THE INFLUENCE OF ELECTROPHILIC ADDITIVES
ON PLASMA ARC JETS

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SUMMARY

The fundamental reason for the enthalpy and efficiency limits of plasma arc jets is the high electrical conductivity of the arc column plasma and its rapid increase with increasing temperature. Injection of electrophilic compounds into the arc column plasma depletes the free electrons in the plasma and hence decreases its electrical conductivity. This dissertation investigates the effectiveness of electrophilic additive injection into the arc column plasma in reducing the arc column conductivity and increasing the arc jet enthalpy and efficiency. Experiments were conducted in a 300 kW, d.c., plasma arc jet facility with argon as the arc gas and sulphur hexafluoride and carbon tetrafluoride as the electrophilic additives, for a temperature range of 5500 to 12,200 K. Small quantities of these electrophilic additives were injected into the arc column plasma and enthalpies and efficiencies with and without the additives were determined by a calorimetric approach. The influence of the additive and arc gas flow rates and the arc jet exhaust pressure are also evaluated.

Injection of minute quantities of electrophilic additives into the arc column plasma is extremely effective in reducing the arc column conductivity and increasing the attainable enthalpy and efficiency levels. A substantial increase in the operating arc voltage and a corresponding decrease in the arc current result with both SF₆ and CF₄ for any given power input, over those without any additives, indicating that negative ions are formed from SF₆ and CF₄ up to temperatures in the vicinity of...
12,000°K. The voltage current characteristic of the arc is found to be a very strong function of the electrical conductivity of the arc column plasma. SF₆ is much superior to CF₄ in increasing the attainable enthalpy and efficiency levels. The increments in arc voltage, enthalpy, and efficiency at higher temperatures decrease with increasing temperature showing that there is a temperature limit up to which sufficient amounts of negative ions required for improving the enthalpy and efficiency limits can form.

Increasing the amount of the injection of SF₆ results in its dissociated products reacting with copper surfaces and forming thin electrically insulating layers. Higher CF₄ additive flow rates result in deposits of carbon on the nozzle surface. Excessive amounts of the electrophilic additives can also result in quenching of the arc.
CHAPTER I

INTRODUCTION

Ionized gases, or plasmas, are found abundantly in the atmosphere of the sun and the stars, as well as in lightning. The applications of the physics of plasmas are found in thermonuclear fusion (1,2)*, magneto-hydrodynamic power generators (3,4), lasers, arc heaters, and rocket engines. For many decades, various devices have been used in the laboratory as a means of producing plasmas for a host of experimental purposes. Of particular interest in engineering are applications such as the simulation of re-entry environments, development of advanced optical weapon systems, and the development of MHD devices for power generation and space propulsion. Of the available laboratory devices, the plasma arc jet has been viewed as one of the most attractive systems for producing laboratory plasmas for the above mentioned engineering applications because of its ease in continuous operation for long periods of time at high levels of enthalpy, mass flow rate, and stagnation pressure.

In a conventional arc jet facility, a flowing gas is heated and ionized by arc discharges between electrodes in an arc chamber. The plasma then passes through a nozzle and enters a test chamber as a jet. The temperature and pressure of the plasma are varied by controlling the electrical power input, the arc gas flow rate, and the pressure in the

*The numbers in parentheses refer to the corresponding number of the references listed in the Bibliography.
test chamber. The utility of the arc jet is presently restricted by the temperature level attainable in this type of facility (5,6).

The fundamental reason for the temperature limit of the plasma arc jet is the high electrical conductivity of the arc column plasma and its rapid increase with increasing temperature. In Figure 1 is shown the voltage drop across a typical d.c. plasma arc. This voltage drop can be divided into three distinct regions; (a) the cathode region (cathode and its adjacent fall space) with a large voltage drop and voltage gradient; (b) the arc column with very good electrical conductivity (compared to the electrode regions) and therefore a low voltage drop and voltage gradient; and, (c) the anode region (anode and its adjacent fall space) with a large voltage drop and voltage gradient. Thus the voltage drops at the anode and the cathode regions, known as the electrode region voltage drops, represent a substantial fraction of the total voltage drop. At any given current level, the Joule dissipation in any region of the arc is directly proportional to the voltage drop across that region. Thus a substantial fraction of the electric power input is Joule-dissipated near the electrodes. In an arc jet, the electrodes are cooled externally to maintain their structural integrity and the electric power dissipated near the electrodes is largely transferred to the coolant. This portion of the power input is not useful in heating the gas passing between the electrodes and represents a loss. The Joule-dissipation in the arc column, on the other hand, is more effective in heating the gas. The efficiency of the arc, that is, the fraction of the input power which is transferred to the gas, should therefore increase with increasing ratio of the arc column voltage drop.
Fig. 1. Distribution of the Voltage Drop Across a D.C. Arc
to the total voltage drop.

At any given current level, the electrode voltage drops are relatively insensitive to the gas temperature in the arc column. The voltage drop in the arc column, however, is highly sensitive to the gas temperature. The electrical resistivity of the gas in the arc column, which is partially ionized, decreases rapidly with increasing temperature. As a result, the arc column voltage drop also decreases rapidly with increasing temperature. The efficiency of the arc jet therefore decreases rapidly with increasing temperature.

With a given gas flow rate, an increase in the power input to the arc jet leads to an increase in the arc column temperature and hence a decrease in the efficiency of the arc. As one attempts to obtain a higher arc jet temperature by increasing the electric power input to the arc, the efficiency of the arc jet deteriorates rapidly and substantial increases in power input result in only minor increases in the arc jet temperature. Also, the amount of power lost to the electrodes, because of the deteriorating efficiency, increases rapidly with increasing power input. As this power loss increases it may cause damage to the arc jet facility, such as the burning out of the electrodes. Therefore a limiting situation is approached where the amount of power loss that must be removed by the cooling system becomes excessive. In other words, for a given arc jet operating with a given gas flow rate, the maximum allowable power input level also restricts the maximum attainable enthalpy level. In addition, for any given arc jet, the maximum allowable operating current also restricts the maximum power input level, since the operating arc voltage is mostly a function of the operating pressure, mass flow
rate, and type of gas used. Therefore, for a maximum allowable arc current level, the power input can be increased only if a method can be found to increase the operating arc voltage.

Since the low electrical resistivity of the arc column plasma imposes severe limits on the maximum enthalpy and temperature levels that can be attained in the plasma generated as well as on the maximum attainable efficiencies of transfer of electric energy to the plasma, it is expected that the attainable temperature and efficiency of the arc jet can be increased if a method can be found to increase the electrical resistivity of the gas in the arc column. Since free electrons are the principal charge carriers in an ionized gas, a depletion of free electrons in the arc column should lead to an increase in the electrical resistivity and therefore to an improved efficiency of the arc jet as well as to an increased attainable temperature.

A survey of the literature shows a number of papers on the methods of depletion of free electrons in an ionized gas. The motivations for developing these methods were the possibility of alleviating the re-entry communication black-out problem and the preventing of electric spark breakdown in electrical machinery. The free electrons in the plasma surrounding a spacecraft during its re-entry phase attenuate the electromagnetic waves and cause the blackout of communication. In the case of electrical machinery, the free electrons, released by one or another mechanism, are found to initiate a spark breakdown in devices such as transformers. The most promising method of depleting such free electrons has been found to be an injection of electrophilic compounds (7-9).

The molecules of electrophilic compounds have high electron
affinity. That is, free electrons tend to attach themselves to electrophilic molecules and thus form negative ions. The attached electrons no longer possess the high mobility of the free electrons. Thus the suppression of free electrons through negative ion formation is found to be effective. Because of the interest in the re-entry communication problem, several investigations have been made in different laboratories in which electrophilic compounds were injected into jets of ionized gases produced in arc-jet facilities. It was found in these investigations that the injection of minute quantities of electrophilic compounds such as UF₆, SF₆, or freon fluorocarbons into the jet substantially depletes the free electrons in the jet (7,8).

It is therefore expected that if a minute quantity of these electrophilic compounds is injected into the arc region of the arc chamber, the electron density of the arc region will be substantially reduced. The efficiency and enthalpy of the arc jet should therefore be improved. This dissertation evaluates this promising method of increasing the enthalpy and efficiency levels of the plasma arc jet by the use of electrophilic additives. Experiments were conducted in a 300 KW, d.c., plasma arc jet facility to gain insight into this approach. The electrophilic additives used in this investigation were sulphur hexafluoride and carbon tetrafluoride, and the arc gas used was argon.
CHAPTER II

BACKGROUND LITERATURE

This chapter presents a summary of the characteristics of the major arc regions. In addition, it provides a summary of the modes of formation of negative ions, the reasons for the selection of SF$_6$ and CF$_4$ as the electrophilic additives for the investigation, and the properties of SF$_6$ and CF$_4$. The chapter closes with a section on plasma diagnostic techniques and the reasons for the selection of the calorimetric method for determining the plasma properties in this investigation.

A. Plasma Arcs

The plasma arc jet in this investigation is a d.c., vortex and magnetic (Axial) stabilized, low pressure (below atmosphere), plasma arc using a water cooled thoriated tungsten cathode and a hollow cylindrical water cooled copper anode. The characteristics of the major regions of such an arc (the electrodes and their fall regions and the arc column), the voltage current characteristics of arcs, and the transpiration cooling of plasma arcs are briefly summarized in this section.

In the most common form of the arc, the interelectrode space involved in current transport consists of the three distinct regions - cathode fall, the arc column and the anode fall. The fall spaces represent transition regions between the electrodes and the arc column. Their properties are determined by the requirements for energy balance.
and current transport at the boundaries between the gaseous and solid conducting media (10). These fall regions are of the order of a mean free path thick and exhibit a variable and much steeper voltage gradient than that of the arc column. They are also characterized by a noticeable contraction of the conduction region between the electrodes and the column, the contraction being more pronounced at the cathode. The voltage drop at the fall regions is of the order of the lowest ionization potential of the arc gas (10-12). The voltage drop at the cathode fall region is usually larger than that at the anode fall (10) while the voltage gradient at the arc column is much lower than the gradients at the fall regions. The fall regions were studied by several investigators for idealized cases (theoretical) such as very low currents and temperatures. In the cathode fall region the electrons emitted from the cathode are accelerated towards the anode by the cathode fall potential (10,13,14).

**Cathode Region**

The cathode emits electrons by several mechanisms; namely, thermionic emission, field emission, photoelectric emission, emissions due to electron and ion bombardment, or bombardment by neutral gas molecules (5). Dominance of one emission mechanism over the other depends on the cathode material, its surface conditions, and the conditions of the column (5,10). The "hot cathodes", made of materials like tungsten and graphite, which have low current densities, are dominated by thermionic emission while the "cold cathodes" like copper, that have higher current densities, are dominated by field emission (5).

In the present investigation the cathode (thoriated tungsten)
emits electrons mainly by thermionic emission. Usually tungsten is thoriated, when used as a cathode, to reduce the work function of the emitting surface in order to enhance the electron emission. Thermionic emission is the excitation of the electrons from the cathode surface due to its high surface temperature which is gained through the ions and neutrals striking the surface and releasing part of their kinetic energy to the surface. Thermionic emission is thus a function of the cathode temperature. The tungsten cathode is cooled by the boiling of the electrons in thermionic emission, by radiation and convective heat transfer to the surrounding gas, by vaporization of the cathode, and also by conduction to an external coolant. The external cooling increases the life of the cathode.

Anode Region

The electrons as well as the neutral gas particles strike the anode surface and dissipate part of their kinetic energy on its surface thereby raising its temperature. Energy is dissipated as heat on the anode surface when the electrons enter the anode (10). Eckert & Pfender (15) conducted experimental studies on the plasma energy transfer to a surface with and without the electric current. Their results show that the presence of the electron flow to a surface leads to an energy transfer to the surface (anode) which is predominant over the convection and radiation heat transfer to the surface. They found that in the case of a cascaded arc the energy acquired by the electrons in the fall region is seen to be the most important single factor in determining the heat transfer to the anode. Convection and radiation in this case were found to be at least an order of magnitude smaller than the total
contribution of the current to the anode energy flux. They concluded that high energy electrons entering the anode are the main reason for the large increase in heat flux on a surface through which an electron current flows compared to a surface with zero current.

In any d.c. arc system the anode receives more heating than the cathode, due to this electron bombardment. As the current is increased in the arc, a situation is reached where normal conduction, convection and radiation losses from the anode are not large enough to dissipate this heat generated. Then a third transfer mechanism occurs - vaporization of the anode - at a rate that is a function of the power input (10). This vaporization leads to the hissing (characteristic noise) of carbon arcs (10,16,17). The vaporization in turn leads to the release of the positive ions from the anode surface, which migrate to the cathode. (These vaporizing regions are termed "spots".) To reduce this vaporization rate, and to increase the life of the anode, the anode is usually externally water cooled. To achieve this, the anode surface should be at a temperature less than the melting point of its material, which for copper is 1080°C. It was found through experiments that the composition of the anode material as well as its surface conditions have marked effects on the electrical characteristics and stability of the arc. Nottingham (18) has found that the boiling point of the anode material has a profound effect on the volt ampere characteristics of the arc, while the cathode does not have any such effect.

The usual ideas of gas behavior suggest that the gas temperature just above the anode surface is near the surface temperature. This
relatively low gas temperature near the anode implies a very low value for the gas electrical conductivity and therefore a steep voltage gradient. This region of relatively cold gas with low electrical conductivity is referred to as the anode fall. Several investigators (16-26) have studied this anode fall.

The Arc Column

The arc column, also known as positive column or arc conduction column, is visually the most prominent region of the gas conduction space. It is characterized by a comparatively low voltage gradient compared to the fall spaces because of its high electrical conductivity. It is a well defined column of hot ionized gas with macroscopic charge neutrality, i.e., equal charge densities of positively and negatively charged particles. In a typical arc column, these charges consist of free electrons and positive ions, which drift toward the anode and cathode respectively, under the influence of the applied electric field. Both the electrons and ions are subjected to the same voltage gradient in the arc column. Since the electrons have a much smaller mass than the ions, they are subjected to a much greater acceleration from the applied field and hence carry most of the current. The collisions of electrons and ions with the neutrals result in ionization of the neutrals. Collisions between electrons and neutrals are the most efficient in ionization, while those between neutrals and neutrals, or ions are less efficient. The arc may thus be thought of as a very high energy region of electrons, ions, neutrals and excited particles, surrounded by a cool region of neutrals. Thus a steep concentration gradient exists between the core and its surroundings. Energy is lost
by conduction to the cooler regions and by radiation to the electrode and nozzle surfaces. The arc column was studied for various purposes by several investigators (27-40).

The column is usually found to be unsteady (in time) and unstable (in space). Unstable refers to the movement of the arc in an erratic manner and to its straying from the center line. These lead to severe local heating and wall erosion and eventual extinguishing of the arc.

In an arc device, usually the arc is stabilized using several methods like vortex, wall, magnetic, and liquid stabilizations. The stabilization directs and limits the discharge path, maintains a continuous current path by constriction and compression of the arc column, and efficiently cools the outer plasma layers. This confinement increases the current density, voltage gradient, column temperature and conductivity in the core of the column, while it cools the outer regions resulting in lower conductivity there. In a vortex stabilized unit, gas is fed tangentially into the chamber between the electrodes to provide an intense vortex within the hollow cylindrical water cooled anode. This vortex forces the arc to travel from the cathode through the hollow anode, until the arc can find a spot to strike through the swirling gas sheath. When a heated gas moves as a vortex, it is well known that cooler and heavier gas particles seek the outer regions of the vortex, so that the center is composed of hotter, lighter particles - thus of highest electrical conductivity. The center of the vortex thus becomes the preferred arc location. In stabilization using an axial magnetic field, the point where the arc column attaches to the anode is rotated, resulting in a rotation of the anode spots, which increases the life of the anode by
reducing the anode vaporization and erosion rates (41).

Voltage Current Characteristic of Arcs

Figure 2 shows a typical voltage current characteristic for an arc (stabilized) and is typical of argon as the arc gas. The part of the curve to the left of the minimum voltage - the negative characteristic where the voltage decreases with increasing current - is called the normal mode and the portion to the right - the positive characteristic - is the arc mode. Arcs operating in plasma jets in the normal mode are found to be usually unstable and they return to the arc mode for stable operation. The peculiar shape of the voltage current characteristic is a result of the dependence of the transport properties of the plasma on the temperature of the plasma column. It is found that the thermal and electrical conductivities play a major role in the shape of the voltage current characteristics (11,42,43). A striking variation in arc voltage with gas type is seen from studies of arcs without forced convection and is attributed to the corresponding variation in thermal conductivity (44).

Transpiration Cooling of Plasma Arcs

It is worthy to note that in any d.c. arc system, and especially in the one used for plasma arc jets which have long cylindrical anodes, the anode receives more heating than the cathode, due to the electron bombardment and also due to the fact that a much larger anode area is exposed to the hot gases for heat transfer as compared to that of the cathode. As a result of this large dissipation of heat in the anode region, various investigators have resorted to transpiration cooling of the anode surface so as to regain a portion of the anode region energy.
Fig. 2. Voltage Current Characteristic of an Arc
losses and thus to increase the efficiency of the plasma arc jets (45-53). This is done by injecting a major portion of the arc gas transversely into the arc chamber through holes drilled on the surface of the anode electrode. Such a cooling arrangement regains a portion of the heat which otherwise would have been lost to the external anode coolant. To make this method useful in reducing the anode losses, a network of holes has to be precisely drilled very close to one another on the surface of the anode. This turns out to be a very cumbersome and expensive operation. Moreover, the interaction of the longitudinal and transverse gas flows and the arc can lead to unevenness in the whole plasma arc structure. This method does not aid in reducing the operating current level, nor does it increase the arc column resistivity.

A theoretical study by Anderson (46) in hydrogen for a transpiration cooled arc shows that while the axis temperature is higher for a transpiration cooled arc, the mass-average enthalpy is higher for a water cooled arc. Hence transpiration cooled arcs will be advantageous only in those applications where it is possible to utilize the hot central core only, or where the need for water cooling is a disadvantage. He also notes that gases which radiate strongly (N₂, Ar) are not suited for transpiration cooling of arc heaters, because too much of the joule heat generated is transferred directly to the wall without being absorbed in the gas blown radially inward.

B. Electrophilic Additives

This section is divided into four subdivisions. The first subdivision discusses the negative ions. It defines the stability of negative ions and summarizes their modes of formation and detachment.
The second subdivision outlines the qualities desired of electrophilic additives to be selected for injection into the arc column. The third subdivision considers sulphur hexafluoride as a possible electrophilic additive. It summarizes the aspects of SF\textsubscript{6} which are necessary for understanding the mode of formation of negative ions from SF\textsubscript{6} such as its physical and chemical properties, negative ion formation from slow speed electrons and in the presence of other atoms and molecules, the composition of SF\textsubscript{6} as a function of temperature, radiation from SF\textsubscript{6} arcs compared to pure argon and nitrogen arcs, and coatings by the dissociated products of the SF\textsubscript{6} additive on electrodes. The last subdivision is on carbon tetrafluoride as an electrophilic additive. It outlines the physical and chemical properties of CF\textsubscript{4} and negative ion formation from CF\textsubscript{4}.

**Negative Ions**

Negative ions, both atomic and molecular, have been observed under varying conditions. They have been found in the atmosphere of the earth, sun and stars as well as in glow discharges. The negative ion plays an important role in gas discharges and plasma phenomena, in the study of the spectra of complex molecules, in electrostatic accelerators, and in space research. Massey's "Negative Ions" (54) gives a good description of negative ions, their stability, modes of formation and detachment. This description is summarized below in this section.

The stability of a negative ion depends on its electron affinity. The electron affinity of an atom can be defined as its ionization potential to form a negative ion, or the difference in energy between the normal state of the atom E\textsubscript{0} and that of its negative ion E\textsubscript{-.} For the
negative ion to be stable, \( E_{-} \leq E_{0} \). This energy difference is also equal to that necessary to detach an electron from the ion, and so may be called the detachment energy of the ion. A positive electron affinity indicates a stable negative ion. The Pauli exclusion principle must be taken into account in discussing the possibilities of formation of negative ions. This principle makes it impossible for more than two electrons (with opposite spins) to occupy the same orbital quantum state, and, in conjunction with the limited number of possible stationary states for the attached electron, severely restricts the number of elements which can form negative ions. The general rule of formation is that those atoms with completely filled electron shells will be unlikely to form negative ions. In such cases, the attached electron must be bound in a state with total quantum number greater by one than that of the outer electrons. The effective field is usually too weak to give such a stationary state. Those atoms in which the shells are most nearly complete will form the most stable negative ions, as in these the outer atomic electrons are least effective in screening the nuclear charge from the extra electron (e.g.: the halogens F, Cl, Br, I). Of these four halogen atoms, F has the greatest electron affinity as the attachment takes place to a shell with the lowest total quantum number.

When an electron becomes attached to an atom or a molecule to form a negative ion, an amount of energy equal to the electron affinity of the atom or molecule plus the relative kinetic energy of the colliding particles must be dissipated. The disposal of this energy depends upon the process of formation of the ion.

In the dissociation process, the impinging electron dissociates
the molecule and attaches itself to one of the products of dissociation, the energy of the electron in excess of that necessary for dissociation together with the electron affinity of the resulting negative ion being carried away in kinetic form by the products of dissociation.

The radiative process is a direct attachment of the electron to the atom or molecule without dissociation, the kinetic energy of the electron together with the electron affinity of the parent molecule being radiated.

Other important negative ion formations include capture of a free electron by an atom in the presence of a third body which takes up the excess energy and the dissociation of a molecule into positive and negative ions by electron impact.

In the formation of negative ions from molecules containing two or more atoms, the motion of the nuclei must be taken into account, as this provides another means of absorbing the energy released on capture of the electron, i.e. by changing the kinetic energy of the relative motion of the atomic nuclei. This may be thought of as a three body attachment process, in which the third body is bound to the capturing atom and not freely moving in the gas. In this process either or both the electronic and vibrational energy states of the newly formed ion could have increased values after the attachment so that there is neither radiation nor a third body collision involvement. In this 'resonance capture' process, the attachment can occur only when the electron energy is equal to the energy difference between the ground state (xy) and the excited state (xy")*, for example (9):

\[
e + (xy) \rightarrow (xy^-)^* \rightarrow (xy^-).
\]
Negative ions are also formed by the capture of bound electrons, in atoms or in a metal, by neutral atoms and molecules (54-61). For the capture from atoms, the reaction is of the type \( X + Y \rightarrow X^- + Y^+ \), which is usually possible only if the electron affinity of \( X \) is greater than the ionization energy of \( Y \). Capture of electrons from metal surfaces by neutral atoms is possible if their electron affinity is greater than the work function of the metal (54).

Detachment processes for electrons from negative ions include negative ion collisions with heavy particles and electrons, collisions with metal surfaces, and detachments involving molecular formation. It is found that in collisions with a metal surface, a negative ion can lose its electron easily to the metal, provided the work function of the metal is greater than the detachment energy of the ion.

**Qualities Desired of Electrophilic Additives for Injection into Plasma Jets**

The following qualities are desired of the electrophilic additives which are to be injected into the plasma arc jet in order to increase the electrical resistivity of its arc column plasma. The electrophilic additives should be in the gaseous state since the arc gases used in arc jets are in the gaseous state. Should the additive be in the liquid state, they will absorb energy for vaporization thus reducing the available energy in the arc column. Vaporization of the liquid additives also can cause unwanted phenomena such as oscillations in the arc column plasma. Finally, the injection of liquid additives is more complicated than injection of the gaseous additives. The electrophilic additives which are chosen should be nontoxic, nonpoisonous, and nonflammable. The electrophilic additives should be readily available.
and economical. They should be stable in the gaseous state at moderate temperatures and pressures, should have high electron affinity, and should form stable negative ions. They should not chemically react with the components of the arc jet or those of the exhaust system or the models to be tested in the plasma produced. Also the exhausting gases which contain these electrophilic additives should not cause any hazards when exhausted to the atmosphere. The above considerations led to the selection of sulphur hexafluoride and carbon tetrafluoride as the electrophilic additives for the present investigation. The physical and chemical properties as well as the mode of formation and temperature dependence of their negative ions are summarized in the following pages.

**Sulphur Hexafluoride**

$\text{SF}_6$ is a colorless, odorless, tasteless gas that is not flammable and is nontoxic. It is readily available and economical. Its high chemical stability and good electrical characteristics have led to its widespread use in various electrical and electronic equipment and in the field of medical science and space research. Its molecular weight is 146.054. The dissociation energy of $\text{SF}_6$ is 22.4 ev for the process $\text{SF}_6 \rightarrow \text{S} + 6\text{F}_2$, (9). $\text{SF}_6$ is one of the most stable gases known. It does not react with water, alkali hydrides, ammonia, or hydrochloric acid. In the presence of certain metals, $\text{SF}_6$ is slightly decomposed at temperatures in excess of 200°C (62). $\text{SF}_6$ has an electron affinity of 1.518 ev at 0°C referred to the gas phase (63). $\text{SF}_5$, a radical formed from $\text{SF}_6$, also forms negative ions (62). It has an electron affinity of 3.645 ev (63).

Several investigators (9,64-67) have studied the formation of
negative ions from SF$_6$ when SF$_6$ is bombarded with low energy electrons alone. They found that SF$_6^-$ and SF$_5^-$ ions are formed by the resonance capture process in large quantities at and near zero electron volts unlike the amounts formed at higher electron volts.

Several investigators (68-78) conducted experimental studies of SF$_6$ arcs to determine the properties of SF$_6$ under various conditions. For example, Richard, et al. (69) studied the material properties of SF$_6$ in a wall-stabilized arc and found, from a calculated equilibrium composition of the SF$_6$ discharge, that its electrical conductivity increases rapidly in the temperature range 4000 to 7000°K and gradually from 7000 to 10,000°K.

Investigations of negative ion formation from SF$_6$ when SF$_6$ is injected into an argon or air plasma were conducted for various plasma conditions by several investigators (7,8,79-82). They added SF$_6$ and other electrophilic additives (such as C$_2$F$_6$, CCl$_4$, freon 113, freon C-51-12, water, and trichloroethylene) into the plasma and found that SF$_6$ successfully depleted the free electrons and formed negative ions. In these investigations, the electrophilic additives were not injected into the arc region. The temperature of the plasma in these investigations varied from 800 to 8000°K. However, the mode of formation or the type of negative ions formed in the above experiments were not investigated.

Composition of SF$_6$ as a Function of Temperature. In order to study the negative ions in the arc region, it is essential to know the type of negative ions formed from SF$_6$ and the dependence of their formation on temperature. The experimental data available in this
respect are only for relatively low temperatures. At higher temperatures, which are of interest here, only theoretical predictions exist. To get a better insight into this topic of importance, the data available are summarized in the following paragraphs.

Fehsenfeld (83) studied the electron attachment to SF$_6$ at 293 and 530°K and found that at 293°K almost 100% of the negative ions formed are SF$_6^-$ while at 530°K 90% of the negative ions formed are SF$_6^-$ and 10% are SF$_5^-$. Chen & Chantry (84,85) studied the temperature dependence of negative ion formation from SF$_6$ in the temperature range of 300 to 1200°K using monoenergetic electrons of 0 to 3 ev. They found sharp SF$_6^-$ and SF$_5^-$ peaks (which are proportional to their concentrations) at zero ev and that as temperature goes up the SF$_6^-$ peak decreases while the SF$_5^-$ peak increases. Above 500°K the SF$_5^-$ peak was greater than that of SF$_6^-$. No F$^-$ ions were seen below 600°K but above this temperature the F$^-$ peak was seen to increase with temperature. They also found a decrease in SF$_4^-$ and SF$_2^-$ peaks while an increase in SF$_3^-$ and F$^-$ peaks with increase in temperature.

Mullen, et al. (86) added SF$_6$, C$_2$F$_6$, CBrF$_2$ and O$_2$ into an argon plasma and conducted studies in the temperature range of interest for re-entry (2000 to 3500°K). F$^-$ was the predominant negative ion seen in their experiments. They found complete disintegration of SF$_6$ at 2500°K and noted that electron attachment and collisional dissociation appear to be the dominant mechanisms controlling the formation of negative ions.

Wilkins (87) calculated the composition of 1 mole % SF$_6$ and 99 mole % argon mixture as a function of temperature, up to 3000°K at 1 atm. His calculations show that F is the predominant component present above
2000°K at 1 atm pressure.

Frie (88) made calculations for the dissociation and ionization of SF$_6$ molecules at 1 atm pressure. He found that SF$_6$ starts dissociation at 1000°K and completes it around 2000°K. SF$_6$ initially dissociated into SF$_4$ + 2F. SF$_4$ later dissociated around 2000°K and complete dissociation into S + 4F occurred around 3000°K. Sulphur started ionization at 3000°K and reached complete single ionization around 12,000°K. Negative ions of F$^-$ started forming at 3000°K and reached a peak from 6000 to 10,000°K. F started ionization at 8000°K and complete ionization of F to F$^+$ occurred around 20,000°K. S$^+$ was subjected to one more ionization from 13,000°K onwards. But here it must be clearly noted that the electrons available for the F$^-$ negative ion formation were those available only from the S$^+$ ionization.

Belov & Semenov (89) calculated the composition of SF$_6$ at temperatures up to 20,000°K and pressures from 1 to 10 atm and found that at 1 atm F is the predominant component up to 17,500°K and above that S$^+$ and F$^+$ take over. F$^-$, even though at low concentrations, is seen up to 20,000°K. S$^-$ is seen in the range of 5,000 to 12,500°K. Sulphur, with an electron affinity of 2.08 ev (referred to the gas phase) and an ionization potential of 10.357 ev, is found to form stable negative ions (63).

From the above findings, it may be concluded that F is the predominant component seen in the plasma in the temperature range of interest to the present investigation, i.e., from 5000 to 15,000°K. These findings also show that F$^-$ is the predominant negative ion formed from SF$_6$ in the temperature range of interest. The electron affinity of the F atom is
3.45 ev at 0°C, referred to the gas phase (experimental) and its ionization potential is 17.418 volts (63). The electron affinity of F₂ is less than that of the F atom (54).

Radiation from the SF₆ Additive. Motschmann (90) conducted experiments for an SF₆ arc in a wall stabilized cascaded arc. His experiments revealed that the radiation from an SF₆ arc at 13,800°K and 100 amperes is less than 5% of the power input and is small compared with that of an arc in argon and even lower than that of an arc in nitrogen. From this it may be concluded that the presence of the SF₆ additive in the plasma arc does not result in any significant additional radiation losses to the electrode surfaces or the nozzle walls. Calculations by Lowke and Liebermann (91) for SF₆ arcs revealed that radiation from F⁻ was negligible.

Coating on the Electrodes by the Dissociated Products of the SF₆ Additive. The dissociated component S of the SF₆ is found to react with the anode and nozzle surfaces and form CuS. Motschmann (92,93) conducted experiments for an arc in SF₆ in a wall stabilized cascaded arc. He found the components, resulting from the dissociation of SF₆, reacting with the electrode and the cascade wall surfaces. Hence he passed argon gas on these surfaces wherever SF₆ was present, so as to avoid these coatings. Richard, et al. (69) noticed insulating surface layers formed on copper plates when conducting experiments with SF₆ in a wall stabilized arc. Bolin, et al. (71) also found products of reaction between SF₆ and metal electrodes precipitating on the surface. But it may be noted that since the amount of additive by volume added is much smaller than the arc gas in the present investigation the coating
would be much less severe than had the whole arc gas been sulphur hexafluoride.

As mentioned earlier in the probable modes of formation of negative ions, as well as from the above findings, it can be seen that SF₆ dissociates into components like S, F, F₂, SF₄, and SF₅. But these components may also react with the electrode components - especially the copper anode. The properties of chemical compounds that may be formed by the above mentioned components are briefly outlined in the following paragraph.

Copper has a greater affinity for sulphur than all other common metals except Ag and Mn (94). Cu and S when heated readily form Cu₂S, cuprous sulphide. Artificial Cu₂S is black with perhaps a bluish luster. It melts at about 1100 to 1300°C, depending on the form. Under certain conditions, its electrical conductivity is much like a metal, resulting in its use as electrodes in certain electric cells (63). Artificial cupric sulphide, CuS, is an off-black hue with a green, brown or blue tinge (63). When dry it is stable in air, but in the presence of moisture it gradually oxides to sulphate. The electrical conductivity of CuS is higher than that of Cu₂S (94). Fluorine is the most reactive element in the periodic table. Fluorine combines with all elements, even with some of the noble gases (62). Fluorine reacts with Cu to form a surface film of fluoride which retards further attack, so that the temperature must be increased to obtain further reaction (62). Cupric fluoride, CuF₂, exists at room temperature. It is a white solid and melts at 780°F (62). The anhydrous CuF₂ in contact with moist air, slowly shows blue coloration because of the hydrate (62).
Carbon Tetrafluoride

Carbon tetrafluoride (CF\textsubscript{4}) is chosen for its following good physical and chemical properties as well as its low cost. CF\textsubscript{4} is an inert, colorless, nonflammable gas, available as a nonliquified compressed gas at 70°F and pressures of 500 psig and above. It has a low order of toxicity, showing no noticeable physiological effects at low concentrations. It is noncorrosive and hence can be used along with common structural materials.

CF\textsubscript{4} is extremely stable, reacting only slightly even at the temperature of a carbon arc (4700°K). It reacts with the alkali metals at about 400°C, giving metal fluoride and carbon. It shows no reaction with Cu, W, Ni or Mo at 900°C. It reacts with CO\textsubscript{2} at temperatures above 1000°C. CF\textsubscript{4} is resistant to oxidizing and reducing agents except under very drastic conditions (62).

The electron affinity of CF\textsubscript{4} is not known. But it has a low dielectric strength of 1.06 (relative to N\textsubscript{2} = 1). The electron affinity of C is 1.25 ev (95). The molecular weight of CF\textsubscript{4} is 88.01. The energy of dissociation of CF\textsubscript{4} (gas) to C (g) + 4F (g) is 20.4 ev at standard conditions (from calculations using the standard enthalpies of formation). The standard energy of negative ion formation of C\textsuperscript{-} and 4F\textsuperscript{-} ions is approximately 17 ev per mole of CF\textsubscript{4}, by calculations (95). It is seen from the previously discussed findings with SF\textsubscript{6} that it clearly dissociates to S + 6F. So it may be reasoned that CF\textsubscript{4} will also dissociate to C + 4F. With CF\textsubscript{4}, the carbon does not react with copper unlike the behavior of the sulphur in SF\textsubscript{6}.

CF\textsubscript{4}, also known as Freon-14, is used in low temperature refrigerents
and in wind tunnel studies as well as in rocket applications for inertial guidance. Georgiev & Rose (96) studied the carbon contamination in an air arc and found that the reaction $C + O \rightarrow CO$ produces an oxygen starved gas and that the carbon contamination affects the test results on combustible materials only. They also found that the largest fraction of the C contaminant in the plasma is in the gaseous rather than the solid state.

Starner (80) added CF$_4$ into a subsonic air plasma at temperatures below 3300°K and found that CF$_4$ was as effective as SF$_6$ or CB$_r$F$_3$ as an electrophilic additive. For mass concentrations of 3% CF$_4$ in air, the negative and positive ion densities were found to be of the same magnitude. He obtained the same results with SF$_6$ and CB$_r$F$_3$. But at mass ratios of 0.3%, the negative saturation current was found to be much larger than the positive ion current for all these three additives, from the measurements made using a Langmuir probe.

C. Plasma Diagnostic Techniques

The determination of the properties of a plasma is quite involved and the continuous monitoring of the properties of the plasma using very reliable plasma diagnostic techniques is required for accurate diagnosis. The methods mostly employed for plasma diagnosis are the spectroscopic methods (97-100), radiation methods, laser diagnostic techniques, electrostatic probes (7,101-111), microwave techniques, enthalpy probes (112-115), and calorimetric methods (6,100,116).

Most of the plasma diagnostic methods require the satisfaction of certain conditions for the plasma, such as the plasma must be homogeneous and be in complete thermodynamic equilibrium. However, in the
present investigation the main interest is in determining the increase in enthalpy and efficiency of the plasma in the presence of the electrophilic additives over those without any additives. This requires a method that is capable of measuring the total heat content of the jet most accurately. Calorimetric method is a simple method and has been successfully employed for decades in laboratories for measuring the heat balance and for calibrating other diagnostic instruments due to its high accuracy. Since each section of the arc jet in the present investigation is individually cooled, the total balance of energy can be verified by checking against the total electrical power input. Calorimetric method is less tedious compared to the other plasma diagnostic techniques for the present investigation. Hence, the calorimetric method was selected for use in this investigation to obtain the enthalpy and efficiency of the arc jet.

Preliminary measurements made using a spectrometer and an electrostatic probe gave results which were not of sufficient accuracy. Hence they were not used for making any measurements in the present investigation.
CHAPTER III

EXPERIMENTAL FACILITY

The experimental facility consists of a plasma arc jet, flow meters, thermistors, pressure transducers, differential pressure gauges, recording instruments, power supplies, volt meters and an oscilloscope. They are briefly described on the following pages.

A. Plasma Arc Jet

The plasma jet used in this investigation is a Thermal Dynamics Model L-500, 300 kW, d.c., plasma arc jet. The plasma is produced by passing the working gas through a constricted d.c. arc. An arc current of up to 6000 amperes can be maintained. The ionized gas flows through a supersonic nozzle of 3 inches exit diameter into a vacuum test chamber, where measurements can be made to determine the various properties of the plasma. The cathode is made of thoriated tungsten, while the anode and the nozzle are of copper. The remainder of the plasma torch is brass. The vacuum test tank is of stainless steel and is three feet in diameter and four feet long. It has two windows for optical measurements. The power supply to the torch is supplied through five welding type 60 kW rectifiers.

The torch assembly consists of the cathode, a copper floating section, and the anode. The arc gas is injected through primary ports located around the circumference of the cathode and secondary ports located at the periphery of the floating section that is adjacent to the
This L-500 torch is a vortex and magnetic (axial) stabilized plasma arc jet. All materials that come in contact with the plasma are water cooled at high pressure (75 psig) to maintain their structural integrity. The manufacturing specification requires that the temperature rise in any of the external high pressure coolant circuits be limited to 20°F.

The hot gas that leaves the vacuum test chamber is cooled in a cross flow heat exchanger to below 25°C before it is exhausted to the atmosphere by the vacuum pumps. The vacuum pumps are a Stokes Microvac pump Model No. 412H-10 and a Stokes Forepump Model No. 900-170-22. A vacuum of 3 mm Hg can be obtained in the plasma jet (tank and anode chamber) using these pumps. These are capable of pumping up to 1300 cubic feet per minute at low pressures, i.e., below 25 mm Hg. The arc gas is supplied from a manifold that can be connected to as many as six bottles of gas at a time.

B. Instruments and Their Accuracy

Gas Flow Meters

The arc gas flow rates are metered using two Fischer & Porter flowrators. The one connected to the primary ports of the arc head is an F&P Flowrator Model 10A1735A using tube No. B4-27-10/77 and float No. BSVT-45. The flowrator at the secondary ports of the arc head is an F&P Model T7-1104/101-11 (735) with tube No. B4-21-250/70 and float No. BSV-T-45. The electrophilic additives are metered using a Matheson Model No. 622 PSV high accuracy 150 mm flowmeter using a 602 tube. Pressure regulators are connected on the upstream sides of all these three
flowmeters. Throttling valves are connected to each end of these flowmeters and pressure gauges are connected to the upstream end of each F&P flowrator, between the throttle valve and the meter.

A Precision Scientific Wet Test Meter Model No. 63115 was used to calibrate the two flowrators with argon and the electrophilic additive flowmeter with sulphur hexafluoride and carbon tetrafluoride. The wet test meter is factory calibrated to an accuracy of $\frac{1}{2}\%$ of total volume, according to ASTM-D-1071 specifications. The wet test meter has 3 litres of volume per revolution and a total capacity of 680 litres. A water manometer with a 0 to 20" range and a readout accuracy of 0.05" was used along with the wet test meter for calibrating the flow meters. The calibration was repeatable to within 1% (30CC).

Coolant Flow Rates

The cathode, anode and nozzle coolant flows are measured using orifices and differential pressure transducers. These flow rates were calibrated for various pressure differentials which were recorded simultaneously on a Consolidated Electrodynamics Corporation recording oscillograph. The exhaust tank and heat exchanger coolant flow rate is measured directly for each run using a calibrated drum and stop watch. All calibrations were repeatable to within 1%.

Thermistors

Thermistors are used as transducers to monitor the temperature rise in the coolant in the cathode, anode, nozzle and tank coolant circuits and the temperature of the exhausting gas. Thermistors are semi-conductors of ceramic material made by a sintering mixtures of metallic oxides such as manganese, nickel, cobalt, copper, and uranium. The
thermistors have a high negative temperature coefficient of resistance. The thermistors used in these experiments are Uni-Curve Interchangeable curve-matched thermistors, Model UUA 33J1 and assembly. They can be used interchangeably within an error band of ±0.2°C in the temperature range encountered in these coolant circuits, i.e., from 15 to 38°C.

These thermistors are very stable. Hence if they can be calibrated individually, an accuracy of much better than ±0.2°C can be obtained for measuring the required temperature differences. These thermistors were individually calibrated using a Haake Constant Temperature Circulator bath Model NB 68428 and a high precision thermometer having an accuracy of ±0.01°C. The bath temperature can be controlled and set to desired temperatures with an accuracy of ±0.01°C. Eight of the thermistors were calibrated in the temperature range 11.92 to 50.62°C and the ninth one from 11.92 to 88.94°C. This ninth thermistor is used to measure the temperature of the exhausting gas. Each thermistor is connected in series with a 5kΩ resistor. The total voltage drop across the thermistor and resistor and the drop across the resistor alone were measured using a Hewlett Packard Model 2401C integrating digital voltmeter having an accuracy of ±10 microvolts. A sampling period of one second was used. The power supply for the thermistors was a Hewlett-Packard d.c. power supply, Model 6215A with a variation in voltage supply less than a tenth of a millivolt. The thermistor calibrations were repeatable to within ±0.02°C. This leads to an accuracy of better than 7.3% for the lowest temperature rise measured (0.55°C) in the coolant circuits.

**Instrumentation**

An 18-channel Consolidated Electrodynamics Corporation recording
The oscillograph Model No. 5-124A is used to record the pressures of the plenum chamber, nozzle exit, vacuum tank and stagnation region, and the cooling water flow rates in the cathode, anode, and nozzle. In addition, the voltage and current of the electrostatic probe and the output of the spectrograph can be recorded. The static pressures are measured by standard (Bourden type) pressure transducers.

The arc current is measured by measuring the voltage drop across a 6000 ampere air cooled shunt while the total arc voltage is measured directly. Both these voltages and also the voltage at the arc head (used to determine the cable losses) are measured using two Fluke Model 8000A digital voltmeters and a United Systems Corporation Digitec digital d.c. voltmeter having a stated accuracy of better than 0.3%. A Tektronix Model 502 dual-beam oscilloscope is used for measuring the fluctuations and the ripple in the arc voltage with time.

Transducers, thermocouples, readout equipment, etc., are prone to electrical interference due to the high energy electrical and magnetic fields in the vicinity of the arc heaters and, unless careful precautions are taken, can yield erroneous readings. Hence, all cables associated with equipment used with the plasma jet are insulated and properly grounded.
CHAPTER IV

EXPERIMENTS

This chapter is divided into two sections. The first section describes the method of injection of the electrophilic additives into the arc column plasma and the calorimetric energy balance measurements. The second section describes the parameters which are varied for the experiments and the reasons for selecting these parameters.

A. Procedure

Method of Injection of the Electrophilic Additives

A sketch of the electrode and nozzle arrangement of the plasma arc jet is shown in Figure 3. The argon gas is injected tangentially through two sets of ports, the primary ports, located ahead of the cathode, and the secondary ports, located between the cathode and the anode. Letters A & B on the Figure denote the probable arc attachment points on the cathode and the anode, respectively. The arc can attach on the anode surface at any point B from C to D. The electrophilic additive must be injected ahead of the point C in order to be effective in decreasing the arc column conductivity. Electrophilic injection along with the secondary argon flow was chosen for the following reasons:

1. Due to the possibility of any of the dissociated products of the electrophilic additives reacting with the tungsten cathode surface and damaging it, the additive should be injected such that it does not
Fig. 3. A Sketch of the Electrode and Nozzle Arrangement of the Plasma Jet
come in direct contact with the cathode. It may be noted that the cathode used here is very much smaller in size compared to the anode.

(ii) Secondary tangential ports are already provided and as such no new ports need be made.

(iii) Mixing of the argon gas and the electrophilic additive is possible before injection, if the additive can be injected along with the argon gas. This leads to a uniformly mixed flow of gases at the secondary ports, resulting in a more uniform distribution of the additive in the arc.

Measurements

The measurements taken for the experiments are summarized in this section. The temperature rise of the coolants and the coolant mass flow rates in the cathode, anode, nozzle, and tank circuits were monitored separately, as described in Chapter III. The temperature of the exhausting gas was measured separately. The total power input leaving the power supply unit was obtained from the measurements of the arc voltage and current. The voltage drop across the arc head was also measured in order to calculate the voltage drop across the cables. The current to the magnet was fixed for all tests.

Making separate measurements for the coolant losses in each circuit has many advantages. Firstly, it leads to an overall energy balance and determination of the accuracy of the calorimetric measurements. Secondly, the measurement of the anode losses would help to verify whether the reduced electron number density and arc current in the presence of the electrophilic additives would lead to lower anode heating and, hence, lower losses. However, if the temperature of the
plasma is higher in the presence of the electrophilic additives it would lead to higher anode heating. As temperature increases, these two opposing effects may tend to compromise the effectiveness of electrophilic addition in increasing the enthalpy and efficiency. Thus, an understanding of the variation of the anode losses with temperature (or power input) would help to estimate the temperature limit of the effectiveness of the electrophilic additives in increasing the attainable enthalpy and efficiency levels. Determining the cathode, nozzle, tank, and cable losses, with and without the electrophilic additives, is of importance in understanding what effect the electrophilic additives has on each of these losses.

B. Parameters

Power Input Levels

Experiments were conducted at power inputs ranging from 14 to 214 kW, with and without the electrophilic additives, to determine whether the efficiency of transfer of the electrical energy to the plasma and the mass average enthalpy of the plasma could be increased above those presently available in the absence of any electrophilic additives. Such a wide range in power input level was used in order to study:

(i) the temperature range in which this method of electrophilic additive injection was effective; (ii) the temperature dependence of negative ion formation from the electrophilic additives injected into the arc column plasma; and, (iii) the dependence of enthalpy and efficiency on the power input to the arc jet.
Exhaust Tank Pressures

It is expected that the arc chamber pressure has some effect on the stable negative ion formation and on the influence of the electrophilic additives on improving the arc jet's enthalpy and efficiency levels. To study these effects, experiments were conducted for two exhaust tank pressures of 4.5 mm Hg and 40 mm Hg.

Arc Gas

Argon was chosen as the arc gas since it is monatomic, readily available, economical, devoid of any complications of chemical reactions or dissociations, and because a modest amount of experimental data are available for argon. The argon used had a purity of 99.998% and came in cylinders at pressures of 2500 psig. Two argon flow rates of 220 SCFH (0.408 lbs/minute) and 290 SCFH (0.529 lbs/minute) were used for the experiments.

Electrophilic Additives

Two electrophilic additives, sulphur hexafluoride and carbon tetrafluoride, were used for the experiments in order to study their relative performances. The $\text{SF}_6$ gas used had a purity of 99.8% (in the liquid phase) and came at a pressure of 500 psig at 70°F. The $\text{CF}_4$ gas had a purity of 99.7% and was at a pressure of 1500 psig at 70°F. Various electrophilic additive flow rates were used in order to find the influence of these flow rates on the performance of the arc and also to select the optimum additive flow rate for increasing the obtainable enthalpy limit. $\text{SF}_6$ flow rates of 0.35, 0.7 and 1.05% by volume of the argon flow rate and $\text{CF}_4$ flow rates of 0.25 and 0.5%, by volume of the argon flow rate, were used. In addition, further experi-
ments were conducted with 0.60, 0.90 and 1.20% CF₄ by volume of 220 SCFH of argon at 20 mm Hg (tank pressure).
CHAPTER V
ANALYSIS OF RESULTS

This chapter is divided into two sections. The first section discusses the accuracy of measurements and the observations made during the experiments. The second section presents a discussion of the results and their significance.

A. Remarks

Accuracy

The enthalpy of the plasma leaving the nozzle was determined from the sum of the calorimetric measurement of the total heat loss to the exhaust tank and the heat exchanger and the heat carried away by the gas exhausting from the heat exchanger. The overall energy balance which consists of the measured cable, cathode, anode, and nozzle losses and the output agreed with the measured total power input to within 3%. The term "power input" as used in this dissertation refers to the power leaving the power supply unit. Some experiments were repeated for similar conditions and it was found that all the components of the energy balance were reproduced to within 2%.

General Observations

(1) No noticeable coatings on the surfaces of the electrodes and nozzle were seen at low electrophilic additive flow rates of 0.35% SF₆. At the higher flow rates of 0.70 and 1.05% of SF₆, the downstream portions of the anode and the whole nozzle surface were seen to be coated
with the products of reaction between copper and sulphur. The material obtained from the surface was analyzed and it was found to contain copper sulphide. However, the coating was not analysed to determine if it contained fluorine compounds. Coating on the anode surface resulted in an increase in the operating arc voltage by as much as 2.5 volts. This was the difference obtained without any additives, before and after operating the jet in the presence of 0.70 or 1.05% of SF$_6$. The voltage increment slowly diminished and reduced to zero as the arc was operated, without any additive, for as long as 10 minutes. This shows that the coating layer behaves as an electrically insulating layer, and that as it is removed by melting the arc returns to its original operating conditions. The melting results in a gradual erosion of the surface.

At 0.6, 0.9 and 1.2% of CF$_4$ flow rate, a dark deposit (carbon) was seen on the nozzle surface. No deposit was seen on the anode surface even at 1.2% of CF$_4$. Below 0.6% of CF$_4$ no deposits were seen on any surface. The deposits were seen after operating the jet continuously for a period of one hour.

(2) When the SF$_6$ or CF$_4$ flow rates were increased to 1.5% by volume of the argon flow rate, quenching of the arc occurred at power inputs near 80 kW. This is because the rate of loss of free electrons due to attachment to electrophilic additives in the arc column plasma is greater than the rate of production of electrons by ionization of the argon atoms. Since the mobility of the massive negative ions is much smaller than that of the electrons, they do not contribute significantly to the conduction of the arc current. This leads to an inability to sustain a stable arc discharge and to the quenching of the discharge.
(3) With stable arcs, with and without the additives, the following variations in arc voltage and current were noticed:

\[
\text{Arc Voltage} \sim \pm 1\% \\
\text{Arc Current} \sim \pm 1\%
\]

These variations were such that as the arc voltage increased, the current decreased, or vice versa, so as to keep the power input level about the same. This variation had a frequency varying from 1 to 2 cycles per minute.

(4) With stable operation, the arc voltage exhibited a high frequency fluctuation. This ripple had a frequency of 300 Hz with an rms voltage of 8 mV (0.028%) at 40 kW, and a frequency of 500 Hz with an rms voltage of 70 mV (0.2%) at 175 kW. These measurements were made for a non-additive plasma.

(5) In addition, with stable arc operation, oscillations in the operating arc voltage and current were seen when the arc was operated with either of the electrophilic additives. These variations were such that as the voltage increased, the current decreased, or vice versa. The addition of CF₄ gave milder oscillations than SF₆. These oscillations were mild but their prominence (both amplitude and frequency) increased with an increase in additive flow rates, and were not seen when the arc operated without any additive. These oscillations had an amplitude range of approximately 0.05 to 0.20 V and an approximate frequency range of 20 to 60 cycles per minute. (0.1 V corresponds to approximately 0.25%)

(6) Unstable arcs were seen at certain power settings with and
without the electrophilic additives. 'Unstable' here refers to the condition in which, (i) the plasma emerging from the nozzle behaves in an erratic manner, and (ii) the monitoring of the data is impossible due to large and rapid fluctuations in the operating arc voltage and current. These random fluctuations in arc voltage had a variation of as much as 100% in amplitude and a frequency of approximately 10 cycles per minute.

The arc was extremely unstable at an argon flow rate of 290 SCFH at 40 mm Hg tank pressure and could not therefore be operated for this condition without any additives. Also at 220 SCFH of argon at 40 mm Hg, the arc was unstable at certain power settings with 0.70 and 1.05% SF₆. The arc was unstable for certain power settings at 290 SCFH of argon at 4.5 mm Hg and 0.70% SF₆. Unstable arcs existed at some regions intermediate to the data points presented. For example, in the region of 300 to 900 amperes at 4.5 mm Hg, the arc was unstable for an additive flow rate of 0.35% SF₆ in 220 SCFH of argon and could not be operated, as shown by the dashed line in Figure 4.

(7) The temperature of the argon gas exhausting from the heat exchanger was found to be very close to the room temperature. Since the enthalpy is referred to the room temperature in the present experiments, the heat content of this exhausting gas is negligible and, hence, is unaccounted for in the calculations.

B. Discussion of Results

This section presents the results obtained from the experiments together with discussions of the influence of the electrophilic additives (SF₆ and CF₄) in reducing the electrical conductivity of the arc column.
ADDITIVE: 0.35% SF₆

Fig. 4. Arc Voltage Vs Arc Current with 0.35% SF₆
plasma and increasing the arc voltage and the attainable enthalpies and efficiencies, for varying power inputs. It also discusses the type and temperature limit of existence of the negative ions formed and the effects of varying the electrophilic additive flow rate, pressure, and arc gas flow rate. Definitions of the terms used here are given at the beginning of this section.

Definitions

(1) Total arc voltage is the sum of the voltage drop in the cables and the drop across the arc head.

(2) "Power Input" is the power leaving the power supply unit.

(3) Nozzle-exit enthalpy is the average (stagnation) enthalpy per unit mass (BTU/lb) of the plasma leaving the nozzle, reference enthalpy being that of the room temperature.

(4) Nozzle-entrance enthalpy is the enthalpy per unit mass (BTU/lb) of the plasma as it enters the nozzle. It is calculated from the sum of the nozzle-exit enthalpy and the nozzle coolant losses.

(5) The nozzle-exit temperature and nozzle-entrance temperature are those calculated from the corresponding measured mass average enthalpies and static pressures, for equilibrium conditions. The equilibrium thermodynamic tables of Brahinsky and Neel for argon (117) were used for this computation.

(6) The overall efficiency is the ratio of the nozzle-exit enthalpy to the total electrical power input. It is expressed as a percentage.

(7) Calorimetrically measured anode, cathode, and nozzle coolant losses are expressed as a percentage of the total power input.
Cable losses, calculated from the product of the measured voltage drop in cables and the arc current, are expressed as a percentage of the total power input.

Influence of Injecting Electrophilic Additives into the Arc Column Plasma - the Effect of Varying the Power Input Level

This section discusses the effect of injecting minute quantities of electrophilic additives, SF₆ and CF₄, into the arc column plasma in reducing the electrical conductivity of the arc column plasma and increasing the arc voltage and the attainable enthalpies and efficiencies over those presently available in the absence of the electrophilic additives in argon. It also discusses the effect of the additives on the heat losses to the components of the arc jet. In these discussions, the arc gas and electrophilic additive flow rates and the tank pressures are fixed while the power input level is varied.

(1) The Voltage Current Characteristics. The voltage current characteristics, without any electrophilic additives in argon, show that the arc operates only in the arc mode, or positive characteristic, as shown in Figure 5. Similarly, with CF₄ injection, the arc operates only in the arc mode, as shown in Figure 6. However, with SF₆ as the electrophilic additive, the arc operates both in the normal (negative characteristic) and the arc modes, as shown in Figures 4 and 7. In the normal mode, for 0.35% SF₆ by volume of 220 SCFH of argon at 4.5 mm Hg pressure, the arc voltage attains a maximum of 65 volts (the open circuit voltage is 100 volts), as shown in Figure 4. In general, with SF₆ as the electrophilic additive the arc voltage is a maximum at the lowest current (in the normal mode) unlike that found without any electrophilic
Fig. 5. Arc Voltage Vs Arc Current without any Additives
Fig. 6. Arc Voltage Vs Arc Current with CF$_4$
Fig. 7. Arc Voltage Vs Arc Current with SF₆ at 220 SCFH
additives or with CF4 as the additive, where the arc voltage is a maximum at the highest current (in the arc mode).

(2) The Voltage Increment. Significant increases in the arc voltage result from the injection of minute quantities of either of the electrophilic additives, CF4 or SF6, as shown in Figures 6 and 7. The CF4 added plasma gives rise to slightly higher arc voltages than the SF6 added plasma in the arc mode, as illustrated in Figures 6 and 7. These higher arc voltages result in lower arc currents for the same power input, for the plasmas with additives. The higher arc voltages in the presence of the electrophilic additives imply that a significant reduction in the arc column conductivity has resulted due to the replacement of the free electrons by negative ions of low mobility in the arc column plasma.

With SF6 as the electrophilic additive, the voltage increment due to the presence of SF6 decreases with increasing power input, as shown in Figure 8. This trend implies that not enough negative ions are forming as the power input increases (keeping the electrophilic additive flow rate constant). The reason for this is that as the power input increases, the temperature of the plasma increases and the free electron density that would be present if no additives were injected increases very rapidly. The fixed amount of electrophilic additives therefore depletes a smaller fraction of the free electrons present. In other words, the ratio of negative ion number density to free electron density decreases with increasing temperature. Further at high temperatures, the additives start ionizing or the negative ions start de-ionizing immediately after their formation to free the electrons they captured.
Fig. 8. Voltage Increment Vs Power Input with SF<sub>6</sub> at 220 SCFH

Fig. 9. Voltage Increment Vs Power Input with CF<sub>4</sub>
The continual decrease in voltage increment with increasing power input noted with SF$_6$ addition (Figure 8) is not apparent with CF$_4$ addition (Figure 9), although the explanation offered above as regards the effect of negative ions should be equally valid for both the additives. The reason for this different behavior is not evident.

To illustrate the rapid increase of the free electron density with increasing temperature, consider the equilibrium degree of ionization as a function of nozzle-entrance temperature, Figure 10, computed from the tables of reference (117). This figure shows that the degree of ionization increases from approximately 4.5% at 9500°K to 10% at 10,500°K, and to 37% at 12,200°K. These temperatures correspond to approximate power inputs of 50, 80, and 214 kW for a nonadditive plasma (220 SCFH). In the present experiments, the power input level varied from 14 to 214 kW.

Hence, as the nozzle-entrance temperature increases, it results in a rapid rate of increase of the free electron density in the plasma.

(3) The Enthalpy Increment. Addition of SF$_6$ substantially increases the enthalpy of the plasma entering and leaving the nozzle over the enthalpy obtained in the absence of any additives, as illustrated in Figure 11. However, the enthalpy increments due to the presence of SF$_6$ decrease with increasing power input at higher power input levels. The reasons for this are, (i) the percentage depletion of free electrons through ion formation decreases with increasing power input; (ii) the higher enthalpy plasma resulting from the influence of the electrophilic additives gives rise to increased heat transfer to the containing walls as temperature increases.

For an argon flow rate of 220 SCFH at 40 mm Hg, 0.35% SF$_6$ by volume
Fig. 10. Temperature Vs Equilibrium Degree of Ionization for Argon at Nozzle-Entrance Conditions
Fig. 11. Average Nozzle-Entrance and Nozzle-Exit Enthalpies Vs Power Input at 220 SCFH
of argon increases the nozzle-entrance enthalpy from 4100 to 5400 BTU/lb (32% increase) at 80 kW power input, as shown in Figure 11. When these experiments are conducted at 160 kW, the nozzle-entrance enthalpy increase is reduced to 6.7% (the enthalpy increased from 7500 to 8000 BTU/lb) as shown in Figure 11. The corresponding increases in nozzle-exit enthalpy are from 2200 to 3800 BTU/lb at 80 kW (74% increase) and from 5000 to 5800 BTU/lb at 160 kW (16% increase), as shown in Figure 11.

The CF$_4$ additive increases the enthalpy only at lower power input levels, compared to the non-additive plasma, as shown in Figure 11. At high power input levels the CF$_4$ added plasma gives lower enthalpies than the non-additive plasma, even though the CF$_4$ added plasma still gives rise to a higher arc voltage than the non-additive plasma at these power input levels. No reason is evident for this behavior of the CF$_4$ added plasma at higher power inputs.

With the CF$_4$ added plasma, the nozzle-entrance and exit temperatures (calculated for equilibrium conditions at the entrance and exit sections of the nozzle) show the same behavior as that of the enthalpies, as shown in Figure 12. 0.35% SF$_6$ in 220 SCFH of argon at 40 mm Hg increases the nozzle-entrance temperature from 8250° K to 9750° K (18% increase) at 35 kW, and from 11,700° K to 11,800° K (0.86% increase) at 160 kW, as illustrated in Figure 12. The corresponding increases for nozzle-exit temperatures are from 3800 to 8000 K at 35 kW (110%) and from 10,400 to 10,700 K at 160 kW (2.9%), as shown in Figure 12. The increases in temperature at higher power levels are much lower than those at lower power levels because: (i) the enthalpy increments are lower at higher power input levels; and, (ii) the degree of ionization
ARGON FLOW: 220 SCFH
TANK PRESSURE: 40 mm Hg

- ▲ 0.35% SF₆
- △ 0.35% SF₆
- ● 0.5% CF₄
- ○ 0.5% CF₄
- □ NO ADDITIVE
- ■ NO ADDITIVE

CLOSED SYMBOLS: NOZZLE-ENTRANCE
OPEN SYMBOLS: NOZZLE-EXIT

Fig. 12. Average Nozzle-Entrance and Nozzle-Exit Temperatures Vs Power Input at 220 SCFH
is much higher at the higher power input levels meaning that a larger fraction of the enthalpy increment is in the form of the ionization energy rather than the thermal energy of the plasma.

(4) The Overall Efficiency. In general, without any additives, the overall efficiency of the plasma jet (the ratio of nozzle-exit enthalpy to total power input) increases with power input, reaches a maximum, and then decreases, as shown in Figure 13. However, with the electrophilic additives, SF₆ or CF₄, the overall efficiency is highest at the lowest power input level, as illustrated in Figure 14.

For the range of experimental conditions tested, SF₆ addition generally leads to higher overall efficiency. At 40 mm Hg in 220 SCFH of argon, the overall efficiency increases from 17 to 43% (153% increase over that without any additives) for 0.35% SF₆ added plasma, at a power input of 27 kW as shown in Figure 14. At 80 kW, the efficiency increment is only 74% (from 19 to 33%), as illustrated in Figure 14.

The CF₄ added plasma gives rise to higher overall efficiencies at lower power inputs and lower efficiencies at higher power inputs, compared to the non-additive plasma as shown in Figure 14. In this Figure, this crossover occurs for the CF₄ added plasma at a power input of 65 kW, for the experimental condition of 0.50% CF₄ in 220 SCFH of argon at 40 mm Hg. For this power input of 65 kW, the corresponding nozzle-entrance temperature of 10,300°C can be read from Figure 12 for the above experimental condition.

(5) Anode Heat Losses. The plots of anode losses (%) against power input with and without the electrophilic additives follow different trends. Without any additives, the anode losses as a percentage of the
Fig. 13. Overall Efficiency Vs Power Input without any Additives
ARGON FLOW RATE: 220 SCFH
TANK PRESSURE: 40 mm Hg

- ▲ 0.35% SF
- • 0.5% CF
- ■ No Additive

Fig. 14. Overall Efficiency Vs Power Input at 220 SCFH
total power input are highest at the lowest power input level and they
tend to decrease with increasing power input, as illustrated in Figure 15.
However, with the additives - SF\textsubscript{6} and CF\textsubscript{4} - the anode losses are lowest
at the lowest power input, they increase with increasing power input to
a maximum and are not very sensitive to further increases in power input,
as illustrated in Figure 15.

The anode losses with the additives are generally lower than those
without the additives at low power inputs and higher at higher power in­
put levels. For example, in Figure 15, the anode losses are lower with
SF\textsubscript{6} up to 80 kW and with CF\textsubscript{4} up to 40 kW, compared to the non-additive
plasma. Above these power input levels the anode losses are higher than
those without the additives.

The above mentioned trends in the anode losses with the additives
are attributable to the following phenomena. For any given power input
level, the free electron density in the plasma and the arc current are
reduced by the addition of SF\textsubscript{6} or CF\textsubscript{4} into the arc. Consequently, the
joule heating at the anode region (roughly proportional to the square
of the arc current) as well as the energy released to the anode electrode
due to such phenomena as electron bombardment (roughly proportional to
the free electron density) are reduced. On the other hand, the presence
of the electrophilic additives gives a higher temperature plasma and,
therefore, leads to increased heat transfer to the anode. At the lower
power inputs, the effects of the reduced free electron density and arc
current dominate and there is, therefore, a net reduction of the anode heat
losses. However, at the higher power inputs the heat transfer becomes
predominant and there is, therefore, an increase in the anode losses over
ARGON FLOW: 220 SCFH
TANK PRESSURE: 40 mm Hg

- □ NO ADDITIVE, ANODE
- ▲ 0.35% SF₆, ANODE
- ● 0.25% CF₄, ANODE

Fig. 15. Anode Losses Vs Power Input at 220 SCFH
those without any additives.

(6) Cable, Cathode, and Nozzle Losses. Because of the lower arc currents in the presence of the electrophilic additives, for any given power input, the cable losses are much lower (as much as 50% less) than those without any additives. Also, with and without the additives, the cable losses increase with increasing power input (and arc current). It is worthwhile to note that the cable losses can be a significant fraction of the total power available (as high as 20% at high power levels).

The cathode losses as a percentage of the total power input are highest at the lowest power input, with and without the additives, as illustrated in Figure 16. The cathode losses are found to be much lower (as much as 30 to 40%) with the additives - SF\textsubscript{6} as well as CF\textsubscript{4} - compared to those without the additives, as shown in Figure 16.

The nozzle losses are found to be inexplicably lower with SF\textsubscript{6} and higher with CF\textsubscript{4} addition, at all power input levels, compared to the non-additive plasma, as shown in Figure 17. The nozzle losses as a percentage of the power input, with and without the additives, are found to decrease with increasing power input and reach an asymptotic value.

The Effect of Varying the Electrophilic Additive Flow Rate

At a fixed tank pressure of 40 mm Hg and an argon flow rate of 220 SCFH, when the CF\textsubscript{4} flow rate is doubled from 0.25 to 0.50% by volume of argon, some increases in the overall efficiency (and therefore in the enthalpies) are obtained, as shown in Figure 18. However, even an increase in CF\textsubscript{4} flow rate results in efficiency decrements at higher power inputs. The changes in the arc voltage are slight, as seen in Figure 6.
Fig. 16. Cathode Losses Vs Power Input at 220 SCFH

Fig. 17. Nozzle Losses Vs Power Input at 220 SCFH
Fig. 18. Overall Efficiency Vs Power Input with CF$_4$ at 220 SCFH
At a fixed tank pressure of 40 mm Hg and an argon flow rate of 220 SCFH, when the SF$_6$ flow rate is doubled from 0.35 to 0.70% by volume of argon, a higher arc voltage is obtained as shown in Figure 7. The overall efficiency for the 0.70% SF$_6$ case, however, is lower than that for the 0.35% SF$_6$ added plasma, as shown in Figure 19. When the SF$_6$ flow rate is tripled to 1.05% by volume of argon, substantially higher arc voltages are obtained, as shown in Figure 7. However, with this 1.05% SF$_6$, lower efficiency (therefore lower enthalpy) is obtained at lower power inputs and higher efficiency at higher power inputs, compared to the case of 0.35% SF$_6$, as shown in Figure 19.

In a 290 SCFH argon plasma at 4.5 mm Hg, when the SF$_6$ flow rate is doubled from 0.35 to 0.70%, lower arc voltages are seen at lower arc currents, as shown in Figure 20. The overall efficiency is also lower at lower power inputs compared to the 0.35% SF$_6$ case, as shown in Figure 21. The arc becomes unstable at some of the regions intermediate to the data points presented for this 0.70% SF$_6$ addition. When the SF$_6$ flow rate is further increased to 1.05% by volume of 290 SCFH of argon at 4.5 mm Hg, the arc becomes unstable.

In general, addition of SF$_6$ at flow rates higher than 0.35% by volume of argon in the present experiments does not result in any further improvement in the attainable enthalpy and efficiency levels. Furthermore, higher additive flow rates result in the dissociated products of SF$_6$ reacting with Cu and coating the anode and nozzle surfaces.

The Effect of Varying the Arc Gas Flow Rate

This section discusses the effect of varying the argon flow rate from 220 to 290 SCFH on the non-additive plasma and on SF$_6$ and CF$_4$ added
ARGON FLOW RATE: 220 SCFH
TANK PRESSURE: 40 mm Hg
ADDITIVE: SF₆

0.35%
0.70%
1.05%
NO ADDITIVE

Fig. 19. Overall Efficiency Vs Power Input with SF₆ at 220 SCFH
ARGON FLOW: 290 SCFH
TANK PRESSURE: 4.5 mm Hg

ADDITIVE: SF$_6$
- 0.70% SF$_6$
- 0.35% SF$_6$
- NO ADDITIVE

**Fig. 20.** Arc Voltage Vs Arc Current with SF$_6$ at 290 SCFH
**Fig. 21. Overall Efficiency Vs Power Input**

with SF₆ at 290 SCFH
plasmas for fixed additive flow rates.

In a non-additive plasma, when the argon flow rate is increased from 220 to 290 SCFH at a fixed tank pressure of 4.5 mm Hg, the arc operates at a higher arc voltage as shown in Figure 5. Increasing the arc gas flow rate lowers the power input per unit mass and hence the enthalpy of the gas. As a result the arc column conductivity decreases and the arc voltage is higher. However, for any given power input, lower efficiency (therefore lower nozzle-exit enthalpy) is obtained, as illustrated in Figure 13. The higher flow rate also gives higher anode and nozzle losses.

With SF6 as the additive, when the argon flow rate is increased by 32% (from 220 to 290 SCFH) at a fixed tank pressure of 4.5 mm Hg, the changes that occur in the operating arc voltage for 0.35% SF6 addition are shown in Figure 4. In general, lower specific enthalpies are obtained with higher argon flow rates. However, the overall efficiency increases when the argon flow rate is increased, as illustrated in Figure 22. Lower specific enthalpy implies a lower plasma temperature and lower degree of ionization. Since the effectiveness of the electrophilic additives increases with decreasing temperature, SF6 is more effective at the higher argon mass flow rate resulting in higher overall efficiency.

The Effect of Varying the Exhaust Tank Pressure

In this section, the effect of varying the exhaust tank pressure from 4.5 to 40 mm Hg on the non-additive plasma and the SF6 added plasma is discussed, for fixed argon flow rates.

Without any additives, when the tank pressure is increased from 4.5 to 40 mm Hg, the arc operates at a higher arc voltage, as shown in Figure 5. Increasing the pressure also increases the heat transfer
ADDITIVE: 0.35% SF₆

- ▲ 220 SCFH, 4.5 mm Hg
- ■ 220 SCFH, 40 mm Hg
- □ 290 SCFH, 4.5 mm Hg
- ○ 220 SCFH, 40 mm Hg, NO ADDITIVE
- ★ 290 SCFH, 4.5 mm Hg, NO ADDITIVE

Fig. 22. Overall Efficiency Vs Power Input with 0.35% SF₆
to the anode and nozzle surfaces and, hence, higher anode and nozzle coolant losses are obtained. This results in lower efficiencies (and therefore lower enthalpies) as shown in Figure 13.

With SF$_6$ as the electrophilic additive, when the pressure is raised from 4.5 to 40 mm Hg, some changes in arc voltage (Figure 4) and anode losses are seen. Nozzle losses are found to be higher at lower power inputs and lower at higher power inputs, compared to those at the lower pressure. However, an increase in pressure increases the overall efficiency (and therefore the nozzle-exit enthalpy) for the SF$_6$ added plasma, as illustrated in Figure 22. The degree of ionization decreases with increasing pressure. This may be the reason that the SF$_6$ added plasma is more efficient at the higher pressure (for a fixed additive flow rate) unlike that found with the non-additive plasma.

**Type and Temperature Limit of Existence of Negative Ions**

The significant changes in the performance of the plasma arc, resulting from the presence of the electrophilic additives, suggest that negative ions are present over the operating range of the experiments (5600°K and above). The electrophilic additives SF$_6$ and CF$_4$ are most probably dissociated completely, from collisions with the neutrals and argon ions, before the negative ions are formed. The negative ion formation in the present experiments can be any or a combination of the processes: (a) radiative process; (b) negative ion formation in the presence of a third body; and, (c) dissociative process.

Sulphur hexafluoride is composed of one sulphur and six fluorine atoms and carbon tetrafluoride has one carbon and four fluorine atoms. Recalling from Chapter II, the electron affinity of the fluorine atom
is 3.45 ev, sulphur atom 2.08 ev, and carbon atom 1.25 ev. The possibility of formation of one S\(^-\) and six F\(^-\) negative ions from SF\(_6\) compared to only four F\(^-\) and one C\(^-\) from CF\(_4\) is the probable reason for the superior performance of SF\(_6\) over CF\(_4\) as an electrophilic additive.

Recalling from Chapter II, S\(^-\) and F\(^-\) ions are found to exist theoretically (at one atmosphere pressure) in the range of 5000° to 12,500°K and 273° to 17,500°K, respectively (88,89). In the present experiments, substantial increments in the operating arc voltage in the presence of the electrophilic additives are obtained up to average plenum chamber temperatures of 12,200°K for SF\(_6\) and 11,600°K for CF\(_4\). (The arc column temperatures are even higher.) This shows that negative ions are forming up to these temperatures. However, the increments in arc voltage, enthalpy, and efficiency at higher temperatures decrease with increase in temperature. This suggests that only insufficient amounts of negative ions are forming at higher temperatures. Therefore, there is a temperature limit up to which negative ions F\(^-\), S\(^-\), and C\(^-\) can form in substantial quantities. This temperature limit cannot be distinctly defined on the basis of the present experiments. However, this temperature limit may be in the vicinity of 12,000°K.
CHAPTER VI

CONCLUSIONS

The experiments reaffirmed that the fundamental reason for the enthalpy and efficiency limits of plasma arc jets is the high electrical conductivity of the arc column plasma and its rapid increase with increasing temperature. Injection of minute quantities of electrophilic additives (less than 1% by volume of the arc gas) is extremely effective in reducing the arc column conductivity and increasing the attainable enthalpy and efficiency levels. Sulphur hexafluoride is much superior to carbon tetrafluoride in improving the enthalpy and efficiency levels.

The improvement in enthalpy and efficiency at higher temperatures decreases with increase in temperature. SF₆ is most effective at the lowest temperature studied (5500°K) and least effective at the highest (12,000°K). (The degree of ionization in argon is around 33% at 12,000°K and 90 mm Hg.) CF₄ addition increases the efficiency and enthalpy levels up to a temperature of about 10,000°K; however, CF₄ is unsuccessful in raising these levels above this temperature level. With the additives the efficiency is highest at the lowest power input and temperature, unlike the tendency found without any additives. For the experiments conducted, the best electrophilic additive flow rates for improving the enthalpy and efficiency levels are 0.35% by volume of argon for SF₆ and 0.50% for CF₄. Addition of 0.35% SF₆ by volume of 220 SCFH of argon increases the attainable plasma arc jet enthalpy from 2200 to 3800 BTU/lb and the overall efficiency from 19 to 33% (74% increase) at a power input
of 80 kW and the overall efficiency from 17 to 43% (153% increase) for a power input of 27 kW.

The voltage current characteristic of the arc is found to be very strongly dependent on the presence of the electrophilic additives in the arc column plasma. A substantial increase in the operating arc voltage is seen with either SF6 or CF4 for any given power input, with the CF4 added plasma exhibiting higher arc voltages than the SF6 added plasma in the arc mode (positive characteristic). With CF4 and without any additives, the arcs operate in the arc mode. However, with SF6 the arc operates both in the arc and normal (negative characteristic) modes. For the SF6 added plasma, the largest voltage occurs at the lowest arc current (in the normal mode), unlike that found for the CF4 and non-additive plasmas at the highest arc current. The increment in the arc voltage with SF6 decreases with increasing power input and temperature.

The significant changes in the performance of the arc resulting from the injection of the electrophilic additives suggest that the free electrons in the arc column plasma are being replaced by negative ions of low mobility which are formed from SF6 and CF4. The decrease in the increments in the arc voltage, enthalpy, and efficiency at higher temperatures with increasing power input and temperature seen with SF6 and CF4 shows that there is a temperature limit up to which large quantities of negative ions can exist.

For any given power input, the presence of the electrophilic additives results in lower cathode (30 to 40% less) and cable (as much as 50% less) heat losses. Nozzle heat losses are higher with CF4 and lower with SF6, compared to the non-additive plasma. Anode heat losses
are lower with SF$_6$ and CF$_4$ at lower power inputs and temperatures and higher at higher power inputs.

Increasing either the arc gas flow rate by 32% or the exhaust tank pressure from 4.5 to 40 mm Hg results in a reduction of the degree of ionization of argon and, therefore, in an increase in efficiency in the presence of the additives and a decrease in their absence.

Mild fluctuations, increasing with increasing amounts of electrophilic additives, occur in the operating arc voltage and current in the presence of both SF$_6$ and CF$_4$. Products of dissociation of SF$_6$ react with the copper anode and nozzle and form thin electrically insulating layers on the nozzle and downstream portions of the anode surface at SF$_6$ flow rates of 0.70% and above by volume of argon. Carbon deposits on the nozzle surface form at CF$_4$ flow rates of 0.60% and above. Increasing amounts of the electrophilic additives (about 1.5%) lead to the quenching of the arc at lower power inputs. Unstable arcs can result at certain operating conditions and additive flow rates.
CHAPTER VII

RECOMMENDATIONS

The present investigation points out a number of areas worthy of future investigation. Oscillations in the operating arc voltage and current as well as unstable arcs are seen under certain operating conditions in the presence of electrophilic additives in the plasma. The lower electrical conductivity and higher operating arc voltage in the presence of SF$_6$ and CF$_4$ will result in a different operating arc configuration. Therefore studies of the electrophilic additive present plasmas in other electrode configurations would be helpful in determining the best arc operating set up as well as in understanding the oscillations and instability.

In the present case, the flow medium is argon. Further studies should be conducted with other arc gases as well as other electrophilic additives. Especially, studies with simulated air are helpful in many practical applications.

In the present investigation, the arcs operate only in the arc mode with CF$_4$ and without any additives. However, with SF$_6$ as the additive the arc operates both in the normal and arc modes. Further studies are required to understand the reasons for this behavior.

The changes in the increments in the operating arc voltage, enthalpy, efficiency and temperature as well as in the cathode, anode and nozzle coolant losses with varying power input are markedly different for SF$_6$ and CF$_4$ added plasmas. This area needs further studies
to understand the difference in their behavior. Studies into the mechanism of negative ion formation as well as the types of negative ions formed from SF$_6$ and CF$_4$ and their temperature dependence are necessary to understand the above mentioned behavior.

The nozzle coolant losses in the present investigation with SF$_6$ behave in an inexplicable manner. This point needs further understanding.

Number density of the electrons, positive ions and negative ions are difficult to measure. However, recent efforts at Georgia Tech in the use of electrostatic probes (7) indicate that it would be possible to measure these densities under certain operating conditions. Such studies would be helpful to the understanding of the arc plasma in the presence of electrophilic additives.

In addition, the determination of the composition and properties - physical, chemical, and electrical - of the coatings formed by the dissociated products of the electrophilic additives on the electrode and nozzle surfaces would be useful for a better understanding of the behavior of the coatings and their effect on the performance of the plasma arc jet.
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VITA

Poozhikala Chacko Zachariah was born of Reverend P. C. Zachariah and Mrs. Elizaba Zachariah on June 6, 1946 in the beautiful city of Trivandrum, India. He graduated from the Model High School in Trivandrum in 1962 and completed his Pre-University course at the University Intermediate College, Trivandrum in 1963 (under the University of Kerala). He received his B.Sc. degree in Mechanical Engineering from the University of Kerala in 1968 and his M.Tech. degree in Aeronautical Engineering, with specialization in combustion and propulsion, from the Indian Institute of Technology, Madras, India in 1970. In the fall of 1970 he entered Georgia Institute of Technology to work toward his Ph.D.

At Georgia Tech, he served as a graduate research assistant in the School of Aerospace Engineering from September 1970 to March 1975. He is serving as a graduate dormitory counselor for the Office of Housing at Georgia Tech. While still in India, he was inducted as a President's Scout by the President of India. He is a member of the Nuclear and Plasma Sciences Society of the IEEE and the International Combustion Institute. He is also a charter member of the Georgia Tech Lion's Club.

He has two brothers, Mammen and Zachariah, and a sister, Mary.