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University of Arizona, Ph.D., 1966
Physics, electronics and electricity

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THE EFFECT OF IMPURITY GAS ON THE OPERATION OF A
THERMIONIC CESIUM DIODE

by

Charles Edward Backus

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF NUCLEAR ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

1966
I hereby recommend that this dissertation prepared under my
direction by Charles Edward Backus
entitled The Effect of Impurity Gas on the Operation of a
Thermionic Cesium Diode
be accepted as fulfilling the dissertation requirement of the
degree of Doctor of Philosophy

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ACKNOWLEDGMENTS

The author would like to express his very deep gratitude to Dr. Monte V. Davis. If it were not for the constant encouragement of Dr. Davis, this investigation would have been abandoned at several points during the two and one half years of experimental difficulties.

A special thanks is due to Mr. David M. Turner for his help and useful discussions. Others that were helpful in the laboratory include John F. Bregar, Paul S. Pickard, and Glen A. Bernabei.

The author would like to acknowledge the Department of Nuclear Engineering for providing facilities for this research. Support and equipment for the investigation were provided by the Office of Naval Research.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>vi</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ix</td>
</tr>
</tbody>
</table>

## CHAPTER 1 - Introduction
- General: 1
- Thermionic Systems: 3
- Nuclear Thermionic Systems: 6
- Nuclear Challenges: 11
- Research Objective: 15

## CHAPTER 2 - Recent Research on Impurities: 17

## CHAPTER 3 - Analytical Considerations
- Fission Product Gases: 20
- "Arc Mode" Cesium Diode: 23
- Effect of Inert Gases: 28
- Effect of Iodine: 30

## CHAPTER 4 - Experimental Procedure
- General: 32
- Diode Construction: 32
- Diode Assembly Procedure: 35
- Heating of Emitter: 37
- Data Recording Technique: 39
- Preliminary Data Procedure: 41
- Data Procedure: 45

## CHAPTER 5 - Results and Conclusions
- Effect of Inert Gas: 48
- The Effect of Iodine: 58
- Post Analysis of the Electrode Surface: 65
- Conclusions: 66
- Recommendations for Further Investigation: 67
### Table of Contents - Continued

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Thermionic Conversion</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>The Cesium Plasma Diode</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Neutralization of Space Charge</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Detrimental Effects</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Current Status</td>
<td>82</td>
</tr>
<tr>
<td>B</td>
<td>Details of Experimental Equipment</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>List of Equipment Used to Record Data</td>
<td>86</td>
</tr>
<tr>
<td>C</td>
<td>Definition of Symbols</td>
<td>88</td>
</tr>
<tr>
<td>D</td>
<td>Purity of Gases</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>Cesium</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>Krypton</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>Xenon</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>Iodine</td>
<td>93</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic of Thermionic Concepts</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Typical In-Core Fuel Element</td>
<td>12</td>
</tr>
<tr>
<td>3a</td>
<td>Ideal Diode Curve</td>
<td>25</td>
</tr>
<tr>
<td>3b</td>
<td>Motive Diagram for Arc Mode</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>Schematic of Diode System</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>Photograph of Diode System</td>
<td>36</td>
</tr>
<tr>
<td>6</td>
<td>Heating Circuit</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>Measuring Circuit</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>Comparison of Methods (static and dynamic) used to Obtain Diode Curves</td>
<td>42</td>
</tr>
<tr>
<td>9a</td>
<td>Inert Gas Manifold</td>
<td>43</td>
</tr>
<tr>
<td>9b</td>
<td>Iodine Gas Manifold</td>
<td>44</td>
</tr>
<tr>
<td>10</td>
<td>Cesium Dependency</td>
<td>46</td>
</tr>
<tr>
<td>11</td>
<td>Effect of Argon</td>
<td>49</td>
</tr>
<tr>
<td>12</td>
<td>Effect of Krypton</td>
<td>50</td>
</tr>
<tr>
<td>13</td>
<td>Effect of Xenon</td>
<td>51</td>
</tr>
<tr>
<td>14</td>
<td>Comparison of Argon Data with Bullis' Data</td>
<td>53</td>
</tr>
<tr>
<td>15</td>
<td>Inert Gas Cross-sections</td>
<td>54</td>
</tr>
<tr>
<td>16</td>
<td>Variation of Electron Temperature</td>
<td>55</td>
</tr>
<tr>
<td>17</td>
<td>Method of Determining Electron Temperature</td>
<td>56</td>
</tr>
<tr>
<td>18</td>
<td>Effect of Iodine</td>
<td>59</td>
</tr>
<tr>
<td>19</td>
<td>Change of Operating Mode with Iodine Addition</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td>Representation of Iodine</td>
<td>62</td>
</tr>
<tr>
<td>21</td>
<td>Photomicrograph of Damage to Ta Surface</td>
<td>66</td>
</tr>
<tr>
<td>22</td>
<td>Schematic Diagram of Thermionic Converters</td>
<td>69</td>
</tr>
<tr>
<td>23</td>
<td>Hydroelectric Analogy of Thermionic Energy Conversion</td>
<td>70</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES. Continued**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>Electron Potential Energy Diagram for the Ideal Thermionic Converter</td>
<td>72</td>
</tr>
<tr>
<td>25</td>
<td>Output Characteristics for Ideal Converter</td>
<td>74</td>
</tr>
<tr>
<td>26</td>
<td>Relation Between Bare and Cesiated Work Function</td>
<td>77</td>
</tr>
<tr>
<td>27</td>
<td>Mode Diagram for a Diode in Which $\phi_e &gt; \phi_n$</td>
<td>81</td>
</tr>
<tr>
<td>28</td>
<td>Ideal Diode Characteristics With a Patchy Emitter</td>
<td>83</td>
</tr>
<tr>
<td>29</td>
<td>Emitter and Collector</td>
<td>87</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Summary of Anticipated Systems Characteristics</td>
<td>8</td>
</tr>
<tr>
<td>II</td>
<td>Results of Fendley's Experiments</td>
<td>17</td>
</tr>
<tr>
<td>III</td>
<td>Results of Kaplan Experiment</td>
<td>18</td>
</tr>
<tr>
<td>IV</td>
<td>Major Fission Products</td>
<td>21</td>
</tr>
<tr>
<td>V</td>
<td>Fission Products That May Escape The Fuel</td>
<td>22</td>
</tr>
</tbody>
</table>
ABSTRACT

The effects of overpressures of argon, krypton, xenon and iodine on a cesium diode operating in the arc mode were determined. The gases krypton, xenon, and iodine are of interest because they are the only fission products that are gases.

The thermionic diode used in this investigation was a planar converter with a 30 mil spacing, a tantalum emitter and nickel collector. The conditions of the experiment were chosen to be typical for in-core thermionic diodes. The emitter was held at 1850°K and the cesium temperature was at its optimum point of 230°C corresponding to a cesium pressure of 1 torr. The converter operated in the arc mode with an output of about 5 amps/cm² short circuit and about 1.4 watts/cm² maximum power density.

The diode was very tolerant of the addition of the inert gases. All of these gases had a detrimental effect on the diode but required several times the pressure of the cesium to have a significant effect. Argon had the least effect on the diode, reducing the power of the diode to 55% of its original value at a pressure of 30 torr. The krypton gradually reduced the diode power until it was 25% of its original value at a krypton pressure of 30 torr. The xenon extinguished the arc in the diode at a pressure of about 8 torr. This effect of the respective inert gases is a reflection of their electron scattering cross-sections.

By assuming that the effect of the inert gases is only to increase the scattering collisions, their effect can be calculated from the transport equation. The good agreement of the
calculated and experimental results supports the validity of the assumption that the inert gases act only as a diffusion barrier.

The iodine changed the work function of the emitter and also changed the mode of operation from the arc mode to an ion rich mode. The diode power increased with iodine addition until a vapor pressure of about 40 torr. At this point the diode power was 2.1 times the initial power. The output power then decreased with additional iodine pressure until it reached its initial power level at about 120 torr of iodine pressure.
Chapter 1

INTRODUCTION

General

One of the more challenging areas in the field of nuclear engineering today is that aimed at coupling a nuclear reactor with a system for the direct conversion of heat to electricity. The unique method by which heat is produced in a nuclear reactor has many advantages which have not been utilized up to the present. The nuclear power plant of today simply uses a reactor as a new heat source replacing coal or oil. Since the energy conversion equipment (heat exchangers, steam turbines, and generators) is the same as for the fossil fuel plants, the nuclear system is still limited to roughly the same size and efficiency. Nuclear fuel is capable of reducing the cost of electrical power, but it does not do it by appreciably reducing the size or by increasing the efficiency of the plant.

Several methods are under development to eliminate the bulky conversion equipment by converting the heat directly into electrical energy. These methods have the possibility of providing electrical power-plants which are small, efficient, and economical. Their properties also make them attractive for special purpose power sources. Of the many direct conversion processes suggested (thermoelectrics, thermionics, magneto-hydrodynamics, fuel cells, etc.), thermionics is the process currently receiving the most attention. It promises to have the highest efficiency of all direct-conversion schemes.\(^1\)
In its most elementary form, a thermionic converter* consists of two electrodes in a vacuum, separated by an electrical insulator. One electrode (the emitter) is heated to a temperature at which it emits electrons thermionically while the other electrode (the collector) is cooled. The electrons boil off of the emitter and flow to the collector. By electrically connecting the emitter and collector the electrons are passed through an external load to perform useful work.

Although Thomas Edison first observed the emission of electrons from hot lamp filaments more than 80 years ago, thermionic emission was not considered as a heat conversion process until very recently. In 1957 and 1958 there appeared some publications which suggested the use of thermionics in a thermoelectron engine.\(^{(2,3,4,5)}\) Interest quickly grew from these publications and several industrial firms established research programs in thermionics and soon received government support. Today there is a rather extensive effort in this country to understand and develop thermionic systems.

Early thermionic devices produced little power because the space charge that developed between the emitter and the collector retarded the electron flow. This space charge made it impossible to obtain current densities of the order of amperes/cm\(^2\) which will be required in practical systems. Techniques which have been used to reduce electron space charge effects include: close emitter-collector spacing (\(~0.0002\) inches), accelerating electric and magnetic fields, and the introduction of positive ions, such as cesium, into the inter-electrode space.

*Refer to Appendix A for more detail
Research has shown that the most attractive technique is the introduction of cesium vapor. Cesium produces positive ions, since it is so readily ionized (3.89 volts), either by surface ionization at the hot emitter or by electron collisions in the interelectrode space. Cesium also serves the important function of providing a partial coating on the emitter. This coating provides a control on the emission properties as well as furnishing a replenishing surface for a long-lived device. With the development of the vapor thermionic converters, outputs of 20 watts/cm\(^2\) and efficiencies of over 15 percent were soon achieved. As a result of the advantages of cesium converters the research has been concentrated on what are called cesium plasma diodes.

**Thermionic Systems**

When thermionic converters are investigated for integration into a complete electrical power unit, it is found that they possess many advantages and present many problems. The major potential advantages of a thermionic system are:

1. Static operation
2. Compactness
3. High temperature operation
4. High power densities

The static operation of the process means that no moving parts would be required. This infers that it has the potential of being highly reliable since there would be no parts wearing out or needing continuous maintenance. Thus these converters are well suited for operation in isolated areas (e.g. Arctic regions, ocean floors, outer space, etc.) where little or no maintenance is available. The operation being static also makes it silent. This is an important advantage in certain applications such as in submarines where operating noise is used by an enemy as a means of detection.

Compactness mainly results in a lower specific weight for the system. This is not particularly important for central
station power plants but it becomes tremendously important for systems which must be airborne or propelled into space. When one considers that it costs in the order of $1000-5000 for each pound of weight put into earth orbit the advantage of compactness is realized. Thermionics may make feasible missions that have been prohibited up to now because of system weight.

The Carnot efficiency of a thermionic converter system is naturally high because of the high working temperatures. A thermionic system is not restricted by the temperature limitations on components such as a steam turbine. It is only limited by its static components. Besides operating at high temperatures it also provides high temperature heat rejection (\(\sim 600^\circ\text{C}\)). This suggests a thermionic "topping" system in connection with a conventional power plant. In this combined plant the heat rejected from the thermionic converter is used to produce steam for a conventional turbine system. Efficiencies of 50 to 60% have been estimated for these systems.\(^7\) Another advantage of high temperature heat rejection is in space, where the only means of heat transfer is by radiation. The amount of heat transferred from a radiator in space \(^8\) is proportional to \(AT^4\), where \(A\) is the area of the radiator and \(T\) is its absolute temperature. One can see that if the radiator temperature, i.e. the heat rejection temperature, is doubled, then the area of the radiator, \(A\), could be decreased by a factor of 16 and still transfer the same amount of heat (assuming constant emissivity). This would greatly decrease the weight of the system and also decrease the meteoroid collision hazard.\(^9\)

The high power density operation in a thermionic device makes it appear attractive to couple this converter with a high density heat source such as nuclear or solar power.

Although thermionics promises all of the above advantages when incorporated into a system, it also presents many problems. For instance, the thermionic converter operates
efficiently with a direct current output of about 1 volt. Since most electrical equipment cannot operate on 1 volt DC, some means must be provided to transform this output to higher voltages and perhaps change it to alternating current. One way of increasing the output voltage is to connect several diodes in series-parallel circuits. Holland has investigated this type of solution for a nuclear system and found it quite acceptable. The cost of a small diode is not much different from that of a large diode so one would only want a minimum number of diodes to put in series and parallel. A few could be put in series and then passed into an electronic inverter (90% efficient with 3 volt DC input) to convert to alternating current which can be transformed to higher voltages.

Perhaps the largest problem presented by thermionics is that of materials. Due to the high temperature of operation (1000-2000°C) the selection of construction materials is extremely limited. The refractory metals such as Ta, Mo, W, Re, and Ir and certain high temperature metals such as Ni, Cu and stainless steel are acceptable. The machining and forming properties of most of the refractory metals are extremely poor. Also the cost of these metals is high and their properties are not well known.

Another difficulty in obtaining a thermionic system is that the operating point of the diodes in the system will be determined by the best system performance and not by the optimum operating point of the diode. For instance, it may be desirable to operate the collector at a higher than optimum temperature in order to reduce the radiator weight, or to operate at a high power density to reduce the size of the power source. These types of considerations will lower the actual efficiency of the converter and tend to make it less competitive as a power system.

The advantages of a thermionic system are extremely attractive and the problems do not appear to be prohibitive.
There is a general feeling of optimism and enthusiasm among the men doing research in this field. One of these men summed up the future of thermionic systems in 1962.\(^{(11)}\)

"The particular forte of thermionic conversion is simplicity, high power density, and high heat rejection temperature. Also thermionic converters will probably achieve the high reliability, long lifetime and low unit cost which presently characterize the products of the electron tube industry. If the present rate of progress continues as expected, it is likely that thermionic conversion will maintain for some time to come its present status as the most efficient demonstrated static method for converting heat continuously into electrical power."

**Nuclear Thermionic Systems**

Soon after the first papers appeared on the prospect of a thermionic power converter, it was realized that a nuclear reactor had many advantages in common with it. A nuclear reactor can be static and compact, and can operate at high temperatures and power densities. The marriage of the nuclear power source with the thermionic heat converter seemed almost imminent. The first known direct conversion of nuclear reactor energy into electric power was reported in April, 1959 by the Los Alamos Scientific Laboratory.\(^{(12)}\) R. W. Pidd, who played a prominent role in this achievement, was so optimistic that he said that a thermionic research reactor could be in operation in two years.\(^{(12)}\) The problems discovered prevented the fulfillment of this prediction and in 1961, C. P. Stanford of the Martin Co. said that a thermionic-reactor system could be operating by 1966.\(^{(13)}\) Although this expectation is not too unreasonable, it appears very unlikely that it can be realized. Research in one area seems to uncover two more areas that need investigation. The national interest and effort has continued to grow and expand, but the work has largely remained in the research state.
From the analysis of the advantages of the nuclear-thermionic system and the state of development of each of the major components, one sees that the first application will be in one of two possible areas: as a "topping" system for a conventional power plant or as an auxiliary power source in space. There is interest in "topping" systems, but the greatest effort, and government support, is in the area of a space power source.

First, consider the power sources available for a space system. Batteries are best for short periods of time (a few days). For long periods, up to a year, photovoltaic (solar cells) units or direct conversion systems energized by solar or isotopic nuclear heat would be suitable but only for low power outputs of less than 100 watts. For large amounts of power (above 1 kw) and long time periods (1 year), the only reasonable source of power is the nuclear fission reactor. It seems inevitable that space vehicle users and designers will demand more power as our space missions become more ambitious. A fission reactor has already been used in space and it is now a matter of deciding which conversion system best suits the nuclear space environment.

Table I is a summary of the anticipated systems characteristics of the three leading contenders for a nuclear space system. The first converter used with a reactor in space was thermoelectric because of its high state of development and the relatively low power requirements of present day satellites. However, its specific weight is much too high for larger powered systems (1-10kw). The choice of the next type of converter in space will be conditioned by the rate of development of thermionics, but may be the turboelectric converter. Eventually, because of its light weight and high reliability, a nuclear thermionic system appears necessary.
<table>
<thead>
<tr>
<th>System</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turboelectric</td>
<td>Technology moderately developed</td>
<td>Startup difficult</td>
</tr>
<tr>
<td></td>
<td>Moderate reliability</td>
<td>Control difficult</td>
</tr>
<tr>
<td></td>
<td>Moderate weight</td>
<td>Untried working fluids required</td>
</tr>
<tr>
<td></td>
<td>(20 to 25 lbs/kw)</td>
<td>High temperature moving parts required</td>
</tr>
<tr>
<td></td>
<td>Moderate development potential</td>
<td>Complex testing required</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Large size</td>
</tr>
<tr>
<td>Thermoelectric</td>
<td>Highly reliable</td>
<td>Specific weights extremely high</td>
</tr>
<tr>
<td>Conversion</td>
<td>Mechanically static</td>
<td>(50 lb/kw)</td>
</tr>
<tr>
<td></td>
<td>Simple startup</td>
<td>Converters radiation sensitive</td>
</tr>
<tr>
<td></td>
<td>Simple control</td>
<td>Little development potential</td>
</tr>
<tr>
<td></td>
<td>Technology fairly well developed</td>
<td>Many temperature limitations</td>
</tr>
<tr>
<td></td>
<td>Simple testing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Compact</td>
<td></td>
</tr>
<tr>
<td>Thermionic Conversion</td>
<td>High potential reliability</td>
<td>Technology primitive</td>
</tr>
<tr>
<td></td>
<td>Light in weight</td>
<td>Reliability not yet demonstrated</td>
</tr>
<tr>
<td></td>
<td>(10 lb/kw)</td>
<td>High temperatures required</td>
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<tr>
<td></td>
<td>Mechanically static</td>
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<td>Simple control</td>
<td></td>
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<td>Simple testing</td>
<td></td>
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<tr>
<td></td>
<td>Large development potential</td>
<td></td>
</tr>
</tbody>
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There are a number of nuclear-thermionic systems which can be considered. They can be categorized as follows:

1. out-of-core converters, conduction heat source
2. out-of-core converters, convection heat source
3. in-core converters, conduction heat source

The first category would have the diodes affixed directly to the outside of the reactor core and the heat would be conducted from the core to the diodes (see Figure 1a). Part of this heat would be converted to electricity and part would be conducted to the outer surface and radiated into space. The proposed General Electric STAR-R reactor system is an example of this type of arrangement. This concept offers high reliability (completely static) but is restricted to low powers because of the limited radiator space and the requirement of extremely high temperatures in the center of the reactor core. Its specific weight would be around 60 lbs/Kw.

The second category, as seen in Figure 1b, would transfer the heat by forced convection from the reactor core to diodes mounted on heat exchanger tubes. This concept partially eliminates the disadvantages of the first concept, but requires that the entire system be maintained above the emitter temperature. Liquid metal coolants (the only coolants feasible for this application) cannot be successfully operated above about 1200°C, which is a point of small output and efficiency for thermionic diodes. Also an electromagnetic pump, which is the best pump for such applications, cannot be operated above 1100°C because the Curie point of any material is exceeded.

The in-core conversion system (Figure 1c) utilizes the liquid metal coolant at collector temperatures (600-700°C) instead of at the emitter temperature. This operating temperature presents no problem for the fluid, the pump, or the heat exchangers. A cross-section schematic of a typical fuel element for
Neutron Reflectors

Reactor Core (Solid)

Thermionic Converter Cells

Heat Rejection Surface

Cesium Reservoirs

Electrical Insulation

a. Out-of-Core
   Conduction Cooled Concept

b. Convection Out-of-Core Concept

Rotating Pump

Heat Exchange Tubes

Electrical Insulation

Thermionic Converter Cells

Cesium Reservoirs

Radiator

Cesium Reservoir

Heat Rejection Surface

Electromagnetic Pump

Reactor (Converters in Core, Convection Cooled)

c. Convection In-Core Concept

Figure 1 - Schematics of Thermionic Concepts(22)
this concept is shown in Figure 2.\(^{(25)}\) The emitter tempera-
ture is limited only by the maximum permissible fuel tempera-
ture which may be as high as 1800°C. Studies show a specific
weight for this concept to be 5 lb/Kw.\(^{(26)}\)

Nuclear Challenges

With the advantages of the in-core, nuclear-thermionic
system, it seems desirable to make a considerable effort toward
the realization of a practical system of this kind. This con-
cept presents many challenges for the nuclear engineer. Research
and development for a reactor that will operate in the space
enviroment has been in progress for the last several years at
Atomics International. The problems (size, weight, etc.) of
building and operating such a reactor have, for the most part,
been solved.\(^{(27)}\) However, the additional problems of operating
thermionic diodes inside a reactor core are just in the early
research stage.

The design of this reactor is determined by the system
requirements and not primarily by nuclear considerations. For
instance, once the power output has been specified and the
converter operating point has been experimentally established,
the power emission per unit area of emitter will be known and
thus the fuel surface area required. This area restriction
sets a lower limit on core size.

The reactor would most likely have to operate with a
fast energy spectrum of neutrons since the materials of the diode
possess high absorption cross sections for neutrons with thermal
energies. Also, the fast reactor provides for long life at high
power since the system is relatively insensitive to fuel burn-up
and fission product poisoning.

The nuclear engineer must now consider many questions.
What amount of uranium or other fuel is required to achieve
criticality with all of the foreign materials and voids
Figure 2 - Typical In-Core Fuel Element (25)
in the core? What are the highest temperatures that various reactor fuels can operate at and for how long? What about the compatibility of fuels with their cladding materials at these temperatures? By what means is the reactor started up and controlled? Are the cladding materials or the fuels compatible with cesium at high temperatures? What happens to the electrical insulators in the cesium atmosphere and in the high irradiation field? What can be done about the build-up and release of gaseous fission products? These are only a few of the questions that must be answered by researchers before a nuclear thermionic reactor can be built.

Of the questions posed above, consider the last one in more detail. Fission results in the replacement of a uranium atom with two new atoms (fission products). These two atoms require more space than the original site of the uranium and this results in internal stresses and pressures building up inside the fuel element. At the temperatures that the fuel must operate in a thermionic system, many of these new atoms will be gases (about 42%). As gases they will diffuse through the fuel element and build up pressures on the cladding container that may cause a swelling and distortion of the fuel element. This is one of the main factors which limits the burnup of fuel in terrestrial reactor systems. In a thermionic system this factor is considerably more limiting for three reasons. First, there is more distortion from the same fuel burnup because of the greater percentage of gaseous fission products at operating temperatures. Secondly, a slight distortion or swelling of the fuel element, and thus the emitter, could cause great changes in the operation of the diodes. And thirdly, the distortions could crack the electrical insulators which could result in complete system failure.
There are several possible ways of handling this problem. One solution would be to lower the emitter temperature and thus the diode efficiency and allow the element to deform. The limits on this deformation would still restrict fuel burnup to low values. Another solution would be to include void volumes in fuel elements to keep stresses at a reasonable level. However, the resulting core size and shield weight may be too excessive.\(^{15}\)

The achievement of large fuel burnup and therefore lifetime, seems to require removal of the fission gases.\(^{29}\) One way of removing these fission gases is to vent each fuel element to space. The complication of the design needed for this may be tolerable but the main problem is the evaporation of the fuel material into space. Another way to do this may be to vent these gases to the interelectrode space or use a porous coating on the fuel material. An even more desirable design would be to eliminate the cladding material altogether and use the fuel material as the emitter. The carbides and borides look promising for this application.\(^{30}\) In these designs most of the fission products would come out of the fuel. In UC-ZrC it has been found that fission products which form stable carbides, such as ruthenium, rare earths, and molybdenum, will have more chance of remaining in the emitter, while the rest, such as silver, cadmium, iodine, tellurium, strontium, barium, and antimony, will be retained only to a small extent.\(^{31}\) Of the products that leave the emitter, some will immediately condense on the collector while others will remain as gases and yet others will be gettered by the cesium gas. The gaseous products will be free to leave the cell and can be removed by a number of ways.

Since the gaseous products will build up to some equilibrium pressure before removal equals production, the
effects of these impurity gases on converter operation is of great interest. These impurity gases may change the electron work functions of the electrodes and also cause serious back-scattering of the electrons from the emitter. The fission products remaining in the emitter (i.e. as carbides) and the fission products released from the emitter and condensed on the collector may have significant effects on the performance of the converter, but these will be evident only in in-pile tests over long periods of time.

The importance of the fission gas problem has stimulated the nuclear engineering department of the University of Arizona to establish a research program in this area. Another stimulus for this program has been some interesting experimental results obtained by N. S. Rasor concerning impurities in thermionic converters. In his work with various emitters it was found that molybdenum gave the best performance but not reproducible results. Tests led the researchers to suspect the cause to be impurities. A major effort was made to increase the purity of both the emitters and the cesium. As a consequence of this suppression of impurity effects the results were highly reproducible but there was a substantial reduction in performance. It is obvious from these experiments that a systematic approach to the effects of impurities is needed.

Objective

The object of this investigation is to determine how the output characteristics of a cesium diode are affected by the overpressure of various gases. The primary gases of interest are those that originate from the fission process. To make the results of this investigation meaningful for an ultimate diode in a nuclear system, it was necessary to construct a diode that would be typical in such an application.
This means that it needs to be of engineering size with typical materials operating at expected temperatures. The gases investigated include: argon, krypton, xenon, and iodine.
Chapter 2

RECENT RESEARCH ON IMPURITIES

When this investigation was initiated in 1962 no data had been reported in this area of study. During the course of the investigation three papers have been published which have reported data of interest.

In October 1963, J. R. Fendley(32) (RCA) reported the addition of xenon to his diode system. Fendley's diode consisted of a molybdenum emitter (1200°C) and a nickel collector (600°C) with a 31 mil spacing. Xenon was introduced at 20 and 50 torr. He described the data as follows:

"Twenty torr xenon pressure results in some loss of short circuit current, but note that the open circuit voltage has increased somewhat. At 50 torr, the effects are more pronounced. It has been found that arc mode cesium diodes have a remarkable tolerance for the inert gas xenon."

Although no data analysis was made in this report, one can summarize the data from the reported I-V curves in tabular form.

Table II

RESULTS OF FENDLEY'S EXPERIMENTS

<table>
<thead>
<tr>
<th>Xenon Pressure (torr)</th>
<th>Open Circuit Voltage (volts)</th>
<th>Peak Power (watts/cm²)</th>
<th>Increase In Power (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.2</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.3</td>
<td>1.1</td>
<td>31</td>
</tr>
<tr>
<td>50</td>
<td>0.4</td>
<td>1.0</td>
<td>19</td>
</tr>
</tbody>
</table>

17
In October 1964, C. Kaplan and J. B. Merzenich (Marquardt Corp.) also reported a xenon addition experiment. Xenon was introduced at only one pressure, 60 torr, but at two emitter temperatures with a variable spacing diode. The diode used an iridium emitter and a stainless steel collector. The spacing varied between 7 and 20 mils. Their results are given in the following table.

Table III
RESULTS OF KAPLAN EXPERIMENTS

<table>
<thead>
<tr>
<th>Emitter Temperature</th>
<th>Gas</th>
<th>Output Voltage (volts)</th>
<th>Output Power (watts/cm²)</th>
<th>Increase in Output Power (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1260</td>
<td>Cs</td>
<td>0.20</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>1260</td>
<td>Cs+Xe</td>
<td>0.20</td>
<td>3.0</td>
<td>75</td>
</tr>
<tr>
<td>1370</td>
<td>Cs</td>
<td>0.30</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>1370</td>
<td>Cs+Xe</td>
<td>0.30</td>
<td>7.35</td>
<td>45</td>
</tr>
</tbody>
</table>

These results are complicated by the fact that an optimization procedure was followed for each run. After the xenon was introduced the cesium reservoir temperature and the diode spacing were adjusted to optimize the output power. Therefore, the reported increase in power does not compare the output change for a given set of operating conditions. The conclusions for this paper are:

"At an emitter temperature of 1260°C a decrease in the emitter-collector spacing is required to obtain increased power output when xenon is added. At 1370°C, the maximum power output for both Cs and Cs+Xe occur at about the same electrode spacing........The reason for the observed increase in power output cannot be positively identified at the present time. However, the data seems to indicate that the increase in power output is due to a decrease in internal voltage loss required for the production of ions by volume ionization."
Both of the papers reviewed investigated the effect of a specific amount of xenon in low temperature converters. In a nuclear system the emitter temperatures will be in the 1800°-2000°K range in order to obtain reasonable output voltages and efficiencies. Also, all parameters will remain the same.

In March 1965, R. H. Bullis, et al., (United Aircraft Corp.) presented a paper on the addition of argon into a cesium converter. The primary purpose of this study was to measure the plasma properties by employing electrostatic probe techniques. The emitter temperature was 1477°K with a spacing of 82 mils. The arc-mode converter was operated with argon overpressures ranging from 4 to 61 torr. It was found that the maximum pressure at which the arc could be sustained in the interelectrode space of this converter was slightly above 61 torr.

The main conclusion by Bullis is to discount a proposed theory by Witting (35) that the dominant ionization process in the arc-mode converter is a multistage process which depends upon the formation of a cesium molecule in a double excited state to produce a cesium ion.

Since Bullis's investigation was primarily of the plasma properties rather than the output characteristics there was only one curve reported that was of particular interest. This curve showed the short circuit current of the diode as a function of the argon overpressure. This current gradually decreased with increasing pressure to about 40% of its initial value at 60 torr. (see Chapter 5)
Table IV

MAJOR FISSION PRODUCTS

<table>
<thead>
<tr>
<th>Element</th>
<th>% Yield</th>
<th>Boiling Point (°C)</th>
<th>Probable Final State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>30.1</td>
<td>2900</td>
<td>Remain in fuel</td>
</tr>
<tr>
<td>Mo</td>
<td>24.4</td>
<td>4800</td>
<td>Remain in fuel</td>
</tr>
<tr>
<td>Xe</td>
<td>21.8</td>
<td>-107.1</td>
<td>Gas</td>
</tr>
<tr>
<td>Cs</td>
<td>19.2</td>
<td>670</td>
<td>Vapor pressure-condense</td>
</tr>
<tr>
<td>Ce</td>
<td>18.4</td>
<td>1400</td>
<td>Condense on cool surface</td>
</tr>
<tr>
<td>Nd</td>
<td>15.5</td>
<td>(MP 840)</td>
<td>Remain in fuel</td>
</tr>
<tr>
<td>Ru</td>
<td>11.0</td>
<td>2700</td>
<td>Remain in fuel</td>
</tr>
<tr>
<td>St</td>
<td>9.3</td>
<td>1150</td>
<td>Condense on cool surface</td>
</tr>
<tr>
<td>La</td>
<td>6.6</td>
<td>(MP-820)</td>
<td>Remain in fuel</td>
</tr>
<tr>
<td>Pr</td>
<td>6.4</td>
<td>(MP-940)</td>
<td>Unknown</td>
</tr>
<tr>
<td>Te</td>
<td>6.1</td>
<td></td>
<td>Unknown</td>
</tr>
<tr>
<td>Ba</td>
<td>5.7</td>
<td>1140</td>
<td>Condense out</td>
</tr>
<tr>
<td>Y</td>
<td>4.8</td>
<td>2500</td>
<td>Remain in fuel</td>
</tr>
<tr>
<td>Kr</td>
<td>3.9</td>
<td>-152.9</td>
<td>Gas</td>
</tr>
<tr>
<td>Rb</td>
<td>3.5</td>
<td>700</td>
<td>Vapor pressure-condense</td>
</tr>
<tr>
<td>Rh</td>
<td>3.0</td>
<td>2500</td>
<td>Remain in fuel</td>
</tr>
<tr>
<td>Tl</td>
<td>2.4</td>
<td>1390</td>
<td>Condense out</td>
</tr>
<tr>
<td>Pr</td>
<td>2.4</td>
<td></td>
<td>Unknown</td>
</tr>
<tr>
<td>Sa</td>
<td>1.9</td>
<td>(MP-1300)</td>
<td>Unknown</td>
</tr>
<tr>
<td>Pa</td>
<td>1.1</td>
<td>2200</td>
<td>Remain in fuel</td>
</tr>
<tr>
<td>I</td>
<td>0.9</td>
<td>184.35</td>
<td>Gas</td>
</tr>
</tbody>
</table>
Table V
FISSION PRODUCTS THAT MAY ESCAPE THE FUEL

<table>
<thead>
<tr>
<th>Element</th>
<th>% Yield</th>
<th>Vapor Pressure(^{39})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenon</td>
<td>21.8</td>
<td>(Gas @ 300°C)</td>
</tr>
<tr>
<td>Cesium</td>
<td>19.2</td>
<td>1 torr @ 300°C</td>
</tr>
<tr>
<td>Strontium</td>
<td>9.3</td>
<td>(10^{-6}) torr @ 300°C</td>
</tr>
<tr>
<td>Barium</td>
<td>5.7</td>
<td>(10^{-8}) torr @ 300°C</td>
</tr>
<tr>
<td>Krypton</td>
<td>3.9</td>
<td>(Gas @ 300°C)</td>
</tr>
<tr>
<td>Rubidium</td>
<td>3.5</td>
<td>0.6 torr @ 300°C</td>
</tr>
<tr>
<td>Tellurium</td>
<td>2.4</td>
<td>(10^{-4}) torr @ 300°C</td>
</tr>
<tr>
<td>Iodine</td>
<td>0.9</td>
<td>(Gas @ 300°C)</td>
</tr>
</tbody>
</table>
will be xenon, krypton, and iodine. The other elements may have sufficient vapor pressures to affect the work functions of the surfaces but will not be gases as such. The present investigation is concerned with the effect of the gases only.

"Arc Mode" Cesium Diode

There are basically three modes of operation for a cesium vapor diode. One mode uses low pressure cesium (<10^{-2} torr) for space charge reduction without appreciable transport effects. This mode allows fairly wide spacings but requires extremely high emitter temperatures (>1800°C) for efficient operation. The second mode is characterized by high cesium pressures (1-10 torr) and moderate to high emitter temperatures (1500-1800°C). Sufficient ionization to neutralize the space charge can be supplied by surface ionization if the very high work function materials (Ir, Re and W) are used as emitters. This mode also requires a much smaller spacing than the first mode. The third mode of operation combines surface and volume ionization to eliminate the space charge. This mode is characterized by an arc discharge and is referred to as the "arc mode". The arc mode allows the consideration of a larger number of emitter elements and operating temperatures \((T_E > 1200°C)\). If the arc mode of operation is used in a design, the above mentioned list of emitters for efficient operation can be extended to include molybdenum, tantalum, and niobium.

In the arc mode, (or ball of fire mode), part of the potentially available output voltage is used internally in the diode to provide the necessary electrical power for the plasma generation. The effect of this on the ideal converter curve (See Figure 3a) is to shift the exponential line to the left by an amount \(V_a\) for an idealized arc mode curve. \((V_a\) is in units of electron volts). If \(V_a \geq \Theta_e - \Theta_c\) the characteristic would reduce to an exponential.
The motive diagram for the arc discharge mode is thought to be as shown in Figure 3b. Recent experimental measurements have indicated that this is true. A small retarding field region near the emitter is followed by a decrease in potential and the electrons are accelerated into the plasma region. It is thought that there is probably another sheath near the collector. If the difference in surface potential of the two electrodes \( V_d \) is less than the required voltage drop \( V_a \) then the space charge potential barrier of height \( V_e \) is assumed to be formed at the emitter and limits the output current to the value that the potential difference \( V_a = V_d + V_e \) can support. The voltage drop \( V_a \) in the plasma has been treated by Hatsopoulos and an expression obtained:

\[
V_a = \frac{2 V_i}{\ln[B \mu_d 2TM/kT_e]} - 2 kT_e
\]  

(3-1)

where

- \( V_i \) = ionization potential
- \( \mu \) = atom arrival rate
- \( d \) = length of ion generation region
- \( M \) = ion mass
- \( T_e \) = emitter temperature
- \( k \) = Boltzmann constant

and

\[
B = \frac{kT_e}{\pi^2 m} \left( \frac{2kT_e}{\pi m} \right)^{1/2} K \left( 2 + \frac{V_i}{kT_e} \right)
\]

(3-2)

where

- \( T_e \) = electron temperature
- \( m \) = electron mass
- \( K = 6 \times 10^{-4} \text{ cm}^2/\text{erg} \)

Electron Transport

The distribution function of particles, \( f = f(\tau, \omega, \xi) \), obeys the Boltzmann equation.
Figure 3a - Ideal Diode Curve - (Effect of arc voltage drop $V_a$)
Figure 3b - Motive Diagram for Arc Mode
\[ k = \text{Boltzmann constant} \]
\[ E = \text{electric field} \]
\[ T_e = \text{electron temperature} \]
\[ <v_e> = \text{average collision frequency} \]
\[ = \int_0^\infty N(v) \, dv \]
\[ N = \text{density of scattering centers} \]
\[ \sigma_s = \text{scattering cross-section} \]
\[ (v)_\text{ave} = \text{average electron velocity} \]

The reduced form of equation 3-4 is given by
\[ \gamma_e = \frac{m_e \, m_e \, E}{\tau_e} - D_e \, \overline{\gamma e} \]  \hspace{1cm} (3-5)

where \( \mu_e \) is called the electron mobility,
\[ \mu_e = \frac{g_e}{m_e \, <v_e>} \]  \hspace{1cm} (3-6)

and \( D_e \) is called the electron diffusion coefficient,
\[ D_e = \frac{kT_e}{m_e \, <v_e>} \]  \hspace{1cm} (3-7)

Equation 3-5 is not completely valid for the small interelectrode space, but if the mean free path of electrons is small compared with the diode spacing equation 3-5 is a good first approximation. \(^{(50,51)}\)

**Effect of Inert Gases**

In the application of the above theory to thermionic converters many difficulties are encountered. Over the last few years of converter development, no successful theories have been developed that will predict the parameters in a converter. This is mainly because of the interdependence of transport and surface phenomena. (Even the mechanism of ionization in an arc mode converter is a subject of much controversy.)

The present investigation is not concerned with the physics of plasma generation, but rather with the effects of impurities in the interelectrode space. For the case of inert
gases it is expected that their effect on the surface phenomena will be small. Also there should be no appreciable ionization by the thermionic electrons (0.1 - 0.4), since the ionization potentials of Ar, Kr, and Xe are 15.7, 14.0, and 12.1 ev respectively. If the effect of the inert gases is only to increase the number of scattering centers, then their effect on the diode operation can be calculated using equation 3-5 if the other parameters of the system are known. Fortunately all the terms in equation 3-5 except \( n_e \) can be determined by using the data from the present diode system or from other experimental investigations. The electron density can then be calculated for normal operation.

The electron current, \( \bar{J}_e \) (electrons/cm\(^2\)-sec), can be determined from the data, since \( \bar{J}_e = q_e \bar{v}_e \). This value for \( \bar{v}_e \) will be for the collector surface. Also from the data, one can determine the electron temperature. The method used to obtain the temperature assumes a constant electron temperature over all output voltages. The assumption is not quite true but this method does give an average temperature. Once the electron temperature is known, the average velocity can be calculated.

The collision frequency \( \langle \gamma \rangle_e \) is normally calculated in a straightforward manner from cross-section data. However, there is a paucity of cross-section data in the 0.1 - 1.0 ev range, i.e., the range of interest for thermionic conversion. The early measurements made by Brode on cesium and the inert gases appear to be the best accepted values. The cross-section of argon is the most difficult to determine from the data in the energy range of interest.

The shape of the electron density has been fairly well established experimentally for various emitter and cesium temperatures. The ratio of \( \bar{v} n_e/n_e(\text{collector}) \) is constant. An
exponential curve can be fitted to the plot of $n_e$ in this range (which is the inference if this ratio is a constant.) From the data it appears that, in numerical value, $\sqrt[6]{n_e}$ (collector) $\approx 60n_e$ (collector). Thus if $n_e$ is known, $\sqrt[6]{n_e}$ can be determined.

The variation of $n_e$ with argon overpressure has been reported. \(^{(34)}\)

The electrical field in the plasma is perhaps the hardest parameter to estimate. This field is not due to an applied voltage, but rather to the internal distribution of charges. Recent experimental measurement of the actual potentials in a diode have been reported. \(^{(56)}\) From the many graphs reported on the electric fields in the plasma it appears that a retarding field of 8 v/cm at the collector would be reasonable for the diode in this investigation.

The analytical model described above can be used to find the relative effect of inert gases on the operation of a diode. This model assumes no change in the surface characteristics of the diode and also that the mode of operation of the diode does not change. The calculation is, of course, limited by the lack of knowledge of some of the physical constants such as cross-sections.

This model was used to calculate the effect of A, Kr, and Xe on the diode and compared with the experimental data (See Chapter 5). The good agreement is indicative of the validity of the model.

**Effect of Iodine**

The effect of iodine on the operation of a diode is difficult to predict analytically because the iodine affects both the surface and the transport properties. Experiments with CsF have shown that the effective work function of the surface is increased by the CsF addition. \(^{(57,58)}\) Since fluorine and iodine are in the same chemical group it would be expected that CsI would also raise the work function.
The value of the emitter work function can be obtained by the shape of the I-V curve\(^{(52)}\) for a plasma converter in the ion rich mode,

\[
\frac{I_S - I}{I_p + I} = \exp \left( \frac{eV_o}{kT_e} - \frac{\Phi_e - \Phi_c}{kT_e} \right)
\]

where

- \(I_S\) = saturation current
- \(I\) = diode current
- \(I_p\) = ion current
- \(V_o\) = output voltage
- \(T_e\) = electron temperature.

Therefore a plot of \(\ln \left( \frac{I_S - I}{I_p + I} \right)\) versus the output voltage has a slope of \(1/\kappa T_e\) and an intercept of \((\Phi_e - \Phi_c)/\kappa T_e\). From this known value of \(\Phi_e - \Phi_c\) one can obtain the emitter work function \(\Phi_e\) by assuming \(\Phi_c = 1.7\) ev, the work function of bare cesium.

To use this method on the arc mode converter the output voltage must be shifted by the appropriate amount \(V_a\).
Chapter 4

EXPERIMENTAL PROCEDURE

General

Since the results of this investigation are to be used for practical thermionic systems, it was essential to design the experiment to investigate a typical diode. These criteria exclude such designs as a central wire, directly heated emitter or small emitter surfaces operating at relatively low temperatures.

A nuclear converter system will probably have an emitter operating in the 1800-2000°K range. This allows sufficient power densities while staying within the temperature limits of most fuels. The spacing in a normal system will be of the order of 20 to 40 mils. These somewhat large spacings will be necessary for reliable fabrication of fuel elements.

Tantalum was selected for the emitter material. This choice was primarily based on the relatively easy machining and welding properties of tantalum. Other refractory metals were considered and an abortive attempt was made to fabricate a tungsten emitter.

Diode Construction

A schematic of the diode system is shown in Figure 4. A detailed drawing of the diode is given in Appendix B.

The emitter consists of a one-inch diameter tantalum tube with a Ta flange welded on one end and a 1/4 inch thick Ta plug welded on the other end. The plug had a 1/32 inch diameter hole drilled as shown, 3/16 inch deep to facilitate the use of
Figure 4 - Schematic of Diode System
an optical pyrometer for emitter temperatures. All welds were
made at the Argonne National Laboratory with an electron beam
welder. After welding, the emitter surface was finished with
a surface grinder to be parallel with the flange (less than
1 mil variation). The surface was then polished on a polishing
wheel using 0.5 micron alumina abrasive.

The collector was made of 200 series nickel, 1-1/2 inches
long and 15/16 inch in diameter. The outside was threaded on a
lathe for $10^4$ threads per inch. This meant that one complete
revolution would change the collector position by 9.6 mils.
A hole was drilled from the back side of the nickel to within
1/16 inch of the collector surface for the admission of a chromel-
alumel thermocouple. The collector surface was made parallel
to the support flange on a lathe (less than one mil variation).
The surface was then polished in a similar manner as the
emitter.

The support flange for the collector was made of 1/4 inch
thick, 410 series stainless steel. This steel was chosen because
of its small expansion coefficient. The inside surface of this
flange was finished on a lathe and the surface polished with
crocus cloth. The central hole was threaded at $10^4$ threads per
inch to mate with the collector. (A similar flange as shown in
Figure 4 was used as a backup plate for the 50 mil Ta emitter
flange.)

The cylindrical spacer used between the emitter and
the collector was 304 series stainless steel pipe (2.885 inch OD,
2.535 inch ID). Proper size grooves were put on both ends of
this pipe for use of stainless steel "O" rings (Toruseal
C-2625-C). The end surfaces of the pipe were finished parallel
to each other (less than 1 mil variation.)

The electrical insulation for the diode was provided
by a 10 mil thick washer of mica placed between the stainless
spacer and the collector flange. A gold layer was deposited on one side of the mica to insure better sealing.

The diode assembly was held together by eight symmetrically located steel bolts. These bolts were made of 3/8 inch diameter threaded stock. Stiff springs were mounted on the cooler end of the bolts to insure constant forces under expansion of the materials while heating up.

The collector was cooled by water flowing through cooling coils. These 1/4 inch copper coils were silver-soldered to a cooling plate that was placed against the collector flange. The heat transfer to the plate was good and only a minimum amount of water flow was required to maintain the desired temperatures.

Figure 5 is a photograph of the assembled diode system.

**Diode Assembly Procedure**

The diode was assembled in two stages. The first stage was to assemble the device without the metal "O" rings. Due to the care that was taken in the making of the components, the emitter and collector surfaces were parallel to within 1 mil. The collector was movable and, therefore, the interelectrode spacing was variable. After the bolts were tightened to their proper position (using a torque wrench), the collector was backed off enough from the emitter to leave a 55-mil spacing. Previous experiments and calculations had shown that this is the spacing of a cold diode required to provide a 30-mil gap at the operating temperature of 1875°K.

The second stage of the assembly was to take the diode apart and have the collector welded to the support flange at the prescribed collector position. The weld was necessary because the threads provided a leakage path for the cesium and impurity gases. After the welding and necessary cleaning of the components, the final diode was assembled. A torque wrench was used on the spring loaded bolts to insure even compression on
Figure 5 - Photograph of Diode System
the metal "O" rings. All bolts were torqued to 10 lbs-ft.
Six chromel-alumel thermocouples were mounted around on the
diode to monitor the temperatures. The cooling lines were
connected and the heating filament mounted in position.

**Heating of Emitter**

The tungsten filament used to heat the emitter was
obtained from a commercial 500 watt light bulb. The leads
to the filament were made of 20-mil molybdenum wire, supported
by an Al₂O₃ insulator. The emitter was heated by both Joule
heating of the filament and by electron bombardment (E-B heat­
ing) due to a constant potential difference. A schematic of the
heating system is given in Figure 6.

The Joule heating of the filament was used not primarily
to heat the filament but to control the temperature of the
filament and thus the current for electron bombardment. The
E-B heating is about 100% effective whereas some of the Joule
heating is dissipated along the walls of the Ta cup and out the
opening by radiation. A typical AC input was about 215 watts
(70v, 3.1a). For operating the emitter at 1875°K the DC input
was 420 watts (560v, 0.75a). The filament operated at about
2400°K. This temperature was high enough to deposit a thin
layer of tungsten on the inside of the tantalum cup from the
vaporization of the filament over a long period of time.

During the actual experiment, the optical pyrometer
readings were not taken as absolute. Before the cesium was
introduced, a calibration curve was run to relate the emitter
temperature with the power input. This curve was then used for
determining the true emitter temperatures and the pyrometer was
used to detect a change in temperature from standard conditions.
This procedure was necessary because the bell jar developed a
thin coating on the inside during operation, thus introducing
Figure 6 - Heating Circuit
an unknown correction factor for the pyrometer reading. The manufacturer provided correction curves for the pyrex bell jar and the 90° prism used in the experiment.

Data Recording Technique

There are several techniques available for the measurement of the diode I-V curves. (59, 60) The method used in this experiment is schematically shown in Figure 7. This schematic shows how an oscilloscope is used to monitor the characteristic curve. The diode is swept 60 times per second by the AC line at low voltage. The voltage across the diode is measured directly. The current is measured by the voltage drop across a variable shunt (0-1 ohm). The oscilloscope is not grounded. The line from the collector to the baseplate feedthru is No. 4 welding cable, nickel plated. The line from the feedthru to the shunt is No. 4/0 welding cable. Pictures of the oscilloscope trace were taken with a Polaroid* camera and the data analysed at a later time. This method measures the I-V curves "dynamically". There are several advantages to this type of measurement. It records the entire I-V curve simultaneously which saves a great deal of time. Also, the curve can be measured at constant emitter temperature. Normal recording uses a variable load resistance and obtains a point-by-point curve. In the regions of high currents and electron cooling of the emitter changes its temperature and therefore the heat input must constantly be changed to insure constant emitter temperature. Finally the point-by-point procedure cannot yield the true short-circuit current.

Other experimenters have reported that there is no difference between the curves recorded dynamically and statically. (60) In the preliminary experiments on the diode used for this investigation, a comparison was made between the two

*Trade mark
Figure 7 - Measuring Circuit
measuring methods. The curves were measured at low emitter and cesium temperatures to make the currents small and thus reduce the effect of electron cooling. These curves are shown in Figure 8. There appears to be no appreciable difference between them.

The major disadvantage of the dynamic method is the inaccuracy of reading the current values in the small Polaroid picture. The error in this reading was assumed to be equal to the thickness of the line trace. Also, one must be careful to zero the scope properly so the curve will not be shifted up or down.

Preliminary Data Procedure

After the components had been properly cleaned, the diode was assembled in the vacuum system. The vacuum system consisted of a pyrex bell jar on a stainless steel baseplate. A 60 l/s Vaclon* pump was used with the rough pumping being done by a Welch mechanical pump with appropriate cold traps. The stainless steel baseplate had the necessary electrical, water, thermocouple and vacuum pump feedthrus. (See Figure 5)

While the Vaclon pump was in the system, the temperature of the diode was gradually raised to outgas the materials. During this procedure the system was kept below about 5 x 10^-6 torr. When the system was pumped down to below 10^-6 torr with the diode at or above its operating temperature, the diode was considered outgassed. The cesium reservoir (See Figure 9a) was outgassed in a similar manner. After the system had been completely outgassed, the inside of the diode was valved off and the cesium ampoule broken. The pyrex ampoule (See Appendix D) was in a 1/2 inch copper tube and was broken by squeezing the tube with a pinch-off tool. The breakage could be easily heard and felt.

*Trade name of Varian Associates
Figure 8 - Comparison of Methods (static and dynamic) used to Obtain Diode Curve
Figure 9a - Inert Gas Manifold
Figure 9b - Iodine Gas Manifold
It was necessary to run several preliminary I-V curves to determine the normal characteristics of the diode and to establish the best cesium pressure for the desired emitter temperature. It is desired that the diode be operating at its maximum point when the impurities are introduced. This point is determined by holding the emitter temperature constant and varying the cesium reservoir temperature. Figure 10 shows the dependence of the diode output power on the cesium temperature. The maximum point for this diode appears to be at a cesium temperature of about 280°-285°C. The subsequent data runs were made with the cesium temperature at this setting. However, a standard curve for the exact conditions was obtained before each run.

Data Procedure

The high purity inert gases (See Appendix D) used in this investigation were obtained from the Linde Company in 1/4 liter, pyrex bulbs. When the gas manifold system (See Figure 9b) had been evacuated to 10^-5 torr and outgassed, the break-off seal on the gas was broken. A desired amount of gas could then be let into the manifold.

When the system was at the operating point and ready for the test, a standard I-V picture was taken. Then the high temperature valve was opened. The pressure in the manifold first registered a decrease as the gas entered the diode and then read a constant value after the pressure had equalized. The valve was then closed. The total time the valve was open did not exceed two seconds. As the valve was being closed, a Polaroid picture of the I-V curve on the oscilloscope was taken. More gas was let into the manifold as the previous picture was being developed and the pertinent data logged (about 45 seconds required). The valve was again opened and the procedure repeated for a higher pressure of impurity. This was continued
Figure 10 - Cesium Dependency
until a departure from the standard conditions of the diode was detected. An observer was monitoring the emitter temperature with the optical pyrometer to detect any change. When the temperature changed by more than 5°C the test was terminated. Also the DC power input was observed and if it started to increase the test was terminated. A complete run normally required about 10-15 minutes.

The mechanism which caused the termination of a run was the leakage of the gas into the bell jar and thus into the space between the filament and the emitter. The gas would help in the transfer of electrons from the filament and thereby increase the power input to the emitter. The termination was always caused by an increase in power or an increase in emitter temperature. Thus, there was no decrease in emitter temperature observed due to the convection of the purity gas.

The experiment with the iodine was conducted in a manner similar to the experiments with inert gases, except that the iodine source was a reservoir of iodine crystals with the pressure controlled by the temperature of the reservoir. This change of reservoir temperature meant that there was a longer wait required between readings to allow the new temperatures to stabilize. However, there was no problem with the iodine leaking out and affecting the DC power input. The iodine either combined with the cesium or if a small amount leaked out, was pumped by the VacIon.

After the iodine experiment the diode was disassembled and examined for damage. Photomicrographs were made of the emitter and collector surfaces.
Chapter 5

RESULTS AND CONCLUSIONS

Effect of Inert Gases

A diode in a nuclear thermionic system would probably be at steady state and operating at the voltage that gave the maximum power output. Therefore, all the data in this investigation is reported as the effect of impurities at the point of maximum power output, which was about 0.6 volts for this diode. For the ease of comparison the curves were normalized to the initial or standard value. The actual output values for this diode were about 5 amps/cm\(^2\) short circuit and 1.4 watts/cm\(^2\) maximum power. All the data was taken on the diode when it was operating in the arc mode.

The effect of the inert gases argon, krypton, and xenon can be seen in Figures 11, 12, and 13 respectively. The diode was very tolerant of the inert gases and required impurity pressures of several times that of the cesium to have much of an effect. All of these gases eventually had a detrimental effect on the diode power. This of course would be expected from the equations in Chapter 3. The increased scattering in the interelectrode spacing decreases the energy of the electrons and impairs their transfer across the gap.

The increasing effect of argon, krypton, and xenon reflects the increase in the cross-sections of these respective gases. (See Figure 15) The inert gas cross-sections are complicated by the Ramsauer effect near the electron energy of interest in thermionic diodes. The tolerance of the diode is due to the fact that cesium has a much larger cross-section than the inert gases. The cross-section for cesium in the thermionic range is about 40 times that of xenon. (55)
Figure 11 - Effect of Argon
Figure 12 - Effect of Krypton
Figure 13 - Effect of Xenon
The analytical model developed in Chapter 3 was used to calculate the effect of these inert gases. These calculated curves are also shown in Figures 11, 12, and 13. The good agreement of the calculated curves indicates that the effect of the inert gases is perhaps entirely a diffusion phenomenon as assumed in the development of the equations.

The argon had the least effect of all the gases. This is to be expected from its low cross-section. The cross-section is difficult to determine from the literature\(^{(55)}\) because the electron energy is at the maximum point of the Ramsauer effect. This is probably the reason that the calculated curve is slightly above the experimental points. A comparison between the argon data in this investigation and that done by Bullis, et al.\(^{(34)}\) is given in Figure 14. One would expect a greater relative decrease in his larger spaced system since the cesium pressure in his diode was only 65% of the cesium pressure used in this study.

Krypton has a much more drastic effect upon the diode power than argon. This reflects the higher elastic scattering cross-section of krypton. As the electron energy is degraded by the krypton collisions, the probability of more collisions increases (See Figure 15) thus decreasing the diffusion coefficient. The electron temperature as a function of krypton pressure is seen in Figure 16. These values were obtained from the data by the method described in Chapter 3.\(^{(52)}\) An illustration of the plots used in this method is given in Figure 17. It is obvious from equation 3-1 in Chapter 3 that the output voltage reading at point \((I_s-I)/(I+I_p) = 1\), gives \(\phi_e - \phi_c\) for the unignited mode. For the arc mode the voltage drop in the plasma must be added to this. The data indicated that \(I_p\) could be neglected for these plots. The gradual shift
Figure 14 - Comparison of Argon Data with Bullis' Data
Figure 15 - Inert Gas Cross-sections
Figure 16 – Variation of Electron Temperature
Figure 17 - Method of Determining Electron Temperature
of the \((I_s-I)/(I+Ip) = 1\) intercept in Figure 16 does not represent a decrease in \(\Phi_s - \Phi_c\), but rather an increase in the voltage drop in the plasma. This voltage drop in the arc increases as the krypton pressure increases, which is to be expected.

An interesting observation with the krypton addition experiment was the stability provided by the krypton. Before introducing the krypton, the diode curve was unsteady, oscillating between two levels of operation. When the first addition of krypton (1 torr) was made, the curve became very stable and remained so for the rest of the experiment. However, the spread of the experimental data points indicate that the period of oscillation was greatly increased.

The addition of xenon to the diode extinguished the arc at about 8 torr. The extinguishing of the arc is in evidence not only in Figure 13, but also in the data which shows a characteristic increase in open circuit voltage. Unfortunately the point of arc extinction could not be determined for the other gases because the construction of the diode would not permit sufficient pressures. Bullis, et al.\(^{34}\) found that argon extinguished the arc in his diode at 61 torr. The experimental limit in this investigation was about 35 torr for any of the inert gases. The analytical model for xenon gives good agreement until the loss of the arc. The model of course does not hold after a change in the mode of operation.

As discussed in Chapter 2, other investigations of the effect of xenon showed an increase in the output of a diode due to the xenon. Although those investigations were with relatively low temperature diodes as compared to the present investigation, it is very difficult indeed to give a physical
explanation of the results. One would expect the effect of xenon to be very similar to, but perhaps more drastic than, the effect of the other impurity gases reported herein and in the work of Bullis, et al.\(^ {34} \)

**The Effect of Iodine**

Although iodine is not the most important fission product gas, it may well have the most important effect on the operating diode. This is because a small amount of iodine changes the work function of the emitter and perhaps that of the collector as well.

The result of iodine addition to the diode in this investigation was interesting for several reasons. Figure 18 shows that the power (at 0.6 volts) increases for iodine pressures up to about 40 torr and than decreases as the pressure is raised more. The most interesting result of iodine addition is shown in Figure 19. This indicates a complete change in the operating mode of the converter. The diode has gone from the arc-mode to the ion-rich, extinguished mode with ion production at the surface only.

This change in the diode behavior is attributed to the change in work function of the emitter. In the arc-mode of operation the emitter has a work function that is below \( \phi_n \). (\( \phi_n \) is the minimum work function that will provide sufficient surface ionization to neutralize the space charge.) This operational mode is known because the I-V curves are double valved.\(^ {46} \) However, when the iodine is introduced, the I-V curves become single valued, meaning that the emitter work function has been raised sufficiently to produce more ions than are necessary to neutralize the space charge, and all the electrical power needed for plasma generation of the arc-mode is now available for higher output voltages.
Figure 18 - Effect of Iodine
Figure 19 - Change of Operating Mode with Iodine Addition
The maximum power before iodine addition occurred at 0.6 volts. After iodine addition and the change of modes, the maximum power point was at 0.9 volts.

From the 0.3 volt shift in the point of maximum power output, it would appear that the voltage reduction caused by arc-mode operation is about 0.3 volt. A calculation of this voltage using equation 3-1 gives a voltage difference of 0.25 volts. Using this correction in the procedure described in Chapter 3 for determining the work functions (52), the effective emitter work function can be found for normal operation in the arc-mode before iodine addition. The result of this analysis gives an effective emitter work function of 2.3 ev. The critical work function for tantalum is given by Rasor (43) as 2.7 ev. Therefore, the diode's normal operation is in the arc-mode with a work function 0.4 ev below that necessary to provide sufficient surface ionization. With a small amount of iodine (2 torr) the work function went to 2.80 ev., which is greater than $\theta_n = 2.70$, and thus the mode changed to extinguished, ion-rich operation. As the iodine pressure was raised, the effective work function gradually decreased to about 2.72 ev. at 130 torr. This decrease in the effective, cesiated work function is indicative of an increase in the bare work function (43).

The increase in power output with iodine is mainly a result of the change in the work function of the emitter. As the effective work function decreases with iodine addition, more electrons are emitted causing the power to increase. However, after about 40 torr the detrimental effect of I and CsI on electron transport in the gap more than compensates for the change in work function. The physical data is not available for calculation of this phenomena, but the quantitative effect is believed to be as shown in Figure 20. The emitter work function gradually increases to a new value, but the detrimental
Figure 20 - Representation of Iodine Effect
transport effects decrease the power as a function of the iodine concentration.

It was observed that the diode apparently recovered in the time elapsing between each data run shown in Figure 17. The experimental procedure was to open a high temperature valve to expose the iodine to the diode, and take a picture after equilibrium was reached. The valve was then closed to adjust the iodine to a new reservoir temperature. Within a minute after the valve closing the I-V curve would return to the initial curve (curve a in Figure 18). This would indicate that the CsI formed in the diode reached an equilibrium on the emitter surface as long as an iodine source was available. However, when the source was removed, the CsI evaporated from the emitter and condensed out in some colder section of the diode, thus allowing the diode to return to its original cesium operation.

It is very difficult to determine the chemical balance in the CsI operation. Both CsI and iodine exist in the inter-electrode space. If the free iodine atoms do not diffuse into the gap directly from the source, they will be formed on the hot surfaces by dissociation of cesium iodine. The dissociation energy for CsI is 3.3 ev. The concentration of cesium atoms and ions in the gap will also change with the amount of iodine available. Most of the iodine in the gap will probably be ionized because of iodine's high electron affinity. The concentrations of the various molecules in the diode are probably determined not only by the vapor pressure of the iodine source but also by the vapor pressure of CsI which will be controlled by temperature in the diode.

The results of iodine in this study are in good agreement with what would be expected from other experimental data on CsF as an additive. Since iodine and fluorine are in
the same chemical group, one would expect their effects to be similar. Langpage in Germany reported that the bare work function of tantalum was increased by 0.4 ev by exposing the surface to a CsF reservoir at 400°C. *(57)* Also, Jester reported that the addition of CsF to his molybdenum diode increased its power output by a factor of about 2-1/2 *(T = 1900°K, spacing = 0.05 mm, T_{CsF} = 800°K).* *(58)*

The vapor pressure curves for CsF and CsI are not available but can be estimated from the Clapeyron equation, *(62)*

\[
\frac{dP}{dT} = \frac{\Delta H_S}{(\nu_v - V_S)}
\]  

*(5-1)*

where

- \(\Delta H_S\) = heat of sublimation
- \(T\) = temperature (°K)
- \(\nu_v\) = volume of vapor
- \(V_S\) = volume of solid

Assuming that \(\Delta H_S\) is not temperature-dependent, that \(V_S\) is small compared with \(\nu_v\), and that

\[\nu_v = \frac{RT}{p}\]

*(5-2)*

equation *5-1* can be reduced to

\[
\frac{dP}{P} = \frac{\Delta H_S}{R} \frac{dT}{T^2}
\]  

*(5-3)*

or

\[
\ln \frac{P}{P_0} = \frac{\Delta H_S}{R} (\frac{1}{T} - \frac{1}{T_0})
\]  

*(5-4)*

Using this expression, the vapor pressure of CsI is \(3 \times 10^{-4}\) torr at 400°C. The heat of sublimation is not known for CsF but as a first approximation it can be assumed to be the same as that of CsI. (The melting and boiling points for CsI and CsF are 621°C, 682°C, 1300°C and 1250°C respectively.)
Figure 21 - Photomicrograph of Damage to Ta Surface
Post-Analysis of the Electrode Surfaces

After the iodine experiment the diode was disassembled and examined. The tantalum emitter appeared to be relatively clean to the eye. However, several small "pits" could be seen on the emitting surface. A photomicrograph of one of the larger "pits" is shown in Figure 21 (100x and enlarged twice in printing). Analysis of this pit has shown that the center of the rings is at about the same level as the unattacked tantalum, indicating that this is not a "pit" but rather a depression in the form of a circular groove. The black foreign material in the grooves appears at several other places on the emitting surface in a crystalline shape. A microprobe analysis could not be made on this material because the cleaning of the surface would destroy it. It is believed to be iodine or cesium iodine because of its purplish appearance. An electron microscope investigation of the rings in Figure 21 showed that this area contained many pits and holes in it.

The nickel collector had a black film on the collecting surface and the sides of the collector. Arc spectrum and x-ray diffraction analysis of this black film did not yield any definite answer as to its composition.

Conclusions

Although all the results of inert gas addition to the diode showed detrimental effects, they still showed that the diode could tolerate large amounts of impurities. The range of the impurity in the cesium was from 0 to about 3000%. For impurity levels of about 100% (1 torr impurity), there was very little effect on the operation of the diode. In a nuclear system it is possible that these gases could be allowed to exist at a few torr and periodically vented to space.
The iodine presents a different situation. It could, perhaps, counterbalance the effect of krypton and xenon. It may also form a compound with some other fission products and plate out on cooler surfaces. There is no question of iodine using up the cesium by formation of CsI because the fission process produces considerably more cesium than iodine. The results of the iodine experiments indicate fission products that have high vapor pressures may have the most important effect. After these elements have been investigated it is conceivable that a system could be designed to tolerate and control the fission products in the interelectrode space.

**Recommendations for Further Investigation**

The other fission products discussed in Chapter 3 should be investigated for their effects on diode operation.

It would also be of interest to conduct an experiment using a reservoir of CsI as an impurity. For the most complete results it would be best to study the effect at various CsI temperatures, emitter temperatures, cesium temperatures and electrode spacings.

The present work could be extended to find the effect of the inert gases at various emitter temperatures and electrode spacings.
Appendix A

THERMIONIC CONVERSION

A thermionic energy converter is a heat engine which uses electrons as the working fluid. The essential components and processes of this heat engine are schematically illustrated in Figure 22. Electrons escape from the hot electrode by virtue of their kinetic energy, flow through the interelectrode space and are condensed on the cold electrode. Useful work can be obtained from this heat engine if the electrons that have arrived at the collector have a higher potential energy than electrons in the emitter. This potential difference can be used to drive the electrons through an external circuit and back to the emitter.

A natural analogy to this process has been suggested by Dr. N. S. Rasor (11) in the conversion of solar heat into hydropower. Figure 23 illustrates this analogy by showing how solar heat is used to evaporate sea water which is transported to the high potential energy level of a mountain lake. The water can then perform useful work by flowing back to the sea through a turbine. This analogy may be helpful in understanding the operation of a thermionic converter. For example, it should be noted that the concentration of water vapor decreases exponentially with increasing altitude above sea level in a uniform atmosphere, and increases exponentially with increasing temperature of the sea. This means that there is an optimum height of the mountain barrier between the sea and the lake for maximum hydropower generation at a given sea temperature. If the barrier is too high above sea level, not enough water vapor is present to provide significant water
Figure 22 - Schematic Diagram of Thermionic Converter
Figure 23 - Hydroelectric Analogy of Thermionic Energy Conversion
flow through the turbine. Conversely, if it is too low the water pressure or "head" available to drive the turbine is too small. (e.g. High deserts and low swamp lands are notably poor sources of hydropower.) Similarly, if the barrier is too high above the lake, most of the energy is dissipated in raindrops falling from great heights. If it is too low, water vaporizing from the lake will migrate back across the barrier and be lost for power generation, unless the temperature of the lake is maintained sufficiently low.

The basic phenomena involved in a thermionic converter may be divided into two categories: emission processes and transport processes. The emission process is concerned with the mechanics of the release and collection of electrons at the electrodes. The transport process is concerned with the effects arising from the electron space charge and effects arising from the scattering of electrons in transit between the emitter and collector.

The maximum attainable performance for an ideal thermionic converter, in terms of power density or thermal efficiency, depends solely on the properties of the emitter and the collector temperatures. There are maximum emitter and optimum collector work functions which maximize the efficiency of the thermionic converter in the absence of transport effects. By ignoring the transport effects, the performance characteristics of an ideal converter can be determined. A diagram of the electron potential energy in such an idealized converter appears in Figure 24. (This should be compared with its analog in Figure 23)

The current density \( J \) of emitted electrons is given by the Richardson-Dushman equation

\[
J = A T^2 \exp \left[ -\frac{\phi}{kT} \right]. \tag{A-1}
\]

* Symbols used in Appendix A are defined in Appendix C
Figure 24 - Electron Potential Energy Diagram for the Ideal Thermionic Converter
The symbol $\phi$ represents the minimum energy required to remove an electron from the metal and is called the "work function" of that surface. The application of equation A-1 to the potential diagrams in Figure 24 gives the emission currents between the electrodes as:

$$J_e = \begin{cases} A T_e^2 \exp \left[ -\frac{(-eV_o + \phi_e)}{kT_e} \right] & eV_o > \phi_e - \phi_c \quad (A-2) \\ A T_e^1 \exp \left[ -\frac{\phi_e}{kT_e} \right] & eV_o < \phi_e - \phi_c \quad (A-3) \end{cases}$$

$$J_c = \begin{cases} A T_c^2 \exp \left[ -\frac{\phi_c}{kT_c} \right] & eV_o > \phi_e - \phi_c \quad (A-4) \\ A T_c^1 \exp \left[ -(\phi_c - eV_o)/kT_c \right] & eV_o < \phi_e - \phi_c \quad (A-5) \end{cases}$$

$$J_o = J_e - J_c \quad (A-6)$$

The electrical output characteristics for a typical idealized converter is given in Figure 25. This is a plot of the net electrical current $J_o$, as a function of the output voltage $V_o$. The current output is constant at the saturation current of the emitter until $eV_o \approx \phi_e - \phi_c$. At this point of maximum power output the current begins decreasing as an exponential function of $eV_o/kT_e$. The experimental I-V curves vary from this shape because of transport effects and non-uniformity of the emitter surface. These effects will be discussed later.

By inspection of equations A-2 through A-5, one may be tempted to state that the best performance would be obtained by lowering $\phi_e$, thus increasing the current density, and making $\phi_c$ a minimum to increase the voltage output. However, recalling the analogy of Figure 23, if $\phi_e$ is low the potential available will be low, corresponding to hydropower from low swamplands. Also, if $\phi_c$ is too low the back emission of the collector (Equation A-4) will drastically reduce the net current $J_o$. There thus appears to be an optimum set of
Figure 25 - Output Characteristics for Ideal Converter
properties that the materials should possess in order to obtain the best performance.

There are two categories of converters herein distinguished by the terms "vacuum" and "plasma". The vacuum converter consists of electrodes whose emission surface has the same atomic components as the interior of the electrodes. The plasma converter consists of electrodes whose emitting properties are determined by a layer of foreign atoms adsorbed on their surface. These foreign atoms are supplied by a plasma of such atoms which exist between the electrodes.

The vacuum converter has several disadvantages which eliminates it for use in a practical application, but it has proven beneficial for the understanding of the thermionic process. The main disadvantage of the vacuum emitter is that there exists no elementary material that is capable of emitting 10 amps/cm² for periods approaching a year without serious vaporization of the material. The requirement that the emitter must deliver adequate emission current at the available heat source temperature even further restricts the choice of materials. The negative space charge which exists in the interelectrode space is a deterrent to electron emission and transport, and unreasonable spacings of about 0.1 mil is required to eliminate this space charge. A further disadvantage of the vacuum diode is that the evaporated emitter atoms will be deposited on the collector, changing its work function. Fortunately, the use of the alternative type of surface (plasma) almost completely removes the limitations of the vacuum surface.

The Cesium Plasma Diode

The work function of a metal can be lowered and controlled by employing a layer of foreign atoms adsorbed on the
elementary surface. By introducing the foreign atoms from a plasma between the electrodes, this layer can be replenished as rapidly as it vaporizes thus avoiding the intolerable erosion of the electrode material by vaporization. The negative space charge is eliminated by the presence of positive ions in the interelectrode space. These ions can be produced by surface ionization of the plasma atoms impinging on the emitter, or by collisions of plasma atoms with energetic electrons in the interelectrode space. This latter mechanism is referred to as volume ionization. Cesium is almost a universal choice for the plasma vapor, because it has the lowest electron affinity of any stable element and also has a desirable work function.

The operation of a cesium plasma diode requires a small cesium reservoir to be added to the diode. Since the cesium vapor is maintained in equilibrium with this reservoir, it is not consumed and its pressure is determined by the temperature $T_R$ of the reservoir. The pressure of the cesium will determine the surface coverage of the electrodes by cesium atoms and thus will change their effective work functions. The work function of a surface is now dependent on three parameters: the cesium pressure (reservoir temperature), the temperature of the surface, and the work function of the elementary surface in a vacuum (referred to as the "bare" work function $\Phi_0$). Figure 26 shows the relationship between bare and cesiated work functions for constant emitter-to-reservoir temperatures of 3.5, 3.75, and 4.0. Cesium has the greatest effect on work functions in the range of 4 to 6 ev. The refractory metals that have work functions in this range are indicated in Figure 26.

Analysis by Rasor has shown that materials in this range
Figure 26 - Relation Between Bare and Cesium Work Function
give both adequate ion and electron emission; and are therefore best suited for diode operation.\(^{43}\)

**Neutralization of Space Charge**

Successful suppression of the energy barrier arising from the negative space charge of the emitted electrons is the principal development which has led to the achievement of practical thermionic converters. Although the positive ions provided to neutralize this space charge can be produced by volume ionization, it appears that surface ion emission is a necessary mechanism for sustaining the discharge at all practical temperatures. Conditions can be found by which ion emission alone is sufficient to neutralize the electron emission. To be emitted from the surface, the positive ions must surmount an energy barrier which is similar to the barrier for the electrons, and is therefore called the "ion work function" \(\Phi_i\). Similarly, a cesium atom on the surface would have an "atom work function" \(\Phi_a\). These emission processes obey laws similar to those for electrons, and may be described by:

\[
\begin{align*}
\dot{g}_i &= Q_0 \exp\left[-\frac{\Phi_i}{kT_e}\right] \\
\dot{g}_a &= 2Q_0 \exp\left[-\frac{\Phi_a}{kT_e}\right] \\
\dot{m} &= \dot{g}_i + \dot{g}_a
\end{align*}
\]  

(A-7)  
(A-8)  
(A-9)

Equations A-7 and A-8 are for the emission flux of ions \(q_i\) and atoms \(q_a\) respectively. Equation A-9 simply expresses the fact that at equilibrium the rate of arrival of cesium atoms \(\dot{m}\) must equal the sum of the ion and atom emission rates. The factor of 2 in \(q_a\) reflects the two spin states of the electron in the emitted atom.
The emission parameters are related to the ionization potential $V_i$ of the cesium atom by:

$$\phi_e + \phi_i = \phi_a + V_i \quad (A-10)$$

This equation states that the amount of energy required to emit an electron and an ion from a surface is equal to the energy required to emit an atom and then ionize it.

By combining the above equations the rate of ion emission is found to be

$$\dot{q}_i = \frac{\lambda}{1 + 2 \exp[(V_i - \phi_e)/kT_e]} \quad (A-11)$$

The electron space charge $\rho_e = J_e/v_e$ is neutralized by the positive ion space charge $\rho_i = e q_i/v_i$ when they are equal.

$$\frac{e \dot{q}_i}{n_i} = \frac{j_e}{n_e} \quad (A-12)$$

Assuming that the ions and electrons are emitted with the same kinetic energy ($M_i v_i^2/2 = m_e v_e^2/2$), neutralization occurs when the electron and ion currents are in the ratio,

$$\frac{J_e}{e \dot{q}_i} = \frac{n_e}{n_i} = \frac{M_i}{m_e} \quad (A-13)$$

where $v_e$, $v_i$, $m_e$, and $M_i$ are the respective average velocities and masses of the electrons and ions. By combining equations A-3, A-11, and A-13 the minimum work function of a surface emitting enough ions to neutralize its maximum electron current is found to be

$$\phi_n = \frac{V_i}{2} + \frac{kT_e}{2} \ln \left[ \frac{m_e}{M_i} \sqrt{\frac{m_e}{M_i}} \right] \quad (A-14)$$

The development of equation A-14 has assumed that $V_i - \phi_e > 2kT_e$ which is the region of practical importance in converter operation.

Values of $\phi_n$ are indicated on Figure 26. For work functions $\phi$ in the region above $\phi_n$ a surplus of ions is
emitted; in the region below $\Phi_n$ a surplus of electrons is emitted. Therefore, diodes which operate with a work function different from $\Phi_n$ will have either an electron or an ion space-charge barrier near the emitting surface.

Cesium vapor pressures at which the positive ion barriers or sheaths are formed at the electrode surfaces represent the most interesting mode of operation of the plasma converters since it is within these pressure ranges (above 0.1 mm Hg) that the device yields high power densities and high efficiencies without the necessity of operating at extremely high emitter temperatures. Figure 27 shows an electron motive diagram for this mode of operation. The diagram illustrates the results of transport effects by the voltage drop $V_{sh}$ across the plasma.

**Detrimental Effects**

The transport effects in a diode are mostly due to short range scattering of electrons by cesium ions and atoms.\(^{46}\) These effects appear as an internal resistance and become increasingly important for high cesium pressures and large spacings of several mean-free-paths. Another interaction which can occur at high electron and ion densities is the excitation of local oscillations in the plasma by the high current beam of electrons from the emitter. Although the high electron temperature thus generated can possibly be important for ion generation, it can also cause large energy losses by increasing the average kinetic energy of the electrons reaching the collector and by the production of excited cesium atoms. In general, all transport effects seem to be detrimental.

The effect other than transport which seems to be the most important is the non-uniformity of surfaces or the "patch effect". Since most metals have a polycrystalline structure,
Figure 27 - Mode Diagram for a Diode in Which $\phi_E > \phi_n$
their surfaces have various "patches" that present different faces of the metal crystal. It is well known that the bare work function is different for these different faces of the metal crystal. Therefore a metal surface does not have a bare work function as such, but is made up of a combination of patches which may have different work functions. In this case each patch will operate as a thermionic emitter with its characteristics determined by the work function of that particular patch. The total output would thus be equivalent to that of a large number of elementary diodes connected electrically in parallel. This effect complicates the space charge barriers in the converter. For complete neutralization, the $\Phi$ of the patch with the lowest work function must be greater than the $\Phi_n$ discussed earlier.

The patch effect is not very important for low pressure diodes in which a small percentage of the surface area has a high work function. However at high cesium pressures the high work function areas will have preferential adsorption of cesium causing them to emit much more current than the surrounding areas. The possible effect of the patches on the output characteristics of a diode can be seen in Figure 28, where an ideal converter curve has been calculated assuming a surface presenting 92% of its area as 3.0 ev patches and 8% as 2.5 ev patches. These distortions of the ideal converter curve are observed in experimental data.

Current Status

The physics of vacuum and low pressure cesium thermionic diodes is well understood. However, the physics of a high pressure diode operating in the arc mode is not well known. There is a very active controversy in the field about
the actual mechanism that causes this volume ionization or arc. One of the original experimenters in this field recently commented that not much more is known about diodes now than in 1958, except that the more care that is taken in the construction of the diode, the better it performs.(64)

Even if good theoretical models were available it would be difficult to calculate the diode performances because of the lack of complete physical data.

There has been considerable progress and development in the experimental area of thermionics. Many problems have been recognized and overcome or minimized. Some additional problems are foreseen, but none appear to be insurmountable.(15) Many advances have been made with the material problems of fabrication, high temperature operation and capabilities. For example, the development of a chemical vapor deposition for coating refractory metals on surfaces enables the fabrication of components is virtually any required shape or size.

Many experiments are also in progress to measure actual properties in the plasma of an operating diode. These experiments are leading toward an understanding of the arc process.

The operating characteristics of experimental devices are constantly being improved. There are reports of data such as power densities of 57w/cm², converter lifetimes of over 10,000 hours, and in-core lifetimes of over 500 hours.(65) The best emitter performance is given from rhenium and iridium surfaces. Nickel and molybdenum are attractive as collectors, but most research is in the study of additives to the surface of the collector (e.g. cesium-antimony on nickel, etc.) to lower its work function. Alumina and beryllia are emerging as about the best compromise for an insulator in a diode. One of the important tasks for researchers seems to be the
Total Current

Contribution of 2.5 ev Patches
Covering 8% of Emitting Surfaces

Contribution of 3.0 ev Patches
Covering 92% of Emitting Surface

Figure 28 - Ideal Diode Characteristics with a Patchy Emitter
improvement of emission technology. It is very likely, for instance, that present converters are operating with only a small fraction of the emitter area active in the emission process because of the patches. A major task would be to find methods by which this active area can be expanded and maintained as a large fraction of the surface. Another approach to increasing power densities may be to make small holes in the emitter to provide more emitting surface for a given surface area.(66)

The present operating conditions of converters are limited by the properties of the materials available today. Future limitations will depend upon improvement of these properties or the discovery of new materials with more desirable properties.
Appendix B

DETAILS OF EXPERIMENTAL EQUIPMENT

List of Equipment Used to Record Data

Emitter Temperature - Micro Pyrometer
(700-3200°C temperature scale)
The Pyrometer Instrument Co.

Thermocouple Temperatures - Millivolt Potentiometer,
Biddle Gray

Oscilloscope - Type 545 A, oscilloscope
Tektronix, Inc.

Camera - Model 196 A, oscilloscope camera
Hewlett Packard

Film - Type 47 - Polaroid film - 3000 ASA

Impurity Pressure - 8 inch, 0-100 mm absolute pressure gage
Wallace and Tiernan

System Pressure - 60 l/s VacIon pump
Varian Associates
Figure 29 - Emitter and Collector
Appendix C

DEFINITION OF SYMBOLS

A = Richardson emission constant = 120 amps/cm²·°K²
a = Amps
Dₑ = Electron diffusion coefficient
d = Length of ion generation region
\( \overline{E} \) = Electric field
e = Electronic charge
ev = Electron volts
f = Distribution function in Boltzmann Equation
\( \nabla_r f \) = Gradient of the distribution function with respect to position
\( \nabla_v f \) = Gradient of the distribution function with respect to velocity
ΔHₛ = Heat of sublimation
I = Diode currents
Iₛ = Emitter saturation current
Iₚ = Ion current
ID = Inside diameter
J = Current density (Amps/cm²)
Jₐ = Collector current density (Amps/cm²)
Jₑ = Emitter current density (Amps/cm²)
Jₒ = Net current density = Jₑ - Jₐ (Amps/cm²)
K = Constant (6 x 10⁻⁴ cm²/erg)
k = Boltzmann constant = 1.38 x 10⁻¹⁶ erg/°K = 8.62 x 10⁻⁵ ev/°K
1/s = Liters per second
M = Ion mass
Mₑ = Ion mass
m = Electron mass

88
\( m_e = \) Electron mass
\( \text{mil} = 1/1000 \) of an inch
\( \text{MP} = \) Melting point
\( N = \) Density of scattering centers
\( n_e = \) Electron density,
\( \nabla n_e = \) Gradient of electron density with respect to position
\( \text{OD} = \) Outside diameter
\( P = \) Pressure (torr)
\( \text{PPM} = \) Parts per million
\( Q_0 = \) Cesium emission constant
\( q = \) Charge on a molecule
\( q_a = \) Atom emission rate
\( q_e = \) Charge on an electron
\( q_i = \) Ion emission rate
\( R = \) Universal gas constant
\( T = \) Absolute temperature °K
\( T_c = \) Absolute collector temperature °K
\( T_E = \) Absolute emitter temperature °K
\( T_e = \) Absolute electron temperature °K
\( T_r = T_{cs} = \) Absolute cesium reservoir temperature °K
\( t = \) Time
\( \text{torr} = \) Pressure unit 1 mm Hg
\( V_a = \) Arc voltage drop
\( V_d = \) Difference in surface potential of the two electrodes
\( V_e = \) Potential barrier height at emitter
\( V_i = \) Ionization potential (3.87 ev for Cs)
\( V_o = \) Output voltage
\( V_s = \) Volume of solid
\( V_{ss} = \) Potential drop across the interelectrode plasma region
\( V_v = \) Volume of vapor
\( v = \) Volts
\( \overline{v} = \) Velocity of electron
\( (v)_{ave} = v_e = \text{Average electron velocity} \)
\( v_i = \text{Average ion velocity} \)
\( \vec{a} = \text{Acceleration imposed on a particle by external forces} \)
\( J_e = \text{Particle current (electrons/cm}^2\text{-sec)} \)
\( \epsilon = \text{Emissivity} \)
\( \mu = \text{Atom arrival rate} \)
\( \mu_e = \text{Electron mobility} = \frac{q_e}{m_e} <\gamma_e> \)
\( <\gamma_e> = \text{Average collision frequency} = \sqrt{N(v)_{ave}} \)
\( \rho_e = \text{Electron space charge} \)
\( \rho_i = \text{Ion space charge} \)
\( \sigma_e = \text{Electron scattering cross-section} \)
\( \varphi = \text{Work function (ev)} \)
\( \varphi_a = \text{Cesium atom work function (ev)} \)
\( \varphi_c = \text{Collector work function (ev)} \)
\( \varphi_e = \text{Emitter work function (ev)} \)
\( \varphi_i = \text{Cesium ion work function (ev)} \)
\( \varphi_n = \text{Work function for which space charge neutralization occurs} \)
\( \varphi_o = \text{Bare work function of surface (ev)} \)
Appendix D

PURITY OF GASES

Cesium

The cesium was obtained from the Dow Chemical Company in small pyrex ampules. These ampules were 3/8 inch in diameter and 3 inches in length and contained one gram of cesium metal. This cesium is well adapted to thermionic work because of its high purity and the care used in packaging it.

The impurity analysis for this cesium is:

<table>
<thead>
<tr>
<th>Impurity</th>
<th>PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>145</td>
</tr>
<tr>
<td>Na</td>
<td>40</td>
</tr>
<tr>
<td>O</td>
<td>36</td>
</tr>
<tr>
<td>Ca</td>
<td>23</td>
</tr>
<tr>
<td>Fe</td>
<td>18</td>
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<tr>
<td>Si</td>
<td>13</td>
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<tr>
<td>Cu</td>
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</tr>
<tr>
<td>K</td>
<td>6</td>
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<tr>
<td>Mn</td>
<td>5</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
</tr>
<tr>
<td>Mg</td>
<td>3</td>
</tr>
<tr>
<td>Ni</td>
<td>3</td>
</tr>
</tbody>
</table>

Argon

The argon was obtained from the Linde Company, Rare Gas Department. It was supplied in 1 liter pyrex bulbs with a break-off tip. A short steel rod encased in glass was moved by use of a magnet to break the tip at the desired time.
The impurity analysis for this argon is:

<table>
<thead>
<tr>
<th>Impurity</th>
<th>PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>10</td>
</tr>
<tr>
<td>O</td>
<td>5</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td>5</td>
</tr>
<tr>
<td>H₂O</td>
<td>3</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
</tr>
</tbody>
</table>

Krypton

The krypton was obtained from the Linde Company, Rare Gas Department in the same form as the argon.

The impurity analysis of the krypton is:

<table>
<thead>
<tr>
<th>Impurity</th>
<th>PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>50</td>
</tr>
<tr>
<td>Xe</td>
<td>25</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td>15</td>
</tr>
<tr>
<td>H₂O</td>
<td>5</td>
</tr>
<tr>
<td>H</td>
<td>5</td>
</tr>
<tr>
<td>O</td>
<td>5</td>
</tr>
</tbody>
</table>

Xenon

The xenon was obtained from the Linde Company in 1/4 liter pyrex bulbs.

The analysis for xenon is:

<table>
<thead>
<tr>
<th>Impurity</th>
<th>PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>50</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td>15</td>
</tr>
<tr>
<td>Kr</td>
<td>10</td>
</tr>
<tr>
<td>H₂O</td>
<td>5</td>
</tr>
<tr>
<td>O</td>
<td>5</td>
</tr>
<tr>
<td>H</td>
<td>5</td>
</tr>
</tbody>
</table>
**Iodine**

The resublimed iodine was obtained from the Fisher Scientific Company in the crystalline form.

The impurities in the iodine are:

- Chlorine and bromine - 0.005%
- Non-volatile matter - 0.006%
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