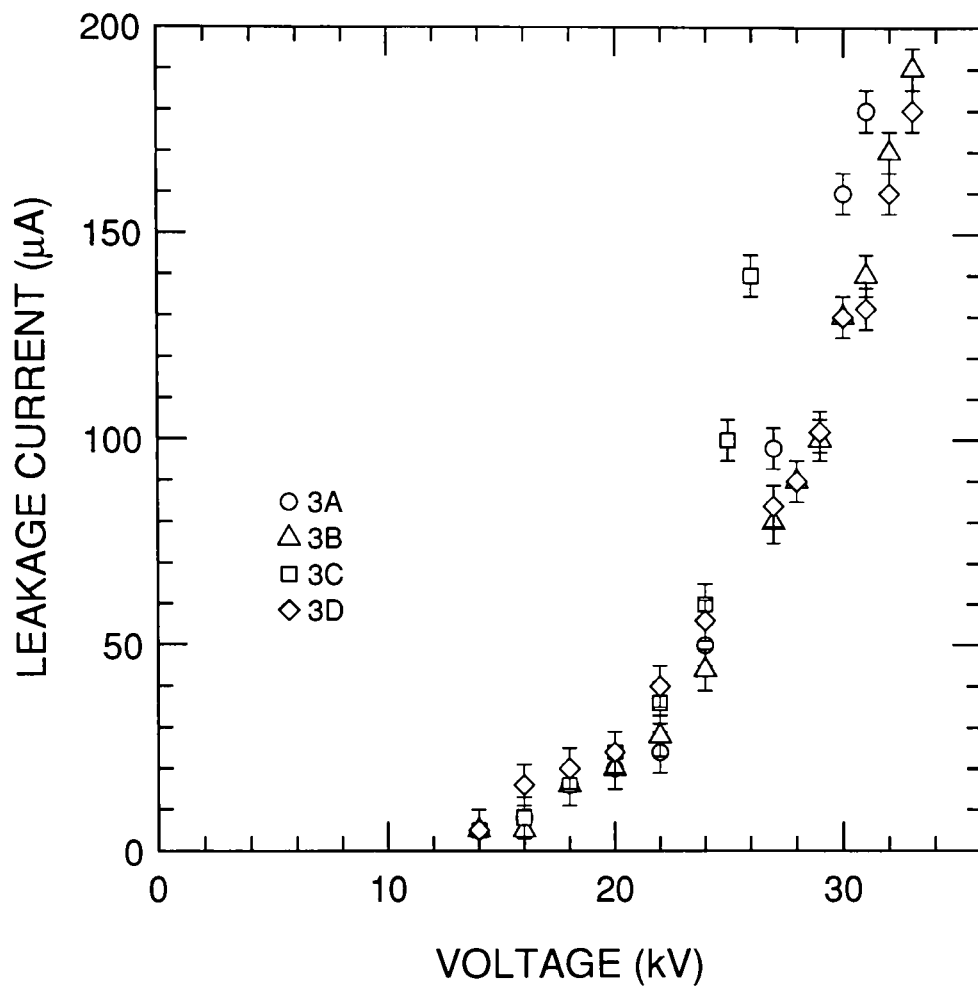
Figure 20 - Nominal (No Reaction) Leakage Currents for Geometry 1

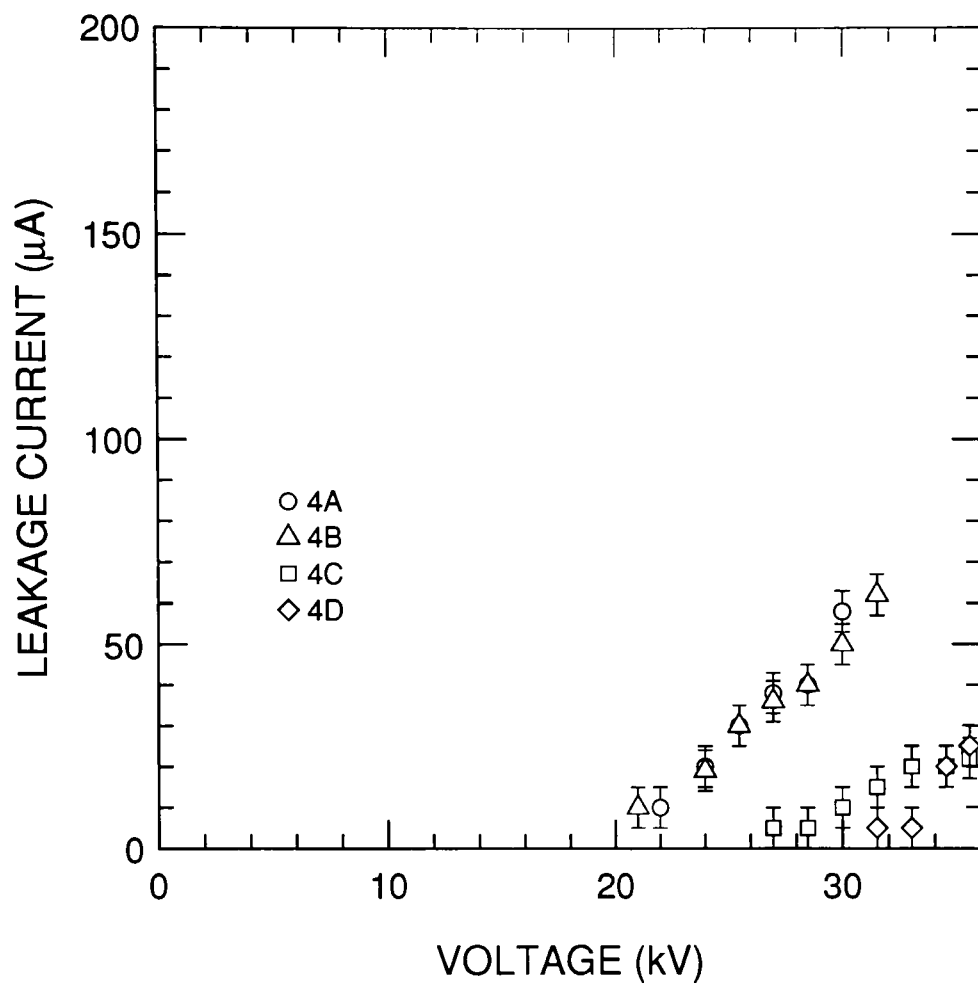Figure 21 - Nominal (No Reaction) Leakage Currents for Geometry 2

Figure 22 - Nominal (No Reaction) Leakage Currents for Geometry 3

Figure 23 - Nominal (No Reaction) Leakage Currents for Geometry 4

indication of the amount of flow ionization (i.e. formation of positively and negatively charged gas-phase species) resulting from the applied field. This data was collected with the natural gas-air mixture flowing over the unreacting platinum wire(s). Two important points can be made by examining this data.

First of all, a measurable leakage current in produced in all electronic configurations. Although there is some variation, the leakage currents for Geometries 1 and 2 (Fig. 8) are similar. This is to be expected, since the geometries of these cases are electronically equivalent. Data for Geometry 3 (Fig. 9), however, shows significantly higher nominal leakage current. This is consistent with the assumption that this geometry will produce a stronger electric field (as discussed in section 2.3.1) than Geometries 1 or 2 for the same applied voltage. Likewise, nominal leakage currents for Geometry 4 are less than for the other cases because this case uses two (approximately) flat plate electrodes, and the field resulting from the same applied voltage is weaker.

When this nominal leakage current data is compared to current data from actual test runs, the test current is almost always greater for a given applied voltage. This confirms that the reacting wire enhances ionization through one or more of the mechanisms discussed in Chapter 2.
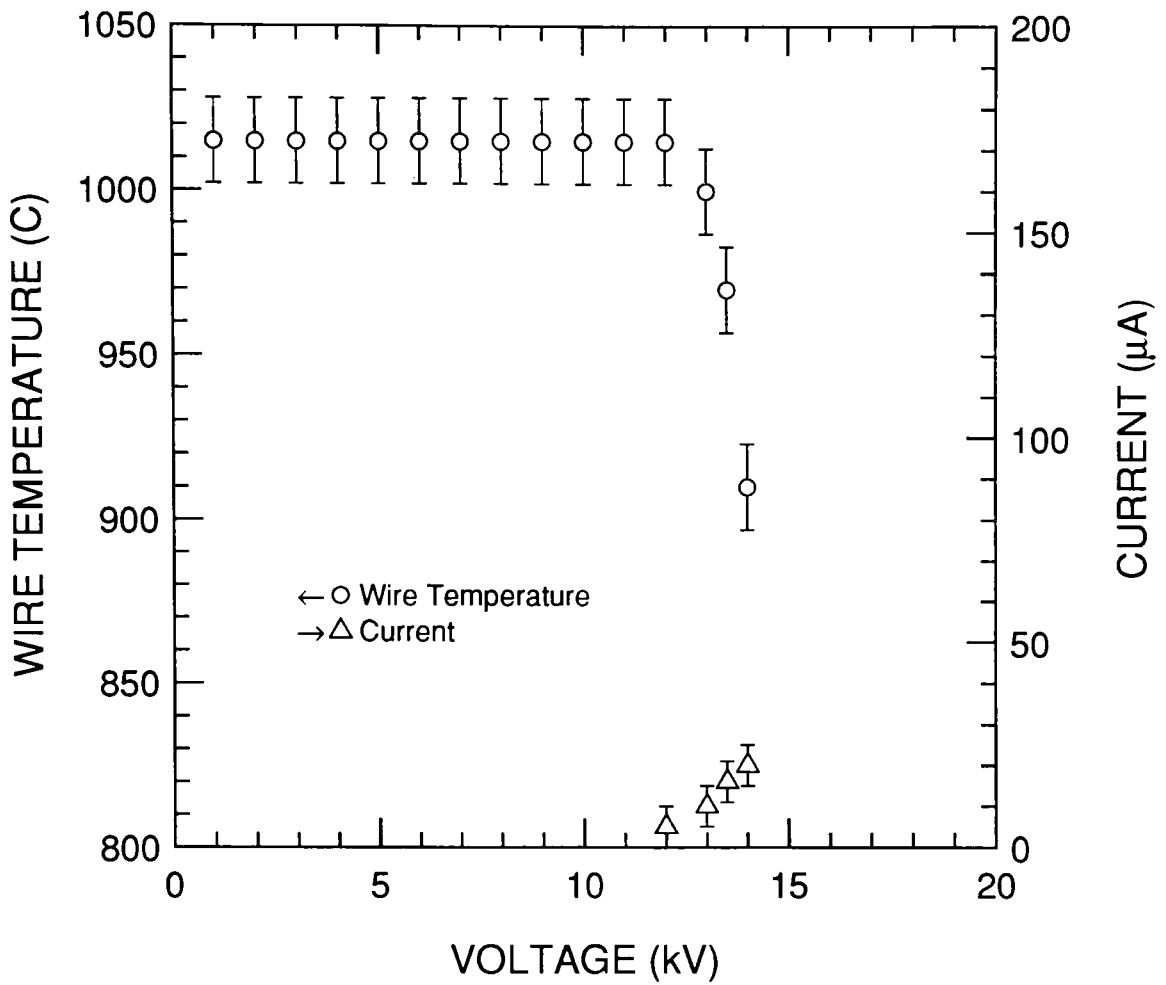
5.2 Charged Catalyst Surface; Field Applied Upstream of Catalyst

For the test cases in this group, the electric field was applied across the gas mixture upstream of the catalyst, and the catalyst had a positive or negative bias. This arrangement was used in test cases 1A, 1B, 3A, and 3B. Plots of temperature versus applied voltage are given in Figs. 24 through 27, respectively. As seen in Table 2, in each of these four cases the wire surface temperature (and hence the reaction rate) falls off and is extinguished around 14 kV. In addition, each of these four tests exhibits a measurable current, indicating ion formation.

In tests 3A and 3B, measurements for the upper wire were taken with the lower wire reacting and also with the lower wire intentionally extinguished. Data for these two cases were found to be identical.

As explained in section 2.3.1, the electric field strength of the two wire tests (3A, 3B) is expected to be larger than the wire-burner tests (1A, 1B). This could account for the higher currents observed in the two wire test cases. Very near the charged wire, however, the fields are expected to be similar since, in both cases, the field strength varies as $1/r$.

It is interesting to note that the effect on quenching is the same for both positive and negative wire biases. This fact suggests that a similar mechanism is at work in both configurations. This could be explained by what will be termed "charged species inhibition".

Figure 24 - Reaction Temperature and Current vs Applied Voltage, Test 1A

Figure 25 - Reaction Temperature and Current vs Applied Voltage, Test 1B
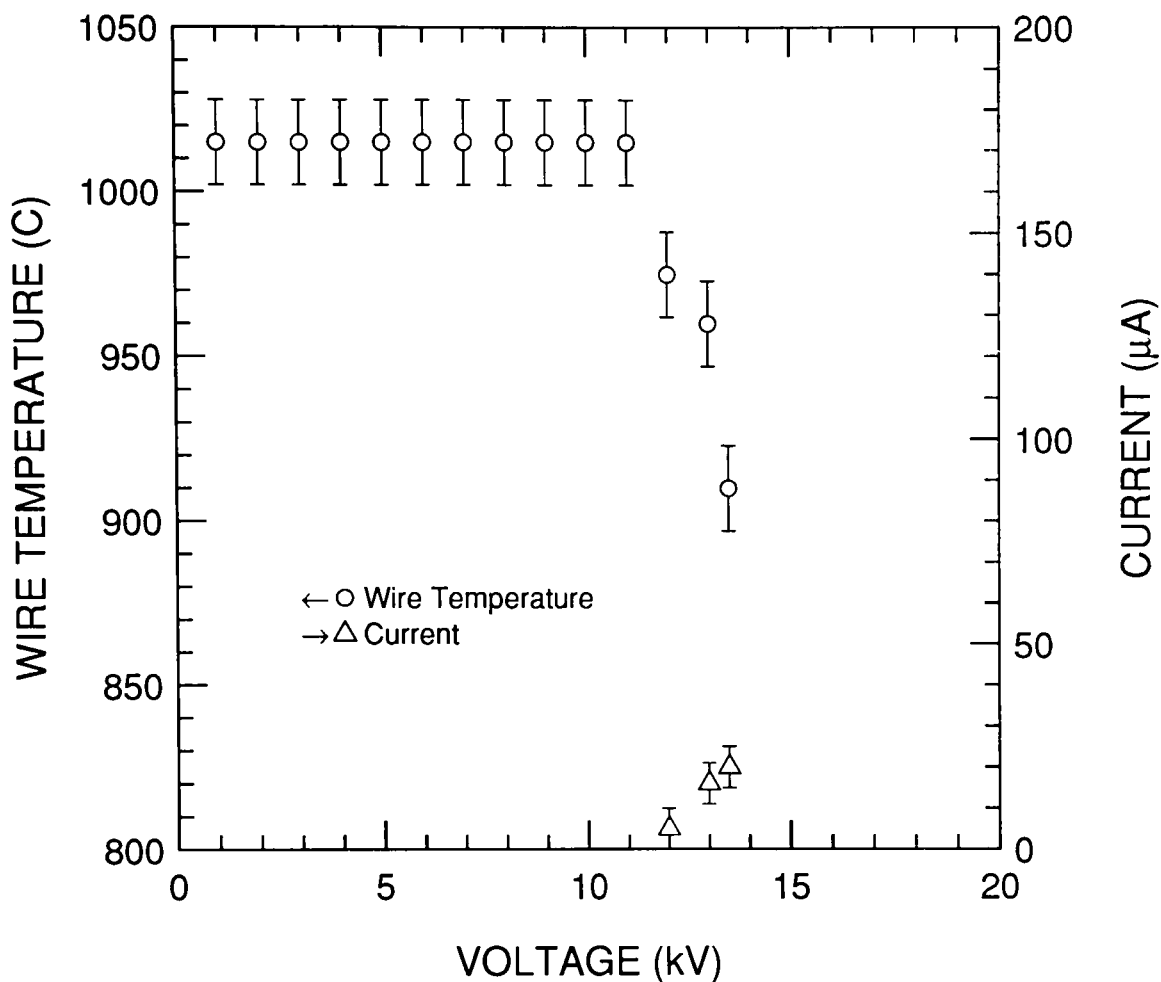
GEOMETRY 3A CONFIGURATION

Upper Wire Bias = POSITIVE [+]
Lower Wire & Burner Bias = GROUND
Field Applied = UPSTREAM OF WIRE
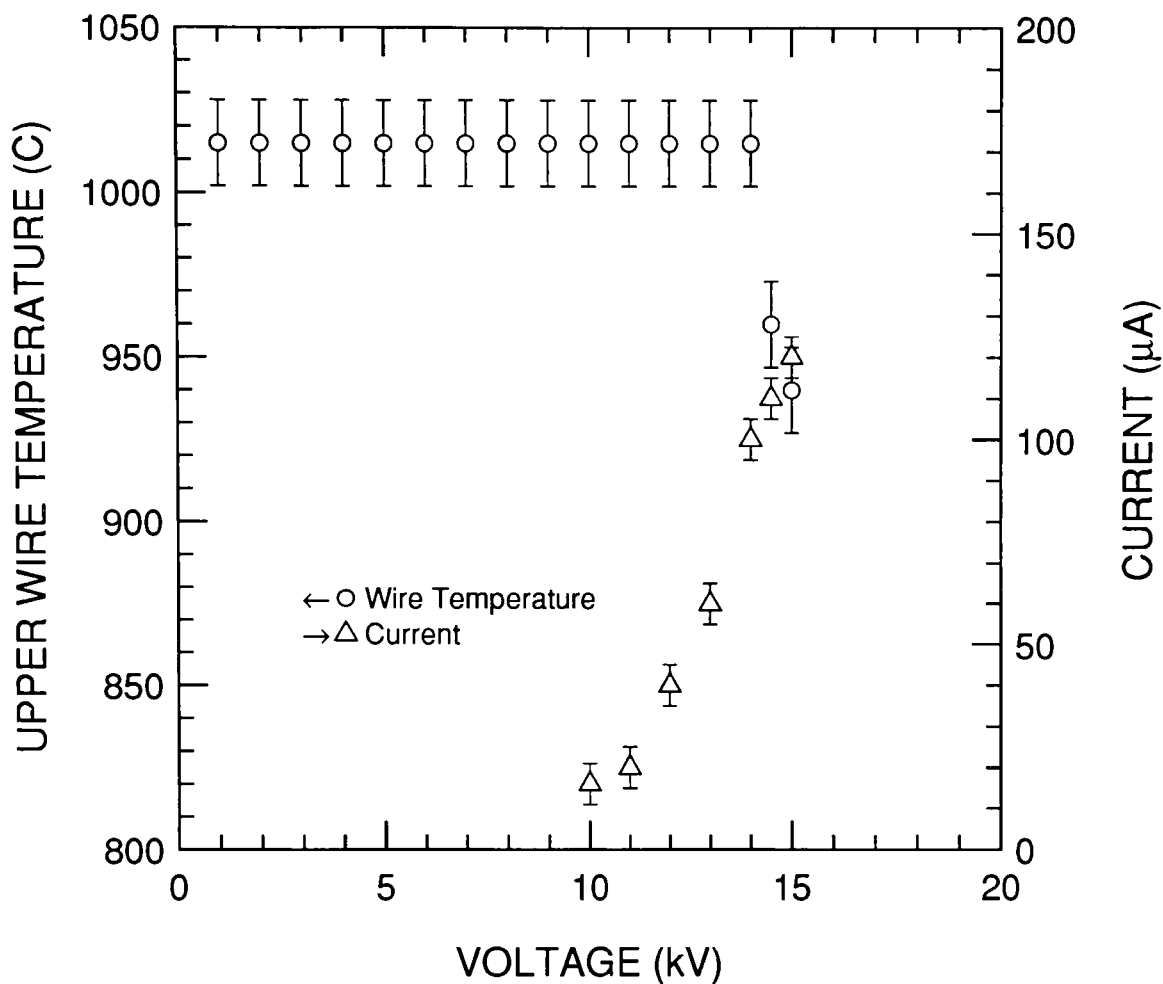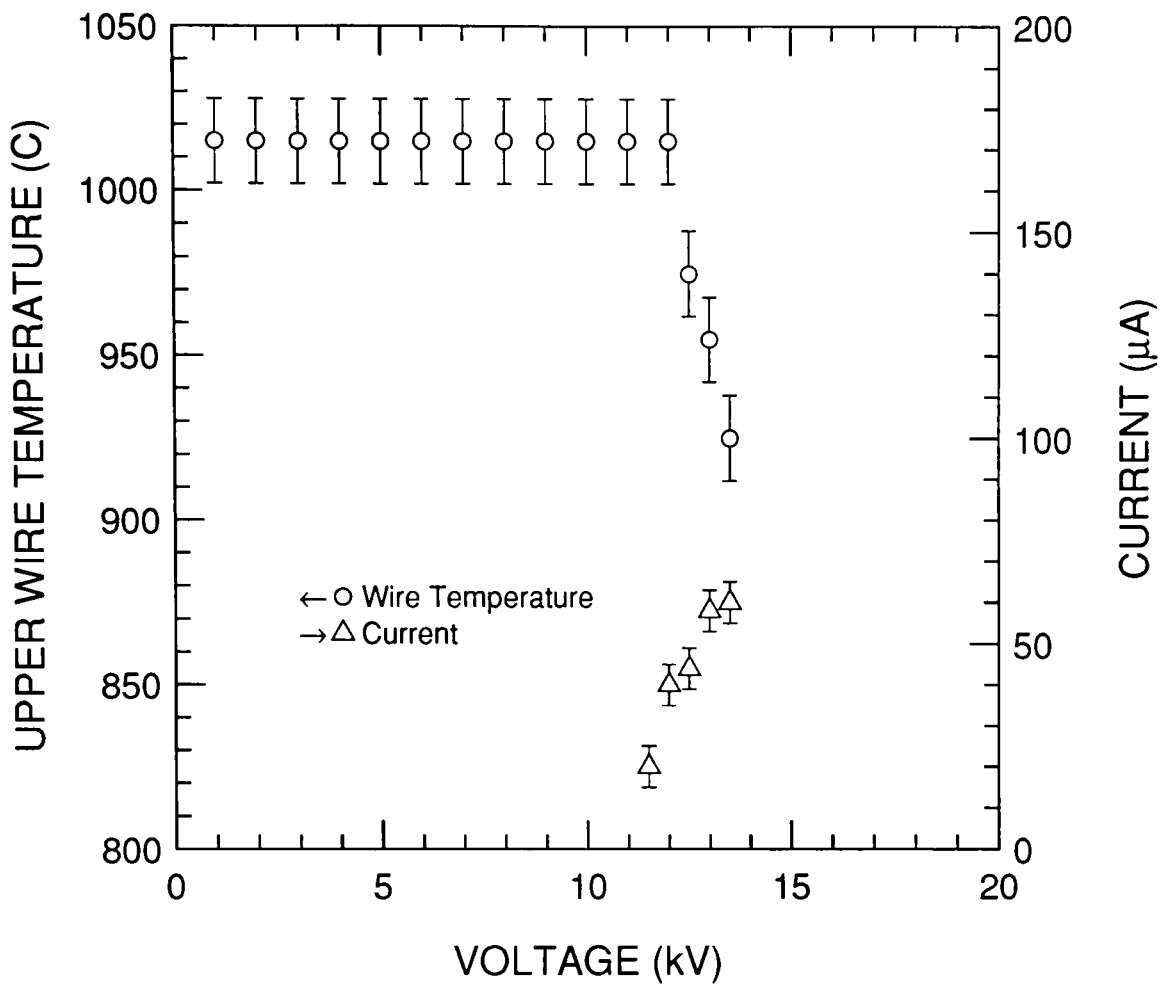Reaction Extinguished = 15 kV

Figure 26 - Reaction Temperature and Current vs Applied Voltage, Test 3A

Figure 27 - Reaction Temperature and Current vs Applied Voltage, Test 3B

While the exact nature of this inhibition is unclear, there are two possibilities. In both cases significant numbers of charged gas phase species are drawn to the (oppositely charged) platinum surface. The electronic interaction between the charged gas phase species and the charged surface might provide enough energy to overcome certain energy barriers that could not be bridged under normal conditions. This could, for example, allow for the formation of different types of adsorbate-metal bonds than are normally formed.

Since the activity of a catalyst is very sensitive to the adsorbate-surface bond strengths, a change in these bonding characteristics could have a profound effect on surface reactions. One possibility is that the species chemically bonded to the platinum under these conditions forms a stronger or more "ionic" bond instead of the normal covalent bond. These "pseudo-ionic" bonds would be stronger and thus harder to break. This would make the progression of surface reactions difficult, since this initial adsorption bond must be broken for the reaction mechanism to proceed.

Formation of these "pseudo-ionic" bonds could inhibit the surface reaction in two ways. First, species normally unreactive with regard to the platinum surface might overcome an energy barrier and form a bond. A possible example is the N_2^+ species. Ionized nitrogen might be able to form an "ionic" bond with the negatively charged platinum surface, even though molecular nitrogen (N_2) does not. These nitrogen atoms would then occupy the

"active sites" needed by methane and oxygen, and the reaction would gradually be extinguished.

Even if N_2^+ does not significantly inhibit adsorption of reactants, "ionic" bonding of reactants to the surface could prevent the completion of the surface reactions. If the reactant species are bonded too strongly to the platinum surface during adsorption, they will not be able to dissolve these bonds and react with other adsorbed species. In this case, the reactants themselves block the active sites, and again the reaction is extinguished.

In the case of a positively charged wire, the above discussion would hold true for negative gas phase ions. Although von Engel [25] suggests that a significant number of O_2^- are formed from air, there is another likely source of negative ions. As stated previously, Talley et al. [26] and others have confirmed the presence of hydroxyl species desorbing from a platinum surface. These OH can be negatively charged and might be involved in this process.

The other possibility is that most of the charged gas-phase species drawn to the platinum surface do not actually form chemical bonds. Rather, they may merely be held near the wire surface by the electric field. This process could be termed "enhanced physisorption", the difference from normal physisorption being that the charged species would be held near the surface by electronic (from the applied field) rather than van der Waals forces.

This clustering of charged species near the wire surface would interfere with normal gas phase diffusion, blocking reactants from reaching the catalyst surface. This would preventing adsorption and eventually quench the reaction.

If it is assumed that the magnitude of the charge on the ions involved is the same (mostly 1^+ or 1^-, for example), the quenching results for the positive and negative wires is expected to be similar. This is because the wire has acquired some net charge which is a function of applied voltage. Thus, when the force between the surface and the gas phase ions is strong enough, charged species inhibition will occur regardless of which is positive or negative, assuming a pool of both positive and negative gas phase species. If the electrical conditions near the wire are similar in Geometries 1 and 3, results for all four of these cases should be similar.
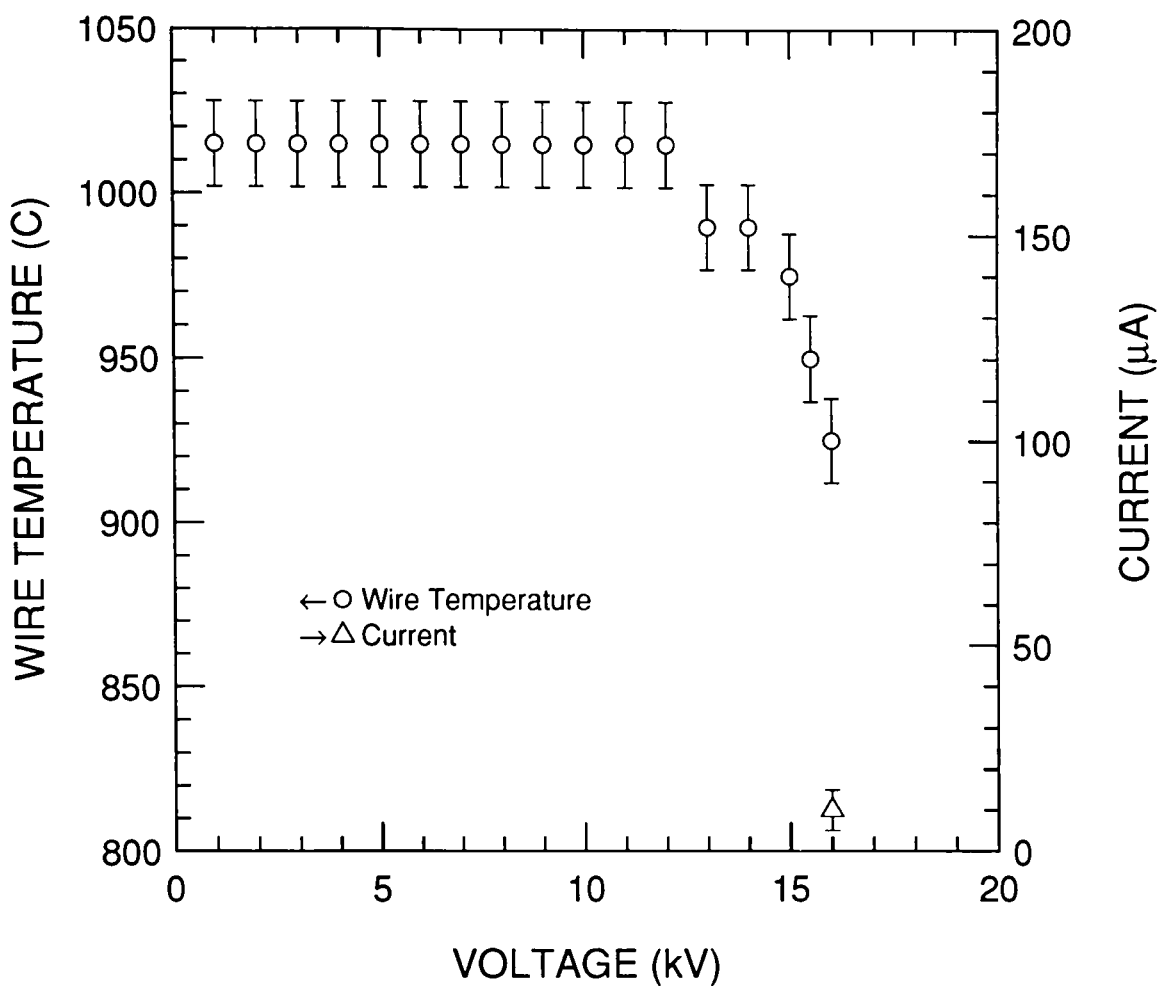
If the field is reduced, the wire surface will rapidly lose its electric charge. In addition to greatly reducing the number of gas phase ions formed, this reduction of the applied field will cause the "pseudo-ionic" bonds already formed to take on a more covalent character. As a result, any N_2^+ species would desorb, and any "pseudo-ionically" bonded reactant species would be free to progress in surface reactions. In addition any species blocking catalytic sites that are held by "enhanced physisorption" would be released. These processes would restore the original catalytic activity, which is in agreement with observation.

5.3   Grounded Catalyst Surface; Field Applied Upstream of Catalyst

In all test runs discussed in this section, the platinum wire was grounded and did not have a surface charge. Four test runs fit this description: 1C, 1D, 3C, and 3D. These results are presented in Figs. 28 through 31, respectively.

The pseudo-ionic bonding or enhanced physisorption proposed in section 5.2 might still occur in these configurations, since gas-phase ionization and surface interaction may still occur. However, if these processes are enhanced by a surface charge, it is expected that they would be less important in these configurations.
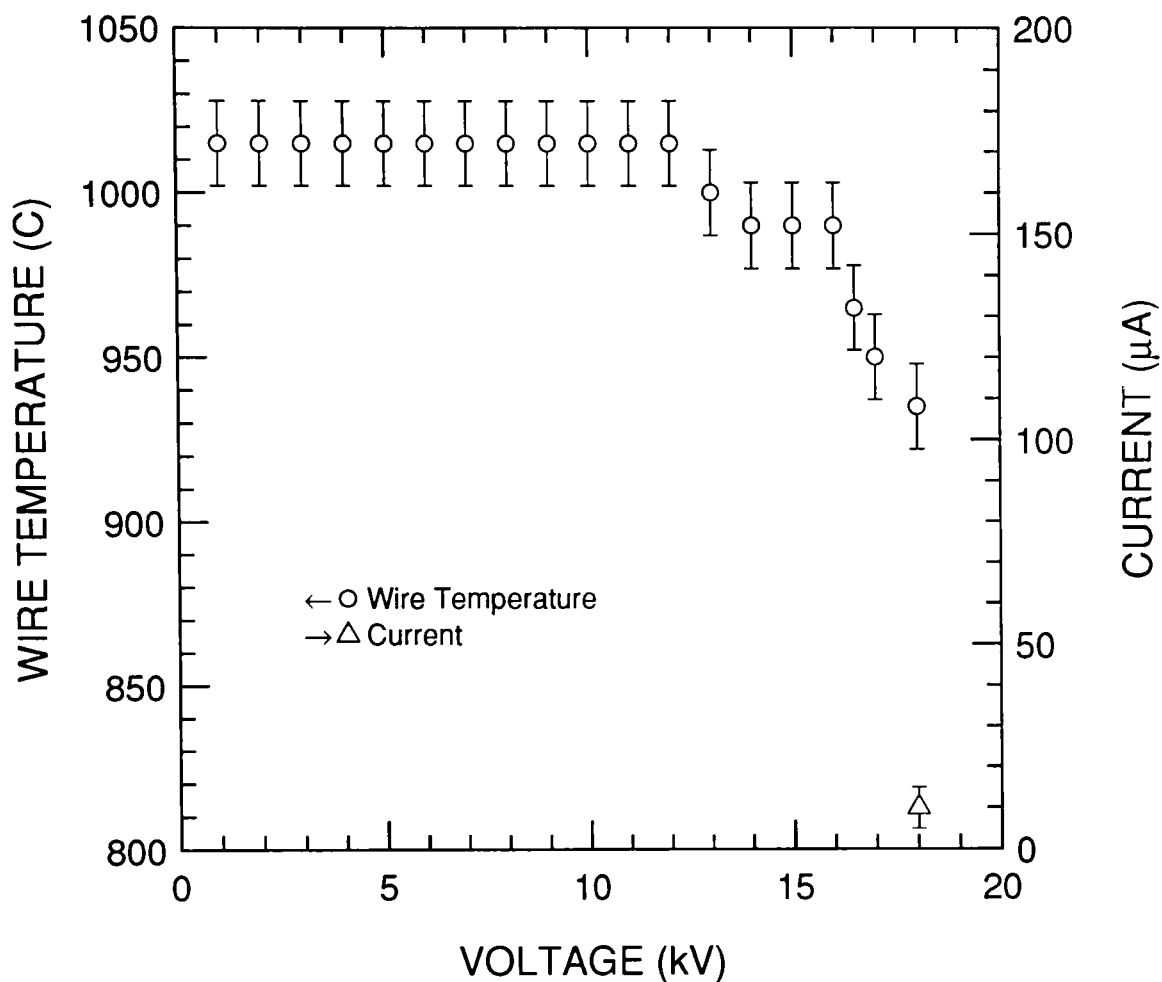
The current for Geometry 3 is expected to be greater than that for Geometry 1; however, variations within these geometries are unexpected. Although some ionization does occur (indicated by the currents in tests 3C and 3D), the amount is significantly less than that measured for cases 1A, 1B, 3A, and 3C. No current was observed in cases 1C and 1D. The electric field strength resulting from a given voltage does not depend on which electrodes are charged or grounded, so the currents measured for a given geometry should be the same. Since the observed variations in current depend on electrode bias and not field direction, the variations cannot be explained be thermionic emission.

Figure 28 - Reaction Temperature and Current vs Applied Voltage, Test 1C

Figure 29 - Reaction Temperature and Current vs Applied Voltage, Test 1D
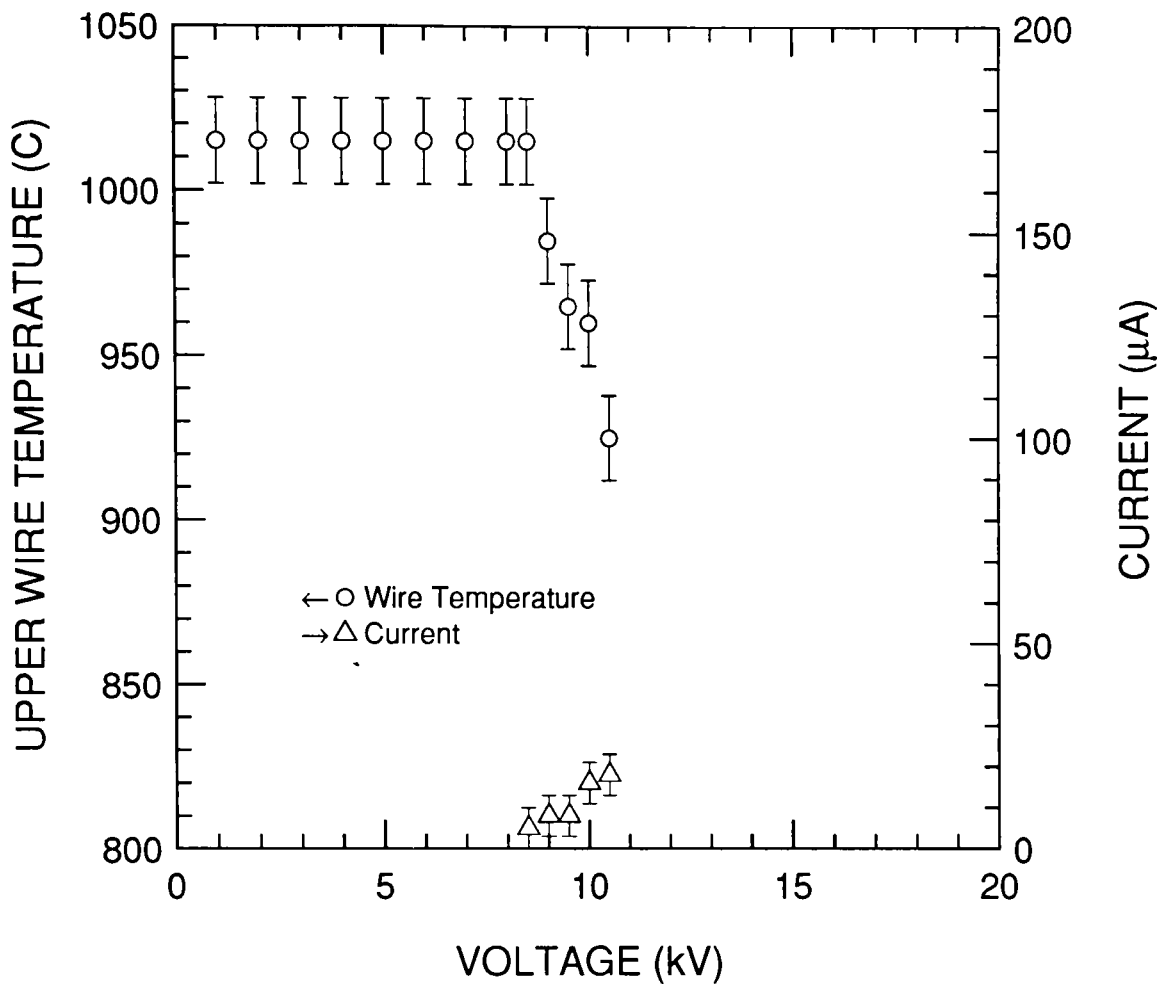
Figure 30 - Reaction Temperature and Current vs Applied Voltage, Test 3C

Figure 31 - Reaction Temperature and Current vs Applied Voltage, Test 3D

Physically a smaller current indicates that fewer charged species (electrons and ionized molecules) are impacting on the electrodes. Although not predicted from electrostatics, this current data seems to indicate that the trajectories of charged particles are different near an oppositely charged wire (stronger attraction resulting in higher observed current) than near a grounded wire (weaker attraction resulting in lower observed current). Differing ion trajectories near the catalyst could explain the difference in reaction quenching characteristics between charged and grounded wires.

Another explanation for the different quenching characteristics observed is that some of the effects discussed in section 2.3 are involved. These include possible field effects on adsorbate interaction stability proposed by Grimley and Blyholder in section 2.3.3. The variations could also be explained in terms of field distortion of molecular (surface) orbitals described in section 2.3.4.

The possible effects of different ion trajectories near a charged or grounded wire surface, the influence of applied voltage on adsorbate stability, and the distortion of "dangling" bonding orbitals will be referred to collectively as "secondary quantum effects."

In tests 3C and 3D, reaction quenching is observed at a lower applied voltage than in tests 3A and 3B. The opposite is true in Geometry 1; tests 1C and 1D quench at a higher applied voltage that tests 1A and 1B. Since the secondary quantum effects described above are only dependent on field strength, they should appear in tests in which the wire is charged as well as

the tests in which the wire was grounded. The data for these two geometries indicates that these quantum effects are secondary to the charged species interactions described in the previous section. Thus, whenever the wire is charged, the formation of pseudo-ionic bonds or enhanced physisorption will dominate over the effects of differing ion trajectories, adsorbate stability, and distortion of "dangling" orbitals. When the lack of a surface charge density on the catalyst makes charged species inhibition less likely, the influence of these secondary quantum effects is observed.

5.4   Grounded Catalyst Surface; Field Applied Downstream of Catalyst

Like the tests considered in section 5.3, the configurations discussed in this section have catalysts with no net surface charge. However, the field in these tests was applied downstream of the catalyst. These results of these tests (2C and 2D) are given in Figs. 32 and 33.

Because the electronic configuration is the same as in tests 1C and 1D (i.e. the surface has no charge density), it is expected that the quenching effects will be the result of the secondary quantum effects described in the previous section. In tests 2C and 2D, however, quenching of the reaction occurs at a much higher voltage.
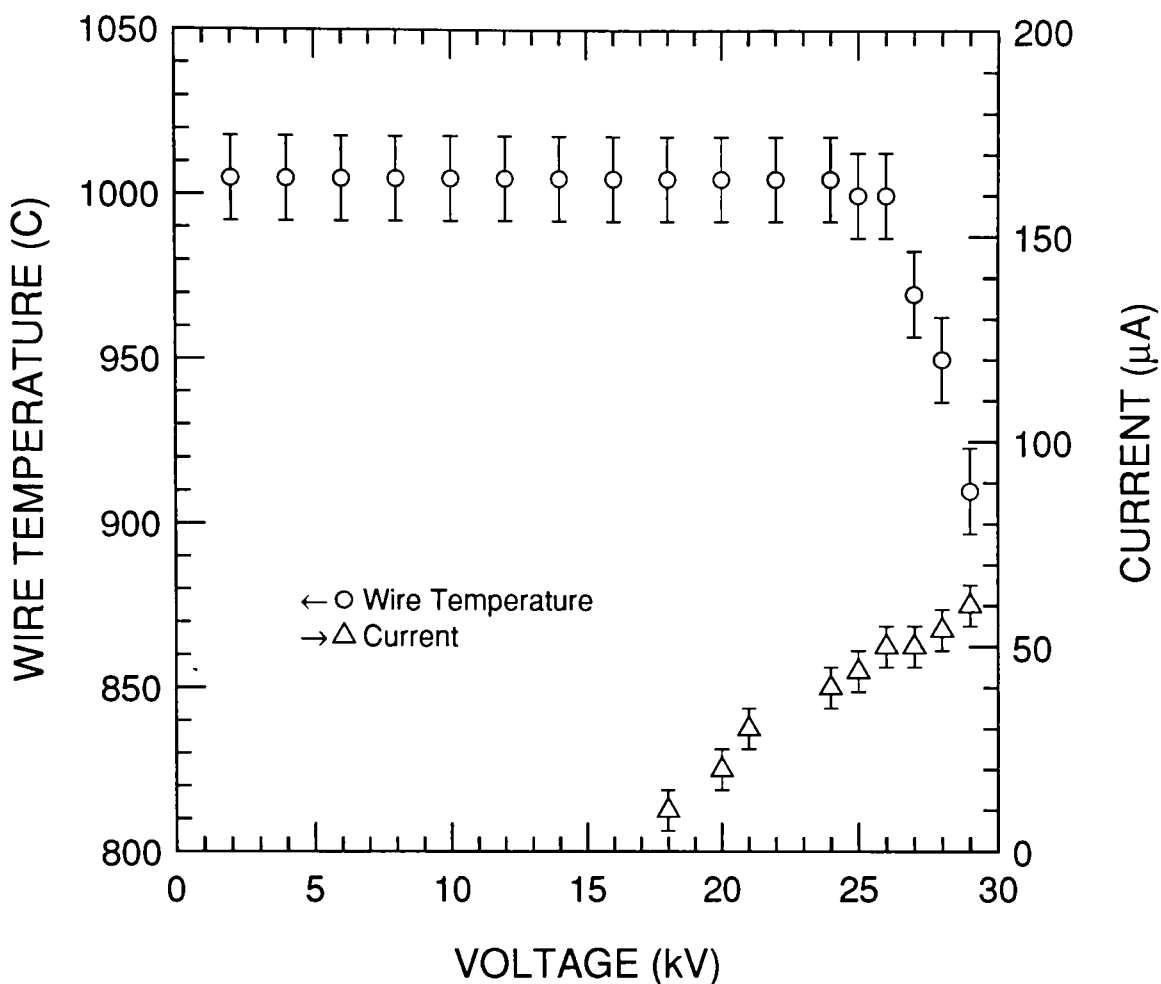
The number of ions formed by the field (of similar intensity) should not depend on whether it is applied upstream or downstream of the catalyst. This
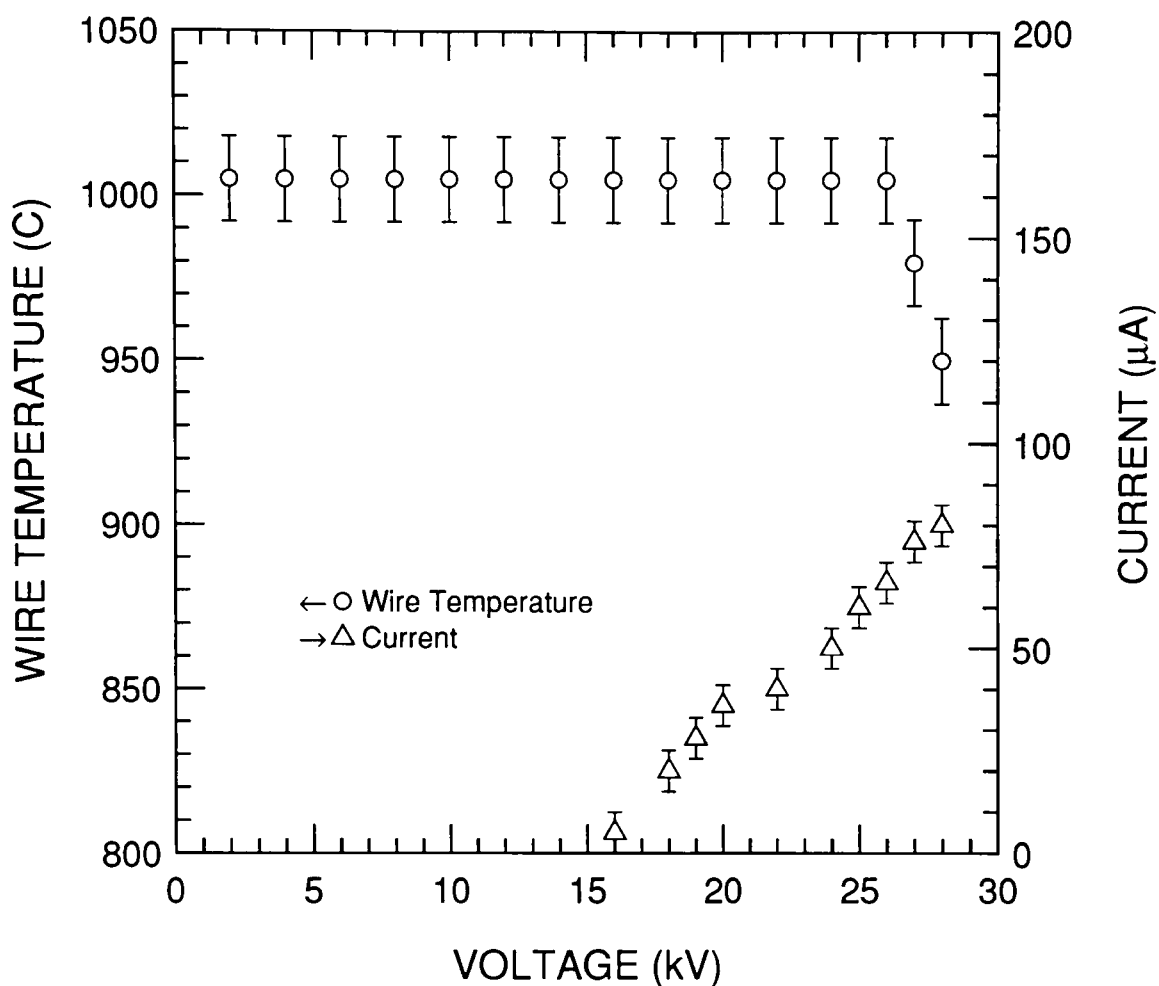
Figure 32 - Reaction Temperature and Current vs Applied Voltage, Test 2C

Figure 33 - Reaction Temperature and Current vs Applied Voltage, Test 2D

is qualitatively confirmed by comparison of the current data in Figs. 26, 27, 30, and 31. In tests 1C and 1D, no current (within the sensitivity of the meter) is observed up to 16 and 18 kV, respectively. In 2C and 2D, these are the threshold voltages where current first appears. Since much higher voltages (resulting in significant currents) are reached in tests 2C and 2D, many more ionized species are present when the reaction quenches in these cases.

In order to account for the different quenching voltages observed in these two configurations, these ionized species could be involved in the quenching mechanism through charged species inhibition (which appears to mask the influence of secondary effects). As discussed in the previous section, it is unlikely that these ionized species could form "ionic" bonds with the uncharged metal surface. Higher voltages and field strength, however, might allow these interactions on a grounded surface. Even if this process did occur, it would be difficult for the ions formed to migrate around to the upstream surface of the catalyst where these ionic bonds would have the most quenching effect (see Fig. 34).

The other possibility is that secondary quantum effects are again responsible for the observed reaction quenching. The higher field strengths are apparently necessary, since the adsorbed species and/or the surface molecular orbitals on the upstream side of the catalyst are shielded from the field by the metal bulk.

Electric Field Interferes with Reaction on
Downstream Surface

Platinum
Wire
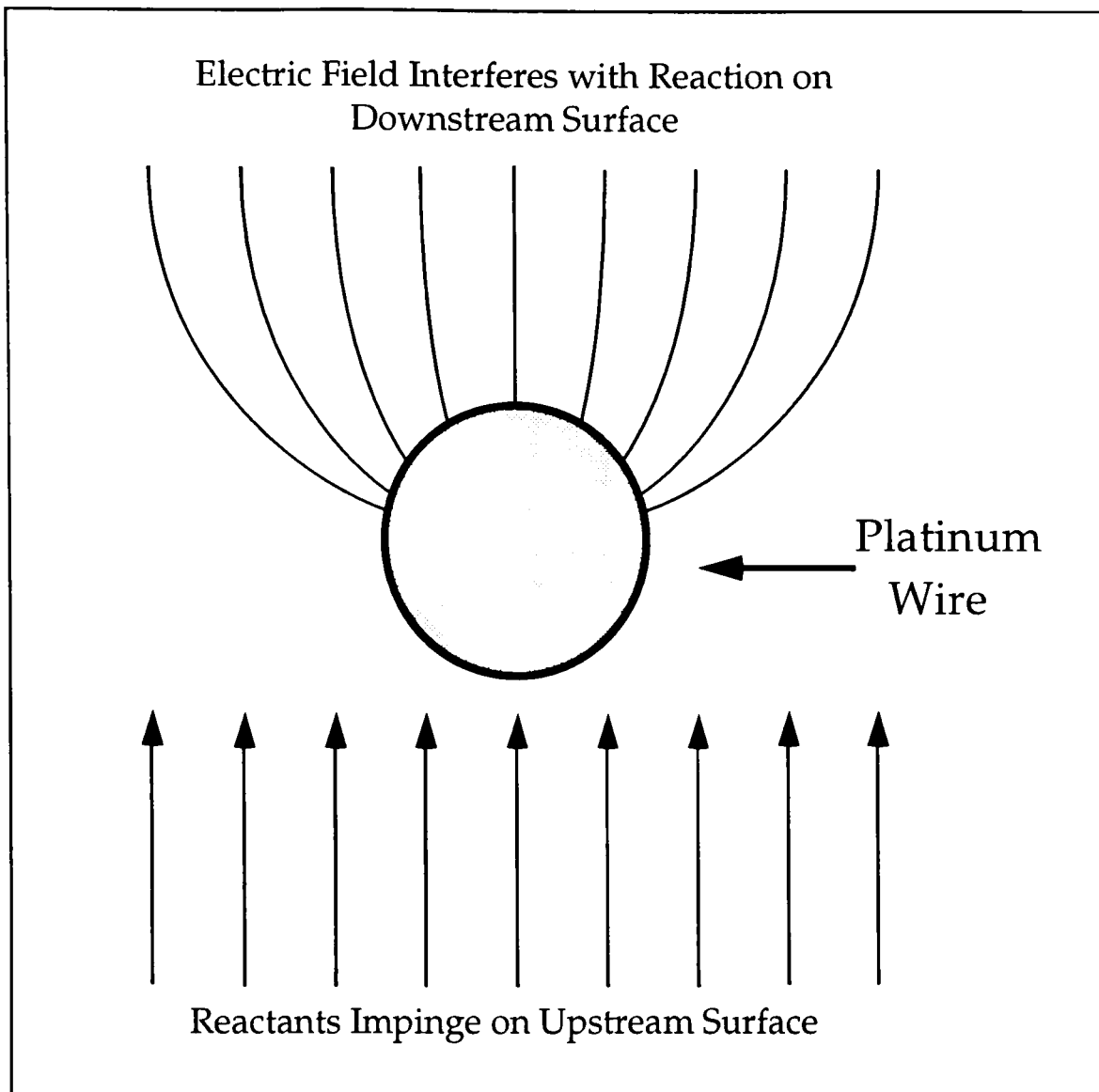
Reactants Impinge on Upstream Surface

Figure 34 - Illustration of Reduced Field Effectiveness when Applied to the
Downstream Surface of the Catalyst Wire

Data in this section shows that the quenching effects are dependent on field orientation. This suggests that the upstream side of the catalyst is more susceptible to "deactivation" than the downstream side. This is intuitively obvious, since most reactants are expected to impinge on the upstream side.

5.5 Charged Catalyst Surface; Field Applied Downstream of Catalyst

Results for the 2B test (wire negatively charged) and the 2A test (wire positively charged) were significantly different; they will be discussed separately below.

5.5.1 Test 2B - Wire Negatively Charged

Results for test 2B are shown in Fig. 35. Quenching voltage for this case is similar to the quenching voltages in 2C and 2D; however, the quenching effect first appears much sooner and is more gradual. This suggests that a different mechanism is responsible.

With the wire negatively charged and a significant ion pool formed (deduced from the observed leakage current), charged species inhibition is expected to occur as in cases 1B and 3B. In this configuration, however, most of the ions formed would collide with the downstream side of the catalyst. Inhibition in this location would have less impact on the catalytic reaction,
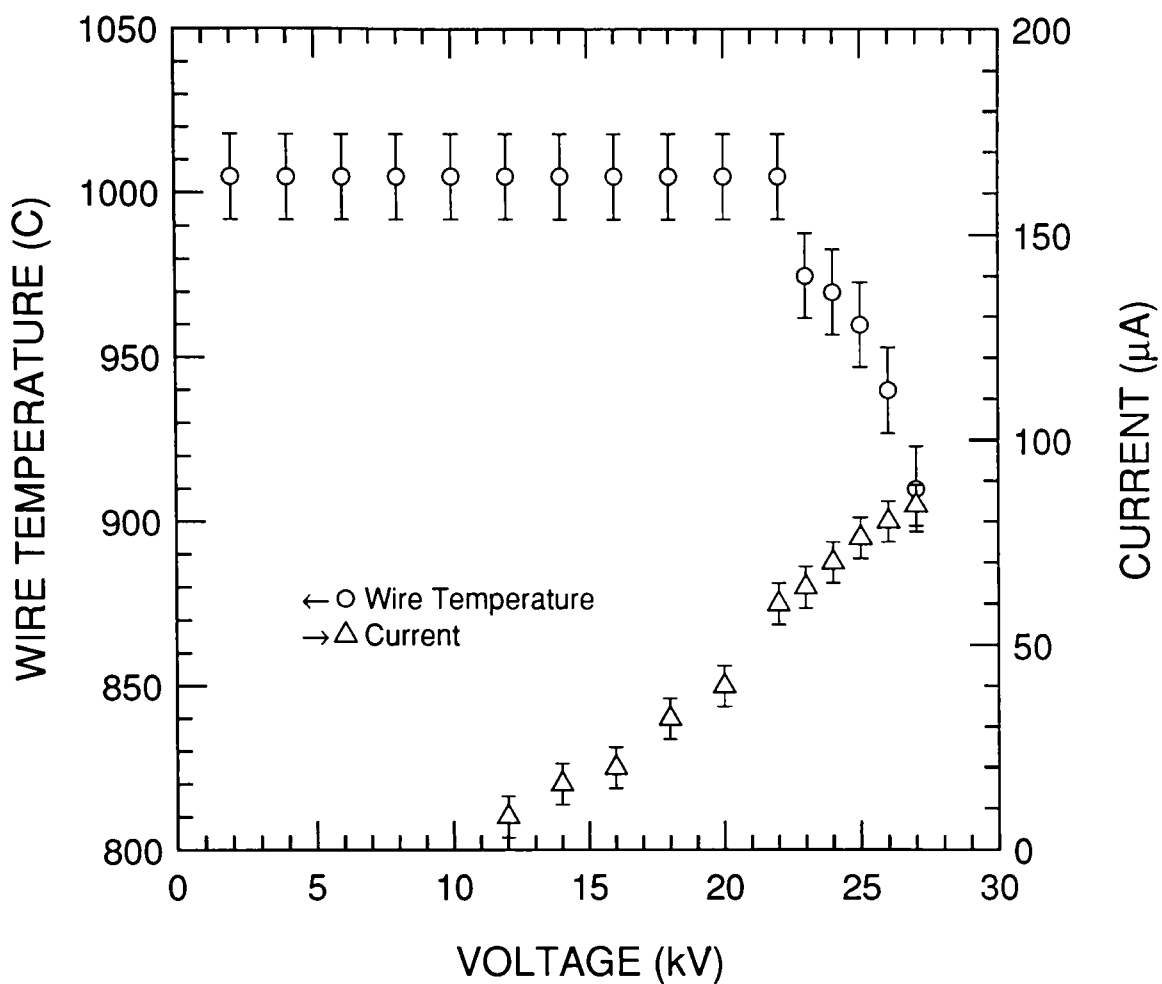
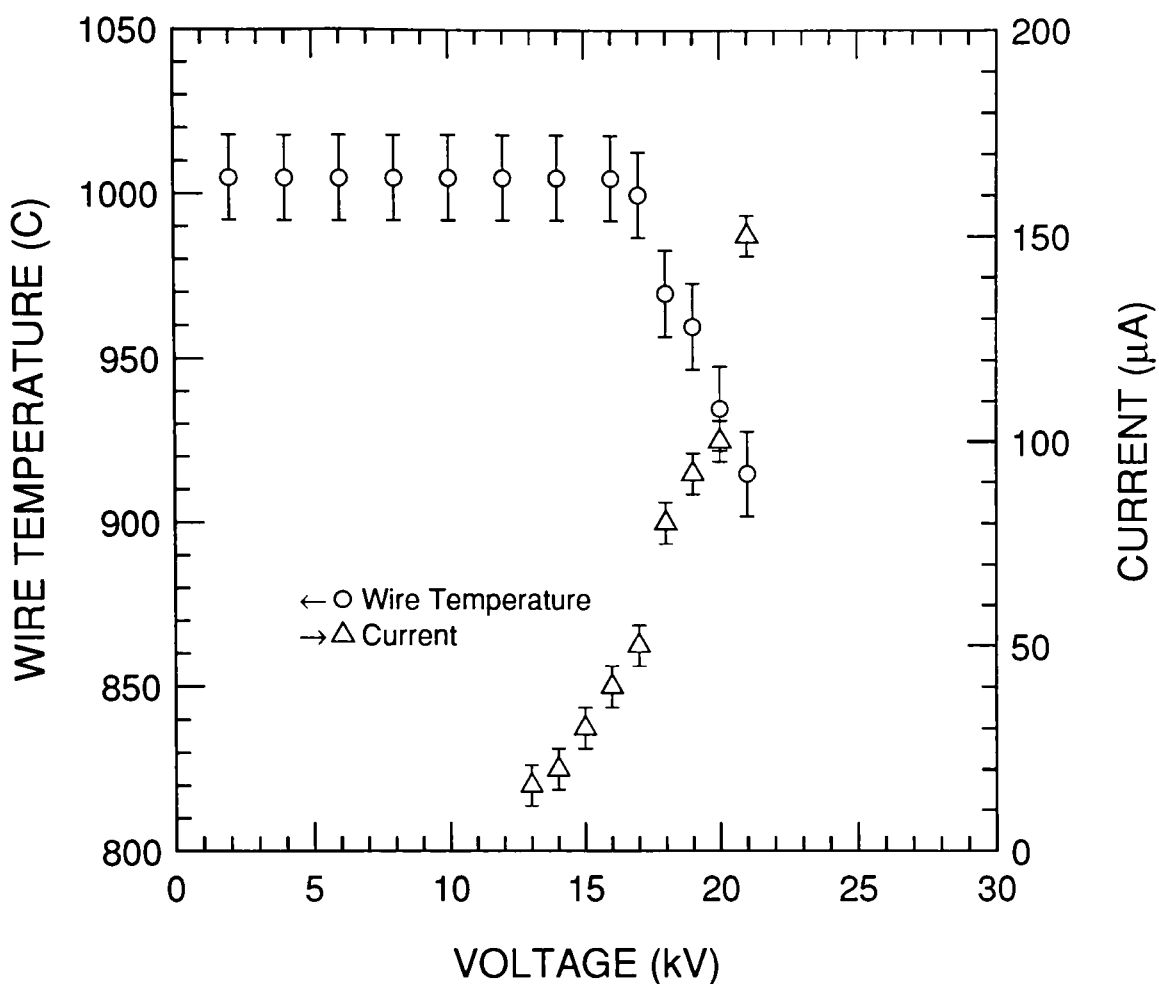Figure 35 - Reaction Temperature and Current vs Applied Voltage, Test 2B

since more reactants are expected to bond to the upstream surface of the wire. The additional voltage required to force these ions around to the upstream side of the wire could account for the difference in quenching voltage between this case and case 1B.

In addition there also probably exists a "reactant poor" boundary layer around the wire. In this region, reactants have been depleted, and diffusion through this region limits the rate at which reactants can reach the surface. The existence of this region could also greatly affect the reaction rate in the downstream configurations.

5.5.2 Test 2A - Wire Positively Charged

Test results for case 2A are shown in Fig. 36. As in case 2B, charged species inhibition is expected since the wire is charged. However in case 2A the quenching voltage is much lower. Assuming that the quenching effect is the result of charged species inhibition, this indicates a large increase in the number of negative gas phase ions.

As discussed in section 5.2, these negative ions could be formed from the gas phase or be hydroxyl radicals desorbed (or prevented from doing so) from the platinum surface. If only gas phase ions were involved, the results of tests 2A and 2B should be similar (as are 1A and 1B). This could indicate that OH species are important only in this case.

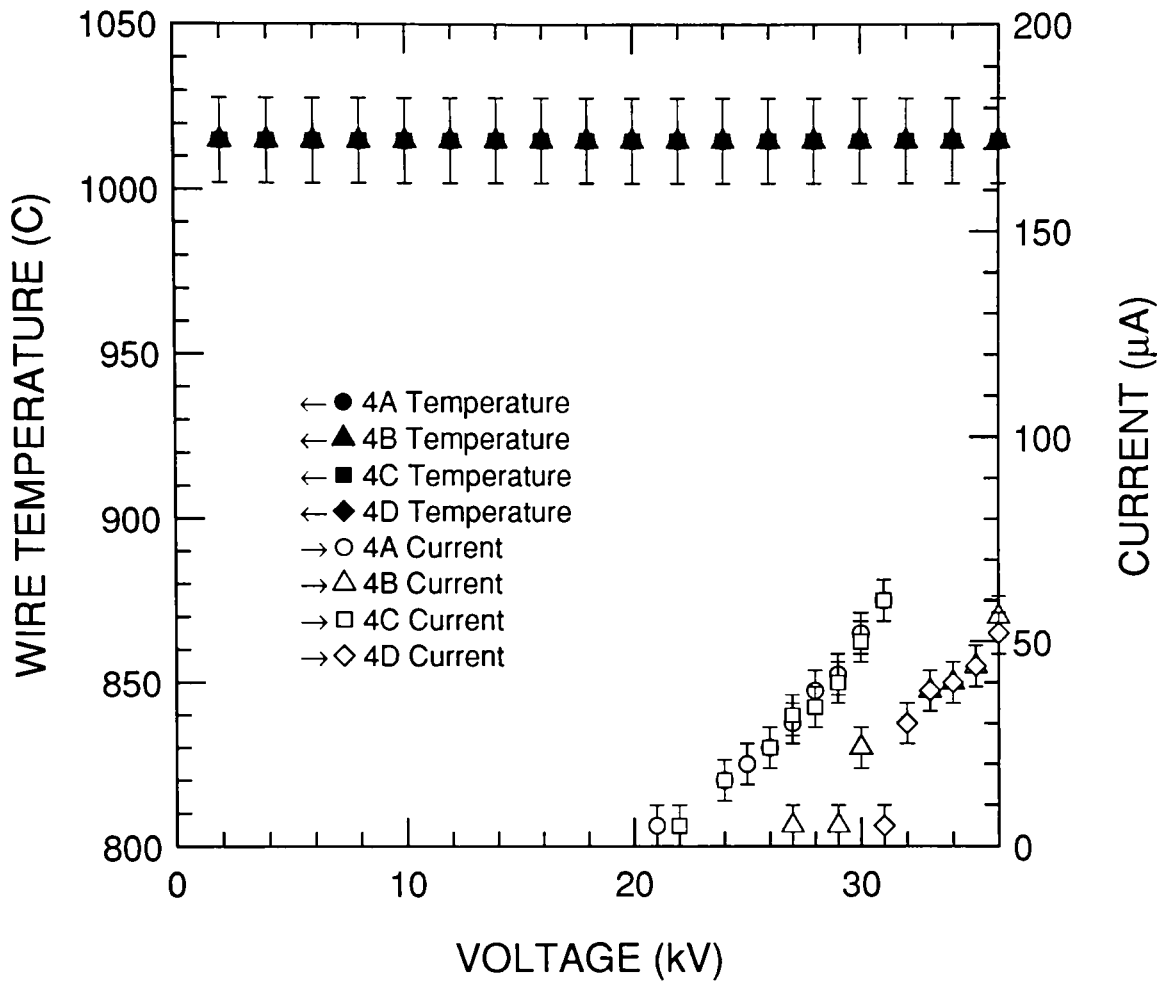Figure 36 - Reaction Temperature and Current vs Applied Voltage, Test 2A

Desorbed hydroxyls could be important in this case (and not apparently in 1A) for two reasons. First, hydroxyl species desorbed from the wire will end up downstream of the wire. If the field is applied upstream of the wire, these OH radicals will not be effected as much as they would be if the field were applied downstream.

A second possibility is that the field/surface charge prevents the hydroxyls from desorbing at all. If this were the case, their effect should be seen in both cases 1A and 2A. If, however, the voltage needed to prevent desorption was greater than the quenching voltage in case 1A, they would only effect the results of test 2A.

5.6 Electrically Isolated Wire (catalyst) Between Two Plane Electrodes

Tests 4A, 4B, 4C, and 4D examined the effect of placing a platinum wire between two (approximately) flat plate electrodes. Applied voltage had no measurable effect on wire temperature in these configurations. Leakage current data is provided in Fig. 37.

These tests were significant because the wire was not one of the electrodes (as it was in all other configurations). This is important because, in this configuration, the surface charge density and potential of the wire are not clearly known. For example, in test 4A, the upper electrode is positively charged and the lower electrode is grounded. In this case the field would tend

Figure 37 - Reaction Temperature and Current vs Applied Voltage, Tests 4A, 4B, 4C, and 4D

to pull electrons away from the downstream side of the wire. On the other hand, electrons on the lower surface of the wire would be forced closer to the upstream wire surface.

Since there are a large number of charge carriers present on the metal surface, we don't expect to see any significant variations in charge distribution. However, if the wire were behaving as a dielectric material, region of partial charge distribution could occur as illustrated in Fig. 38.

Although the current data indicates that ions are present in the reaction zone, their presence alone does not appear to inhibit the surface reaction. This could be because not enough ion trajectories terminate on the wire surface in this electronic configuration. Also, for the same electrode spacing, the field resulting from two flat plate electrodes is significantly less than that for Geometry 3 (two wires) or for Geometries 1 and 2 (wire-plane).

5.7 Lower Wire Quenching in Geometry 3

As noted above, tests to quench the reaction on the lower wire in Geometry 3 are considered separately. This is because the electric field could not easily be approximated by the infinite line and infinite plane of charge used for other cases. The reaction on the lower wire was quenched in three out of the four test configurations. In the fourth case, electric breakdown occurred before any quenching effects were observed. In fact, breakdown was
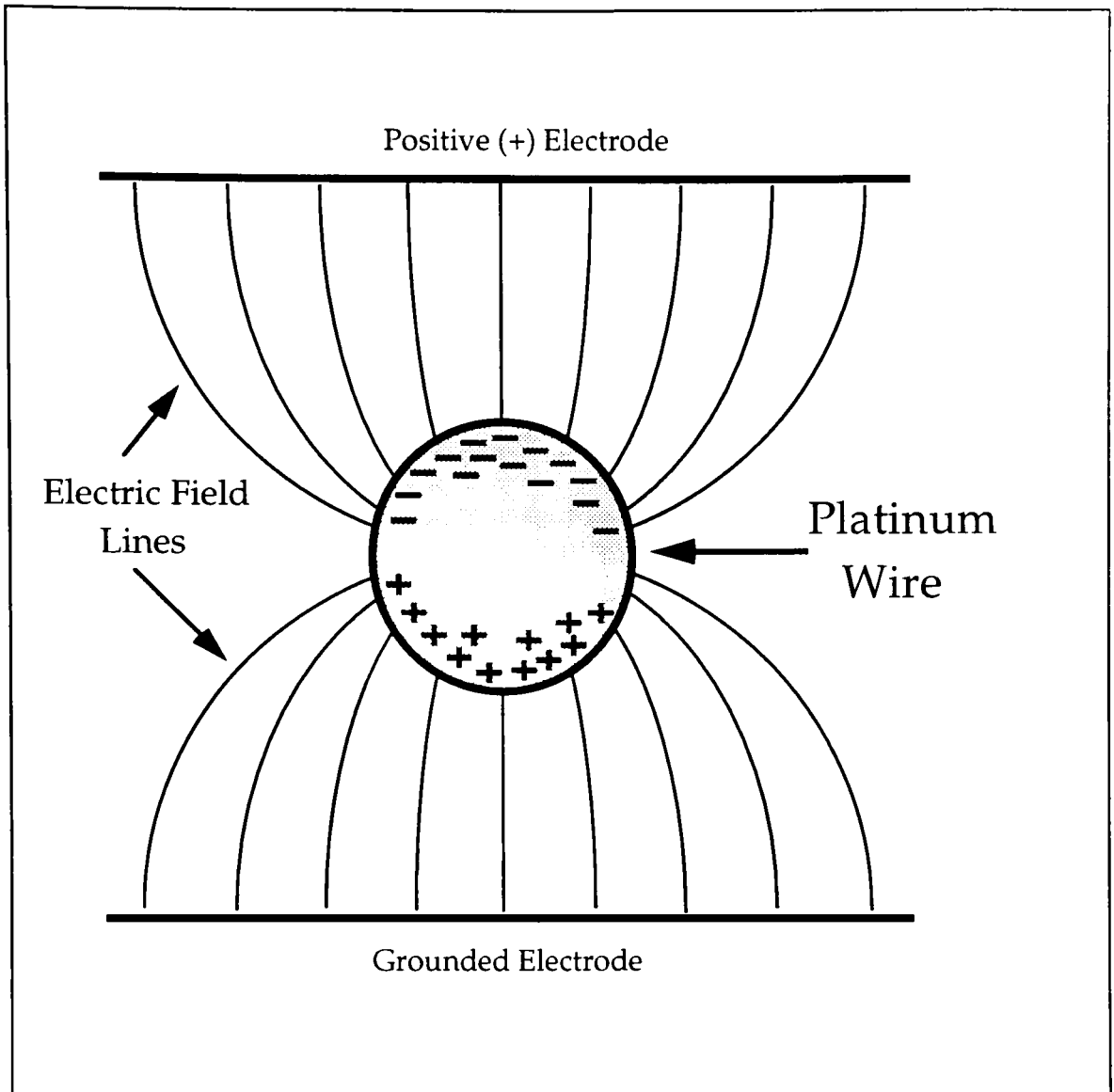
Figure 38 - Non-Uniform Surface Charge Distribution on a Dielectric Wire
Suspended Between 2 Flat Plate Electrodes

more likely to occur in all of these test cases. This is probably because of the increased ion pool generated by the lower wire. It is interesting to note, however, that these lower wire ions did not have an effect on the quenching of the upper wire (see section 5.2).

Although only briefly discussed, these results are included for completeness in Figs. 39 through 42.

Figure 39 - Upper and Lower Wire Quenching, Test 3A
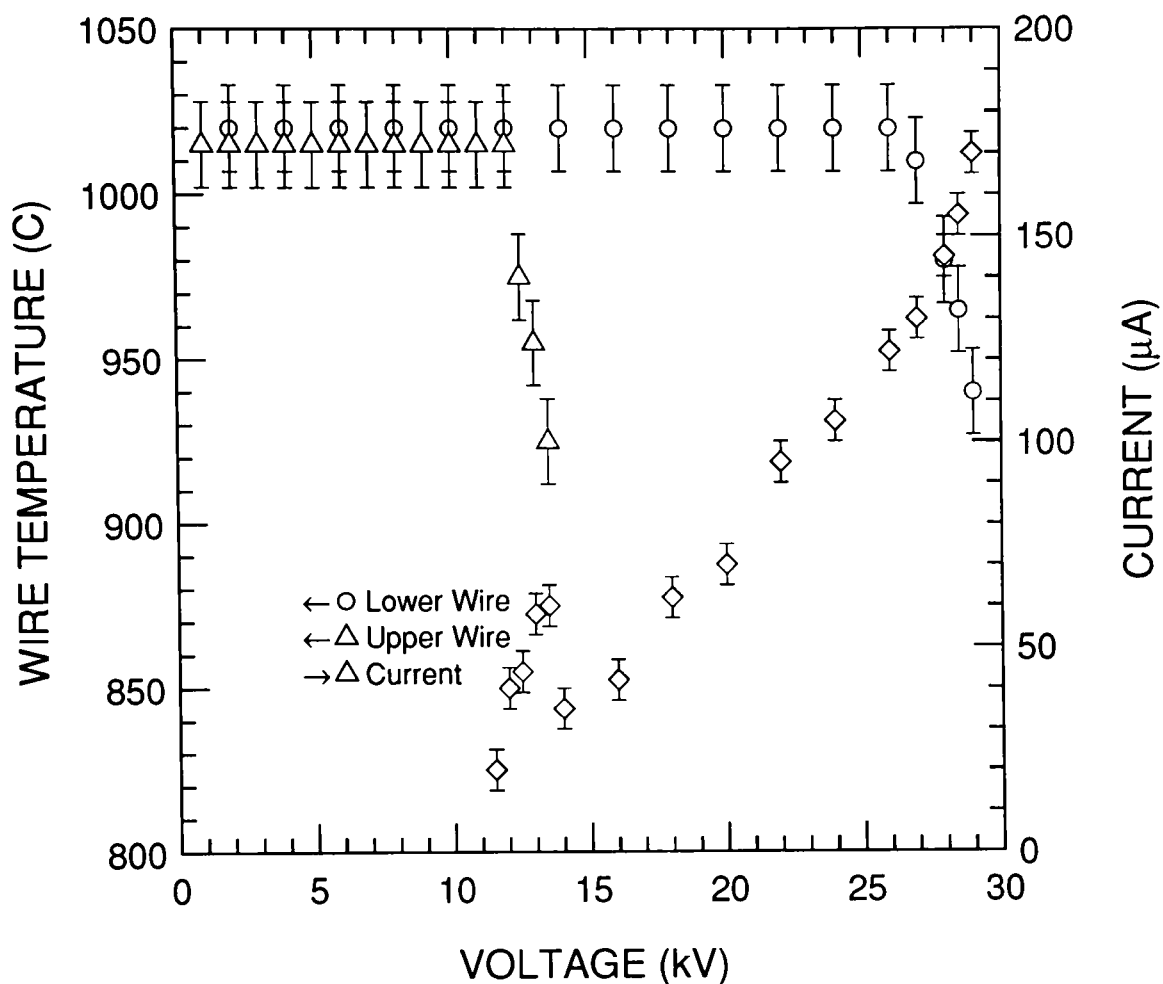
Figure 40 - Upper and Lower Wire Quenching, Test 3B
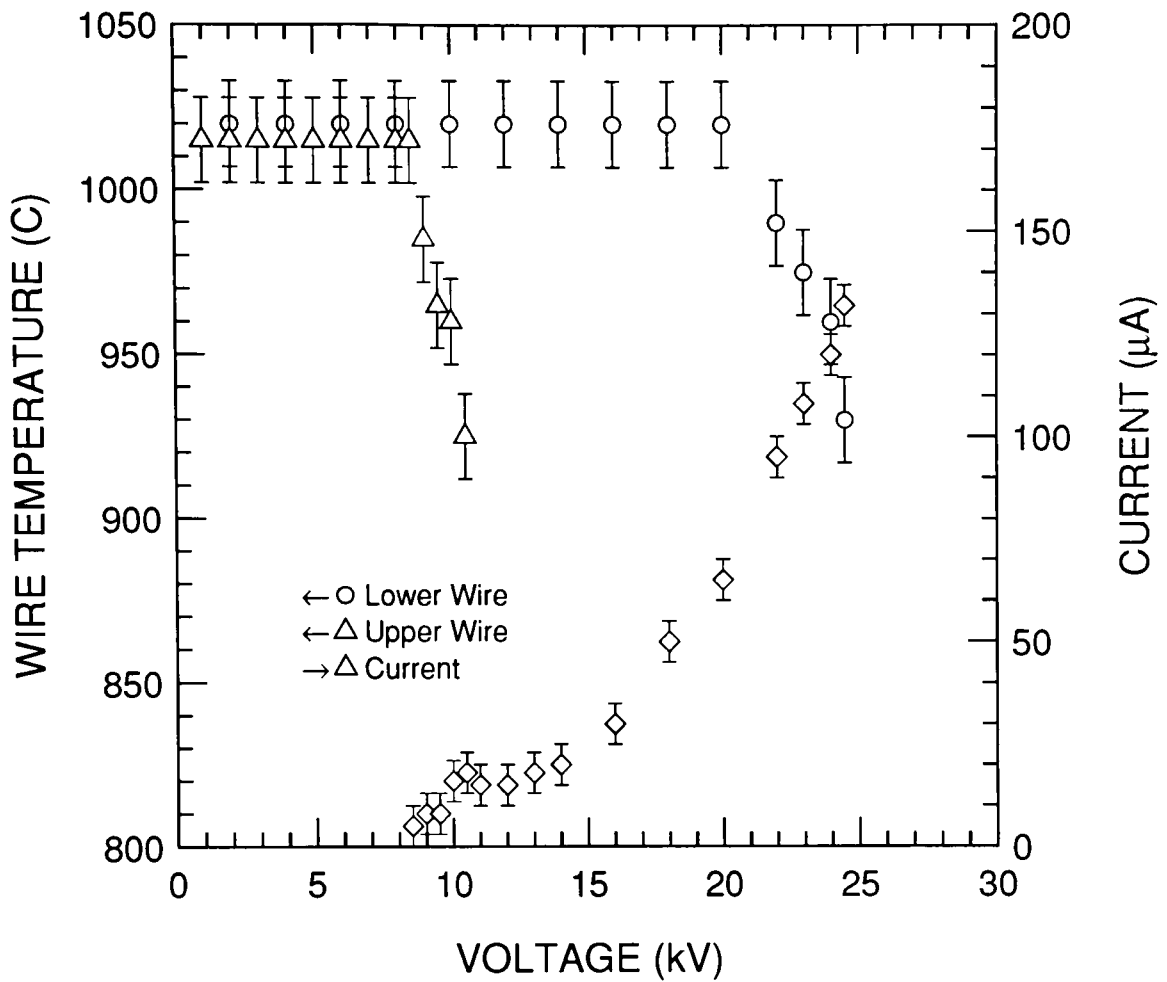
Figure 41 - Upper and Lower Wire Quenching, Test 3C
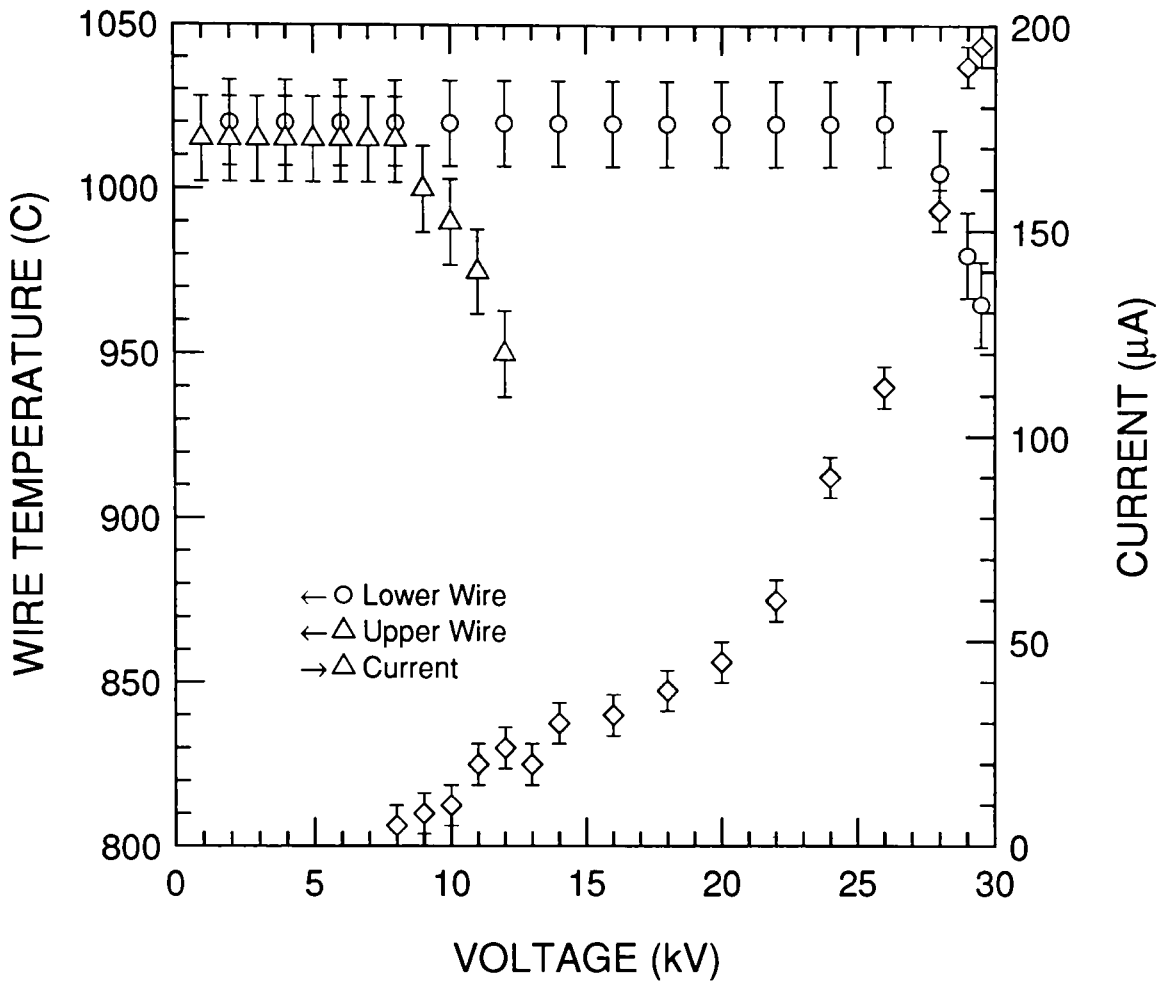
Figure 42 - Upper and Lower Wire Quenching, Test 3D

6. Summary and Conclusions

6.1 Summary

This thesis has examined the effect of an applied DC electrostatic field on the catalytic combustion of natural gas in air over platinum. In most cases a sufficiently strong field was found to extinguish the catalytic reaction. In no case was the reaction enhanced by the field. The voltages at which the reaction was affected varied with the electronic configuration. An explanation for these variations involving flow ionization and quantum effects on metal surfaces is suggested and summarized below.

For configurations in which the field was applied upstream of the (positively or negatively) charged platinum wire, it was suggested that charged species inhibition was responsible for the observed quenching effect. This inhibition could take two forms. First, charged gas-phase ions could be forming "pseudo-ionic" bonds with electrically charged wire surface. Because "ionically" bonded reactants would be too strongly held to react with other adsorbed species, the surface reaction does not proceed. The other possibility is that other non-reactive species are adsorbed and block the active sites. This makes further reactant adsorption increasingly difficult and again the reaction is quenched.

The other mechanism for charged species inhibition would involve the applied field holding charged species near the wire in a sort of "enhanced physisorption." This process would result in the formation of a layer of species blocking diffusion to the catalytic sites. Without reactant access to the active sites, adsorption would not occur and the reaction would be quenched.

For configurations in which the field was applied upstream of an uncharged (grounded) platinum wire, the charged species inhibition described above would be less likely. It was suggested that in this case secondary quantum effects could contribute to the quenching mechanism.

One effect is the interaction of adsorbed species through the conduction band. If the bonding energy levels of the adsorbate are near the Fermi level of the metal, it is possible that the application of a potential could redistribute the bonding electrons in such a way as to destablize the metal-adsorbate bond. Adsorbed hydrogen is a likely candidate for this type on interaction.

The other quantum effect discussed involved the molecular orbital (rather than the band) model of a catalytic surface. This model attributes the catalytic activity of transition metals to "dangling" d orbitals that are localized on the metal surface. It was suggested that at small distances from the surface, the applied field might be strong enough to compete with the local electron repulsive field. Changing the orientation of these orbitals could greatly change the catalytic activity of the surface.

These quantum effects only appear when the wire is uncharged. Apparently the effects caused by charged species inhibition dominate whenever the catalyst has a net charge density.

Cases in which the field was applied downstream of the uncharged platinum wire required significantly higher applied voltages to quench the surface reaction. Although gas phase ions may be directly involved in the surface mechanism in these cases, it was suggested that a higher field strength was required to attain the same secondary effects on the upstream side of the wire. This is because this surface of the catalyst is shielded from the field by the metal bulk. Activity on the upstream side of the wire was more important because apparently most of the reactants are adsorbing there.

The effects of a field applied downstream of a charged wire were different depending on the wire's charge. For a negatively charged wire, charged species inhibition is expected. In this configuration, however, most of the ions drawn to the wire will arrive on the downstream side. Apparently charged species inhibition in this location has less of an effect on the surface reaction than on the upstream side, or a stronger field is needed to force the charged species around to the upstream side.

The positively charged wire was the easiest to quench in these (field applied downstream) configurations. This could be the result of charged species inhibition involving recently desorbed OH^- radicals from the platinum surface. These hydroxyls did not appear to have as much of an effect in

upstream field configurations. This could be because they appear primarily downstream of the wire, or the field strength required to influence them was larger than that used in upstream configurations.

The catalytic reaction on a platinum wire located between two (approximately) flat plate electrodes appeared to be unaffected by the applied field. Leakage currents, indicating the presence of ions, were measured. This suggests that the presence of gas phase ions alone is not enough to quench the reaction when the wire is electrically isolated. In this case, the surface of the wire is partially biased positive and partially biased negative, so some interaction with the gas-phase ions is expected. However, there doesn't appear to be a sufficient surface charge density under the conditions used in this study to cause charged species inhibition.

6.2 Conclusions

This thesis has shown that the rate of a catalytic combustion reaction can be controlled by an applied electric field. Specifically the rate of the catalytic combustion reaction of natural gas over platinum was decreased and eventually quenched at strong applied fields in various configurations. In no case was that reaction rate increased. The quenching mechanism appears to involve both the generation of gas phase ions and their interactions with the catalytic surface, as well as variations in the electronic structure of the metal.

Although theoretical calculations to predict reaction quenching resulting from these effects are presently intractable, several interesting experimental observations can be noted.

The most striking differences in the observed quenching effects occurred between the upstream and downstream field orientation. Much higher voltages were required to quench the reaction when the field was applied downstream of the catalyst. This suggests that whatever mechanism is involved in quenching the surface reaction, it is much more effective when applied to the upstream side of the wire. This is presumably because most of the reactants adsorb on the upstream side of the wire.

The quenching mechanism observed in this study is apparently very complex, involving formation of gas phase ions, diffusion to the catalyst surface, and surface interactions. While it isn't possible to completely decouple these effects, several general statements about it can be made.

First, the quenching effect must involve some sort of change in the mechanism of adsorption, desorption, or surface reactions. If this were only a gas phase diffusion effect, quenching results would not have been dependant on the charge density on the surface of the catalyst. This indicates a more complex phenomena.

Another interesting observation is that the mechanism involved in quenching a charged catalyst surface dominates over that responsible for quenching a grounded surface. The reason for this is not clear.

The specific quenching effect observed in this study could find application in the chemical industry. Since hydrocarbon oxidation reactions are very exothermic, they tend to go to completion. In the catalytic synthesis of certain organic chemicals, however, it is desired to halt the oxidation process before this occurs. It is possible that the effect described in this thesis could be used to moderate such a reaction. This would only be the case, however, if intermediate reaction products were desorbed from the platinum surface.

Another application for this quenching effect could be as a control for a catalytic combustor. Although the maximum catalytic rate could not be increased, lower temperature operation could be attained or controlled by an applied voltage. A problem with current catalytic combustor designs is that the temperature distribution tends to be nonuniform. The "hot spots" that result from this temperature variation greatly diminish the emissions (NO_x) reduction potential of the system. The quenching effect observed in this thesis might be used to cool these "hot spots" and provide a more uniform temperature distribution, increasing emissions performance.

Before any commercial application of this effect can be considered, however, significantly more research needs to be done to clarify the actual mechanism, especially the identity of any desorbed reaction intermediates.

6.3 Suggestions for Future Work

6.3.1 Improvements to this Study

One thing that could be changed with the apparatus used in this thesis is the geometry of the platinum catalyst. Computation of the exact field strengths corresponding to the various electrode configurations was not attempted because of the complexities involved. Use of two relatively large platinum screens as electrodes would make approximation of the electric field strength much more reliable. Better knowledge of the field strengths would allow for more quantitative comparison of quenching in different geometries.

A possibility not discussed is that a small amount of a contaminant (such as water vapor or more complex hydrocarbons like propane) could be involved in the observed quenching effect. Significant amounts of these and other contaminants are present in both the natural gas (assumed to be methane) and line air used. Additional contaminants are also entrained from the room, since the reaction zone is open.

The problem of contaminants could be greatly reduced by using a sealed reaction zone and high purity methane, oxygen, and nitrogen. The sealed reaction zone would also eliminate some of the (relatively minor) uncertainty as to the actual fuel-air mixture at the platinum wire.

With these improvements and a more precise optical measurement system it would be possible to more closely examine the transient or quenching region in the various configurations. This might provide additional evidence that different mechanisms are responsible for the observed effect in different electronic configurations. A study of various normalized parameters such as the slope of the quenching region was done; this showed no additional information. The amount of data collected, however, was judged to be insufficient to justify a statistically sound parameter analysis. A more accurate pyrometer and automated data acquisition would alleviate this problem.

6.3.2 Spectroscopy

In order to verify the actual quenching mechanism observed here, several additional studies should be done. One of the most useful would be to observe the reaction intermediaries on the platinum surface. One way to determine the adsorbate concentrations on the platinum surface would be to do some type of surface spectroscopy. This would require a thin, flat piece of platinum rather than the wires used in this study.

Although spectroscopy would reveal any strongly bonded contaminants on the platinum, it probably would not help in clarifying the quenching mechanism. This is because the platinum surface returns to "normal" when

the applied field is removed. Thus, any quenching resulting from either charged species inhibition or enhanced physisorption would not be detectable once the platinum was removed from the electric field and reactant flow. Secondary quantum effects would similarly be undetectable by spectroscopy once the platinum wire was removed from the field.

6.3.3 Gas-Phase Species Identification

The next most useful bit of information would be to know the composition of gas-phase species near the platinum wire during various tests. These measurements would need to be done optically, since any short-lived species would recombine before reaching a gas analyzer. Also, we would be primarily interested in species concentrations very near the platinum surface.

Information about gas phase species could confirm (or refute) some of the mechanisms suggested in this thesis. For example, a large increase in the N_2 concentration near a charged wire when the voltage is reduced could indicate that nitrogen was blocking the surface, either by pseudo-ionically bonding to the surface, or by enhanced physisorption. Also, it is expected that the OH concentration downstream of the wire would decrease as the reaction is quenched in configuration 2A.

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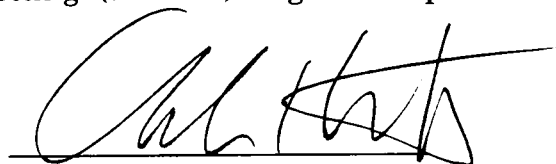
Vita

Andrew Clark "Andy" Halsey was born on Christmas Eve, 1968. After living in Wilmington, Delaware and Deerfield, Illinois, his family settled down in Emmaus (near Allentown) Pennsylvania.

Andy graduated from Emmaus High School in 1987 and decided to attend Virginia Tech. Four grueling years later he graduated cum laude with a B.S. in aerospace engineering with an English minor. Feeling his academic experience was not yet complete (and rethinking his desire to enter the aerospace industry), Andy stayed on at Tech and entered the mechanical engineering department in the fall of 1991.

Fortunately he was able to convince his fiance and high school sweetheart to enroll in grad school at Tech as well. After years of commuting back and forth to Penn State on weekends, Andy Halsey and Tracy Stauffer were married in July of 1992. Tracy also finished her M.S. degree in Engineering Mechanics in April, 1993.

Andy will soon (hopefully) begin a career in mechanical engineering, and Tracy intends to pursue her interest in engineering education. Both look forward to starting a family and getting (another) dog to keep Hershey company.

Andy Halsey