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**FINAL REPORTS OF THE
HIGH EFFICIENCY THERMIONICS (HET-IV)
and
CONVERTER ADVANCEMENT (CAP) PROGRAMS**

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April 1996

**BETTIS ATOMIC POWER LABORATORY
WEST MIFFLIN PENNSYLVANIA 15122-0079
Operated for the U.S. Department of Energy by
WESTINGHOUSE ELECTRIC CORPORATION**

Final Reports of the High Efficiency Thermionics (HET-IV) and Converter Advancement (CAP)
Programs

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Contents:

- I. Transmitting Note (C. B. Geller - Bettis)
- II. Attachment A: High Efficiency Thermionics Program (HET-IV) Final Report
(J-L Desplat et al, Rasor Associates)
- III. Attachment B: Converter Advancement Program Final Report
(D. R. Riley, and C. S. Murray - Bettis)

I. Transmitting Note

This letter transmits the final report of the High Efficiency Thermionics (HET-IV) Program, Attachment A, performed at Rasor Associates, Inc. (RAI); and the final report of the Converter Advancement Program (CAP), performed at the Bettis Atomic Power Laboratory, Attachment B. The phenomenology of cesium-oxygen thermionic converters was elucidated in these programs, and the factors that had prevented the achievement of stable, enhanced cesium-oxygen converter performance for the previous thirty years were identified. Based on these discoveries, cesium-oxygen vapor sources were developed that achieved stable performance with factor-of-two improvements in power density and thermal efficiency, relative to conventional, cesium-only ignited mode thermionic converters. Key achievements of the HET-IV/CAP programs are as follows:

- a new technique for measuring minute traces of oxygen in cesium atmospheres
- the determination of the proper range of oxygen partial pressures for optimum converter performance - 10^{-7} to 10^{-9} torr.
- the discovery, and analysis of the cesium-oxygen liquid migration and compositional segregation phenomena
- the successful use of capillary forces to contain the migration phenomenon
- the use of differential heating to control compositional segregation, and induce vapor circulation
- the development of mechanically and chemically stable, porous reservoir structures
- the development of precise, *in situ* oxygen charging methods
- stable improvements in emitter performance, up to effective emitter bare work functions of 5.4 eV
- stable improvements in barrier index, to values below 1.8 Volts
- the development of detailed microscopic models for cesium-oxygen reservoir dynamics and collector work function behavior
- the discovery of new relationships between electrode geometry and Schock Instability

These developments are detailed in the attachments.

RASOR ASSOCIATES, INC.

HIGH EFFICIENCY THERMIONICS PROGRAM

HET-IV FINAL REPORT

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Vol. 1

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PREFACE

At first, in HET-I and HET-II, a development approach was attempted, as if the utilization of beneficial oxygen effects in cesium vapor thermionic converters could be accomplished by employing known principles in modified conventional converter designs. It was found, however, that the obstacles of instability and irreproducibility encountered by many other competent groups over the previous 20 years could not be overcome by design innovation alone. In HET-III, therefore, a Physical Understanding Experiment (PUE) task was added to define and overcome the unknown rogue process causing the basic obstacles.

The PUE experiments were designed specifically to define the rogue process. In experiments PUE-1 and PUE-2 the instability and irreproducibility were again encountered without determining their underlying cause. In PUE-3, however, the rogue process was discovered.

With the rogue process identified, an attempt in PUE-4 to control the process by isolating the Cs/O source in a porous pellet was highly successful. The newly discovered Cs/O vapor source was named the Dynamic Equilibrium Cesium-Oxygen Reservoir (DECOR). The high degree of vapor stability and control obtained in PUE-4 was reproduced in PUE-5 over a 1000-hour test period.

The HET-IV program reported here was formulated and initiated prior to discovery of the rogue process. Accordingly, it included development-type tasks that were rendered either infeasible or irrelevant by the discovery of the rogue process. These obsolete tasks were converted to experiments intended to exploit the DECOR discovery in a more practical configuration. A cartridge configuration was chosen based on the primitive understanding and data base for the DECOR process at the time. The PUE-6 and PUE-7 experiments with this cartridge DECOR design again achieved stable Cs/O vapor composition, but the operating point was found to be different than that of the pellet DECOR and to be strongly dependent on other factors such as the level of gaseous impurities and equilibration time.

The HET program was terminated in September 1995 as a result of system down-selection. At the time of the termination an experiment PUE-8 for evaluation of a new DECOR design, and an experiment PUE-9 using a mass spectrometer for direct determination of the Cs/O vapor composition had been initiated at Rasor Associates.

It is now possible, in retrospect, to interpret many of the DECOR characteristics and behavior observed in the PUE-4 to -7 experiments that seemed anomalous at the time the data were obtained but that now are explained by the theoretical model subsequently developed from those observations. Insufficient time and resources were available to re-examine and re-interpret the data from those completed experiments in light of the more recently obtained understanding, however.

Accordingly, the HET-IV experimental results and their interpretation are reported here in the form they were originally obtained, followed by a description of the successful theoretical model and a newly developed test vehicle appropriate for future work.

1.0 EXECUTIVE SUMMARY

The primary objective of the HET program was to define and utilize the beneficial effects of oxygen in cesium vapor thermionic energy converters. The HET-IV program phase reported here included the development of a stable cesium/oxygen (Cs/O) vapor source, and its associated experimental and basic analytical characterization.

Experimental Characterization

Cs/O Vapor Properties

- The Sputter Pulse Recovery Emission Elevation (SPREE) method initiated in HET-III was fully developed to permit continuous digital recording of both oxygen and cesium equivalent pressures, from 10^{-10} to 10^{-6} torr equivalent oxygen pressure.
- A three-stage mass spectrometer was developed to accurately measure species of mass 2-1500 AMU, having partial pressures as low as 10^{-7} torr in 1 torr cesium vapor, sampled directly from a gated hot orifice; Cs_2O , CsOH and Cs_2 were identified as dominant species.

Electrode Properties in Cs/O Vapor

- Converter J-V characteristics were measured using guarded planar electrodes.
- Emission work functions were measured using a guarded filament emitter.

Analytical Characterization

Cs/O System

- A thermochemical computer model was formulated that characterizes the vapor from Cs/O, Cs/O/H and Cs/O/C associated solutions.
- A physical/analytical model was formulated characterizing the liquid and vapor composition, together with mass and heat transfer, for the DECOR Cs/O vapor source.

Electrode System

- Physical/analytical models were formulated for time-dependent emission properties of electrodes immersed in Cs/O vapor with monolayer and multilayer coadsorbed cesium and oxygen-containing molecules.

Plasma/Electrode System

- A unique fundamental transport model of the ignited cesium diode thermionic converter was formulated with the associated computer program PLAS1D.
- The model was extended to obtain the first general two-dimensional transport model of the converter for coexisting ignited and unignited local plasmas and the associated PLAS2D computer program.
- PLAS2D and a modified TECMDL programs were used to characterize converters with grooved and hybrid mode emitters.

Dynamic Equilibrium Cs/O Reservoir (DECOR) Vapor Source Development

- A method was discovered for suppression of the basic physical instability of Cs/O solutions found in HET-III to arise via oxygen and cesium segregation due to cyclical distillation from a creeping film.
- It was discovered that this process could be confined and controlled within a porous medium to obtain long-term stability and reproducibility in its initial pellet configuration.
- In a more practical cartridge configuration it was found that additional factors must be controlled, primarily impurities such as H₂ and CO that were retained in the initial cartridge design.
- It was found that H₂ and CO impurities were abundant in the cesium ampules received from the vendor, and that they can be removed by a cesium still and suppressed thereafter by a commercially available getter.
- Based on the analytical model for DECOR, testing was initiated just prior to program termination on a system in which the Cs/O vapor is automatically circulated through the converter by DECOR.

Test Vehicles

- Most of the work in HET-III and HET-IV was performed in the "cube" test vehicle; this reduced cycle time for testing converter innovations from 3-6 months for conventional test converters to 3-6 weeks for the cube, but at the cost of troublesome failure modes of the demountable and valvable cube system.
- A new test vehicle, the sapphire tube, has been developed to overcome these limitations; it is revolutionary in its simplicity, reliability and low cost, and its cycle time can be a few hours or less; at the time of program termination, it was being used to evaluate a DECOR suitable for integration in a cylindrical converter.

Outstanding Accomplishments of the HET-IV Program

- A stable and controllable source of Cs/O vapor, including the basic theory of its operation and of diffusion-limited vapor equilibration time.
- New test methods:
 - Cube and tube test vehicles.
 - SPREE measurement of Cs/O vapor composition.
 - Hot-orifice three-stage mass spectrometry of Cs/O vapor.
- Greatly increased converter performance (see Fig. 1-1):
 - Output power increased 300%, efficiency increased 80% compared with cesium vapor only at large electrode spacing.
 - Stable performance increase obtained in Cs/O vapor without special electrode material or surface preparation.

Fig. 1-1 Converter performance improvement achieved through use of cesium-oxygen vapor, and projected further performance improvement through suppression of electron reflection from the Cs/O adsorbed layer. Emitter temperature 1800 K, collector temperature 800 K, electrode spacing 0.5 mm (20 mils), cesium pressure 1 torr.

2.0 PHYSICAL UNDERSTANDING EXPERIMENTS (PUE)

The Physical Understanding Experiments were initiated in the HET-III program to determine the conditions under which a single reservoir supplying Cs- and O-bearing gaseous species could improve thermionic performance. The initial approach was therefore to proceed through a sequence of oxidation steps on a Cs reservoir and to correlate vapor pressures with electrode performance. However, during the course of that investigation, experimental observations pointed to the unintentional development of a dual reservoir due to migration of cesium oxide (likely Cs_2O) out of the Cs reservoir as oxidation progressed.

Thus, in HET-IV, the PUE tests were redirected toward control and confinement of this cesium oxide segregation, while at the same time improving the description of the Cs-O vapor by adding species identification to the effective vapor pressures measurement successfully implemented in HET-III. To achieve vapor species identification, a time-of-flight mass spectrometer (TOF/MS), coupled with a special sampling valve, was operated to study the gas phase from a cesium-oxygen source in a converter environment. A complete test stand was built to operate the TOF/MS, the sampling valve and a planar converter (the "cube" converter with its required vacuum and temperature controls).

2.1 TOF/MS Sampling Valve and Test Stand

2.1.1 TOF/MS

It has become increasingly apparent that significant advances in converter performance require a better understanding of the molecular species in a converter gas phase, including Cs-O species: conceivably from H_2 to Cs_{11}O_3 (that is, masses from 2 amu to over 1500 amu). Unfortunately, commercial quadrupole systems that can go to 2000 amu are very expensive and suffer from a transmission loss of about one order of magnitude every 200 amu.

A combination of a standard quadrupole spectrometer and quadrupole trap to a time-of-flight spectrometer with a reflected flight path appeared to be an ideal instrument for the study of the mass spectra of cesium/oxygen vapors. Some of the advantages of such an instrument are the following:

- a. The time-of-flight instrument does not have the drop-off of transmission with mass number that the quadrupole mass spectrometer has, and it has the capability (in principle) of very good resolution, so it can be used to study large molecules such as Cs_2O and Cs_{11}O_3 .

b. The use of the quadrupole storage trap (with collisional damping) added to the time-of-flight spectrometer avoids some of the conflicts encountered between duty cycle, sensitivity, and resolution that a time-of-flight device alone would have. That is, with a time-of-flight device alone, high resolution requires short pulses from the source with pauses to separate pulse trains, resulting in a low duty cycle. And short pulses from a non-enhanced source results in low sensitivity. With the quadrupole trap, ions for a period equal to or long compared to the flight time can be gathered and dumped into the flight tube as a short burst, and more gathered while the first group of ions are being resolved in the flight tube. Further enhancement of the sensitivity occurs if the signals from repetitive dumps are added. Essentially, an extended-time, full duty cycle can be achieved [1].

c. The addition of a standard quadrupole in front of the trap [2] provides new capabilities:

- i. The front-end quadrupole mass spectrometer can be used as a Brubaker lens to get the ions from the sampling aperture near the cube (placed there for maximum solid angle) out through the vacuum wall where they can be analyzed by the trap and the time-of-flight spectrometer. In this function it becomes a broad-band mass transport device for loading the trap.
- ii. The front-end quadrupole mass spectrometer can be used by itself as a mass spectrometer for low-mass species. The trap and the flight tube then become just a complicated geometry the ions from the quadrupole spectrometer must go through before reaching the detector.
- iii. Finally, the front-end quadrupole mass spectrometer can be used for mass-selective loading of the trap, which is then analyzed by the time-of-flight spectrometer. The physics behind the operation of the Brubaker lens and of the ion trap can be found in detail in Ref. 3. To summarize the analyses, for practical purposes the Brubaker lens in our system lets through a mass range in amu between $M_1 = 0.116 V_{RF1}$ and $M_2 = 1.05 V_{RF1}$ while the ion trap retains ions between $M_3 = 0.054 V_{RF2}$ and $M_4 = 0.488 V_{RF2}$, where V_{RF1} and V_{RF2} are the peak-to-peak amplitudes of the RF voltages applied respectively to the quadrupole rods and to the ion trap ring. Thus, by changing these two voltages, it is possible to prevent species with an overwhelming concentration, e.g. Cs^+ , from entering the trap and then to

select the mass range of the ions for which an increased sensitivity is desired.

- iv. The reflected flight path improves the resolution of the instrument by causing ions of the same mass but different energies to reach the detector at about the same time. Another advantage of the reflected flight path is that it permits the shielding of the detector from the cesium neutral beam. A cold surface at the end of the flight tube can condense out the neutral cesium while only the ions are reflected back to the detector.

2.1.1.1 Structure of the TOF/MS

The structure of the TOF/MS is shown in Fig. 2-1 and the front-end pieces - the ionizer, quadrupole (Brubaker) lens, and the ion trap -- are shown in Fig. 2-2 in greater detail. The ionizer generates positive ions by electron impact and a 3-aperture electrostatic lens accelerates them into the quadrupole lens.

At the end of the quadrupole (Brubaker) lens or mass filter, the ions enter the quadrupole ion trap which consists of two end caps and a central ring with the geometry of hyperboloids of revolution around the mass spectrometer main axis. Usually the end caps are grounded and an RF potential is applied to the ring. Ions entering the trap are accelerated into complex orbits that are temporarily contained within the trap. A buffer gas (e.g., helium) is injected into the trap by a side tube, as shown by Figs. 2-1 and 2-2. The rate of injection is adjusted to give a background gas in the trap of about 10^{-5} torr, or in the chamber external to the trap of about 10^{-6} torr. The ions in the trap gradually lose energy by collisions with the buffer gas atoms and become permanently trapped. The ion density in the trap gradually increases and the ions trapped gradually become concentrated near the center of the trap.

This ion cluster is then accelerated into the flight tube by applying a negative pulse to the end cap. There is an additional, beam-defining, cone-shaped aperture within the field-free flight tube. The grid and aperture at the beginning of the flight tube and the flight tube itself are biased at about -1200 volts relative to ground. Immediately after entering the flight tube, the ions pass through an Einzel lens, which can be used to focus the ion beam, so as to cause the beam to fully cover the active surface of the detector. At the far end of the flight tube the ions enter the retarding field of the reflector, are reversed in direction, accelerated back into the flight tube, and sent to the

Fig. 2-1 TOF/MS Layout

Fig. 2-2 TOF/MS Front-End Components

detector. A deflection electrode is used to maximize the coverage of the detector by the reflected ion beam. The detector is a three-stage, micro-channel plate.

The mass spectrometer is contained in a double-chamber vacuum system (Fig. 2-3). The Brubaker lens and the quadrupole trap are in one chamber, and the flight tube is in the other. The two chambers are evacuated by separate turbo pumps. The pump for the quadrupole trap provide the forevacuum for the turbo pump which evacuates the flight tube chamber. A oil-free, two-stage diaphragm pump acts as a backing pump for the turbo pumps. Later a four-stage pump was substituted to lower the base pressure in the ion trap and the contribution of the residual gases to the spectrum. Without buffer gas the residual pressure, as seen by the first Bayard-Alpert gauge, is $\sim 1 \times 10^{-7}$ torr and in the flight tube $\sim 1 \times 10^{-8}$ torr. With He as a buffer gas at 1×10^{-5} , the pressure in the flight tube chamber is only $\sim 1 \times 10^{-7}$ torr.

Venting of the turbo pumps upon stopping is done with high-purity argon instead of air to avoid bringing reactive gases (O_2 , H_2O) in contact with surfaces with condensed cesium species.

Neutral cesium species entering the flight tube are condensed on a cold plate at $\sim 2^\circ C$ behind the ion-reflecting electrodes.

2.1.1.2 Coupling of the TOF/MS to the Cube: Sampling Valve

The planar converter from which gaseous species are mass-analyzed in the TOF/MS is similar in design to the "cube" converter, amply used in the HET-III program.

The cube needs to be centered in its vacuum chamber to allow full access to the ports of the cube. The TOF/MS, therefore, must pass through a vacuum collar (at the level of the cube) and penetrate far enough through the collar to come close to the cube. It needs to be close so the entrance aperture of the TOF/MS will intercept a maximum solid angle of the neutral beam from the cube and therefore maximize the sensitivity of the measurement. As shown in Fig. 2-4, this is accomplished by means of a stainless steel fitting (the shape of a "coke" bottle) that has been welded into the collar. A double sided flange attached to the small end of the "coke" bottle contains copper, fluid-cooled, beam-forming apertures. This flange is also attached to the valve that isolates the cube from the mass spectrometer. The cross sections of the aperture flange and the valve are shown in Fig. 2-5. The valve is operated from outside the vacuum chamber by means of a rotary feedthrough that attaches to the valve stem and to a tilt mounting flange which compensates for small misalignments.

Fig. 2-3 TOF/MS Vacuum System

Fig. 2-4 Coupling between the TOF/MS and the Cube Planar Converter

Fig. 2-5 Sampling Valve Connecting the Cube to the TOF/MS

Between the valve and the cube (and attached to the valve) is a hot, knife-edged, removable aperture with an opening about 10 mils in diameter. The hot aperture in conjunction with the fluid-cooled apertures of the double-sided flange define the neutral beam entering the ionizer.

The performance requirements for the valve are quite severe. Since the valve is attached to the cube, the end of the valve must operate at cube temperatures. Also, the other end of the valve must be attached to the flange which holds the fluid-cooled apertures, and those apertures need to be cooled to about zero degrees centigrade. So there is a severe temperature gradient through the valve. Also, the distance between the cube aperture and the spectrometer aperture must be short since the beam intensity from the cube aperture will go down inversely with the square of the distance. So the valve must be very short. In addition, to allow the beam to pass through, the valve must be in-line, with the sealing structure completely retractable out of the beam. The valve parts must be made from metals that are compatible with cesium at cube temperatures. And finally, the valve must be demountable for cleaning.

The shortest bakeable valve available commercially with 2.75" flanges is 7" long, which is unacceptable. A valve suitable for our needs was, therefore, designed and constructed using many of the parts of a high-temperature SS6UWTW-HT NUPRO valve from the Swagelok Co. The new valve body is machined from SS316 as in the NUPRO valve, and the valve tip is from the NUPRO valve, too. The overall valve length is down to 2.8".

Closing and opening of the valve are done by a "Tech-Motive" nutrunner manufactured by GSE, Inc. That tool is based on a dc electric motor and was developed as a CAM tool for the automotive industry. It is completely computer-controlled, can operate in the forward or backward direction, and can move to a specified rotation or to a specified torque. With these capabilities the valve action can be automatic, fast, and repeatable. In particular, the repeatability with respect to rotation and torque specifications allows to open the valve with just enough motion for the valve stem to clear the beam and then close to a precise torque. The proper operation of the sampling valve stem and the absence of any obstruction on the sampling orifice or the cooled skimmer can easily be ascertained by running the TOF/MS ionizer filament at high temperature (emission ~2 mA): if there is a clear line of sight, the bounced filament light will make the sampling hole shine when the valve opens.

2.1.2 System Operation

The hardware and software integration for the operating TOF/MS is shown in Fig. 2-6. The computer which controls the operation is shown by the large dashed box in the lower half of the diagram, which is shown to contain two computer cards and two software packages. One computer card is the LabView PC+ board of the National Instrument Co. that is used in conjunction with the LabView software. The LabView software sets the parameters for the operation cycle of the TOF/MS. The other computer card is the PI9845 signal capture board. Its associated software package sets the data-gathering parameters for the board, operates the signal digitizer, and displays the resulting mass spectral data.

Once the parameters are set up in PI9845 software and the data-gathering electronics activated, the operator moves to the software package LabView to initiate the measurement cycle. Once the cycle is initiated in LabView, LabView actuates the PC+ board, which sends appropriate signals out to the digital relays or digital actuators for the electric nutrunner. These electronic relays choose the desired operation for the nutrunner and turn the nutrunner on by means of the CS-40 controller. LabView applies a short delay, needed for the cleanup of cesium from surfaces in the valve, and then actuates the Precision Instruments 9845 board in the PC.

The spectrometer flight tube, ion reflector and detector are shown on the right side of Fig. 2-6. Voltages needed for the liner, a focus Einzel lens for adjusting the beam size to the detector, a deflector electrode, reflection grids at the end of the flight tube, and the MCP (micro channel plate) detector are provided by the AREF (Angular Reflection) power supply. The quadrupole rods are activated by a standard quadrupole mass spectrometer r.f. power supply (QUAD P.S.).

The rest of the spectrometer connections depends on the mode of operation. The bold-line connections shown above the spectrometer are the connections for the standard quadrupole mode. In this case, the focus or extraction aperture is connected to the standard focus voltage supply. In addition, power supplies are connected to the three electrodes of the trap to try focussing the ions coming out of the quadrupole rods onto the exit aperture of the trap. The quadrupole supply is operated in a standard way with the usual sweep, resolution, and center-of-mass adjustments. The sweep or ramp signal (as shown in Fig. 2-6) is passed through a pulse shaper to turn the beginning of the sweep into a TTL signal to trigger the sweep of the signal digitizer.

When the spectrometer is operated as a quadrupole-trap time-of-flight device, the bold-line connections below the spectrometer are used. The focus or extraction aperture of the ionizer

is now triggered by a pulse sequence generator. That is, an A/B pulse through the IT/RF supply triggers the IF/RP (ion focus remote pulser). An IT/RF (ion trap r.f.) power supply supplies the r.f. power to the trap. Another pulse from the pulse sequence generator (the C/D pulse) triggers the IT/RP (ion trap remote pulser) that dumps the ions of the trap into the flight tube. The reason the C/D pulse must trigger the IT/RP through the IT/RF power supply is that arrangement is made in the latter device to that when the C/D pulse arrives an r.f. phase detector waits until the r.f. voltage passes through zero in a positive-going direction before turning off the r.f. Then the device waits until the r.f. dies down sufficiently for the extraction process to be efficient and waits again until the r.f. passes zero in a positive-going direction before the trap end cap is actually pulsed with the IT//RP to empty the trap. At that moment of emptying the trap a TTL pulse appears on the pulse monitor of the IT/RF supply. This pulse is used to trigger the beginning of the data signal digitizing scan.

2.1.3 Operation Cycle and Electronic Control

The operating cycle and some associated electronic signals are shown in Fig. 2-7. As the top panel of that figure shows -- first, the valve is opened; second, a cleanup time is allowed (for cleanup of cesium from all surfaces outside the cube sampling aperture). Much of that cesium will move to the cold aperture system and be captured. With the pulse generator in free-run, the trap is repeatedly loaded during the A/B pulses, ions are cooled in the trap between points B and C, and the trapped ions are dumped into the flight tube as triggered by the C/D pulses. As the figure shows, at the appearance of the C/D pulses this is accomplished by phase-sensing waiting until the r.f. is going through zero in a positive direction, the r.f. first being turned off, a delay added to let the r.f. decay somewhat, phase-sensing again waiting until the r.f. is going through zero in a positive direction, and then dumping the trapped ions into the flight tube with a pulse of set duration. The trap RF is then turned on again. After the requested number of scans are recorded, the valve is closed. With the use of a pulse delay generator the beam can load the trap for a time independent of the trap cooling time. This can be used, for example, when it is desired to maximize resolution by minimizing the loading of the trap to avoid space charge problems and by maximizing the cooling of the ions before firing them into the flight tube to avoid ion energy spread. A simplified version of the phase sensing circuit of the IT/RF power supply is shown in Fig. 2-8.

Fig. 2-8 Schematic of the Ion Trap RF Timing

2.1.4 TOF/MS Operational Tests

2.1.4.1 TOF Mode

Some samples of TOF spectra are shown in Figs. 2-9 and 2-10. Fig. 2-9 shows an Xe spectrum with its various isotopes: the mass resolution is about 200, lower than expected. According to R. Jordan, this could be due to the smaller size of the ion trap, as some of his later units with the same Brubaker lens have achieved resolutions of 1000 with a bigger trap. Nevertheless, our resolution is good enough to separate Cs_2 (266) from $(\text{CsOH})_2$ (300) and just enough to differentiate Cs_2O_2 (298) from $(\text{CsOH})_2$.

Fig. 2-10 is a collage of scans for perfluorotributylamine ($\text{C}_{12}\text{F}_{27}\text{N}$ or FC43). One setting of the Brubaker lens is not enough to see the whole mass range at once: a setting of 100 amu loads the lighter fragments (up to ~300 amu) in the trap, while a setting of 380 amu is needed to let in the heaviest fragments (up to 614 amu). For the spectra shown in Fig. 2-10 the same RF voltage on the ion trap ring was used; i.e., keeping constant the trapped amu range.

For a fixed set of DC voltages applied to the TOF electrodes, a single mass-time correlation can be obtained, as shown in Fig. 2-11.

2.1.4.2 Quadrupole Mode

Fig. 2-12 is a scan of the residual atmosphere with argon added, obtained when using the front quadrupole as a mass analyzer. The trigger for the scan occurs as the RF voltage sweep starts to return to its minimum value, so there is a fast backward spectrum before the slow forward one. The signal-to-noise ratio and the resolution are both poor because the ions which would get trapped in the ion trap now have to fly through it without the possibility of storage and axial confinement. Attempts to use the three ion-trap electrodes as an electrostatic lens to refocus the ions axially did not produce any significant improvement. It should also be noted that in a regular quadrupole mass spectrometer the ion detector would be located right where the front trap electrode is, and present a wide acceptance angle able to capture ions with significant radial velocities. The poor sensitivity obtained in the quadrupole mode appears to preclude the detection of H_2 and CO as constituents of the cube gas phase, given the attenuation of the neutral beam as it expands out of the sampling hole into the TOF/MS vacuum system.

XENON TOF SPECTRUM

Fig. 2-9 Xenon TOF Spectrum

"FC 43" TOF SPECTRUM

Fig. 2-10 FC43 Spectra at Various Settings of the Quadrupole Lens Window

Fig. 2-11 Calibration of Mass vs Time-of-Flight Using Various Gases

Fig. 2-12 Using the quadrupole of the TOF/MS to detect low masses

2.1.4.3 Detection Sensitivity in the TOF Mode

Direct measurements of the equivalent oxygen pressure (i.e., the sum of the partial pressures of oxygen bearing species that are absorbable at ≥ 1300 K) by the sputter-reabsorb method give values in the range 10^{-10} to 10^{-6} torr, when the cesium pressure is about 1 torr (see Section 4.3). Thus, if these oxygen-bearing species are of the type Cs-O-X, the TOF/MS must detect such low pressures at amu's beyond 133. A scan around the Cs peak indicates a signal-to-noise ratio of about 800 (Fig. 2-13) which obviously is inadequate. However, if the loading time of the ion trap and the storage time (i.e., axial confinement time) are increased for the investigated species, the detection limits can be raised. The signal amplitude was, therefore, studied as a function of loading and storage times, using in this particular case for convenience the remnant Cs peak coming from Cs layers condensed on the ionizer electrodes (see Section 2.3). The results, shown in Figs. 2-14 and 2-15, indicate that indeed the signal can be increased by at least three orders of magnitude if the loading and storage times are increased in the same amount. The drawback of this approach is that the Cs losses out of the cube also increase in proportion, as the sampling valve is kept open during the loading, storage and spectrum-averaging. (At $P_{Cs} = 1$ torr, the cube will lose $15 \mu\text{g}$ of Cs for each second of open time.) Two experiments were then conducted to see if partial pressures of 1×10^{-6} torr could be detected in the presence of a major constituent at a pressure approaching 1 torr using standard molecules, e.g. Xe for Cs and $\text{C}_2\text{H}_5\text{I}$ (156) for CsOH (150). The set-up is shown in Fig. 2-16: the low pressure range is covered by a cold cathode gauge calibrated against a Bayard-Alpert gauge (using a sensitivity factor of 4.5 for $\text{C}_2\text{H}_5\text{I}$), the high pressure range up to 10 torr is covered by a capacitance gauge and leak valves are used to adjust each pressure.

In the first experiment the two pressures of $\text{C}_2\text{H}_5\text{I}$ and Xe were obtained in a dynamic equilibrium in which the leak rates were adjusted to obtain stable pressure readings while pumping on the system, i.e. with the butterfly valve in Fig. 2-16 open. The results of this test are shown in Fig. 2-17, when a sequence of spectra is displayed: a, b, c, d, obtained with increasing P_{Xe} and letting Xe ions in the ion trap show the progressive disappearance of the $\text{C}_2\text{H}_5\text{I}$ signal. However, in spectrum e, when Xe ions were excluded from the trap by adjusting the Brubaker lens RF voltage, the Xe peak is almost gone, even at 2 torr, while $\text{C}_2\text{H}_5\text{I}$ at 2×10^{-6} torr is very prominent. (For all spectra in Fig. 2-17, the loading time was 0.3s, and the storage time 0.5 s.)

In the second experiment the two pressures were established in a static fashion: first, the $\text{C}_2\text{H}_5\text{I}$ leak valve was gradually opened until $P(\text{C}_2\text{H}_5\text{I})$ reached the desired value

Fig. 2-13 Cesium TOF Signal from Cube with $P_{\text{Cs}} \sim 0.1 \text{ torr}$.
 (On this time scale, CsOH , Cs_2O , Cs_2O_2 would
 appear at 56.1, 77 and 79.1 μs , respectively)

Fig. 2-14 Influence of ion trap loading time on signal

Fig. 2-15 Influence of ion trap storage time on signal

Fig. 2-16 Set-up to test the detection limits of the TOF/MS

Fig. 2-17 TOF Spectra from the Cube with 2×10^{-6} torr of $\text{C}_2\text{H}_5\text{I}$ and rising Xe pressures in dynamic regime. Scans a, b, c while accepting Xe^+ in trap.

Fig. 2-17 (continued) Spectrum d while accepting Xe^+ in trap,
 and Spectrum e while rejecting Xe^+ from trap.

above the background; second, while maintaining $P(\text{C}_2\text{H}_5\text{I})$ the leak valve and the butterfly valve were gradually closed; third, with these two valves closed, Xe was added to reach its desired pressure at which point its leak valve was also closed. Despite the disparity in the two pressures, the concentration of $\text{C}_2\text{H}_5\text{I}$ in Xe should become uniform in about 1 minute, as shown in Appendix A. As seen in Fig. 2-18, adding 0.6 torr of Xe to 1×10^{-6} torr of $\text{C}_2\text{H}_5\text{I}$ wiped out the iodide peak when Xe ions were allowed in the trap, but the iodide peak reappeared when the Brubaker lens was set to reject Xe ions. (This rejection is not perfect since Xe peaks are still seen.) Spectrum c in Fig. 2-18 was obtained by averaging 8 scans for which the loading time was 0.3s and the storage time 0.5s: increasing the number of averages and these loading/storage times would clearly make $\text{C}_2\text{H}_5\text{I}$ pressures below 1×10^{-7} torr detectable. Direct demonstration of the ability to detect Cs_2 , Cs_2O and Cs_2O_2 at this pressure level was obtained during PUE-9 testing (see Section 2.3).

2.1.5 Cube Converter Test Stand

Fig. 2-19 shows schematics of the two vacuum systems used to pump-down/outgas a cube converter and to bring its various components to their operating temperatures.

Pumping down the cube was done by a turbo pump backed by an oil-sealed mechanical pump. The small volume between the two butterfly valves was intended for adding measured amounts of oxygen if needed. After outgassing the vacuum plumbing outside the bell jar, the base pressure read by a cold cathode gauge was usually below 1×10^{-7} torr.

The bell jar pumping was accomplished by a 230 l/s ion pump with most of the initial outgassing being dumped into an outside turbo cart. Appendix B described the operating procedure for the TOF/MS vacuum system shown in Fig. 2-3, as well as those for the cube test stand. The rest of the hardware provided temperature controls to the various components of the cube converter (reservoirs, electrodes, plumbing), shown in Fig. 2-4. Fig. 2-20 shows two views of the complete set-up.

2.2 PUE-9: TOF/MS Analysis of Cube Vapor Species

After the successful operation of a DECOR source in the previous PUE tests and the development of internal diagnostics to determine the effective cesium and oxygen pressures, the purpose of this task was to identify the oxygen-carrying vapor species responsible for these oxygen pressures so as to provide experimental data to the theoretical thermochemical modeling.

Fig. 2-18 TOF Spectra with static pressures in the cube:
 a. C₂H₅I at 1x10⁻⁶ torr and residual Xe
 b. Same C₂H₅I pressure, 0.6 torr of Xe
 c. Same as b, but preventing Xe loading of the ion trap

Fig. 2-19 Schematic of the vacuum systems for the cube connected to the TOF/MS

Fig. 2-20 Complete TOF/MS set-up for the PUE tests

As will be shown in Section 4.3, the first attempt to sample the vapor phase in PUE-6 was based on a redesign of the DECOR which provided a wealth of data on P_{Cs} and P_{Ox} , but did not lead to very good thermionic performance. It was, therefore, considered preferable to return to the original pellet design of DECOR, such as tested in PUE-4 and PUE-5 (see Section 4-1 and 4-2).

Radiant heating of the top DECOR surface, which occurred in these two tests, was first simulated by having a filament above the Pt pellet (PUE-7 test, Section 4-4). But voltage breakdown in the cesium atmosphere between the filament ends limited the available heat flux, so it was decided to use the emitter itself as the sole heat source for the pellet top.

2.2.1 PUE-9 Test Set-up

Using existing components -- emitter, oxygen/cesium detector, window, cup -- leaves only one port available on the cube as the fifth port is needed for the sampling valve. To avoid having to redesign one of these components or the collector assembly, the last port was therefore assigned to carry a mirror and an internal thermocouple to measure the temperature at the top of the pellet, thereby omitting the collector. This is only a very minor inconvenience since the main objective of the test is to sample the vapor phase supplied by a DECOR source.

Fig. 2-21 shows the PUE-9 set-up. The Mo emitter located about 0.8" above the pellet was heated by electron bombardment as usual. The Pt pellet (ϕ 0.43" x L 0.13") had a sintered density of 15% of bulk Pt, which made it very similar to that in PUE-5.

A type E (Ni-Cr/Cu-Ni) 5 mil wire thermocouple was shaped to make a springy contact inside a small hole (ϕ ~0.02" x L 0.04") drilled in the top pellet surface. The thermocouple wires were spot-welded to type E rods (ϕ = 0.05"). A polished Ni mirror was brazed to the same flange. A small Ni shield (~ 0.25" square) was located above the thermocouple junction to prevent radiation from the emitter from reaching it directly, which could have lead to false temperature readings. The Pt pellet rested in the center of a Mo cup whose temperature was regulated.

The original dimensions of the sampling valve handle were reduced to allow the removal from or installation in the bell jar of the whole plumbing with the sampling valve attached to the cube without having to tilt the cube (Fig. 2-22). For instance, to install the system inside the bell jar, the following operations were performed sequentially:

Fig. 2-21 PUE-9 Set-up

Fig. 2-22 PUE-9 cube with plumbing and sampling valve attached

- Outside the argon box, the cube with its attachments, except the pellet cup, was connected to the closed sampling valve and to the plumbing, and all flanges tightened.
- Inside the argon box, the pellet cup was raised with the Pt pellet in place while aiming the internal thermocouple junction at the pellet hole.
- After tightening this last flange, the whole system was brought to the test stand with the beam skimmer placed inside the sampling valve, and lowered in position, without having to tilt the system, thereby guaranteeing that the Pt pellet would stay in the cup with the internal thermocouple in place.

Removing the system from the bell jar would proceed exactly in reverse, after backfilling the cube and the TOF/MS with argon. In addition to the usual reservoirs and valves, the plumbing also included a getter canister with its own heater. This canister contained a 2 cm x 80 cm strip of Zr-V-Fe getter material from SAES, rolled into a coil. As explained in Section 2.4, this getter was found to be very effective in removing gaseous impurities from the cesium gas phase.

2.2.2 PUE-9 Outgassing

PUE-9 was pumped down during outgassing with the outside pumping system (shown in Fig. 2-19) to which a quadrupole mass spectrometer had been added to monitor the evolved gases. The outgassing proceeded as follows:

- Outside pumping system at ~150 C using heat lamps to remove H₂O.
- Plumbing, cube, cup at 350 C and pellet top at 410 C: mostly CO released.
- Emitter at 1550 C: mostly CO, some H₂.
- Getter at 600 C on its own (isolation valve closed): very large amounts of H₂.

The cesium contained in both fast and calibrated reservoirs was purified by bringing Cs vapor at ~1 torr in contact with the getter at 320 C overnight.

2.2.3 Sampling of the Cube Atmosphere in the TOF/MS Quadrupole Mode

Attempts were made to detect differentially partial pressures of CO or H₂ in the cube vapor. These attempts were unsuccessful for two reasons:

- Expansion of the beam coming from the sampling orifice. When this beam reaches the ionizer its intensity has been reduced by a factor of $\sim 1 \times 10^6$ (see Appendix D).
- Background pressure in the ionizer region was too high. With partial pressures of H_2 , H_2O and CO about equal at $\sim 1 \times 10^{-7}$ torr each, anything coming from the cube at these masses at a partial pressure of 1×10^{-6} torr would be seen at the ionizer as having an effective partial pressure of 1×10^{-12} torr and would not be detected above the background. To detect such cube vapor species one would have to reduce the residual gases down into the 10^{-11} torr range. To achieve this the TOF/MS vacuum system would need to be upgraded to strict UHV standards (all Cu-gaskets, bake-out above 200 C, Ti getter pumping with cryo-panels).

2.2.4 Sampling of the Cube Atmosphere in the TOF Mode.

Early TOF spectra showed great promise, as Cs_2 , Cs_2O and Cs_2O_2 (or the CsOH dimer) were very prominent. However, each of them started growing in time as the sampling valve was operated, while the ionizer electron current started showing leakage (emission current varying with electron energy, for a cold ionizer filament). Turning off the ionizer filament lead to a drop in the leakage and the peak heights, but they rose again as the filament was left on. This provided strong evidence that Cs-O compounds were condensing and building up on the ionizer electrodes and insulators, leading to spurious signals as these ionizer components were slowly heated by the filament.

Microscope examination of the grid on the anode entrance aperture revealed at each wire intersection a liquid droplet attributed to deliquescent CsOH . The ionizer was then modified mechanically in two ways (Fig. 2-23): removal of all grids in the ionizer, bigger diameter of all ionizer electrodes so as not to offer condensing surfaces to the beam coming out of the cooled skimmer. To reduce the temperature of the ionizer parts, copper strips (cold-worked to achieve some springiness) were added to make contact with the cooled flange and other parts connected to it.

After these modifications, the spurious background at Cs_2 , Cs_2O and Cs_2O_2 was much lower and leaving the ionizer filament on for 1 hour did not cause these peaks to rise. Resuming the test produced qualitatively satisfying results such as seen in Fig. 2-24: two spectra are

Fig. 2-23 Modifications to the ionizer assembly to reduce the amount of build-up on the electrodes

Fig. 2-24 Two TOF Spectra, with the sampling valve open (top) and closed (bottom)

shown, the top one with the sampling valve open and the bottom one with the valve closed: the major difference is, aside from the Cs peak, the Cs₂O peak with is ~2.5 times above its background signal when the sampling valve is open. However, the background signals of Cs₂, Cs₂O and Cs₂O₂ obtained with the valve closed were still noticeable above the noise, despite the changes to the ionizer described previously. One possible explanation for the existence of a background for these species is that, after the first valve opening, adsorbates on that sector of the hemispherical valve tip in permanent line of sight of the sampling orifice, can diffuse over the entire tip from which some can be desorbed into the ionizer. To mitigate this problem either the time between valve openings would have to be increased to allow that desorption to self-exhaust or a way to supply localized heating to the valve tip would have to be found to accelerate that desorption.

In the top scan of Fig. 2-24, values are given for P_{Cs}, P_{ox} and P_{Cs2}. The first two were obtained from the detector filament inside the cube, using the SPREE method. P_{Cs2}, on the other hand, was calculated using a thermodynamic approach described in Appendix E, assuming that, due to the overwhelming Cs pressure, the dimmer Cs₂ comes only from the reaction

which leads to:

$$\text{Log } P_{\text{Cs}_2} \text{ (torr)} = 3.317 \text{ Log } P_{\text{Cs}} \text{ (torr)} - 7.513.$$

So, the presence of a Cs₂ peak provided a way of calibrating the partial pressures of Cs₂O and Cs₂O₂. To be as accurate as possible, three processes would have to be quantified: the relative ionization cross-sections, the contribution of the cesium oxides to the Cs₂ peak by fragmentation and the relative secondary electron coefficients of the electron multiplier. As a first approximation, these corrections were ignored and, indeed, based on the peak heights in the top spectrum, some consistency is reached as

$$P_{\text{Cs}_2\text{O}} \sim 2 P_{\text{Cs}_2} \sim 1 \times 10^{-7} \text{ torr} \sim P_{\text{ox}}$$

It should also be noted that the scans in Fig. 2-24 were obtained with ion trap loading and storing times of 0.6s and averaging 16 spectra, in effect leaving the sampling valve open for 19s, thereby

losing at that P_{Cs} about 330 μg of Cs. If higher Cs losses can be tolerated, partial pressures of cesium oxides well below 10^{-8} torr should be detectable. This approach was unfortunately not tried on Cs_{11}O_3 , so at this point we can only say that its pressure probably did not exceed 2×10^{-8} torr.

Using the fast Cs reservoir, it was possible to vary the Cs pressure inside the cube over an order of magnitude. Two examples of TOF spectra are given in Fig. 2-25 and 2-26 in which the Brubaker lens setting was changed to allow or not Cs^+ in the ion trap. Plotting the peak heights of Cs and Cs_2 versus P_{Cs} after background subtraction results in Fig. 2-27. In this log-log plot, the graph of the Cs peak height versus P_{Cs} should have had a slope of 1, which suggests that the ion trap was saturated at all cesium pressures for the trap loading and storage times of 0.6s, common to all spectra in Figs. 2-25 and 2-26. (In retrospect, instead of attenuating the signal after the detector, it would have been preferable to reduce the ion current into the detector by dropping the ionizer electron current and both loading and storage times.) According to thermodynamics, the Cs_2 peak height should have had a slope of 3.32 as a function of P_{Cs} (see Fig. 2-28), but it is 1.86 instead. This discrepancy is not understood at this time.

2.2.5 Conclusions on the PUE-9 Test and Suggestions for Future Work

Despite considerable obstacles (impurity levels below 1 ppm, condensable species) the data obtained in the PUE-9 test have finally shown that the initial choice of a time-of-flight mass spectrometer, coupled to an ion trap, itself preceded by a quadrupole lens, had all the required properties to detect Cs_2O in 1 torr of Cs at pressures below 1×10^{-7} torr while allowing a very small amount of cesium to escape. The main unresolved question is the reduction of spurious peaks in the mass range of interest.

Although the work required in this task was successfully completed, it would be informative to vary the effective oxygen pressure inside PUE-9 over a wide range and to correlate it with measurements of the various cesium oxide partial pressures with the TOF/MS. This would therefore constitute a natural extension of the present research. (It might actually be easier to affect the oxygen pressure over a wider range by adding other gaseous species such as H_2 or CO .) Even though the sensitivity proved quite adequate, it would be highly desirable to reduce the amount of cesium loss when the sampling valve is operated by reducing the sampling orifice size. One suggestion is to increase the efficiency of the ionization process by using a magnetic field to

Fig. 2-25 Two TOF Spectra for $PCs = 0.25$ torr in PUE-9. A Brubaker lens setting of 420 lets Cs ions reach the trap, while at 500 they are excluded.

Fig. 2-26 Two TOF Spectra for PCs = 1 torr in PUE-9

Fig. 2-27 TOF/MS Cs and Cs₂ signals vs Cs pressure

Fig. 2-28 Equilibrium pressure of the dimer Cs_2 vs the Cs pressure

cause the ionizing electrons to travel a long distance. Based on the process described in Ref. 9 a possible implementation is shown in Fig. 2-29.

2.3 Cesium Purification System

2.3.1 Experimental Background

The objective of this task was to develop and test a system that can guarantee availability of a high purity cesium supply for future experiments. Experiments PUE-6, PUE-7, and PUE-7A showed evidence of large quantities of hydrogen as a contaminant in the cube vapor, which was suspected of affecting thermionic performance. The cube atmospheres were sampled by briefly opening the valves which isolate the cube from the external vacuum plumbing. The valve was open for a short enough time (≤ 2 seconds) that loss of cesium from the cube was negligible. A standard quadrupole mass spectrometer was present in the external plumbing in each experiment. All cesium vapor released from the cube would condense before reaching the quadrupole, but non-condensable gasses could be detected. Quadrupole results consistently showed that hydrogen was the dominant gas released during a brief opening of the isolation valve.

Quadrupole measurements in the PUE-7 experiment showed that the external liquid cesium reservoir, from which cesium was transferred into the cube, was also a strong source of hydrogen, as well as some carbon monoxide and methane. This raised the suspicion that the original source of hydrogen in the cube was that it was present in the liquid cesium when it was placed in the external reservoir, and was then transferred into the cube when cesium was distilled from the reservoir to the pellet cup.

The cesium-loading procedure for the PUE experiments was suspected to be a source of contamination. In this procedure, cesium was loaded into the external reservoir in a purified argon-atmosphere glove box. Heated glass cesium ampules were broken open, and the liquid metal was drawn into a hypodermic needle. It was then injected into the reservoir tube, and the reservoir was closed.

2.3.2 Description of cesium purifier prototype experiment

A prototype cesium purification system was designed and constructed in order to answer the questions:

- Is cesium the source of the observed hydrogen contamination?

Fig. 2-29 Possible way to increase the ionization efficiency

- What other gas species are evolved from the cesium?
- If cesium is the source of the contamination, is the contamination due to the injection procedure in the argon glove box, or is it present in the cesium as received from the vendor?

A sketch of the apparatus is shown in Fig. 2-30. Cesium was transferred into the reservoir by distillation from an ampule holder. The heated cesium liberated gasses which were measured by the quadrupole mass spectrometer. Vacuum was maintained by a 20 liter/second triode ion pump, which pumped the gasses as they were evolved. Total gas pressure was measured using the ion pump current. The water-cooled baffle isolated the ion pump and quadrupole from cesium vapor

Fig. 2-30 Cs purification prototype.

by condensing the cesium so that it dripped back into the lower "tee". Care was taken to keep the water temperature above the melting point of cesium (29°C) to prevent freezing of the entire cesium charge in the baffle. All-metal components were used throughout, so that the system could be baked at 250-300 °C. This enabled a low background pressure of $\sim 1 \times 10^{-8}$ torr to be achieved, ensuring that any measured gasses came from the cesium rather than the plumbing.

Two experiments were performed. In the first, a glass ampule containing 1 gram of cesium was placed in the ampule holder, outgassed at 180 °C, then crushed from outside the vacuum

envelope in order to release cesium. In the second, cesium was injected into the ampule holder using the hypodermic injection procedure as was used in the PUE experiments. If the second experiment showed substantially more gas than the first, that would implicate the injection procedure as a source of contamination. Both experiments used cesium from the same lot number (#2070) as were used in PUE-6, -7, and -7A. There is a high probability that this lot also supplied PUE-5, but this cannot be definitely confirmed.

In the prototype design it was found that cesium which dripped back into the lower tee from the baffle could not find its way back into the small reservoir tube quickly enough, so that the lower tee effectively functioned as the reservoir. This was not a problem for gas measurements done during cesium transfer from the ampule holder, which provided the primary information in the experiment. Also, since all temperatures (including the lower tee) were the same in the first and second experiments, contamination from as-received and from injected cesium could be directly compared.

In addition, since the section above the water-cooled baffle must be continuously pumped in order to operate the quadrupole, the gas pressure as measured at the ion pump was lower than that in the actual reservoir. Two factors contributed to this. The first was the conductance between the reservoir and ion pump, which was dominated by the conductance of the baffle. The gas pressure in the reservoir was estimated using the known value of the ion pump pumping speed and calculated values of the conductance. The second factor is that when cesium condenses in the baffle, it forms a cold, fairly pure layer of cesium over the entire interior surface of the baffle. When impurity gases pass through the baffle they are partially re-absorbed by this layer. The impurities are returned to the reservoir when cesium drips back down from the baffle. This effect possibly caused a further reduction in gas pressure as measured at the ion pump.

2.3.3 Measurement of Evolved Gases

Total pressure and composition were measured during cesium transfer, when cesium in the ampule holder was heated to about 180 °C. A strip chart showing total pressure vs. time is shown in Fig. 2-31. The peak total pressure at the ion pump was 4×10^{-6} torr. Correcting for conductance gives an estimated pressure of 1.8×10^{-5} torr in the reservoir/lower tee area.

The gas composition consisted of three primary species: H₂, CH₄, and CO. A sample spectrum is shown in Fig. 2-32. Hydrogen accounted for over half the total pressure at the beginning

Fig. 2-31 Pressure vs. time strip chart for first cesium transfer.

Fig. 2-32 Mass spectrum at total pressure of 8×10^{-7} torr.

quickly, so that after about 1 ½ hours hydrogen was almost 80% of the total. This would seem to indicate that the inventory of hydrogen dissolved in the cesium was much larger than that of methane or CO. Pressures vs. time and gas compositions were nearly identical for cesium in as-received condition and for cesium injected with a hypodermic needle.

After transfer, the ampule holder was valved off and the cesium reservoir brought to 300 °C. However, as previously mentioned, the design of the prototype was such that re-condensed cesium from the baffle tended to stay in the lower tee rather than the reservoir. Results indicated that reservoir temperature had a negligible effect on impurity pressure, while the temperature of the lower tee had a very strong effect. Post-test disassembly found no evidence of cesium in the reservoir, while cesium was found both in the lower tee and in the ampule holder. As a result, the actual cesium temperature and pressure during this second phase of the experiment is not known precisely, so that it is difficult to be quantitative about the level of impurities evolved at high temperature. However, the results confirmed the gas composition as consisting of hydrogen, methane, and carbon monoxide, with hydrogen the dominant species.

Conclusions

Some conclusions reached during experiments with the cesium purification prototype were:

- Heating liquid cesium produced a relatively high pressure of impurity gas, which consisted primarily of hydrogen. It is therefore very likely that the cesium was the source of the contamination observed in PUE-6, -7, and -7A.
- Methane and carbon monoxide were present in smaller quantities.
- The impurities were present in cesium as it was received from the vendor. There was no evidence that handling in the argon box or contact with the hypodermic needle caused further contamination.

2.3.4 Advanced Cesium Purification System Design

This task produced a design for a system which could produce pure cesium (hydrogen-free) on a long-term basis. The design goals were for a system with the ability to:

- add new cesium from time to time without exposing any cesium remaining in the system to the atmosphere,
- provide cesium to multiple experiments,

- operate for an extended period of time and over multiple cesium fillings without disassembly and cleaning.

The purifier shown schematically in Fig. 2-33 utilizes both gettering and active pumping, with a continuous flow of cesium through the purifying components. Gettering with a Zr-V-Fe alloy was found to be effective in removing hydrogen in the PUE-7B experiment (see section 4.4). Active pumping was shown to be effective in the prototype experiment, and is useful in removing methane, which is not gettered well. Cesium container 1 is held at a higher temperature than cesium container 2, so that cesium vapor continuously flows through the getter canister, past the water-cooled baffle, recondenses in cesium container 2, and flows by gravity back to container 1. The system is continually pumped through the water-cooled baffle, in which cesium vapor condenses and then drips back down into cesium container 2. The loss of cesium over time is very small. A small heater heats the inlet cooling water above 30°C so that the cesium will not freeze out in the baffle. The composition of non-condensable impurity gasses can be continuously monitored by an RGA.

The arrangement of valves in Fig. 2-40 is such that new cesium ampules can be added by distillation from crushed glass ampules into cesium container 1, pumped down, and outgassed while preventing contamination of the system by exposure to atmosphere. An argon purge would be used to prevent exposure of the ampule holder connection to air when installing new ampules. A design for the above system was produced to meet the requirements of this task and is shown in Fig. 2-34 and Fig. 2-35.

2.4 PUE Emitter Model

2.4.1 Background

COAD, a physical-analytical model [4], was developed for computing the emission and vaporization properties of a surface immersed in a multi-species vapor, based on the original Rasor-Warner model for cesium adsorption alone [5]. The evaporation and condensation processes are assumed to be identical to those for an equilibrium adsorbed phase in equilibrium with its vapor, hence leading to a statistical mechanics computation of the sticking coefficient for the practical non-equilibrium condensation condition. The model uses available and estimated properties for 17 species of cesium, oxygen, tungsten, and their compounds to compute the work function for tungsten immersed in Cs/O vapor. The work function is computed by the summation over the dipole moments of the various coadsorbed species in their mutual electric field. Two classes of adsorption sites are defined corresponding to superficial and interstitial coadsorption.

Fig. 2-33 Cesium purifier using a cesium still and active pumping.

Fig. 2-34 Top view of design for a re-usable, long-term cesium purification system.

SECTION B-B

Fig. 2-35 Side view of design for a long-term cesium purification system.

Earlier evaluations indicated that the model provided an adequate description of emission and evaporation processes a tungsten surfaces that were immersed in pure cesium vapor as well as those immersed in pure oxygen vapor. Electrodes immersed in Cs/O vapor have been shown to remarkably increase the performance of cesium vapor thermionic converters [6]. Practical use of this technology has been restricted by the incomplete understanding of the thermochemical complexity of the surface system and the concomitant lack of control over the processes involved. Therefore, the ultimate usefulness of the model requires a comprehensive description of the coadsorption of cesium, oxygen, cesium oxides and tungsten oxides on tungsten.

The COAD model is, however, restricted to the emitter work function as it allows for the formation of submonolayers (coverage <1) for each of the electropositive and electronegative adsorbates, e.g. Cs and O. The collector work function, especially at low collector temperatures, does not fit into the COAD formulation as both coverages approach and exceed unity (see Section 2.5 below).

An attempt has been made during this work to systematically test the COAD model in order to ascertain the following:

- a. A general overview of the effect of the changes in the converter parameters (P_{Cs} , P_{O_2}).
- b. Isolation of the most influential species by evaluating each species for the effect due to caused by changes in key physical parameters (i.e. the density of adsorption sites, σ , and adsorption energy, ϕ_A).
- c. Estimation of the possible effect of ambiguities in thermodynamic parameters, especially with respect to the most influential species. (Variation in the enthalpy of formation, H .)
- d. Evaluation of the effect of introducing additional species not present in the existing model set, but which would be likely to play an important role. (Demonstrated by replacing the Cs_2O parameters in the matrix with those appropriate to $CsOH$.)

2.4.2 Effect of Converter Parameters (P_{Cs} , P_{O_2})

Table 1 contains the matrix of parameters for 17 species which were used as baseline data for the preliminary COAD computations. These matrix values were used in the earlier evaluation

Table 1.

SPECIES PROPERTY ARRAY FOR TUNGSTEN IMMERSED IN Cs/O VAPOR

SPECIES	CLASS	σ $10^{14}/\text{cm}^2$	f $10^{12}/\text{sec}$	α 10^{-24}cm^3	M_o 10^{-14}esu	ϕ_j eV	ΔH eV	ΔS $10^{-3}\text{eV}/^\circ\text{K}$
O	1	14.0	10	5.0	-0.1	5.40	2.630	0.698
O ₂	1	14.0	7	6.0	-0.2	5.00	0.000	0.000
WO	1	14.0	5	6.0	-0.2	5.00	4.350	0.963
WO ₂	1	7.0	5	7.0	-0.4	5.00	0.492	0.343
W ₃ O ₈	1	2.0	5	11.0	-1.2	5.00	-16.900	-3.850
WO ₃	1	5.0	5	8.0	-0.5	5.50	-3.200	-0.591
W ₂ O ₆	1	2.5	5	16.0	-1.0	5.00	-11.300	-2.340
W ₃ O ₉	1	1.7	5	24.0	-1.5	5.00	-20.300	-4.680
W ₄ O ₁₂	1	1.3	5	32.0	-2.0	5.00	-28.600	-6.890
W ₅ O ₁₅	1	1.0	5	40.0	-2.5	5.00	-35.900	-9.290
Cs	2	3.6	1	10.0	0.4	1.70	0.000	-0.000
Cs ₂	2	1.8	1	12.0	0.8	1.70	-0.508	-0.729
Cs ₂ O	2	1.8	2	15.0	1.7	5.70	-3.060	-1.350
CsO	2	3.6	3	12.0	2.2	5.50	-0.344	-0.217
Cs ₂ O ₂	2	1.8	3	20.0	1.7	6.00	-4.060	-2.140
Cs ₂ WO ₄	2	1.2	1	25.0	2.5	3.00	-2.750	-1.290
Cs ⁺	2	3.6	1	40.0	1.3	2.00	4.120	0.501
		R_1 Å 0.7	R_2 Å 1.5	ϕ_o eV 4.6	T_{Cs} °K 330.0	μ_{Cs} $\text{cm}^2 \text{sec}^{-1}$.425 E+16	P_{O_2} torr .500 E-07	μ_{O_2} $\text{cm}^2 \text{sec}^{-1}$.241 E+14

by Rasor [4]. The arrival rates of cesium and oxygen are interactive parameters based on the input values of the reservoir temperature, T_{Cs} , and the oxygen partial pressure, P_{O_2} , respectively.

Fig. 2-36 shows the effect of varying P_{O_2} on the theoretical curves work function vs temperature using two different cesium pressures in the correlation. Curves a, b & c correspond to $T_{Cs} = 551$ K ($P_{Cs} = 1$ torr) and curves p and q correspond to $T_{Cs} = 577$ K ($P_{Cs} = 2$ torr). It can be seen that the curves approach the Rasor-Warner plots as the oxygen pressure is increased.

Fig. 2-37 shows the effect of changing the cesium pressure at a fixed value of P_{O_2} (0.5×10^{-7} torr). The cesium pressures used included 0.1 torr ($T_{Cs} = 430$ K), 0.5 torr ($T_{Cs} = 528$ K), 1 torr (551 K) and 2 torr (577 K).

2.4.3. Most Influential Species

a. This analysis was performed by inputting large variations in the density of adsorption sites, σ , for a particular species while keeping the rest of species unchanged and gauging the net change in the theoretical ϕ vs T plot. The exercise was repeated for each species. Fig. 2-38 shows the plots corresponding to the species that resulted in a perceptible change in the theoretical plot. The "baseline curve" corresponds to the matrix of parameters shown in Table 1. The rest of the curves have been marked to indicate the change in the value of σ used to produce the curve. In spite of large changes in σ , only six species showed some effect: O, Cs, Cs⁺, CsO, Cs₂O and WO₃. The remaining 11 species displayed no effect whatsoever.

b. The above systematic analysis was also performed by inputting large variations in the adsorption energy, ϕ_A . Here only four species appeared to result in changes from the baseline curve: O, Cs₂, CsO and Cs₂O. Fig. 2-39 shows the plots corresponding to the sensitive species along with the change in adsorption energy used.

2.4.4. Experimental Data Fitting

A fitting exercise was performed on experimental data for the PD-4 oxygenated converter which was tested in the TTP program [7]. Fig. 2-40 shows the theoretical curve obtained by using the matrix shown in Table 2. The σ values for the cesium species have been altered to reflect the currently accepted value of $5.0 \times 10^{14}/\text{cm}^2$. The density of adsorption sites for CsO, however, was set at a higher level of $8.0 \times 10^{14}/\text{cm}^2$ to obtain a good fit over the whole range of temperatures. Another important observation is that lowering the value for the adsorption energy for atomic oxygen

Fig. 2-36 COAD Work Function Plots at the Conditions Indicated

Fig. 2-37 COAD Work Function Plots at the Conditions Indicated

Fig. 2-38 Influence of Adsorbate Surface Densities on COAD Work Function Plots

Fig. 2-39 Influence of Adsorbate Adsorption Energies on COAD Work Function Plots

Table 2.

CLASS		σ	f	α	Mo	ϕ_a	H	S
O	1	14.0	10.	5.0	-1.0	4.40	2.630	0.698
O ₂	1	14.0	7.	6.0	-0.2	5.00	0.000	0.000
WO	1	14.0	5.	6.0	-0.2	5.00	4.350	0.963
WO ₂	1	7.0	5.	7.0	-0.4	5.00	0.492	0.343
W ₃ O ₈	1	2.0	5.	11.0	-1.2	5.00	-16.900	-3.850
WO ₃	1	5.0	5.	8.0	-0.5	5.50	-3.200	-0.591
W ₂ O ₆	1	2.5	5.	16.0	-1.0	5.00	-11.300	-2.340
W ₃ O ₉	1	1.7	5.	24.0	-1.5	5.00	-20.300	-4.680
W ₄ O ₁₂	1	1.3	5.	32.0	-2.0	5.00	-28.600	-6.890
W ₅ O ₁₅	1	1.0	5.	40.0	-2.5	5.00	-35.900	-9.290
Cs	2	5.0	3.	10.0	04.	1.70	0.000	0.000
Cs ₂	2	2.5	3.	12.0	0.8	1.70	-0.508	-0.729
Cs ₂ O	2	2.5	2.	15.0	1.7	5.70	-3.060	-1.350
CsO	2	8.0	1.	12.0	2.2	5.50	-0.344	-0.217
Cs ₂ O ₂	2	2.5	1.	20.0	1.7	6.00	-4.060	-2.410
Cs ₂ WO ₄	2	1.2	1.	25.0	2.5	3.00	-2.750	-1.290
Cs ⁺	2	5.0	3.	40.0	1.3	2.00	4.120	0.501
	R1 0.7	R2 1.5	ϕ_o 4.6	T _{Cs} 551.0			Po ₂ 5x10 ⁻⁶

Fig. 2-40 Fitting PD-4 data with Cs_2O parameters and two atomic oxygen adsorption energies

results in a bump in the theoretical curve. The size of the bump was found to increase significantly when $\phi_A(O)$ is lowered to 4.4 eV.

2.4.5. Introducing New Species

A new species was introduced into the matrix of species by replacing the data for Cs_2O with $CsOH$. Fig. 2-41 shows the resulting theoretical plot. It should be pointed out that the entropy of formation used for $CsOH$ (0.25×10^{-3} eV/K) is lower than that calculated from available thermodynamic data (see Appendix C). The value used is the maximum value allowed by the program in order to produce a solution. A higher value of ΔS_f led to a singularity. Experimental work function plots (Fig. 2-42), similar to the one in Fig. 2-41, have been obtained in past studies at much smaller cesium and oxygen pressures [8].

In summary, the COAD model was shown to be adaptable to various coadsorbed species in the emitter temperature range. Experimental results on Cs-O species and their vapor pressures from the TOF/MS would then be fitted to the COAD model as they become available.

2.5 Collector Work Function Modeling

Since a reduction in the collector work function constitutes the most effective way of increasing thermionic converter performance in terrestrial applications, this task was undertaken in HET-IV to improve understanding and analytical modeling of the collector surface which always requires high adsorbate coverages, extending even into the multilayer region.

2.5.1 Introduction

There have been several analytical models aimed at describing the observed emission from metal surfaces with adsorbed alkali metals. Rasor and Warner [5] presented an analysis which adopted many of the critical elements of Langmuir's approach [10] and its subsequent refinements. While the Langmuir approach is not valid for coverages greater than 0.5, the Rasor and Warner analysis maintained analytical coherence well into the region of high coverage. This was accomplished by modifying the calculation of work function change due to the adsorbed layer to include the relative probability of atomic and ionic states.

Fig. 2-41 COAD results with CsOH as the main oxygen species

Fig. 2-42 Experimental work function plots obtained on W(100) with constant cesium and oxygen fluxes

Another important advantage of the Rasor and Warner analysis was that it permitted extension to a variety of materials and a wide range of variables. The analysis was, therefore, remarkably successful in explaining many features of existing data. Nevertheless, the authors found conditions which were outside the domain of validity of their framework. Since no data exists for those conditions to begin with, any further refinements of the framework so as to include these conditions would require verification using appropriate experimental data.

The conditions under which the Rasor and Warner analysis may not be valid are as follows:

- I. when $T/T_R < 1.7$ in general
- ii. when $\phi_o < 3.3$ eV
- iii. when $\phi_o > 5.1$ eV and $T/T_R < 3.5$

These conditions directly affect the validity of an important assumption in the Rasor-Warner analysis, namely that "only repulsive interactions exist between adsorbed particles." Under this assumption, the image plane corresponding to the adsorbed particles which sets up the dipole field remains fixed near the surface of the substrate, allowing the electrons to be confined inside the substrate surface as they interact with particles outside the surface.

When coverages become large (approaching full coverage) a larger proportion of the adsorbed particles are in atomic states and the electrons would now be free to move in the adsorbed layer. As a result, the net work function ϕ becomes less dependent on the bare work function and more dependent on the properties of the adsorbate. Also, as coverage becomes large and particles in atomic states begin to predominate, the short range attractive forces between adsorbed particles are no longer negligible compared to the long range repulsive forces. Physically, this would coincide with the formation of a condensed phase, hence violating an important assumption of Rasor-Warner analysis, namely the existence of a uniform surface.

In addition to the changes in energetic interactions between adsorbed particles, the mass balance of the analysis is also affected when large coverages are reached. Due to the rapid change in the density of states as the perfect monolayer is reached, the factor $[\exp(\theta/1-\theta)]/1-\theta$ which appears in the expression for the evaporation rate [11] may not be strictly valid. As in initial attempt to study some of these issues, it would be useful to include the formation of a second layer with a coverage proportional to the fourth power of the first layer coverage as well as the ratio of surface temperature the cesium reservoir temperature, T/T_R . The dependence on the fourth power of the first

layer coverage arises out of the geometrical reasoning that at any instant four first-layer particles would have to be sufficiently close by to support the presence of a single second-layer particle [10]. In the Rasor-Warner framework the presence of the second layer has to be included both in A) the calculation of the dipole field associated with the adsorbed layer; and B) the kinetic balance between arriving and evaporating particles.

2.5.1.1 Dipole Field Associated with Adsorbed Layer Supporting a Secondary Layer

As pointed out above, a second layer attachment has the geometric requirement that four first-layer atom be sufficiently close by to support an atom in the second layer. Assuming that the surface is uniform and that only long range repulsive interactions exist, the success of attachment to the second layer is significant only at high coverages. Under these conditions the depolarization of first layer particles by adjacent first layer particles is high due to their proximity at high coverages. But, more important is the fact that the second-layer ions provide an additional depolarizing effect by virtue of the fact that they compete with the substrate for the available electrons.

2.5.1.2 The Kinetic Balance Between Arriving and Evaporating Particles

For the monolayer case at steady state is $\beta\mu = v$, where β is the sticking coefficient, μ is the arrival rate; v is the evaporation rate. For the two-layer case the following holds at steady state

$$(1 - \theta_1) \beta_1 \mu + \theta_1 \beta_2 \mu = v_1 + v_2$$

where β_1, β_2 are the sticking coefficients for first and second layer attachment, respectively, θ_1 is the coverage for the first layer, and v_1, v_2 are the evaporation rates for particles in the first and second layers, respectively.

2.5.1.3 Solving the Differential Equation Governing Adsorption

The time-dependent coverage associated with adsorption on a surface is related to the arrival rate and evaporation rate as follows:

$$\frac{d\sigma}{dt} = \beta\mu - v$$

where σ = number of atoms adsorbed on the surface.

The coverage θ is defined as follows: $\theta = \sigma/\sigma_1$, where σ_1 is the number of available adsorption sites. Therefore,

$$\sigma_1 \frac{d\theta}{dt} = \beta\mu - v$$

A complete formulation can now be presented for the two-layer, time-dependent calculations using the Rasor and Warner framework. The equation above is an initial valued, first order ordinary differential equation. Such a problem is readily solvable using the "Runge-Kutta method with adaptive step size control." A standard numerical package was utilized for this purpose [12].

The underlying idea of any routine for solving the initial value problem is to rewrite the differential equation in terms of finite steps for the independent variable (t in our case) and the function (θ in our case).

$$\frac{d\theta}{dt} = f(t, \theta)$$

The Euler's method is then applied to add small increments to the function (θ in our case) obtained by multiplying the derivative $f(t, \theta)$ with the increment in the independent variable, h . Therefore,

$$\theta_{n+1} = \theta_n + hf(t_n, \theta_n)$$

and

$$h = t_{n+1} - t_n$$

Runge-Kutta methods propagate a solution over an interval by combining the information from several Euler-style steps (each involving one evaluation of the right hand function,

f) and then using the information obtained to match a Taylor series expansion up to some higher order (usually up to fourth order). Adaptive step size control features imply that the integrator routine utilized in the Runge-Kutta method allows for frequent changes in the step-size (i.e., increments in the independent variable) over its progress over an interval. Usually the purpose of this adaptive step size control is to achieve some predetermined accuracy in the solution with minimum computational effort.

2.5.2 Mathematical Framework

2.5.2.1 General Formulation for Time Dependence of Coverage

$$\frac{d\sigma}{dt} = \beta\mu - v \quad (1)$$

- σ = total number of atoms adsorbed on surface
- β = sticking coefficient
- μ = arrival rate
- v = evaporation rate

NOTE: - at steady state

$$\frac{d\sigma}{dt} = 0 \quad (2)$$

$$\therefore \beta\mu = v \quad (3)$$

By definition, coverage $\theta = \sigma/\sigma_1$ where σ_1 = total number of sites available for adsorption of atoms. Therefore, Eq. (1) becomes

$$\sigma_1 \frac{d\theta}{dt} = \beta\mu - v \quad (4)$$

and steady state is represented by

$$\frac{d\theta}{dt} = 0 \quad (5)$$

In the Rasor-Warner analysis, the coverage θ was composed of θ_i , the coverage corresponding to the adsorbed particles in the ionic state, and θ_a , the coverage corresponding to the adsorbed particles in the atomic state. So that,

$$\theta = \theta_i + \theta_a \quad (6)$$

The fraction of particles in either state depended on the mean energy difference between the atomic and ionic states on the surface, E , as follows:

$$\frac{\theta_a}{\theta_i} = 2 \exp \left(\frac{-E}{kT} \right) \quad (7)$$

NOTE: This expression originated by considering the quantum-mechanical interaction between a surface and an incident atom under the assumption that a "weak interaction" exists between the two; i.e., the distance of the ion core from the surface is great enough that the valence energy level is only slightly broadened due to the interaction with the surface.

Rasor and Warner evaluated E as follows:

$$E = E_o - (1 - f) \Delta\phi \quad (8)$$

$\Delta\phi$ = The change in work function of the surface due to the adsorbed layer. It is the energy received by an emitted electron as it traverses the entire exterior electric field of the dipole layer.

f = Geometrical factor

NOTE: The factor f arises from the fact that the nucleus of the ion does not reach the surface when the ion is adsorbed. Hence, only a fraction f of the dipole potential difference is available to the ion. As a result, the dipole field increases the ion adsorption energy by $f \Delta\phi$.

E_o = The energy expended to transform the adsorbed particle from the ionic state to the atomic state by extracting an electron from the metal.

NOTE: Rasor and Warner obtained E_o as follows:

$$E_o + \phi_{ao} + I - \phi_{io} - \phi_o = 0 \quad (9)$$

where,

ϕ_{ao} = atom adsorption energy for the bare surface
 I = ionization potential of the adsorbing atom
 ϕ_{io} = ion adsorption energy for the bare surface
 ϕ_o = bare work function of the surface

2.5.2.2 Expressions for Arrival Rate and Evaporation Rate

$$\text{Arrival rate, } \mu = \frac{p}{(2\pi mkT)^{1/2}} \quad (10)$$

$$\text{Evaporation rate, } v = (\sigma_1 f) \theta_a \gamma \exp\left(\frac{-\phi_a}{kT}\right) \quad (11)$$

where,

p = partial pressure of the arriving species in the vapor
 m = mass of the arriving atom
 k = Boltzmann constant
 T = temperature of the surface
 f_o = oscillation frequency of the ion
 ϕ_a = adsorption energy of the atom on the substrate

The term γ is a parameter related to the configurational entropy of the atoms adsorbed on the surface. As derived in [11].

$$\gamma = \frac{\exp\left(\frac{\theta}{1-\theta}\right)}{1-\theta} \quad (12)$$

From Eq. (7) and Eq. (11) we can obtain an expression for the evaporation rate in term of the total coverage, θ .

$$v = \sigma_1 f_o \theta \cdot \exp \frac{\theta}{1-\theta} \cdot \exp \left(\frac{-\phi_a}{kT} \right) \cdot \frac{2 \exp \left[\frac{-E}{kT} \right]}{1 + 2 \exp \left[\frac{-E}{kT} \right]} \quad (13)$$

2.5.2.3 Formation of a Second Layer from Early Stages of Adsorption

$$\sigma_1 \frac{d\theta_1}{dt} + \sigma_1 \frac{d\theta_2}{dt} = \frac{d\sigma}{dt} = (1 - \theta_1) \beta_1 \mu + \theta_1 \beta_2 \mu - v_1 - v_2 \quad (14)$$

where	μ	=	arrival rate of atoms
	v_1	=	evaporation rate from exposed regions of layer 1
	v_2	=	evaporation rate from layer 2
	β_1	=	sticking coefficient for layer 1 = 1.0 (Langmuir)
	β_2	=	sticking coefficient for layer 2 = 1.0 (Langmuir)
	θ_1	=	coverage for layer 1
	θ_2	=	coverage for layer 2
	μ_s	=	arrival rate when vapor is saturated vapor pressure
	ϕ_1	=	adsorption energy of atoms on substrate
	ϕ_2	=	adsorption energy of atoms on the 1st layer

Expressions for evaporation rates are analogous to Eq. (12):

$$v_1 = \sigma_1 f_o (\theta_1 - \theta_2) \gamma_1 \exp \left[\frac{-\phi_{a1}}{kT} \right] \cdot \frac{2 \exp \left[\frac{-E_1}{kT} \right]}{1 + 2 \exp \left[\frac{-E_1}{kT} \right]} \quad (15)$$

$$v_2 = \sigma_1 f_o \theta_2 \gamma_2 \exp \left[\frac{-\phi_{a2}}{kT} \right] \cdot \frac{2 \exp \left[\frac{-E_2}{kT} \right]}{1 + 2 \exp \left[\frac{-E_2}{kT} \right]} \quad (16)$$

where

$$\gamma_1 = \frac{\exp \left[\frac{\theta_1}{1 - \theta_1} \right]}{1 - \theta_1} \quad (17)$$

$$\gamma_2 = \frac{\exp \left[\frac{\theta_2}{1 - \theta_2} \right]}{1 - \theta_2} \quad (18)$$

furthermore,

$$\theta_2 = \theta_1^4 \cdot \frac{\mu}{\mu_s} \quad (19)$$

E_1 and E_2 and analogous to Eq. (8).

$$E^{(1)} = E_o^{(1)} - (1 - f) \Delta\phi^{(1)} \quad (20)$$

$$E^{(2)} = E_o^{(2)} - (1 - f) \Delta\phi^{(2)} \quad (21)$$

where $\Delta\phi^{(1)}$ = the energy gained by an emitted electron as it traverses the exterior field of the first dipole layer as though in layer were not on

$\Delta\phi^{(2)}$ = the energy gained/lost by an emitted electron as it traverses the entire exterior electric field of the second dipole layer

the net $\Delta\phi$ is

$\Delta\phi^{(1)} + \Delta\phi^{(2)}$ if the two dipole layer produce fields that reinforce each other

or

$\Delta\phi^{(1)} - \Delta\phi^{(2)}$ if the two dipole layers produce fields that oppose each other.

2.5.2.4. Calculating the Dependence of Work Function on T/T_R

i. The Monolayer Case

The dependence of the work function on temperature and total surface coverage θ was given by Rasor and Warner:

$$\Delta\phi = \frac{4\pi e^2 \sigma_1 \left\{ r_i - \left[\frac{\alpha_i (1 - f)}{2e^2 r_i} \right] \Delta\phi \right\} \theta}{1 + q \exp\left(\frac{-E}{kT}\right)} \quad (22)$$

where: $E = E_o - (1 - f) \Delta\phi$. (See Eq. (8).)

They used:

$$1 - f \approx 0.18\theta + 0.20$$

$$q = 2$$

$$\sigma_1 = 3.56 \times 10^{14} \text{ cm}^{-2}$$

They found that Taylor and Langmuir data at 640 K was well described by the above formulation when the following values were used:

$$\begin{aligned} r_i &= 1.4 \times 10^{-8} \text{ cm} \\ \alpha_i &= 28 \times 10^{-24} \text{ cm}^3 \\ E_o &= 1.05 \text{ eV} \end{aligned}$$

The ionic radius of cesium is $1.7 \times 10^{-8} \text{ cm}$ and the atomic polarizability of cesium is in the range $40\text{-}60 \times 10^{-24} \text{ cm}^3$. E_o , the energy required for transition of the adsorbed particle from the ionic to the atomic state on the "base" surface was obtained indirectly from the atom adsorption energy for the "bare" surface, ϕ_{ao} , the ionization potential of cesium, I and the adsorption energy for the cesium ion on the "bare" surface, ϕ_{io} :

$$E_o = \phi_o - \phi_{ao} - I + \phi_{io}$$

where ϕ_o is the bare work function of the surface. For the Cs on W case, Rasor and Warner used the following:

$$\phi_o = 4.6 \text{ eV}, \phi_{ao} = 1.7 \text{ eV}, I = 3.9 \text{ eV} \text{ and } \phi_{io} = 2.05 \text{ eV}$$

which resulted in the value of $E_o = 1.05 \text{ eV}$, which was deemed compatible with the accepted values at the time.

ii. Extension to Two Layer Case

For the two-layer calculations two values of $\Delta\phi$, one for each layer, are calculated in the manner described above (see Eqs. 20 and 21). $E_o^{(1)}$ and $E_o^{(2)}$ essentially result in $\Delta\phi^{(1)}$ and $\Delta\phi^{(2)}$. $E_o^{(1)}$ is the same as that calculated in the monolayer case:

$$E_o^{(1)} = \phi_o - \phi_{ao} - I + \phi_{io}$$

E_o for the second layer was calculated using an analogous expression:

$$E_o^{(2)} = \phi_o^{(2)} - \phi_{ao}^{(2)} - I + \phi_{io}^{(2)}$$

In the case of cesium adsorption on tungsten we can establish ranges for each of these parameters. Here, $\phi_o^{(2)}$ is physically viewed as the surface work function seen by the

cesium atoms joining the second layer. The value of $\phi_o^{(2)}$, therefore, should be lower than ϕ_o , the bare work function of tungsten, but higher than the work function of bulk Cs (2.1 eV). Also, $\phi_{ao}^{(2)}$, the adsorption energy of Cs in the second layer, is likely to be lower than that for the first layer but higher than the sublimation energy for bulk Cs (0.75 eV).

2.5.2.5 Comparison with Experimental Data

i. Rasor and Warner Formulation for Steady State Monolayer Adsorption

Langmuir's data at 473°K and Houston's data at 473°K were used for comparisons with the model calculations. Fig. 2-43 shows T/T_R plots corresponding to the steady state monolayer calculations by Rasor and Warner. The plots show the effect of varying a) the density of sites available for cesium adsorption, and b) the polarization of cesium ions. It can be seen that slight variations of these two parameters can result in a good fit between theory and experiment.

ii. Results Using the Time-Dependent Formulation

The time-dependent formulation evolved in this work was applied to evaluate monolayer adsorption at steady state. The T/T_R plots obtained were identical with the Rasor-Warner calculations. Fig. 2-44 shows these results at 473 K along with the Houston and Langmuir data.

iii. Effect of the Second Layer

The second layer was introduced into the time-dependent formulation as described previously. The possible effects of the second layer can be evaluated in terms of three cases.

Case "A": Depolarization of First Layer Dipoles by Second Layer

This is applicable to the hypothetical situation where the bare surface and the cesium is completely free of impurities such as oxygen. Here the net decrease in work function $\Delta\phi^{net}$,

$$\Delta\phi^{net} = \Delta\phi^{(1)} - \Delta\phi^{(2)}$$

where $\Delta\phi^{(1)}$ and $\Delta\phi^{(2)}$ are the work function changes associated with the first and second layer, respectively, which are calculated from Eqs. (20), (21) and (22), using appropriate physical parameters for each layer. Curve 'a' in Fig. 2-45 is the calculated T/T_R plot corresponding to this case.

Fig. 2-43 T/T_R Plots for Steady-State Monolayer Adsorption Obtained from Rasor-Warner Formulation (NEDSPH1)

Fig. 2-44 T/T_R plots obtained from time dependent formulation evolved in this work

Fig. 2-45 Three cases considered for the evaluation of the effect of second layer atoms on the first layer dipole field

The parameters used for the first and second layers are:

$$\begin{aligned}\phi_o^{(1)} &= 4.5 \text{ eV}; & \phi_a^{(1)} &= 1.7 \text{ eV} \\ \phi_o^{(2)} &= 2.8 \text{ eV}; & \phi_a^{(2)} &= 0.8 \text{ eV}\end{aligned}$$

Case "B": No Effect of Second Layer

Here the adsorption energy for the second layer particles are assumed to be the same as the first layer. As a result the effect of the second layer is minimal and the calculations become identical with the monolayer calculations. Curve 'b' in Fig. 2-45 is the T/T_R plot corresponding to this case. The parameters used for the first and second layers are:

$$\begin{aligned}\phi_o^{(1)} &= 4.5 \text{ eV}; & \phi_a^{(1)} &= 1.7 \text{ eV} \\ \phi_o^{(2)} &= 2.8 \text{ eV}; & \phi_a^{(2)} &= 1.7 \text{ eV}\end{aligned}$$

Case "C": Polarizing Effect of Second Layer

This case applies to the situation where dipoles associated with the second layer reinforce the dipole field associated with the first layer. Here the net decrease in work function, $\Delta\phi^{\text{net}}$, is given by

$$\Delta\phi^{\text{net}} = \Delta\phi^{(1)} + \Delta\phi^{(2)}$$

where $\Delta\phi^{(1)}$ and $\Delta\phi^{(2)}$ are the work function changes associated with the first and second layer, respectively, which are calculated from Eqs. (20), (21) and (22), using appropriate physical parameters for each layer.

Curve 'c' in Fig. 2-45 is the calculated T/T_R plot corresponding to this case. The parameters used for the first and second layers are the same as those used in Case 'A'.

$$\begin{aligned}\phi_o^{(1)} &= 4.5 \text{ eV}; & \phi_a^{(1)} &= 1.7 \text{ eV} \\ \phi_o^{(2)} &= 2.8 \text{ eV}; & \phi_a^{(2)} &= 0.8 \text{ eV}\end{aligned}$$

Fig. 2-46 compares the T/T_R plots and work function vs. coverage for Case "B" and Case "C".

Work function vs coverage curves, similar to case 'c' have been observed in UHV experiments, such as that shown in Fig. 2-47 where a preadsorbed oxygen layer allowed the start of the second layer [13].

The Case "C" described here is also appropriate to the situation where electronegative impurities populate the surface and the adsorbed layers. Qualitative support for this

Fig. 2-46 Comparison of Case "B" and Case "C"
 Top : T/T_R plot
 Bottom: Work function vs coverage

Fig. 2-47 Work function vs Cs coverage on O-W(110)

reasoning is based on data for Mo(110)-Cs and Mo(110)-O-Cs [14]. Fig. 2-48 shows these data along with corresponding best-fit curves calculated from the two-layer model with the case 'c' hypothesis.

2.5.3 Thoughts on Cesium-Oxygen Multilayer Modeling

2.5.3.1 Survey of Experimental Data

Many experimental studies on multilayer deposition of O and Cs in UHV systems, at room temperature and on a variety of substrates point to the possibility of reaching very low work functions, i.e. ≤ 1.1 eV (e.g. Refs. 15-17). An in-depth study using surface analytical techniques showed that the lowest work function was obtained for a cesium oxide layer between 30 and 50 Å (see Fig. 2-49) and that the thermal desorption products from such a layer were Cs and Cs₂O [16].

A few experiments conducted under equilibrium conditions at low Cs and Cs₂O pressures [14] showed work functions decreasing below 1.4 eV as the substrate temperature dropped below 620K. Also, in quasi-equilibrium situations with directed molecular beams of Cs and O₂, work functions as low as 1 eV were obtained [18].

2.5.3.2 Nature of the Cesium Oxide Layer

For thick layers of Cs₂O deposited on a metallic substrate, the work function models for submonolayer coadsorption which emphasize dipole interaction are no longer applicable. Instead, since a metal-insulator transition was shown to occur during the progressive oxidation of thick Cs films into Cs₂O [19], the composite layer must be seen as constituting a metal-semiconductor Schottky barrier with band-bending in the Cs₂O layer [20]. Such a model has also been proposed to describe the S-1 photocathode (Ag-Cs₂O), whose exact structure is still being debated [21].

2.5.3.3 Suggestions for Future Work

This completes the work required in this task. In future work, however, the Schottky barrier model of a metal-Cs₂O junction should be included. It is likely to contain some unknown quantities such as dopant level and concentration. So in parallel, an experimental investigation of the electronic properties of cesium oxide layers of varying composition should be undertaken to determine these unknowns.

Fig. 2-48 Comparison between Case "C" Calculations and Data for Mo-Cs-Cs₂O

Fig. 2-49 Work Functions Obtained During Codeposition of Cs and O₂ on W(110) at 295 K

2.5.4 Influence of Electron Reflection at the Collector

Although the issue of electron reflection at the collector surface does not affect the previous analyses, the net effect of such a reflection is to introduce a voltage loss which can be perceived as coming from a higher collector work function.

A detailed analysis of this effect is given in Appendix F. To summarize the results, a 50% reflection at the collector increases the barrier index by 0.2 eV. At 70% reflection, the barrier index is increased by nearly 0.3 eV. Even though direct measurements of the reflection coefficient are not available for energies between 0 and 0.4 eV, there is evidence that Cs adsorption on W increases the reflection and that Cs-O coadsorption can lead to a 70% reflection at 1 eV, suggesting that such high reflection coefficients could also be present at 0.4 eV. The overall potential impact on converter performance also is illustrated in Fig. 1-1.

3.0 STRUCTURED EMITTER DEVELOPMENT

3.1 Structured Emitter Model

The PLAS2D code was intended to be used to

- develop understanding of the physical processes involved in the grooved emitter effect,
- predict performance in grooved-emitter thermionic converters,
- aid in optimizing the groove geometry.

The approach was to implement a 2-dimensional numerical solution of the set of plasma transport equations and associated sheath boundary conditions for a region representing the interelectrode space in a grooved-emitter device. The solution region is illustrated in Fig. 3-1. The code was designed to be able to easily specify different geometries of emitter grooves.

All previous experience with thermionic converter performance models has been in 1-D.

Modeling a 2-D geometry introduced some new complications, specifically that existing 1-D models specified the value of current density J , which is invariant over the interelectrode gap. This resulted in simplification of the plasma differential equations and the sheath boundary conditions. For a 2-D case current density can be a function of position, since current can move parallel to the electrodes. The invariant quantity in the 2-D problem is (in the absence of ohmic losses) the electrode voltage. This new problem was somewhat more complicated for two primary reasons. First, at the boundaries the sheath heights depend on the difference between the plasma potential, which comes from solution

Fig. 3-1 PLAS2D solution region for an example with rectangular grooves in the emitter.

of the transport equations, and the electrode surface potential. Charged particle currents depend exponentially on the sheath heights; therefore, small changes in the potential can result in large changes in plasma and energy loss at the boundaries. This does not happen in the current density-specified case since the sheath heights come from solving the sheath equations for the given current density.

Secondly, the electron current density in the plasma was obtained from the transport equations, rather than from a specified value of total current density as in previous 1-D models. For a poor initial guess, the current density may differ from its converged value by an order of magnitude. This feeds back into the plasma formulation through the ohmic heating term in the electron energy conservation equation.

An additional complication for modeling the grooved emitter was that the plasma conditions vary over the solution region, with ignited conditions in the main gap smoothly varying to unignited conditions deep in the emitter grooves. In previous ignited mode models, such as TECMDL and IMD-4, approximations were made which were specific to the ignited mode. These were primarily in the sheath boundary conditions. For PLAS2D we required comprehensive boundary conditions which could function all the way from the ignited mode to the unignited mode. TOR/TOR-N and THRIVE accomplish this by considering only monotonic sheaths. PLAS2D includes non-monotonic "virtual emitter" sheaths in order to be accurate and comprehensive. As will be discussed below, inclusion of boundary conditions of this type pointed out a deficiency in our physical understanding of the ignited mode.

In order to be able to test PLAS2D against a standard, and to get around delays in development due to PLAS2D's slow speed, 1-D models were developed in parallel which contain the same basic plasma and sheath formulations. The first of these was a version of the existing MASTERPC code in which the new boundary conditions were added. This continued to use specification of current density rather than voltage, and used a shooting method rather than finite differences. The second 1-D model was PLAS1D, which solved the same equation set as PLAS2D using a similar finite-difference scheme. It had the advantage that it could test the same voltage-specified equation set as PLAS2D, but in much less time. A variation of PLAS1D which specified current density was also produced.

Three primary iterations occurred in the code development. The first was conversion of the numerical method from ADI (alternating-direction, implicit) to the non-linear SOR (successive over-

relaxation) technique. Some reformulation of the plasma equations was also done in order to improve convergence and eliminate problems with the ohmic-heating feedback. In the second iteration, the boundary conditions were reformulated in an attempt to accommodate emitted ions, to simplify the formulation, and to improve numerical robustness. The third iteration involved the brief effort necessary to convert from the SOR method to a globally-convergent Newton-Raphson method, which had much improved convergence characteristics.

Calculated results for a smooth emitter and a grooved emitter are compared in Fig. 3-2. The grooved-emitter case used the same geometry at the GR-1 converter tested under HET-III: 10-mil deep by 3-mil wide grooves separated by 3-mil wide lands. These results show features which are qualitatively similar to experimental conclusions from HET-III; the grooved emitter has greater output current density in the quasi-saturation region, and the current approaches that of the smooth emitter as output voltage is increased.

The grooved emitter calculation stops at the voltage where the plasma becomes unignited at the bottom of the grooves, while the smooth emitter calculation does not go into the obstructed mode. The reasons behind this have pointed up a gap in understanding of the physics of the ignited mode. As previously stated, PLAS2D was designed to have boundary conditions which could accurately describe both monotonic and non-monotonic sheaths ranging from ignited to unignited mode conditions. In most previous ignited-mode models, emitted ions were neglected as being inconsequential compared with the ions produced in the plasma. In developing PLAS1D and PLAS2D, it was found that inclusion of the space charge of the emitted ions completely eliminated the non-monotonic emitter sheath for an ion-richness ratio (β) greater than or nearly equal to one, as for the case shown in Fig. 3-2. Inclusion of trapped positive ions, which was not attempted in the present formulation, would further reduce the parameter space in which a double-valued sheath can exist. Without a double-valued sheath, the calculated J-V curves had negative resistance regions below the "knee", which could not be calculated by the constant-voltage PLASXD models. Other models such as THRIVE (using the Norcross and Stone ionization coefficients) and TOR, which only allow monotonic sheaths, have also shown negative resistance in the obstructed mode. The existence of negative resistance for $\beta \approx 1$ was confirmed by the constant-current version of PLAS1D and is shown in Fig. 3-3. The higher cesium reservoir case shown in Fig. 3-3 has $\beta < 1$ and only shows the low current density negative resistance caused by radiation loss. Experimental data have repeatedly shown that actual I-V curves have positive resistance in the obstructed mode, even for $\beta \geq 1$. Our

Fig. 3-2

PLAS2D-calculated J-V curves for smooth and grooved emitters. Current density J is referenced to the collector area. Dashed curves show expected behavior in regions not yet calculated.

understanding of the physics of the ignited mode must therefore be incomplete. It is therefore difficult to devise a formulation which smoothly transitions from the ignited to the unignited modes, which may account for the difficulty of continuing the grooved-emitter calculation in Fig. 3-2 to higher voltages, in which the grooves are unignited.

Fig. 3-4-Fig. 3-8 summarize the state of the interelectrode plasma at one point on the I-V curve for the calculated grooved-emitter case of Fig. 3-2. Fig. 3-4 shows a 3-D representation of the plasma density for an interelectrode region between an emitter groove and half of the adjacent emitter lands. The plasma between the collector and the emitter lands shows the sinusoidal behavior typical of the ignited mode. The density decreases with depth into the emitter groove, showing that for this point the penetration of the plasma into the grooves is only partial. Fig. 3-5 shows the electron temperature, with a typical quasi-linear drop in temperature from the emitter to the collector in the region between the lands. The electron temperature initially rises in the groove, then decreases to low values characteristic of the unignited mode near the groove bottom. Fig. 3-6 shows the electron potential, or 3-D motive diagram. The emitter sheath is large on the surface of the emitter lands, and decreases gradually down the groove as the plasma potential in the groove increases.

Fig. 3-7 is a 2-D vector plot of the electron current density. Electron current increases gradually from the bottom of the groove to the entrance. The "plume" of electrons spreads out very quickly after leaving the groove, so that electron current becomes uniform in the x-axis direction. A vector plot of ion current density is shown in Fig. 3-8. Ion current to the emitter is very low deep in the grooves, due to the low plasma density. Ion current is most intense at the entrance to the groove.

At the beginning of the HET-IV program speculation on the source of the experimentally observed grooved emitter effect included increased ion current and the anomalous Schottky effect. PLAS2D calculations revealed that the grooved emitter effect is primarily due to increased electron current as the ignited plasma penetrates deeper into the grooves at high applied (lower output) voltages. Limitations in the calculable range were encountered, but these appear to be due to the state of physical understanding rather than the formulation.

3.2 Adaptation of TECMDL for Grooved Emitters

The objective of this task was to produce a modified version of the TECMDL computer code which would reproduce the effects of grooved emitters on performance and thermal stability. This

Fig. 3-3 J-V curves calculated by PLAS1D, showing negative resistance ("tuck-under") in the obstructed mode for the ion-rich case at $T_R=577 \text{ K}$.

Fig. 3-4 3D representation of the plasma density for the grooved emitter case of Fig. 3-2. Calculation was done at 0.2 volts.

Fig. 3-5 3D representation of the electron temperature for the grooved emitter case of Fig. 3-2. Calculation was done at 0.2 volts.

Fig. 3-6 3D representation of the electron potential for the grooved emitter case of . Calculation was done at 0.2 volts. Emitter and collector sheaths are included in the diagram.

Fig. 3-7 Vector plot of electron current density in a grooved emitter for the case in Fig. 3-2. Calculation is from PLAS2D at an output voltage of 0.2 volts.

CURRENT SCALE IS
15X SCALE FOR
ELECTRON CURRENT
VECTOR PLOT

Fig. 3-8 Vector plot of ion current density in a grooved emitter for the case in Fig. 3-2. Calculation is from PLAS2D at an output voltage of 0.2 volts.

was needed as the basis of a reactor system code which could determine the increase in the region of stable operation due to use of grooved emitters.

The first part of the task was to improve TECMDL's accuracy for smooth emitters in the deep quasi-saturation region. In its present form, TECMDL overestimates current in this region, so that its results already mimic the grooved emitter effect to some extent. This is illustrated by the comparison of I-V curves in Fig. 3-9, where electrode work functions have been chosen to match the experimental I-V curve at the "knee".

The second part of the task was to introduce semi-empirical expressions for increasing the effective electron emission in TECMDL, based on the experimental results obtained in HET-III and on the PLAS2D results discussed previously in Section 3.1.

Initial efforts to improve quasi-saturation mode accuracy focused on the neglect of the plasma resistance in TECMDL. A new formulation which approximated resistance effects was developed and implemented; however, it failed to produce the expected improvement in accuracy. In order to resolve the issue, the numerical PLAS1D code discussed in Section 3.1 was updated and used as a basis of comparison for the approximations used in TECMDL. PLAS1D produced I-V curves with significantly more realistic I-V curve shapes, as shown in Fig. 3-9.

Comparison between the two models indicated that the new formulation for plasma resistance was reasonably accurate, and that the problem in the quasi-saturation mode was not due to neglect of plasma resistance but to an overestimation of electron scattering in TECMDL. This caused the I-V curve knee to be depressed with respect to the saturation current, so that when the emitter bare work function was adjusted to fit the knee of an experimental curve, the saturation current was then too high. Lowering the electron-scattering parameter in TECMDL produced better agreement at low cesium pressures, as shown in Fig. 3-10. However, as shown in Fig. 3-11, this change caused a significant degradation in accuracy at high pressure-spacing product values. It is likely that further work would resolve the remaining problems. The modified version represents the data in the practical pressure region, however, which meets the objective of this task.

3.3 Grooved Emitter Scoping Tests

The objective of this task was to develop a method for fast-turnaround scoping tests to aid in optimization of groove geometry. Experience with sapphire tube cold-seal tests, described in Section

Fig. 3-9 Improved fit between an experimental I-V curve and a calculation using PLAS1D as opposed to TECMDL version F. Agreement is particularly improved in the quasi-saturation region.

Fig. 3-10 TECMDL modification to improve accuracy in the quasi-saturation region of the I-V curve.

Fig. 3-11 Loss of accuracy at high pressure-spacing product in the modified TECMDL.

5.0, showed that these could provide an easily constructed system which could quickly test an iterative series of grooved emitters. Comparison of volt-ampere characteristics in the quasi-saturation region would select those groove shapes and sizes which gave the greatest degree of current enhancement.

Modification of the sapphire tube concept presented the following design challenges.

- Incorporation of plane-parallel electrodes with variable spacing.
- Accurate measurement and control of emitter and collector temperatures.
- Operation at emitter temperatures up to 2000 K. This was required since grooved emitter tests in HET-III showed that the enhancement effect was greatest at high emitter temperature.
- Elimination of impurities, especially hydrogen and oxygen, in order to produce repeatable results. The effort in all previous sapphire tube work (Section 5.0) was to deliberately *introduce* oxygen.

The double-ended design developed is shown in Fig. 3-12 and in the electrode region detail of Fig. 3-13 and addresses the above design issues. Variable spacing was accomplished by sliding the entire collector assembly through a compression fitting, with three screws providing spacing and alignment control. Electron-bombardment heating was selected over resistive heating due to the high required temperature. RF heating was considered but rejected due to the complexity of shielding the collector and other parts. The sapphire tube was $\frac{3}{4}$ inch outside diameter, with a 0.040 inch wall. A rolled-screen wick was selected rather than the sintered-metal rods of the double ended experiment described in Section 5.1, since the larger diameter tube required greater symmetry in the cesium vapor flow in order to establish a distinct cesium-argon interface (Section 5.1.3). A Zr-V-Fe getter (SAES Getter type St 707) was incorporated into the wick, primarily to remove hydrogen from the liquid cesium.

This grooved emitter scoping test design meets the objectives of this task.

3.4 Analysis of Hybrid Mode

3.4.1 Overview

The objective of this task was to use the PLAS2D 2-dimensional thermionic converter plasma code, discussed in Section 3.1, to study the grooved-emitter hybrid mode concept¹. PLAS2D's

¹ N.S. Rasor, U.S. Patent 3,983,423, "Thermionic Converter", filed January 9, 1975; issued September 28, 1976.

Fig. 3-12 Schematic for design of a double-ended sapphire tube experiment for testing structured emitters.

Fig. 3-13 Close-up of the electrodes in the structured emitter scoping experiment design.

physics is applicable to the regime and geometry of previous experimental hybrid mode converters. Code upgrades to improve speed and convergence were made. Modifications to handle the spatial variation of emitter bare work function were planned to compare calculations with existing experimental data in the literature, and to explore optimizations of converter performance.

The hybrid mode thermionic energy converter illustrated in Fig. 3-14 is a variation on the ignited mode triode in which ion-producing regions are formed by grooves cut into the emitter. Ions from these regions diffuse into the regions between the collector and the "land" areas of the grooved emitter, which then operate in an enhanced unignited condition. The ion-producing grooves are formed from a low bare work function (high cesiated work function) material in order to facilitate formation of an intense arc. The land areas are coated with a very high bare work function material (low cesiated work function) to maximize emitted current density.

Fig. 3-14 Hybrid Mode Converter Schematic.

3.4.2 Literature Search and Preliminary Analyses

Experimental hybrid mode converters were constructed and tested in the late 1970's both at JPL and at Thermo Electron. These used grooved molybdenum emitters with a thin coating of rhenium deposited on the lands. A literature search and initial analysis of these published results were conducted. These results [22-26] were somewhat contradictory and difficult to interpret. In [22],

	Groove width (mm)	Groove depth (mm)	Land width (mm)	Interelectrode gap (mm)
JPL-Mk II	0.5	0.5	1.0	0.25-2.4
JPL-Mk III	0.5	0.5	0.25	0.076-?
TECO	0.5	0.5	1.0	0.36-1.78
PLAS2D solved cases	0.076	0.254	0.076	0.254

Table 3 Comparison of various hybrid mode emitter geometries with geometry solved by PLAS2D.

Shimada stated that his converter operated in the hybrid mode only at large interelectrode spacing; however, in his later paper [23] hybrid mode analyses were performed on data taken at 3 mil (0.076 mm) spacing. Thermo Electron was unable to attain Shimada's improved performance in converters with similar geometry, and concluded that Shimada's results were the result of oxygen contamination of his converter [24]. Thermo Electron also concluded, based on spectroscopic measurements, that their converter operated in the ignited mode in all regions [25-26].

As a result, a certain amount of uncertainty remains concerning the operating modes and performance benefits of such grooved-emitter, hybrid-mode converters.

3.4.3 Analysis of the Applicability of PLAS2D to the Hybrid Mode

PLAS2D had already been shown to give good results for a grooved emitter with groove dimensions 6.6 times smaller than those used by JPL and Thermo Electron (see Table 3). Scaling the dimensions up was not a problem since the plasma in the grooves would be even more strongly diffusion-dominated, which is the regime best analyzed by PLAS2D, and early tests using 6-mil wide grooves and lands rather than 3-mils show that PLAS2D converged even faster for the larger grooves. The cesium pressure previously used in PLAS2D cases was 2 torr. Hybrid mode results range from 0.5 to 8 torr, which should easily be in the range of validity for PLAS2D.

3.4.4 PLAS2D Code Modifications and Upgrades

Since a fairly extensive amount of calculation was required for the hybrid mode analysis, the slow speed of PLAS2D was a limiting factor. Therefore, in preparation for the hybrid mode study, improvements were made to the PLAS2D code which improved its calculational speed by a factor of seven. This was done by changing the algorithm used to solve the very large set of simultaneous linear equations resulting from the Newton-Raphson method so as to take advantage of the sparse nature of the Jacobian matrix. Further speed improvements are possible by substitution of a Broyden algorithm for the Newton-Raphson method.

PLAS2D calculations using stepwise approximations to trapezoidal emitter grooves uncovered convergence problems associated with inside corners. An effort was made to resolve the inside-corner issue in order to ensure that code results were accurate. Review of the formulation and the computer code did not uncover any problems.

As previously stated, the primary change to PLAS2D required for this study was to make the emitter bare work function a position-dependent variable.

3.4.5 Enabled Analyses

The computations made possible by the work in this task should be focused on the following areas:

- Calculation matched to reported experimental data from JPL and TECO. This can verify the code and address the question of whether the reported experiments achieved hybrid mode operation or not.
- Exploration and optimization. This can vary groove/land geometry, interelectrode gap, cesium pressure, and the bare work functions of the grooves and lands in order to locate the most promising conditions for hybrid mode operation.

4.0 DECOR SOURCE DEVELOPMENT

4.1 PUE-4: Source Stabilization

One of the significant discoveries made in the HET-III program was that upon gradual oxidation of a cesium pool, cesium oxide would migrate out of the container against the temperature gradient and thereby establish a dual reservoir at different compositions and temperatures. The physical mechanism responsible for this migration was then described as electrostatic repulsion

between polarized Cs-O molecules, which leads to spreading in a liquid film. To prevent this migration it was therefore decided to adapt a technique which proved successful at containing the spread of molten Na₂SO₄ [27]. The original technique was to mix ground Na₂SO₄ and Pt black powder.

4.1.1 Source Design: Porous Pt Pellet

Pt black powder in its raw form has a specific area of at least 10 m²/g which translates in an average particle size of 200-300 Å. It is also a very fluffy material with an apparent density between 3 and 7% of that of bulk Pt.

Since it absorbs large amounts of water it needs to be outgassed, which also results in a partial sintering. This sintering has the advantage of making the finished product considerably easier to handle, but also likely results in a drop in the specific area. Many sintering tests were performed during the HET-IV program and the particulars are gathered in the Table 4 below.

Scanning Electron Microscope examinations were not performed on representative samples of sintered Pt used in PUE-4 to PUE-6, but outgassing spectra during sintering, and the SEM pictures obtained later should provide good clues as to how the early samples behaved during and looked like after processing: these data are therefore introduced now, against the chronology of events, to simplify the presentation.

4.1.1.1 Platinum Outgassing/Sintering

The Pt black powder was loaded inside a hollow stainless steel container and, except for PUE-4, lightly compacted. The container was then slowly outgassed inside a bell jar first pumped down by a turbo and later by an ion pump.

The outgassing temperature first chosen at 850 C was later reduced to 700 C to reduce the amount of shrinking. As can be seen from the preceding table, at 700 C there was a fairly constant ratio (~3) between the sintered density and the starting density after compaction.

Monitoring the gases released with a quadrupole mass spectrometer during the Pt processing showed the following:

- prominent H₂O and CO₂ desorption starting at 85 C and peaking at ~600 C.
- amu 30 (?) and 32 (O₂?) between 300 C and 400 C.

Table 4

#	Pt Powder			Meas. Initial Density	Sintering Temperature	Measure Final Density, Dimensions	Pt Weight
	Lot	Loose	Compacted				
PUE-4	F01 D09	X		2.5%	850 C	~ 11% ϕ .40" x L .09"	0.43
PUE-5	?		X	5.4%	700 C	18% ϕ .50" x L .08"	0.95
PUE-6 (granules)	H25 E16		X	6.6%	"	26.3% ϕ .56" x L .22"	4.60
PUE-7 (granules)	"		X	11.5%	"	32.2% ϕ .51" x L .20"	4.72
PUE-7b	"		35 psi	9.6%	"	27.1% ϕ .44" x L .11"	1.56
PUE-8 CVC	"		18 psi	8.8%	"	26.4% ϕ .28" x L .63"	3.50
PUE-9	"	X		0.055	"	15.2% ϕ .43" x L .13"	1.02

- CO between 500 C and 650 C.
- H₂ between 500 C and 700 C.

After two hours at 700 C the residual pressure in the bell jar was usually down below 2×10^{-7} torr, and the temperature was dropped.

The sintered Pt was then transferred into an argon box, but this necessitated an exposure to ambient air for about two minutes, likely leading to some O₂, H₂O and CO₂ readsorption. SEM pictures of the initial Pt powder and of a chunk of sintered Pt are shown in Fig. 4-1. At the same magnification, they show a dramatic evolution: the unprocessed powder exhibits features as small as 300Å, in line with particle size estimates, but all this fine structure has vanished from the sintered Pt which shows a coalescence in ~3000-5000Å modules with pores in the μm range. The surface of the modules looks very smooth, which suggests that they are probably fully densified. A very rough estimate of the new specific area, S_p , can be obtained by assuming a body-centered cube of identical spheres (diameter D): $S_p = 6/\rho D$, where ρ is the Pt density (21 g/cm³), so for $D = 3000\text{\AA}$; $S_p \sim 1 \text{ m}^2/\text{g}$, which means that the sintering has reduced the specific area by an order of magnitude.

4.1.1.2 PUE-4 Cs-O Source

The first Pt pellet for PUE-4 was sintered inside the final Mo cup to be attached to the cube (the cup inner surface had actually been Pt-coated prior to the sintering to reproduce as much as possible the experimental conditions of Ref. 27, in which Na₂SO₄ was held in a Pt Knudsen cell). After shrinkage the Pt pellet ended up free standing in the middle of the cup. The PUE-4 pellet, ϕ 0.40" x L 0.09" and 0.43 g in weight, had little mechanical strength and was crumbly.

4.1.2 PUE-4 Setup

Fig. 4-2 shows two side views at 90° of each other of the PUE-4 cube converter, and Fig. 4-3 the plumbing needed to outgas the cube and transfer measured Cs amounts into the Pt pellet cup.

The CVD W on Mo emitter and the Mo collector were carryovers from PUE-3, leading to the same spacing ~23 mils at the usual operating temperatures. A stainless steel mirror located inside the cube slightly below and behind the emitter allowed to see from outside the bell jar most of the Pt pellet and the cup and also partially the conical Kovar heat dam where the temperature

Fig. 4-1 SEM pictures of Pt powder before and after sintering

Fig. 4-2 PUE-4 Converter Setup

Fig. 4-3 Cube Plumbing

gradient would be. A camcorder with a close-up lens was used to record whatever was occurring at the cup.

Outgassing *in situ* of the various components was as follows: the emitter at 1800 K, the collector at 900 K, the cup at 650 K, the cube at 450 C. Cracking open briefly ("burping") the Cs valve showed H₂ contamination in the liquid Cs, but without a getter which came later, not much could be done about it.

Using the resistance method developed in HET-III, 80 mg of cesium were transferred from the calibrated reservoir into the cup. This amount corresponds to about 1/4 of the Cs weight needed to fill the void volume in the pellet.

Oxygen was also added right away to reach an oxygen atom concentration of 1.5%. In retrospect, adding oxygen was probably unnecessary, as discussed later.

4.1.3 PUE-4 Performance Summary

- * Performance was very good from the start without activation. Fig. 4-4 shows a comparison of a reservoir family between PUE-4 (reservoir = cup) and HET-4R (reservoir = Cs) under similar conditions. (HET-4R had cesium oxide in the collector and required extensive sputtering to achieve its performance level.)
- * Even at comparatively low collector temperatures, the output voltage was higher than for conventional converters. Fig. 4-5 shows that even at $T_C = 650$ K, V_B (5 A/cm^2) = 2.04. Raising T_C to 800 K increases the emission and reduces V_B down to ~1.95 eV, effects usually associated with the presence of an oxygen-carrying compound on the collector.
- * Oxygen effects were also obtained by changing the cube temperature, Fig. 4-6.
- * Despite recurring Cs losses out of the cube the performance remained stable for hundreds of hours. In particular, after one such loss adding more Cs to the pellet restored good performance (Fig. 4-7). These Cs losses were later attributed to leaky valves, which exhibited marred sealing surfaces probably caused by overtightening.

PUE-4 CUP TEMPERATURE FAMILY (O_2 - 1.5%)

COMPARED WITH HET-4R DATA

Fig. 4-4 Comparison of reservoir temperature families for PUE-4 and HET-4R at the conditions indicated

PUE-4 COLLECTOR TEMPERATURE FAMILY ($O_2=1.5\%$)

Fig. 4-5 PUE-4 collector family at the conditions indicated

PUE-4 CUBE TEMPERATURE FAMILY ($O_2=1.5\%$)

Fig. 4-6 Cube temperature family for PUE-4 at the conditions indicated

DURING TEST PERIOD, EMITTER APPARENT BARE
 WORK FUNCTION REMAINED CONSTANT $\phi_o \approx 5.4$ eV

Fig. 4-7 PUE-4 barrier index history

- * Oxygen pressures obtained by the sputter-readsorption technique were consistently lower than those obtained in PUE-3, which did not have a Pt pellet, as shown in Fig. 4-8. Assuming that the specific area estimate after sintering is valid, the total area in the pellet is about 0.4 m^2 where 6×10^{18} oxygen atoms can be chemisorbed (and most likely are, since chemisorbed oxygen desorbs around 700 K, and the oxide is stable up to 1300 K, Ref. 28). Taking into account the added oxygen, the average oxygen concentration in the Cs would be 3 atoms%. Comparing Lamoreaux's theoretical estimates of P_{ox} versus oxygen concentration and temperature (see Fig. 4-8) with the P_{ox} obtained in PUE-4 shows a better agreement when the wall temperature is the parameter, but for an oxygen content around 0.1%.

4.1.4 Other Observations

- * Cesium condensation into the cup left a thin film on portions of the cup floor and on small Pt particles which had fallen from the pellet. Not surprisingly, the cesium pressure measured by the valving technique followed closely the cup temperature.
- * In the center of the pellet top a pale discoloration appeared after Cs condensation in the cup.
- * The cube walls and the copper gaskets visible through the sapphire window retained their metallic shine, without signs of attack or oxidation.
- * No cesium oxide migration out of the cup was ever observed. This shows that the porous Pt pellet had suppressed the migration of a liquid cesium oxide out of the cup, as intended.
- * After operation the Pt pellet appeared to have lost mechanical cohesion around the upper edge which looked eroded and crumbly (Fig. 4-9). Its weight had increased, however, by 35 mg.

Fig. 4-8 Summary and comparison of oxygen equivalent pressures (all species) measured during operation of the cube experiments with and without a Pt-black pellet in the reservoir cup. Oxygen pressure dependence on cup temperature is much weaker than thermochemical estimates by Lamoreaux, but dependence on cube wall temperature approaches than expected for Cs/O mixtures.

Fig. 4-9 Appearance of Pt pellet in PUE-4 cup

- * A radial cut through the pellet showed what looked like small shiny globules (diameter ~2 mils) dispersed in the bulk, thought to be Cs droplets, and a dense region near the center top surface. Fig. 4-10 is a sketch of these observations.
- * The internal mirror which darkened over time showed S contamination, attributed to segregation induced by overheating.

4.1.5 PUE-4 Test Conclusions

The purpose of the PUE-4 test was to see if porous Pt would, in effect, prevent cesium oxide migration out of the Cs-O reservoir and, from that stand point above, the test was very successful. Moreover, the ability of Pt to retain adsorbed oxygen and the large specific area left after sintering point to the possibility of using porous Pt as a common source of cesium and oxygen species without having to add oxygen and without impregnating the collector with cesium oxide.

An empirical phenomenology on the operating principles of this common source is given in Section 4.6 based on the various observations made in the PUE-4 test. In summary, cesium and cesium oxide segregated along the porous Pt pellet thickness with Cs at the cold end and cesium oxide concentrated at the hot end, which was the pellet top due to radiant heating from the emitter. The whole process has been called DECOR (Dynamic Equilibrium Cesium Oxygen Reservoir).

4.2 PUE-5 1000-Hour Test

After the successful demonstration of cesium oxide migration containment inside the PUE-4 Pt pellet, as well as PUE-4 very promising thermionic performance, it was decided to run a short life test, 1000 hours, during which thermionic performance and oxygen/cesium pressures would be monitored.

Fig. 4-10 Sketch of post-test appearance of pellet interior structure

4.2.1

PUE-5 Converter

- * The emitter is the same as for PUE-4 (CVD W on Mo). However, a floating Mo shield was added, surrounding the emitter cylinder to prevent emission from the side (Fig. 4-11). Furthermore, since barrier index data are dependent on the emitter temperature, a black body hole (ϕ 0.04" x L 0.20") was EDM-drilled near the emitting surface to allow pyrometric calibration of the emitter thermocouple.
- * A new Mo collector was assembled.
- * The new Pt pellet was sintered in a slightly different way. To improve its mechanical integrity, before sintering the Pt black was compacted in the Mo cup, resulting in a higher starting density and weight (see table in Section 4.1.1). The sintering temperature was also reduced from 850 C to 700 C to reduce the shrinking. The finished density after sintering was 18% of bulk Pt.
- * The Pt coating in the Mo cup was removed since it had substantially debonded during the PUE-4 test and was judged to be non-essential to the operating process.
- * An Ni mirror was substituted to the stainless steel one to evolve fewer impurities when heated, and heat-sunk to the flange through a 0.25" Ni rod to reduce its temperature.
- * To avoid excessive openings and closures of the various valves involved in the direct Cs pressure measurement, which might have lead to valve leaks, an indirect method was developed to infer P_{Cs} from the emission after sputtering of the oxygen detector filament. (See "Cesium/oxide Pressure Measurement Software User Manual", Document E-1130-039-A-091295.)

Fig. 4-11 PUE-5 Emitter with Floating Shield

- * Outgassing *in situ* of the various components: emitter at 1900 K, collector at 900 K, plumbing at 350 C, cube at 400 C, cup at 380 C. The calibrated Cs reservoir was pumped down while at ~100 C, but still released H₂ when heated at 230 C the usual transfer temperature. The Cs load introduced into the pellet was 170 mg, corresponding to the increased Pt weight in PUE-5 with respect to PUE-4.

4.2.2 Life Test Results

Upon the first heating of the emitter at 1800 K, a collector optimum temperature was found at 860 K, and the life test began immediately thereafter, with the cup holding the Pt pellet at 525 K. Converter performance and vapor pressures were found to be remarkably stable over the 1000 accumulated hours of operation and generally reproduced the results obtained in PUE-4. Fig. 4-12 shows the time histories of the barrier index V_B (5 A/cm²) and the short circuit current density J_{sc} (even though J_{sc} has no particular meaning *per se*, it is a quick way of characterizing the emission). Fig. 4-13 shows the time histories of the cesium and oxygen pressures.

Several experimental difficulties occurred that affected the performance results slightly. The most disruptive of these was continued cesium loss from the cube through the valves, even though the leaking valves in the previous experiment had been replaced and valve operation was minimized in this test. Fortunately, no detectable loss of cesium from the external cesium reservoir occurred through its valve, such that the cube could be recharged with cesium after its apparent exhaustion at 300 and 700 hours of operation (the down-time during the recharge cycles is not included in the total operating time shown in the above figures). The reoccurrence of the leaks through the valves in contact with Cs/O vapor and not through the cesium reservoir valve suggests that corrosion by or deposits of Cs/O on the valve seats may be responsible for the leaks.

As in the previous experiment, a distinct orange discoloration occurred on the top surface of the Pt-black pellet during operation of the system after initial charging of the cube with cesium. In the previous experiment this discoloration disappeared when the cesium became exhausted, but always reappeared after recharge with cesium. In the present experiment, however, the pellet discoloration returned only weakly after the first cesium recharge, and was barely detectable after the second. The reason for this is not known, but the great observed stability and reproducibility

PUE-5 LIFE TEST

Fig. 4-12 Time history of V_B (5 A/cm²) and J ($V=0$) during the PUE-5 Life Test

PUE-5 LIFE TEST

Fig. 4-13 Time History of P_{ox} and P_{Cs} during the PUE-5 Life Test

of the vapor composition suggests that the discoloration is not an essential feature of DECOR operation.

Another difficulty affecting the results was an apparent change in the calibration of the emitter thermocouple relative to the temperature of a black body hole in the emitter observed by optical pyrometer through the sapphire window. This was a small temperature uncertainty, amounting to only about 20 K at 1800 K, but the associated adjustment caused changes in the computed values of V_B that were as large as all other observed changes after the 100-hour initial startup transient. Unusual erratic behavior of the thermocouple (± 5 K instantaneous fluctuations) tend to identify the temperature uncertainty as arising from the thermocouple rather than the pyrometer. Although no clouding of the window was visible directly, some scattering at the pyrometer wave length ($0.65\mu\text{m}$) developed during the test, as indicated by a progressive but slight degradation in sharpness of the filament image in the pyrometer. Although these are quite small uncertainties in the emitter temperature, they tend to diminish the significance of the very small trends in observed performance over the 1000 hour test.

A significant exception to the nearly identical reproduction of performance in the PUE-4 and PUE-5 tests is the observed optimum collector temperature of about 850 K in this test, as compared with the 650 K optimum in the previous test. Attempts after the stability test to seek conditions for a lower optimum collector temperature in this system were unsuccessful.

In general, the performance (i.e., short circuit current and barrier index) and the Cs/O vapor composition (cesium and oxygen partial pressures) were remarkably reproduced after excursions in operating conditions. The most severe of these excursions were the exhaustion and recharging of cesium on two occasions, which involved cooling and reheating the electrodes, as well as the possibility for changes in the level of impurities. While some step changes were observed in performance and Cs/O vapor just before exhaustion and just after recharge, these changes generally were small and the steady-state level was recovered afterward.

Worth mentioning, perhaps, is the exceptional performance obtained briefly on a few occasions which were not accompanied by significant changes in Cs/O vapor composition. The most significant of these occurred immediately after the electrodes were first heated, and persisted over the first three days of operation. In Fig. 4-14 J-V curves at the beginning and after 600 hours are shown. On two other occasions (one being after the Cs recharge at 700 hours), V_B decreased to about 1.92 eV for two days without significant change in short circuit current. This could not have been due to a

PUE-5 LIFE TEST

Fig. 4-14 Comparison of J-V curves at the conditions indicated at the beginning of the life test and at 600 hours. (There was little change afterwards.)

change in emitter temperature, therefore, and was not accompanied by changes in Cs/O vapor properties.

4.2.3 Post-Stability Test Experiments

Following the 1000-hour stability test, a set of collector temperature, Cs/O cup temperature and cube temperature J-V families were obtained (Figs. 4-15 to 4-17). These were unremarkable and showed that the conditions during the stability test were near optimum. The onset of strong back emission effects at ~900 K collector temperature suggests that the collector work function was near 1.4 eV. The overall performance and Cs/O vapor composition was not significantly affected by the temperature excursions.

It was suspected that the high optimum collector temperature may have arisen because the collector was equilibrated initially at that temperature. Equilibrating the collector at 750 K for several days did not change the optimum temperature, however.

To test whether formation of a layer of impurities on the electrode surfaces during the first 100 hours of operation might have caused the increase in V_B and decrease in current observed during that time, the electrodes were given sputtering pulses (8 cycles each, 9 volts peak forward, 30 volts peak inverse). The first two such pulses resulted in performance nearly the same as that in Fig. 4-14 at the beginning of the life test, but the improvement gradually disappeared during the following hour. Subsequent pulses did not result in increased current, and V_B actually was increased. These pulses also caused some darkening of the mirror with a transparent golden-brown layer, presumably due to overheating from the discharge to it.

No oxygen had been added to the PUE-5 cube up to this point, except what was adsorbed on the platinum black. Enough gaseous oxygen then was injected into the cube to give about 10 atomic percent Cs/O if reacted with the entire cesium inventory in the cube. An increase in cup temperature during the injection indicated that reaction with the liquid cesium had occurred there. Only a very slight discoloration of the pellet top was discernable. The oxygen was added to determine whether the initial quantity of adsorbed oxygen was adequate to fully implement the DECOR process. No consequent increase in performance or change in vapor properties was observed, however, indicating that the total quantity of oxygen present is not a critical factor in DECOR operation above a sufficient amount.

PUE-5 COLLECTOR TEMPERATURE FAMILY

Fig. 4-15 PUE-5 Collector Family after the Life Test

PUE-5 CUP TEMPERATURE FAMILY

Fig. 4-16 PUE-5 Cup Temperature Family after the Life Test

PUE-5 CUBE/OVEN TEMPERATURE FAMILY

Fig. 4-17 PUE-5 Cube Temperature Family after the Life Test

4.2.4 Discussion

Aside from the different collector temperatures in PUE-4 and PUE-5, their thermionic performances were quite similar and so were the Cs/O vapor compositions. So, the main goal of the PUE-5 test -- to demonstrate the stability of a DECOR source in an operating converter -- was achieved and at a performance level only previously obtained in dual-reservoir mode converters with oxide-containing collectors.

However, the slight drop in performance, mostly over the first 200 hours, does not seem to correspond to any obvious changes in the Cs/O vapor composition as measured by the detector filament. This suggests that surface structures evolved over that period of time on both electrodes (leading to a rise of 0.05 eV and 0.09 eV in emitter and collector work functions, respectively), or that some impurity not seen by the detector filament was influencing these work functions. The possibilities would have to be examined in future studies, in test vehicles more controllable from a purity standpoint than a demountable cube converter.

The control of gaseous impurities, however, such as H_2 and CO, in the cube itself by the use of getters was tried later on in PUE-7 and after.

The stability of the DECOR source having been shown, it became apparent that, in order to verify its mode of operation based on cesium oxide segregation across the non-isothermal Pt pellet, the temperature gradient inside the pellet would have to be controlled and measured. This led to several redesigns of the DECOR, tested in subsequent experiments starting with PUE-6.

4.3 PUE-6: Source Diagnostics Test

4.3.1 DECOR Cs/O Source Design

In the previous experiments, the temperature of the top of the Pt-black pellet could not be measured or directly controlled. That temperature was determined by the radiant heat flux from its surroundings, i.e., by a complex combination of cube, emitter and collector temperatures. Yet, virtually the entire inventory of oxygen is in this Cs-soaked, pellet-top region, so that its temperature determines both the oxygen pressure and cesium pressure. The DECOR vapor source structure shown in Fig. 4-18 was constructed to provide mechanically stable and well-defined confinement of the Pt-black, as well as the ability to measure and control the temperatures at both ends of the Pt-black compact. A radiation shield suppressed the effect of radiation from surrounding components and an axial tube provided a return path for cesium vapor outside the Pt-black. This

Fig. 4-18 Schematic of Cartridge-style DECOR as used in PUE-6, PUE-7 and PUE-7A

return path was present in the previous pellet and probably reduces equilibration time in the cube chamber by convective stirring.

This structure was designed and constructed before DECOR operation was better defined by subsequent work. The ten-fold extended length of the Pt-black region was intended to provide sufficient isolation of the oxygen-containing region to measure and independently control its temperature. It was subsequently realized, however, that the associated ten-fold increase in the amount of Pt-black and adsorbed oxygen would introduce a ten-fold greater amount of oxygen transported into the oxygen-containing region which might plug its pores or otherwise affect the poorly-understood but crucial process in this important region. Accordingly, a molybdenum plug was inserted to halve the amount of Pt-black required.

Another aspect of the design appears in retrospect to introduce an unnecessary uncertainty based on present understanding. In the previous pellet configuration, the top of the pellet was the hottest point in the vapor source such that vaporization occurs only there and no path exists for film creep from this region to a hotter region. Because the heater adjacent to the top of the structure in Fig. 4-18 might be hotter than the surface of the Pt-black, the possibility for Cs/O migration to it and deposition of oxide there exists. Whether this was a significant factor in the performance of this version of DECOR must be determined by examination upon post-test disassembly.

Because shrinkage of the Pt-black during outgassing cannot be tolerated in this confined configuration, the Pt-black was compacted and outgassed as before but in a separate container at 700 C, with a final density of 26%. The sintered compact then was crushed into granules less than about 1 mm diameter in a purified argon atmosphere and compacted under mild pressure into the DECOR cavity around a perforated axial tube, as shown in Fig. 4-18.

4.3.2 Test System

This DECOR assembly then was mounted in a new stainless steel cube having a sapphire window, detector filament and converter electrodes similar to those in the previous cube tests except that in this case the emitter and collector both were molybdenum (see Fig. 4-19). The cube itself was mounted in a new test stand having provisions for connecting the time-of-flight mass spectrometer (TOF) and hot-orifice valve to the cube (Fig. 4-20). The additional complexity of this vacuum system has caused the bell jar to have a disappointingly high base pressure ($\sim 2 \times 10^{-6}$ torr)

Fig. 4-19 Schematic of PUE-6 Cube Experiment with DECOR Cartridge

when the test system is fully heated and operating. This is to be compared with the $< 2 \times 10^{-7}$ torr bell jar pressure in the PUE-5 tests. The cause of this high pressure in PUE-6 has firmly resisted efforts to identify it. Ordinarily, a bell jar vacuum near 10^{-6} torr would be considered to be adequate for converter tests in conventional practice, but it might have more significance here, as discussed later.

4.3.3 DECOR Parametric Results

Initially, it was found that the thermocouple imbedded in the oxide-containing region of the Pt-black (Fig. 4-18) was not functioning properly. The experiment was continued, however, with an external thermocouple that sensed the temperature of the Mo ring in thermal contact with this region. This is referred to as the "top temperature" in the following results. The "bottom temperature" is that sensed by the thermocouple imbedded in the temperature-regulated base, which is estimated to be typically less than 2 K lower than the temperature at the bottom of the Pt-black compact.

Initial exploration also showed that nearly two hours were required to reach a steady oxygen pressure after a change in operating conditions of the vapor source, as shown in Fig. 4-21. Since this is the same order of magnitude as the estimated diffusion-limited vapor equilibration time within the cube volume (Section 4.6.5.4), this is assumed to be the limiting process here rather than an equilibration process within the DECOR source itself. Obviously, such a long equilibration time significantly impedes the rate at which parametric data can be acquired.

Figs. 4-22 and 4-23 show the dependence of the equivalent oxygen pressure and cesium pressure on the DECOR top temperature for given bottom temperatures. These pressures were determined by new and improved methods that are described in detail elsewhere. The sputter-readsorption emission (SPREE) method of measuring the total equivalent pressure of all oxygen-bearing species was basically the same as that employed in previous cube experiments, but improved instrumentation allowed continuous measurements during rapid sputter pulsing which is especially important at high and rapidly-changing oxygen pressures ($\geq 10^{-6}$ torr) such as those encountered in the PUE-6 tests. The new cesium pressure measurement method utilized the emission current immediately after the sputter pulses, i.e. the maximum emission from oxygen-free tungsten, to infer the cesium pressure required for that emission at the tungsten filament temperature. The great advantages of this method over the previously used cumbersome valving method are that it gives continuous cesium pressure data simultaneous with continuous oxygen pressure data, using the same

Fig. 4-21 Time Response of Oxygen to DECOR Temperature Change in PUE-6

Fig. 4-22 Oxygen Dependence on DECOR Top Temperature in PUE-6

Fig. 4-23 Effect of DECOR Top Temperature on Cs Pressure in PUE-6

simple filament assembly. Both pressures can be recorded on a strip chart to show fluctuations, trends, and correlations with each other and with data from other components immersed in the same vapor.

The principal disadvantage of this method is that it is not an absolute measurement of the cesium pressure as is the valving method; i.e., the cesium pressure inference in this method depends on the constancy of the bare tungsten emission properties. For example, in the data obtained for the dependence of oxygen and cesium pressure on the DECOR bottom temperature, Figs. 4-24 and 4-25, the observed cesium pressures obtained by this method on one occasion correspond to a bare (cesium-free) work function of $\phi_o = 4.60$ eV and on another occasion to $\phi_o = 4.66$ eV (Fig. 4-25), resulting in a $\pm 15\%$ uncertainty in cesium pressure. The possibility of this difference arising from the presence of an uncontrolled impurity in the vapor, and of the potential ability of using this effect to detect and quantify the presence of impurities, is discussed briefly later.

4.3.4 Performance and Emission Results

Fig. 4-26 shows J-V characteristics obtained initially using the planar molybdenum electrodes (spacing ≈ 21 mils). Although this is very good performance for a molybdenum emitter at this large electrode spacing, the data were taken before full control and mapping of the DECOR reservoir had been performed and probably before the cube and DECOR system had equilibrated.

Unfortunately, the converter performance deteriorated rapidly thereafter. At the same time, the appearance and growth of crystalline structures between the electrodes at this time indicated that massive mass transfer was occurring. This was suspected to be due to the water cycle which causes rapid erosion of molybdenum emitters. It was subsequently confirmed by an external quadrupole mass spectrometer (QMS) that the hydrogen partial pressure in the cube was entirely adequate to support the observed degree of erosion via the water cycle. Because efforts to suppress the hydrogen pressure were not successful, and because the corrosion that already had occurred rendered further data useless, the electrodes were cooled and inactive during the subsequent DECOR tests.

As an alternative to J-V data in the DECOR vapor, saturation emission currents in the ignited mode were measured from the tungsten filament used for oxygen and cesium pressure measurements. Such data are notoriously difficult to interpret because of nonuniformity and other inadequacies in filament temperature and discharge configuration control. Nevertheless, the observed

Fig. 4-24 Effect of DECOR Bottom Temperature on Oxygen Pressure in PUE-6

Fig. 4-25 Effect of DECOR Bottom Temperature on Cesium Pressure in PUE-6

Fig. 4-26 PUE-6 Volt-Ampere Curve Data

data in Fig. 4-27 suggest strong oxygen adsorption effects that could not be obtained by atomic oxygen adsorption alone at the corresponding filament temperatures and cesium pressures.

4.3.5 First TOF/MS Tests

PUE-6 provided for the first time the opportunity to test the TOF/MS connected to an operating converter via the sampling valve. The first such tests shows very large Cs peaks, as expected, but nothing but noise above 133 when the ion trap RF was adjusted to exclude Cs. The occurrence of a cesium build-up, downstream from the sampling valve seat itself, became later evident as the Cs peak would decrease very slowly after closing the valve. The presence of such a quasi-constant Cs peak was actually utilized to show the effects of raising both loading and storage times on the signal amplitude (Section 2.1.4.3).

These techniques used to boost the signal failed, however, to reveal any new peaks in these early TOF/MS tests and eventually lead over a period of a few days to a plugging of the beam skimmer front hole by cesium condensation. (The cesium amount needed to plug that hole completely is only about 9 mg.)

4.3.6 Discussion of PUE-6 Results

4.3.6.1 Stability Issues

The high stability and reproducibility of the PUE-4 and PUE-5 results were at first gratifying from a practical viewpoint and puzzling from a basic science viewpoint. The stability puzzle was solved subsequently when a physical/analytical model (Section 4.6) was developed that explains the basic origin of the stability. The basic stability question that arose was what physical and/or chemical properties of the system are so dominant as to make this particular operating point unique and stable? The controlling property is not a precisely selected overall composition of the Cs/O source alone since this changed over a wide range during the cesium exhaustion and recharge cycles. It is not the structure of the Pt-black pellet alone since this was altered significantly, i.e. from 10% solid volume fraction in PUE-4 to 20% solid volume fraction in PUE-5. The physical-analytical model of DECOR now answers this question (Section 4.6). It identifies a physical (two-phase solid/liquid) Cs/O stabilized operating point or a chemical (coexistence) Cs/O/metalate stabilized operating point.

Fig. 4-27 Oxygen Detector Filament Emission Measurements from PUE-6

As can be seen in Fig. 4-22, the observed dependence of equivalent total oxygen pressure on DECOR top temperature is nearly that estimated for a constant Cs/O composition in the thermochemical analysis of the Cs/O system by Lamoreaux. Furthermore, the observed oxygen and cesium pressures both are near those for the two phase region, shown as the liquidus curve in Figs. 4-22 and 4-23, well within the accuracy of the SPREE method and the thermochemical analysis. These data tend to confirm, therefore, that operation in the two phase region (Section 4.6.5 below) may be the factor responsible for the unique and stable operating point in PUE-6. The Cs/O liquid and vapor properties are constant in the two phase region and the total pressure is that at the liquidus temperature shown in Fig. 4-22.

4.3.6.2 Reproducibility Issues

The basic reproducibility question that arose was why, if operation is stabilized at the liquidus two-phase composition, did the stable operating conditions in PUE-6 give an order of magnitude higher oxygen pressures than those obtained in PUE-4 and PUE-5? In retrospect, based on the improved understanding obtained via the theoretical model (Section 4.6), it appears that the differences in operating point both for PUE-6 and subsequently for PUE-7 arose from two major aspects:

- i. The configuration and wick structure of the cartridge-type DECOR in PUE-6 and PUE-7 is very different than that of the pellet-type DECOR in PUE-4 and PUE-5.
- ii. The level of gaseous impurities in PUE-6 and PUE-7 was much higher in PUE-6 than in PUE-4 and PUE-5 and was shown subsequently in PUE-7 to strongly affect the operating point.

Relative to the configuration issue, the six-fold increase in length of the wick in PUE-6 and PUE-7 now can be seen to be the most important design factor affecting the operating point. The analytical model shows that this length strongly affects both the critical temperature and oxygen concentration at the vapor-generating top of DECOR and their relationship to the bottom temperature.

Eqs. 11 and 12 in Section 4.6, describing two-phase flow and heat transfer through the biporous Pt DECOR structure, can be solved numerically to determine the temperature profile across DECOR. When using parameters applicable to PUE-6, the calculated profiles,

reproduced in Fig. 4-28 for two DECOR bottom temperatures, show that the temperature drop across the interior of DECOR is much greater than across the boundary layer at the DECOR top. For vapor pressures typically less than 1 torr as in DECOR, the latent energy density of the vapor is so small that heat transport by conduction through the solid structure is comparable to or greater than latent heat transport by the vapor. Furthermore, the vapor velocity is so high that a substantial pressure drop occurs across the flow impedance of the biporous structure.

The DECOR structure in PUE-6 (Fig. 4-18) was chosen with a long vapor flow path, about 20 mm, between the vapor formation and condensation regions to facilitate their accurate temperature measurement. By the design convention valid in K-Max, this was expected to have little effect on the source operation. However, with a flow path length about 6 times greater than that in the ~3 mm high PUE-5 Pt-black pellet, the temperature drop across the PUE-6 DECOR structure actually was much greater than that in PUE-5, resulting in a much higher top temperature for a given bottom temperature and, therefore contributing to the order of magnitude higher oxygen pressure in PUE-6 for that same bottom temperature.

Furthermore, it is apparent in the computed example in Fig. 4-28 that the top temperature is only weakly dependent on the bottom temperature; the change in bottom temperature is computed as being 6.0 times the change in top temperature in the numerical example given. For similar conditions, the change in bottom temperature in Fig. 4-25 is observed experimentally to be about 5.6 times the change in the top temperature corresponding to the observed change in cesium pressure in the cube. Similarly, a 30 K change in bottom temperature in Fig. 4-24 is observed experimentally in Fig. 4-22 to give about the same increase in oxygen pressure as a 5 K change in top temperature. These results tend to confirm the validity of the analytical model and indicate that the top temperature of the DECOR indeed primarily controls the cesium and oxygen pressure in the cube.

In addition to greatly increasing the temperature drop across the PUE-6 DECOR, the greater wick length also greatly affects the oxygen concentration. It can be seen from Eq. 26 of Section 4.6 that the oxygen concentrations at the ends of the DECOR structure are exponentially related to the distance d between them. Accordingly, the ratio of the oxygen concentrations at the ends of the structure in PUE-6 would be $e^6 = 400$ times greater than that for the six-fold shorter pellet in PUE-4 and PUE-5 at the same heat flow, again contributing to the much higher oxygen pressure observed in PUE-6.

Fig. 4-28 DECOR temperature profile calculation for estimated PUE-6 conditions (Evaporator is the DECOR top)

Relative to the impurity issue, when the cube vapor is sampled by an external quadrupole mass spectrometer, the impurities H_2 and CO are found to be present in significant amounts, especially in PUE-6. This is an imprecise determination, however, because only non-condensable and non-reactive species can reach the external spectrometer through the cold plumbing. Therefore, other species in the cube vapor, such as cesium compounds, cannot be observed and the possibility exists that the sampled vapor from the cube could liberate H_2 and CO in the plumbing by reacting with condensed impurity species there. Nevertheless, the possibility exists that the high impurity levels in PUE-6 were responsible for the high oxygen levels observed, so their effect was evaluated.

Dr. Robert Lamoreaux has evaluated the effect of hydrogen and carbon impurity levels in the Cs/O/H and Cs/O/C systems by extending the previous associated solution thermochemical model. (The complete report is in Appendix G.) His results, shown in part in Figs. 4-29 and 4-30 involve a factor, $0 < f < 1$. This empirical factor represents the degree of chemical interaction of the impurity compounds with cesium in the condensed phase: 0 for completely inert, and 1 for the same degree of interaction as Cs_2O .

As can be seen in Fig. 4-29, the presence of hydrogen substantially increases the total equivalent oxygen pressure, especially at low oxygen concentrations. This occurs via reaction of hydrogen with cesium oxide to form the more volatile hydroxide via the reaction

The CsOH is more abundant than Cs_2O in the pressure ratio (see Appendix C)

$$\frac{P_{CsOH}}{P_{Cs_2O}} = K^{1/2} \frac{P_{H_2}^{1/2}}{P_{Cs}} \quad (33)$$

where K is the equilibrium constant for the chemical reaction in Eq. 32 and is an exponentially increasing function of the temperature. Since CsOH is substantially more stable than both H_2O and Cs_2O , H_2O effectively does not exist in the system under conditions of interest here, and free H_2 effectively does not exist until all Cs_2O is converted to CsOH (see Appendix C). For example, H_2 persisted at significant pressure ($>10^{-7}$ torr) in the PUE-3 cube until oxygen was admitted, whereupon

Fig. 4-29 Effect of hydrogen impurity on equivalent O_2 pressure in the Cs/O system. $X(\text{O})$ is atomic concentration of oxygen; $f = 0.5$ From R. Lamoreaux

Fig. 4-30 Effect of carbon impurity on equivalent O_2 pressure in the Cs/O system. $f = 0$ From R. Lamoreaux

hydrogen fell to undetectably low pressures ($<10^{-9}$ torr). The hydrogen in the cube did not disappear, it just was all converted to CsOH in the cube which was insufficiently volatile at room temperature to reach the spectrometer.

Because hydrogen readily diffuses through most metals at the cube temperature, it can be expected that the hydrogen activity inside the cube is equal to the hydrogen pressure in the bell jar. In PUE-6 the H_2 pressure inside both the cube and the bell jar were found to be near 10^{-6} torr. This abundance of free H_2 in the cube suggests that all oxygen in the PUE-6 cube is in the form of CsOH which, therefore, is the oxygen-bearing species whose pressure is being measured by the detector filament at $\sim 10^{-7}$ torr rather than Cs_2O for which the equivalent oxygen pressures are computed in Fig. 4-22. Similarly, the hydrogen pressures in the PUE-5 cube and bell jar are near 10^{-7} torr, and the measured equivalent oxygen pressure in the cube is $\sim 10^{-8}$ torr.

All this leads to the following hypothesis:

The hydrogen pressure in the cube, maintained constant at the bell jar pressure, might be a factor affecting the unique and stable operating points in the PUE-4, 5 and 6 cubes.

A corollary of this hypothesis is that the presence of hydrogen might be required to achieve the levels of oxygen observed at the operating temperature in PUE-4, 5 and 6.

It should be recognized that hydrogen should become concentrated in the top region of DECOR by the same process that concentrates oxygen there. High concentrations of hydrogen in the condensed phase can substantially move the liquidus phase boundary. Most important, however, is that the presence of hydrogen can result in compounds that dominate the thermochemistry as described above. The analytical tools to formally evaluate this hypothesis and to assess the consequences are now available, as well as the experimental techniques for its verification. Data from a mass spectrometer are essential in this process.

As can be seen in Fig. 4-30, the presence of carbon can depress the equivalent oxygen pressure by forming Cs_2CO_3 , which is less volatile than Cs_2O . Accordingly, carbon in the form of CO and Cs_2CO_3 are unlikely to be the measured oxygen-bearing species in the cube. As adsorbed species on the electrodes, however, their uncontrolled and undetected presence could be responsible for observed transient changes in performance that are not accompanied by changes in observed oxygen or cesium pressures, including the difference in optimum collector temperatures in PUE-4 and PUE-5, or indeed might limit the minimum V_B .

In summary, the PUE-6 test supplied valuable information on the dependence of cesium and oxygen pressures on the various DECOR temperatures. Unfortunately, TOF/MS sampling had not yet achieved the sensitivity needed for detection at the 1 ppm level. So, the next PUE tests were branched out in two parallel directions: repeat of PUE-6 with a W emitter and improvement of the TOF/MS sensitivity.

4.4 PUE-7 W Emitter-Cartridge and Disc Sources

4.4.1 PUE-7

The objectives of the PUE-7 test were to produce a consistent and repeatable set of performance data from a converter with a DECOR cartridge-type oxygen source, and to expand on previous oxygen and cesium pressure data from PUE-6. The design of the cube was identical to PUE-6, shown in Fig. 4-19 with the following exceptions.

- A tungsten-coated emitter was used as in PUE-4 and PUE-5, rather than the molybdenum emitter used in PUE-6.
- The thermocouple suspended in the platinum granules at the top of the DECOR, which failed in PUE-6, was removed. Instead, a thermocouple hole was provided for the top flange thermocouple in order to improve its accuracy.
- The platinum compact was denser in PUE-7 than in PUE-6 (see Table 4).

The PUE-7 experiment was performed in the same high-vacuum bell jar as the PUE-4 and PUE-5 experiments, since poor external vacuum in the PUE-6 test was blamed for the high hydrogen content of that experiment. It was expected that this change, plus the use of a tungsten emitter, would eliminate the severe electrode oxidation encountered in PUE-6.

Initial oxygen pressure was almost an order of magnitude greater than PUE-6, as seen in the comparison in Fig. 4-31. This was roughly two orders of magnitude above the levels seen in PUE-5, which were associated with long-term improved performance. Hydrogen pressure was measured by the quadrupole mass spectrometer by briefly opening vacuum valves to the cube and found to be in the range of $1.0 - 2.7 \times 10^{-5}$ torr. Both electrodes were kept below 420 °C during this period in an attempt to avoid oxidation.

In order to lower the oxygen pressure to the desired level, all cesium was transferred from the DECOR back into the liquid cesium reservoir. The DECOR cartridge was outgassed into the vacuum system until the background hydrogen pressure dropped to about 7×10^{-7} torr, and the DECOR was

DECOR bottom temperature = 500 K

Fig. 4-31 Comparison between PUE-6 and initial results from PUE-7 for oxygen pressure as a function of DECOR top temperature.

re-cesiated. Also during this period, the liquid cesium was cleaned of hydrogen by operating the titanium getter "scrolls" at a reduced temperature ($\sim 290^\circ\text{C}$). As a result, the oxygen pressure was reduced by about one order of magnitude, as shown in Fig. 4-32, and the hydrogen pressure during cube operation was in the mid-to-low 10^{-6} torr range.

As shown in Fig. 4-33, the cesium pressure at a given DECOR temperature was nearly the same as the previous PUE-6 results.

Volt-ampere curves were obtained at an emitter temperature of 1800 K. Initial I-V sweeps were out of the power quadrant, and visual observation through the sapphire window indicated that they were outside of the interelectrode gap. The I-V curves improved over a period of about 12 hours, with the collector held at 930 K. At the end of this period the minimum barrier index was about 2.15 eV. Performance remained steady at this level. Fig. 4-34 shows a typical volt-ampere characteristic.

The I-V curve from the oxygen detector often had odd features when the emitter was over about 1600K. Oxygen pressure readings were therefore somewhat erratic during this period. Oxygen pressure decreased nearly another order of magnitude during operation at 1800 K, as shown in Fig. 4-32, and then appeared to stabilize.

The cube was backfilled with purified argon twice as part of the procedure to replace the emitter filament. No noticeable effect on performance or oxygen pressure was observed.

The PUE-7 cube was backfilled with argon and partially disassembled and in order to remove and clean the collector. The DECOR was left loaded with cesium during this period. Examination of the collector, shown in the photograph in Fig. 4-35, revealed a thick, yellowish-white, flaky deposit on top and a gray flaky deposit on the sides. An ESCA diagnostic was performed on the deposit. The spectrum, shown in Fig. 4-36, indicated the presence of cesium, oxygen, and tungsten. Further analysis, shown in Fig. 4-37, showed that the tungsten was in the form of WO_3 . It was not possible to determine if the cesium was also in the form of an oxide. These results show that the thick collector deposit was due to oxidation of the tungsten emitter, with consequent deposition of the oxide on the collector.

4.4.2 PUE-7A

After the PUE-7 collector was removed and examined, it was cleaned, electropolished, replaced, and the cube reassembled. As before, the initial oxygen readings at start-up were high ($\sim 6 \times 10^{-7}$ torr),

Fig. 4-32 Summary of oxygen pressure vs. DECOR top flange temperature data from PUE-7.

Fig. 4-33 Comparison of cesium pressure measurements from PUE-7 and PUE-6.

Fig. 4-34 Volt-ampere curve from PUE-7 experiment.

Fig. 4-35 Photograph of PUE-7 collector with oxide deposit.

Fig. 4-36 ESCA spectrum from PUE-7 collector deposit showing the presence of tungsten, oxygen, and cesium.

Fig. 4-37 Analysis of ESCA spectrum showing that the tungsten in the PUE-7 collector deposit is in the form of WO_3 .

although lower than for the PUE-7 start-up. The cesium was again removed from the DECOR, and the DECOR was outgassed and re-cesiumated. Low oxygen pressures were restored, as shown in Fig. 4-38.

Thermionic performance was essentially unchanged from PUE-7, with a barrier index of about 2.15 eV and an emitter bare work function of 5.35 eV. A family of I-V curves, with the DECOR top flange temperature varying, is shown in Fig. 4-39. The cube was completely disassembled. A spotty deposit, shown in the photograph in Fig. 4-40, was observed on the collector. This deposit was much thinner than the thick, flaky deposit found on the collector at the end of PUE-7.

4.4.3 PUE-7B

The objectives of PUE-7B were

- to recover the performance level of PUE-5 by returning to the "Pellet"-style DECOR,
- to minimize contamination by use of an effective hydrogen getter, by pre-cleaning the liquid cesium, and by thorough outgassing of all parts of the experiment.

The "cartridge-style" DECOR, used in PUE-6, PUE-7, and PUE-7A, was designed so that the critical top temperature of the DECOR compact could be measured and controlled. Since no cube experiment with a cartridge-type DECOR had approached the performance level of PUE-4 or -5, a design for an "instrumented pellet" DECOR was produced for PUE-7B, which is illustrated in Fig. 4-41. A radiant heater, provided with radiation shields to thermally isolate the DECOR from the emitter, was used to control the pellet top temperature. A chromel-constantan (ANSI type "E") thermocouple was placed in a 30-40 mil deep hole in the pellet top surface. The hole was then partially filled with DECOR material in order to improve thermal contact. Photographs of the heater/shield/thermocouple assembly are shown in Fig. 4-42 and Fig. 4-43. The new platinum pellet had a diameter of 0.44", a thickness of 0.11", and a density of 27%. The same CVD tungsten emitter and same Mo collector (after cleaning and electropolishing) were used as for previous PUE experiments. Alumina shields were used around the collector as in PUE-7A. The interelectrode gap at typical temperatures was estimated as 22 mils.

PUE-7B was the first experiment to be fitted with a heated canister containing a Zr-V-Fe getter (SAES type St 707). This was in the form of a coiled constantan strip which had getter material bonded to both surfaces. The total amount of getter material was about 12 grams. The material

Fig. 4-38 Oxygen pressure measurements from PUE-7A.

Fig. 4-39. Volt-ampere curves from PUE-7A. DECOR top temperature varies.

Fig. 4-40 Photograph of the PUE-7A collector showing deposit.

getters H_2 , CO , N_2 , and H_2O at an operating temperature of about $300\text{ }^\circ\text{C}$, after being activated at $\sim 500\text{ }^\circ\text{C}$.

Test instrumentation was improved in PUE-7B by addition of a computer-controlled system which could continuously monitor oxygen and cesium levels from the SPREE detector.

A major objective was reduction of contamination in PUE-7B, especially hydrogen. Improved outgassing of all parts was implemented, especially for the external plumbing which had been found to be a strong source of water vapor in previous experiments. The outgassing appeared to be effective in lowering the system base pressure from the mid- 10^{-7} torr range used in previous cube experiments to the high 10^{-8} torr range. The emitter was initially a source of CO , which was eliminated after outgassing at 1900 K . The external plumbing was initially a source of H_2O , and the pellet was a source of H_2 , CO , and CO_2 .

The liquid cesium was cleaned by exposure to the Zr-V-Fe getter. Brief valve openings showed 10^{-4} torr of hydrogen prior to the cleaning procedure. The cesium was heated to $280\text{ }^\circ\text{C}$ and exposed to the getter at $320\text{ }^\circ\text{C}$ for a period of about 20 hours. Valve openings to the mass spectrometer showed hydrogen pressures of about 10^{-7} torr after this process.

Fig. 4-41 Schematic showing the instrumented DECOR pellet and radiative heater installed in the PUE-7B experiment.

Fig. 4-42 Heater and thermocouple assembly for Pt pellet (PUE-7B).

The very first test results showed poor output performance and high oxygen pressure, similar to the tests with cartridge-style DECORs. Baseline operation was at an emitter temperature of 1800 K, collector of 800 K, and cesium pressures. Over the initial 24 period of operation, performance improved and oxygen pressure decreased rapidly. Performance increased slowly over the next 140

Fig. 4-43 Pt pellet with thermocouple and heater mounted in PUE-7B.

hours. Fig. 4-44, Fig. 4-45, and Fig. 4-46 summarize the history of performance (based on the minimum barrier index), the equivalent oxygen pressure, and the cesium pressure over the entire PUE-7B testing cycle. Performance at about 170 hours is indicated by the I-V curve in Fig. 4-47 and the efficiency vs. power density curve in Fig. 4-48. Equivalent PUE-5 data are shown for comparison.

At this point in the experiment it was planned to begin parametric mapping of converter performance. The first such variation was a collector-temperature family from 700 K to 990 K. This excursion to higher collector temperature caused a loss in output voltage which persisted after returning to baseline conditions, indicating either that contaminants had been released into the cube by the high collector temperature, or that some change had occurred in the collector surface itself. To examine this last possibility, the collector surface was sputter-cleaned at a DC voltage of about 25 volts for a brief period.

The sputter-cleaning revealed the existence of a relatively thick coating of material on the collector, which had not been apparent during visual examination of the collector through the sapphire viewport. This coating flaked off during sputtering, with some flakes large enough to bridge the interelectrode gap and adhere to the emitter. Both electrodes were sputtered with AC in an attempt to remove the flakes. The sputtering process resulted in a performance recovery to the level achieved prior to taking the collector temperature family, as indicated in Fig. 4-44, but did not eliminate all of the flakes visible on the electrode surfaces. Increasing emitter temperature to 1900 K also did not eliminate the flakes adhering to the emitter.

The customer requested a 200 hour hold at baseline conditions ($T_E = 1800$ K, $T_C = 800$ K) in order to evaluate how performance was changing with time. During this period performance gradually decreased, as shown in Fig. 4-44.

The inability to reach the performance level of PUE-5, the changes in performance over time, and the presence of the collector-deposit flakes on both electrodes meant that the initial objective of performance mapping in PUE-7B was compromised. However, before disassembly of the cube began, work could still be done on characterization of the vapor source.

The effect of increasing the hydrogen pressure in the cube to $\sim 5 \times 10^{-7}$ torr was examined by increasing the temperature of the getter so that it released hydrogen. No measurable effect on oxygen pressure or the volt-ampere characteristics was found.

Fig. 4-44 PUE-7B performance history.

Fig. 4-45 PUE-7B oxygen pressure history.

Fig. 4-46 : PUE-7B cesium pressure history.

Fig. 4-47 PUE-7B I-V curve after initial performance improvement. PUE-5 data from the 1000 hour test have been added for comparison.

Fig. 4-48 PUE-7B power density and estimated efficiency after initial performance improvement.

The effects of pellet top temperature and cup temperature on both oxygen and cesium pressures were measured and are shown in Fig. 4-49-Fig. 4-52. Fig. 4-49 shows oxygen pressures which are both significantly lower than PUE-6, -7, or -7A and have less dependence on measured top temperature. Fig. 4-51 confirms previous results that the oxygen pressure is essentially unchanged by DECOR bottom temperature. The slight decrease of oxygen pressure with bottom temperature is most likely due to reduction in power to the radiant heater as the cup temperature is increased. The radiant heater was previously observed to affect oxygen readings. Cesium pressure depended on both temperatures, but was most strongly affected by the cup temperature.

The effect of cube temperature on oxygen and cesium pressures was also measured and is shown in Fig. 4-53 and Fig. 4-54. The dependence of oxygen pressure on cube temperature was nearly as strong as that on pellet top temperature, suggesting that at this point the oxygen was dominated by a different source than the pellet.

Operation with separate oxygen and cesium sources was then briefly examined, with the cesium removed from pellet back to the external liquid reservoir, and the external reservoir used as the cesium source while the pellet was used exclusively as an oxygen source. Performance was nearly the same as for the combined pellet source.

On disassembly, PUE-7 was subjected to a post-test visual inspection. The emitter had protruding metallic flakes adhering to it, and an etched appearance on the emitter surface. The collector showed a dark grey deposit, with a few small flakes on its surface. A dark grey deposit was also, surprisingly, on the collector insulator and on the lateral collector surface, which were both shielded from direct deposition by the ceramic collector shield.

The cube's interior surface and the copper gaskets were brilliantly clean, as in PUE-5. The cup which held the DECOR pellet was clean and, unlike PUE-5, showed no evidence of bonding of the pellet to the cup floor. No evidence was found of film creep out of the cup. A slight blue discoloration was seen on the inside surfaces of the stainless-steel mounting flanges for the SPREE oxygen detector, the sapphire window, the electrodes, the DECOR cup, the DECOR heater/thermocouple, and the vacuum pumpout. These flanges were made of the same grade of stainless steel as the cube, which showed no discoloration.

The DECOR pellet itself had a dark appearance, with tinges of orange (the color of Cs_2O) in some regions. The pellet had become structurally weak, and small pieces flaked off when it was removed from its cup.

Fig. 4-49 PUE-7B oxygen pressure vs. DECOR pellet top temperature.

Fig. 4-50 PUE-7B cesium pressure vs. DECOR pellet top temperature.

Slight reduction in oxygen pressure with cup temperature is attributed to reduction in pellet-top heater power in order to maintain constant pellet-top thermocouple reading.

Fig. 4-51 PUE-7B oxygen pressure vs. DECOR cup temperature.

Fig. 4-52 PUE-7B cesium pressure vs. cup temperature.

Fig. 4-53 : PUE-7B oxygen pressure vs. cube temperature.

Fig. 4-54 PUE-7B cesium pressure vs. cube temperature.

The question remains why PUE-7B developed deposits on its collector and emitter, while PUE-4 and PUE-5 had similar pellet oxygen sources but did not develop deposits. The electrodes were unchanged for all the experiments, and the oxygen pressure levels, as measured by the SPREE detectors, were similar between PUE-5 and PUE-7B, even including the initially high pressures at start-up. Some of the distinctions between the two sets of tests are:

- PUE-7B's pellet heater and pellet top thermocouple. One concern was that oxide material could climb the temperature gradient up the thermocouple wire from the pellet top. As an alternative, changes in heat transfer from that in PUE-4 and -5 could have resulted in loss of oxide from the pellet or a different oxide circulation rate.
- PUE-7B's ceramic collector shield. It could be that cesium reacts with alumina at certain temperatures to form different oxide species than the DECOR pellet.
- Better outgassing and cleaner cesium was employed in PUE-7B than in any previous PUE experiment, with the intention of preventing electrode deposits.
- The platinum-black used to fabricate the pellet in PUE-7B was from different lot number, had a higher density, and was slightly thicker than those in PUE-4 and -5.
- The increase in emitter temperature at start-up was limited during the initial period of high oxygen pressure, again, to avoid the formation of deposits. In the PUE-4 and -5 experiments the emitter temperature was increased much more quickly, possibly reducing the time spent in a critical temperature range for emitter oxidation.
- The stainless steel cube *may* have been a different part than PUE-4 or -5, although this cannot be determined for certain.

4.5 PUE-8: Flow-Through and Monolith Source

The PUE-8 design tested in this task evolved from the original DECOR with the intention of providing better temperature control at both ends and of providing some measure of vapor flow control. In all previous tests, whether with free-standing Pt pellets or with the column of porous Pt granules, there were return paths for the vapor outside the porous Pt components, offering hardly any significant flow impedance, as illustrated in Fig. 4-55. (In the particular case of PUE-6 there was not only a return path through the center perforated tube, but also around the Pt granules themselves.)

Fig. 4-55 Vapor flow around a Pt pellet (top) and first DECOR design (bottom)

The PUE-8 source, DECOR2, was designed to eliminate this possibility and to make the vapoflow through the cube variable. This, in turn, would allow us to study the influence of the flow rate on equilibration times, oxygen and cesium pressures, and electrode performance.

4.5.1 DECOR2 Source

Fig. 4-56 shows the DECOR2 source. Its main feature is a porous Pt cylinder (ϕ 0.275", L 0.065") with a very tight fit inside a Mo tube. The porous Pt cylinder was sintered in the usual fashion at 700°C, the final pressure being 1×10^{-7} torr. The Pt powder used was from the same lot as for PUE-7 and given the similar final sintered density (26% vs. 27%), it is very likely that the microscopic structure would be undistinguishable from that shown in Fig. 4-1. (Pore size ~ 0.5 to $1 \mu\text{m}$.)

The dimensions of the Mo container were adjusted to provide a press fit with the Pt cylinder and a 15 mil wall thickness in order to decouple the temperatures at the cylinder top and bottom. The bottom temperature was controlled by a screw-on heater-cooler, while an external heater was used to raise the top temperature when needed.

The vapor conductance of the DECOR2 source was determined from a measurement of the pressure drop as Ar was pumped out of a small vessel through DECOR2: at 25°C and an Ar pressure around 2 torr, the conductance was $\sim 0.6 \text{ cm}^3/\text{s}$. Similar values were obtained on cylinders half as long for which the side had been sealed with vacuum grease, suggesting that the tight fit in DECOR2 did not leave any significant flow leak.

4.5.2 PUE-8 Converter

Fig. 4-57 shows how DECOR2 was integrated into a cube converter to provide vapor flow near the electrodes and the oxygen detector and recondensation at the cold end. A high temperature Nupro valve was included between the cube and the DECOR2 cold end to allow the flow to be varied. However, this type of valve does not provide a high degree of control, even in its "regulating" version: the lowest measured conductance was $1.5 \text{ cm}^3/\text{s}$ and was obtained within 2-3° of complete closure. For future experiments a much better choice would be a bakeable UHV leak valve to achieve conductances several orders of magnitude below that of DECOR2.

Fig. 4-56 DECOR2 design

Fig. 4-57 PUE-8 test converter

The PUE-8 electrode features were:

* *Emitter:* CVD W on Mo previously used in PUE-7B. Separately outgassed for 4h at 1900 K in an ion-pumped bell jar with a residual pressure of 1.5×10^{-7} torr. This step was taken to avoid the apparent release of CO inside the cube upon the first few emitter temperature rises.

* *Collector:* Mo previously used in PUE-7B. Re-electropolished. Lateral alumina shield omitted.

The complete PUE-8 set-up is shown in Fig. 4-58. After mounting the various flanges onto a cube which had been bulk-outgassed separately at 950 C, with a residual pressure of 5×10^{-6} torr, the following outgassings were performed in sequence:

- plumbing (everything inside the oven, except DECOR2) at 350 C: mostly H_2O released.
- getter at 580 C with isolation valve closed: large amount of H_2 released.
- DECOR2 (top at 690 K, bottom at 620 K): H_2 , CO and CO_2 released.
- collector at 850 K, emitter at 1940 K: nothing significant released.

The outgassing was considered completed when the pressure at the pump was $\leq 2 \times 10^{-7}$ torr (~ equal amounts of H_2 , H_2O and CO).

Finally the cesium in the calibrated reservoir was cleaned of H_2 and CH_4 by bringing the Cs vapor in contact with the getter kept at 305 C for 36 hours. After this cleaning, cracking open the cesium valve to sample the vapor phase in the Cs reservoir at 250 C showed only a doubling of the H_2 peak.

4.5.3 Tests in "Dual-Reservoir" Mode

Before transferring cesium into DECOR2, PUE-8 was operated with the cesium calibrated reservoir as the Cs vapor source. Cs vapor in turn upon coming in contact with the porous Pt cylinder would react with the oxygen chemisorbed on the internal Pt surface and form a cesium oxide with an equilibrium Cs pressure precisely equal to that of the Cs liquid reservoir. DECOR2 would then act as a separate oxygen source, providing the opportunity to study this mode of operation not tried before. After opening the cesium and isolation valves, the initial oxygen pressure was 7.0×10^{-9} torr. However, it jumped overnight to 2.3×10^{-7} torr, suggesting a slow reaction kinetics

Fig. 4-58 PUE-8 test set-up

between adsorbed oxygen in DECOR2 and cesium vapor, or a slow penetration of the Cs vapor in DECOR2.

A transient with a time constant of several hours was observed in the J-V curve at one set of parameters, after the isolation valve had been re-opened, bringing Cs vapor in contact with the heated electrodes. Fig. 4-59 illustrates this time evolution.

This transient cannot be correlated to any temperature changes in PUE-8 and during the same period the oxygen pressure actually went down from 5.5×10^{-7} with the electrodes first heated to 1.7×10^{-7} torr. The cause of the J-V transient cannot be established at this early stage, but the changes observed in emission and barrier index suggest the formation of particular surface compounds or structures on the electrodes. The top curve in Fig. 4-59 can be characterized by

$$\phi_{EO} = 5.49 \text{ eV}$$

$$\text{and } V_B (6 \text{ A/cm}^2) = 1.98 \text{ eV}$$

which is comparable to the performance of PUE-5 and PUE-7B.

A collector temperature excursion from 700 to 850 K showed an optimum T_c around 800 K, similar to that of PUE-5.

Finally, J-V curves were found to be nearly insensitive to a change in the DECOR2 top temperature, while the oxygen pressure was only weakly dependent on it, as shown in Fig. 4-60. Closing the flow valve did not affect the performance or the oxygen pressure. Closing the isolation valve, however, resulted in a drop in the Cs pressure (about a factor of 2 in 2 hours), similar to what was obtained with the dual-reservoir converters IC1 and IC2. The insensitivity to the flow valve condition was not unexpected since P_{Cs} was determined outside DECOR2 and because no bulk Cs had been condensed in the pores thereby leaving them open for Cs-O vapor circulation: in the dual-reservoir mode no external flow is needed to keep P_{Cs} and P_{ox} constant.

4.5.4 Tests with a Monolithic Reservoir

Cesium was then condensed at the cold end of DECOR2 (flow valve open): the Cs amount transferred, 0.40 g, corresponded to a 50% filling of the Pt void volume, as for previous PUE converter tests. With the flow valve open, the performance was lower than in the dual reservoir mode, with V_B reaching 2.10 eV. Since the flow valve had too coarse a control to bring reliably its vapor conductance around or below that of DECOR2, it was instead operated as an ON-OFF flow switch.

PUE-8

Fig. 4-59 Evolution of PUE-8 J-V curve in dual-reservoir mode

PUE-8 IN DUAL-RESERVOIR MODE

Fig. 4-60 Oxygen pressure as a function of DECOR2 top temperature at a constant cesium pressure

Closing or opening this flow valve generated several transients in P_{Cs} , P_{Ox} and the temperature distribution in DECOR2. Fig. 4-61 shows at various times after closure a particular J-V curve: the rise in current suggests a P_{Cs} increase. Automated measurement of P_{Cs} and P_{Ox} showed, in fact, that upon closure of the flow valve, P_{Cs} practically doubled (Fig. 4-62) and P_{Ox} increased by 40%, as shown in Fig. 4-63. These pressure changes were completely reversible by re-opening the flow valve. Finally, as shown in Fig. 4-64, opening and closing the flow valve resulted in small but reproducible temperature changes at the DECOR2 top thermocouple.

The P_{Cs} rise in Fig. 4-62 exhibits two time constants: $\tau_1 \sim 22s$ and $\tau_2 \sim 6 \text{ min}$. τ_1 is also observed in the P_{Ox} rise and appears to correlate well with the rapid change in the J-V curve. τ_2 , on the other hand, seems commensurate with the temperature transient observed at the DECOR2 top.

4.5.5 Interpretation of ON-OFF Flow Transients

The simple fact that P_{Cs} and P_{Ox} change very quickly when the flow valve is closed (or opened) validates one of the basic assumptions used to describe the operation of the original DECOR (see Section 4.6 below): the existence of Cs and CsO_x vapor flows outside the porous Pt. With the flow valve open, P_{Cs} is in effect determined by the DECOR2 bottom temperature as the pressure drop along the return path is likely quite low. And, due to the concentration gradient of CsO_x along the temperature gradient inside the porous Pt, P_{Ox} is determined by the location of the cesium oxide with the highest oxygen content inside the Pt. Even though it is argued elsewhere that this oxide (Cs_2O ?) can migrate in its liquid phase against the temperature gradient, it is not obvious that the oxide will reach the top of the Pt column, whose temperature is actually not known (only the temperature of the upper Mo ring in contact with the top outer cylindrical surface of the column is accurately measured).

When the flow valve is closed, P_{Cs} is then determined by the temperature of the liquid Cs interface inside the Pt column and, since the Cs load is only half of the full void filling, the location of that interface is not easily inferred. As shown in Fig. 4-65, with the valve closed P_{Cs} reacts to changes in the DECOR2 top temperature.

The long time constant reflects the establishment of a new temperature profile inside the Pt column when the outside vapor flow is disturbed, leading to new equilibrium P_{Cs} and P_{Ox} .

In conclusion, these tests were highly successful in establishing the validity of describing DECOR as a thermochemical circulating vapor driver, fulfilling the requirements of this task.

PUE-8

Fig. 4-61 Transients in J-V curve when closing the flow valve

Fig. 4-62 Cs pressure transient observed upon flow valve closure

Fig. 4-63 Oxygen pressure transient observed upon flow valve closure

Fig. 4-64 Temperature changes at DECOR2 top upon operating flow valve

Fig. 4-65 With flow valve closed, P_{Cs} dependence on DECOR2 top temperature

4.6 Physical-Analytical Model for a Dynamic Equilibrium Cs/O Reservoir (DECOR)

4.6.1 Introduction

The objective of this task was to develop a physical-analytical model describing DECOR that relates the thermal, chemical and configurational parameters to the composition of the Cs/O vapor that DECOR maintains. The model consists of self-consistent, steady-state coexistence of three classes of processes:

heat transport, which establishes the temperature distribution and its relationship to heat flow and associated vapor and liquid mass transport rates;

chemical equilibrium, which establishes the local Cs/O liquid and vapor composition associated with the temperature distribution; and

mass transport, which establishes the relationship between the local Cs/O composition and cyclical mass transport rates.

Aspects of vapor control by DECOR in system and converter design are considered.

4.6.2 Two-phase Heat Transport in a Biporous Structure

The biporous structure considered here consists of a continuous web of small particles soaked with Cs/O liquid that forms the walls of large interconnecting pores filled with Cs/O vapor (Fig. 4-66). Heat supplied to one region of the structure vaporizes the liquid into the pores through which the vapor flows to condense into the web in a region where heat is removed. The liquid returns by wicking through the web in a continuous cycle. More detail on heat transport in this structure can be found elsewhere [29].

The total heat Q_t added to the end of the biporous structure consists of the heat Q transported through the structure and the heat Q_x transported by the external vapor flow rate $G_{vx} = Q_x/L$. The heat flow Q across a plane at distance x from the high temperature end of the structure is divided between the heat conducted by the web Q_s and heat transported by the vapor Q_v through the pores.

$$Q = \beta Q_v + (1 - \beta) Q_s \quad (1)$$

Fig. 4-66a Process assumed to be occurring in DECOR.
Liquid flow is solid arrows; vapor flow is dashed arrows.

Fig. 4-66b Enlargement of circled region in Fig. 4-66a showing two-phase counter-current flow in a bi-porous structure transporting heat. This "Type A" structure is appropriate for large pore volume fractions. The inverse "Type B" structure (porous ball compact) is appropriate for low pore volume fractions.

$$Q_s = -K \frac{dT}{dx} \quad (2)$$

$$Q_v = LG_v \quad (3)$$

where β is the fraction of the projected area of the slice that is occupied by the pore void, K is the thermal conductivity of the web, G_v is the mass flow rate of the vapor per unit area of void across the slice, and L is the latent heat of vaporization.

Differentiation of Eq. 1, together with Eqs. 2 and 3, gives for heat flow continuity ($dQ/dx = 0$)

$$\frac{dQ_v}{dx} = \frac{1 - \beta}{\beta} K \frac{d^2T}{dx^2} \quad (4)$$

At a surface where heat flux density q is being removed by a net rate of vaporization, acceleration of the vapor away from the surface causes the pressure in the vapor P_v to be less than the vapor pressure of the surface P_{Cs} by an amount

$$\Delta P = P_{Cs} - P_v = (2\pi RT)^{1/2} q/L \quad (5), (6)$$

where $R = R_0/M$ is the gas constant, T the temperature, R_0 the molar gas constant, and M the molecular weight. In a slice dx thick normal to heat flow in the biporous structure, the heat dQ_s is removed from the liquid-filled web at the rate

$$q = -dQ_s / S_p dx \quad (7)$$

where S_p is the surface area of the pores per unit volume of the biporous structure.

Differentiation of Eq. 5 gives

$$\frac{dP_{Cs}}{dx} = \frac{dP_v}{dx} + \frac{d\Delta P}{dx} \quad (8)$$

For laminar vapor flow through the pores neglecting compressibility for small pressure drops, the vapor pressure gradient is

$$\frac{dP_v}{dx} = -r G_v \quad (9)$$

with the vapor flow resistance

$$r = \frac{150 \mu b RT}{P_v D^2}$$

where μ is the vapor viscosity and density, D is the diameter of the web structures, and $b = (1 - \epsilon_v)^2 / \epsilon_v^3 \phi$ is a configuration design parameter involving the void volume fraction ϵ_v and shape factor $\phi \leq 1$.

Differentiation of Eq. 6, together with Eqs. 1, 3, 4 and 7, gives

$$\frac{d\Delta P}{dx} = B \frac{d^3 T}{dx^3} \quad (10)$$

where

$$B = \frac{(2\pi RT)^{1/2} K}{LS_p} \frac{1 - \beta}{\beta}$$

Eq. 8 thereupon becomes, using Eqs. 9 and 10 with 1-3,

$$\frac{dP_{Cs}}{dx} = B \frac{d^3 T}{dx^3} - r \frac{K}{L} \frac{1 - \beta}{\beta} \frac{dT}{dx} - \frac{rQ}{\beta L} \quad (11)$$

Since the partial pressure of oxygen-containing species is negligible, P_{Cs} in Eq. 11 is the vapor pressure of cesium above the liquid Cs/O mixture given by

$$P_{Cs} = \epsilon P_o \exp(-L/RT) \quad (12)$$

where ϵ is the cesium activity, and L and P_o are the values for pure Cs. Fig. 4-67 is a plot of $\epsilon(C_{OL})$ from the associated solution thermochemical estimates by Lamoreaux (Appendix G), along with values of a convenient analytical fit, such that for oxygen mass fraction C_{OL} ,

$$\epsilon = \begin{cases} (1 - 425 C_{OL})^2 & \text{for } 0 < C_{OL} \leq 0.04 \\ 0.32 & \text{for } 0.04 \leq C_{OL} < 0.056 \text{ and } P_{Cs} \leq 1 \text{ torr} \end{cases} \quad (13)$$

The liquid vapor pressure and composition remain constant above the liquidus composition (4 w/o or 26 a/o) because excess oxygen above this composition is precipitated as solid cesium oxide.

Fig. 4-67 and Eq. 13 are preliminary and inaccurate in that they were taken from plots of Lamoreaux's computations rather than directly from numerical calculations. They are adequate for semi-quantitative illustration of the DECOR formalism, however, and are subject to correction by such direct calculations.

Numerical solution of Eq. 11 therefore requires the distribution of oxygen $C_{OL}(x)$ in the biporous structure for use in Eqs. 11-13. This, in turn, requires a model for steady state mass transport in the counterflowing Cs/O liquid and vapor streams.

4.6.3 Two-Phase Cs/O Mass Transport in DECOR

The net oxygen mass transport rate across a plane at distance x from the hot end of the structure is

$$G_O = G_{OL} + G_{OV} + G_{OD} + G_{OX} \quad (14)$$

Fig. 4-67 Cesium activity in liquid Cs-O as computed by Lamoreaux and an analytical approximation

where

G_{OL}	=	$C_{OL} G_{CL}$	= oxygen mass transport rate by liquid flow
G_{OV}	=	$C_{OV} G_V$	= oxygen mass transport rate by vapor flow in pores
G_{OX}	=	$C_{ox} (G_{CsX} + G_{OX})$	= oxygen mass transport rate by external vapor flow
G_{OD}	=	$G_{ODL} + G_{ODV}$	= oxygen mass transfer rate by diffusion
G_{ODL}	=	$-\rho_L D_L dC_{OL}/dx$	= oxygen mass transport rate by diffusion in liquid
G_{ODV}	=	$-\rho_V D_V dC_{OV}/dx$	= oxygen mass transport rate by diffusion in vapor
C_{OL}	=		mass fraction of oxygen in the liquid
C_{OV}	=		mass fraction of oxygen in the pore vapor
C_{OX}	=		mass fraction of oxygen in the external vapor
G_{CL}	=		mass rate of liquid flow
G_V	=		mass rate of pore vapor flow
G_{CsX} and G_{OX}	=		mass transport rates of cesium and oxygen, respectively, in the external vapor stream
ρ_L and ρ_V	=		densities of Cs/O liquid and vapor, respectively
D_L and D_V	=		local interdiffusion coefficients for cesium and oxygen in Cs/O liquid and vapor, respectively

Also note that, by definition, $C_{OL} = 1 - C_{CsL}$, $C_{OV} = 1 - C_{CsV}$ and $C_{OX} = 1 - C_{CsX}$

Similarly, the net cesium mass transport rate is given by

$$G_{Cs} = G_{CsL} + G_{CsV} + G_{CsD} + G_{CsX} \quad (15)$$

where all the definitions in Eqs. 14 apply also in Eq. 15 if the subscript "O" and the term "oxygen" are replaced with "Cs" and "cesium", respectively; i.e. Eqs. 14 and 15 are completely symmetrical in oxygen and cesium.

For a steady-state cyclical process, there can be no net transport of cesium or oxygen across the plane, so that

$$G_o = G_{Cs} = 0 \quad (16)$$

Furthermore, the thermochemical analysis by Lamoreaux in Appendix G gives the equivalent partial pressure of oxygen above Cs/O liquid having oxygen atom fraction C_{OL} at temperature T . A convenient fit to his results is

$$P_{ox} = \begin{cases} 1.4 \times 10^6 \exp\left(80.23C_{OL} - \frac{1.78 \times 10^4}{T}\right) & \text{for } 0.01 \leq C_{OL} \leq 0.04 \\ 3.6 \times 10^7 \exp\left(-\frac{1.78 \times 10^4}{T}\right) & \text{for } C_{OL} \geq 0.04 \end{cases} \quad (17)$$

Accordingly, the local oxygen and cesium mass fractions in the vapor are obtained from Eqs. 12 and 17 as, respectively,

$$C_{OV} = P_{OX}M_{OX}/(P_{Cs}M_{Cs} + P_{OX}M_{OX}) \quad (18)$$

and

$$C_{CsV} = P_{Cs}M_{Cs}/(P_{Cs}M_{Cs} + P_{OX}M_{OX}) \quad (19)$$

The oxygen and cesium mass fractions in the external vapor C_{ox} and C_{Csx} are obtained from Eqs. 12, 17, 18 and 19 for the mass fraction C_{OL} at $x = 0$.

It should be noted that atom fractions X are related to mass fractions C by the relations

$$X_o = \left[1 + \left(\frac{1}{C_o} - 1 \right) \frac{M_o}{M_{Cs}} \right]^{-1} \quad (20)$$

$$X_{Cs} = \left[1 + \left(\frac{1}{C_{Cs}} - 1 \right) \frac{M_{Cs}}{M_o} \right]^{-1} \quad (21)$$

where M_{ox} and M_{Cs} are the oxygen and cesium atomic masses, respectively.

If the dependence of ρ_L , ρ_V , D_L and D_V on temperature and on liquid and vapor composition is known, Eqs. 9 and 11-19 can be solved numerically to obtain the temperature and Cs/O composition distribution in the structure, and the composition of the Cs/O external vapor, as a function of the configurational parameters of the biporous structure and the heat flow through it.

Fig. 4-68 shows the known dependence of ρ_L on C_{OL} . From kinetic theory, the vapor density is given by

$$\rho_V = (P_{ox} M_{ox} + P_{Cs} M_{Cs})/kT \quad (22)$$

Similarly, the interdiffusion coefficient in the Cs/O vapor can be estimated from kinetic theory as

$$D_V = \frac{3}{8} \sqrt{\frac{\pi}{2}} [(M_{Cs} + M_{ox})/M_{Cs} M_{ox}]^{1/2} (kT)^{3/2}/P_{Cs} S \quad (23)$$

where $S = \pi (R_{ox} + R_{Cs})^2$ is the diffusion cross section for the cesium and oxygen-bearing species of radii R_{Cs} and R_{ox} and masses M_{Cs} and M_{ox} . The diffusion coefficient in the Cs/O liquid D_L is unknown, however, and is difficult to estimate analytically with confidence over the wide range of Cs/O compositions in DECOR. The diffusion coefficient D_L and flow resistance r should be determined experimentally.

To obtain intuitive insight into the DECOR process, algebraic solutions can be obtained for Eqs. 14-16 by assuming that internal vapor flow G_{OV} , vapor diffusion G_{ODV} and heat conduction K are negligible, and that ρ_L and D_L are constant at appropriate average values, giving

$$C_{OL} = (C_{OLE} - C_{OX}) \exp(-x/s_p) + C_{OX} \quad (24)$$

where

$$x_s = \rho_L D_L L/Q \quad (25)$$

and C_{OLE} is the oxygen mass fraction in the liquid at the hot (evaporating) surface of the structure (i.e. at $x = 0$). If C_{OLC} is the oxygen mass fraction in the liquid at the cold (condensing) end of a structure of thickness d , Eq. 24 gives, since always $C_{OX} \ll C_{OLE}$,

$$C_{OLC} = C_{OLE} \exp(-d/x_p) + C_{OX} \quad (26)$$

Fig. 4-68 Density of Cs-O compounds as a function of the oxygen atomic content.

4.6.4 Operating Point and Stability

4.6.4.1 Operating Conditions

Eqs. 24 and 25 show that the concentration of oxygen in the structure decreases exponentially with distance from the hot surface with an e-folding distance that is inversely proportional to the heat Q supplied to that surface. A crude estimate for the diffusion coefficient D_L can be obtained from the Stokes-Einstein equation,

$$D_L \approx kT/6\pi\mu R_{OX} \approx 8 \times 10^{-5} \text{ cm}^2/\text{sec} \quad (27)$$

for liquid cesium viscosity $\mu = 0.25$ centipoise and radius of the diffusing oxygen species $R_{OX} = 1.7 \times 10^{-8} \text{ cm}$ at $T = 500 \text{ K}$. For $\rho_L \approx 2.5 \text{ g/cm}^3$ and $L = 540 \text{ J/g}$, Eq. 25 gives an e-folding distance $x_s \approx 1 \text{ mm}$ for $Q = 1 \text{ w/cm}^2$. This distance could be much smaller if the oxygen is bound in a large molecule such as the Cs_{11}O_3 said to characterize dilute Cs/O solutions.

Accordingly, Eq. 26 shows that DECOR biporous structures act as an "oxygen amplifier" in a converter, with a "gain" that is exponentially proportional to the thickness d and heat flow Q through the structure. The circulating cesium vapor scavenges almost all the oxygen in a converter and concentrates most of it in a thin region near the hot surface. For structure thicknesses the order of $d \approx 1 \text{ cm}$, the oxygen concentration in the Cs/O liquid at the hot surface C_{OLE} is many orders of magnitude greater than that at the cold end C_{OLC} . In fact, for large structure thickness $d \gg x_s$, the oxygen concentration in the liquid at the cold end approaches that in the condensing vapor, $C_{OX} \approx 10^{-8}$ typically. As a result, most of the Cs/O liquid in the structure has a very low oxygen content, except near the hot surface, $x \leq x_s$.

The oxygen concentration in the external vapor is a function of the concentration C_{OLH} and temperature T_E of the liquid at the hot surface where it is generated by evaporation, via Eqs. 17, 18 and 20. Accordingly, Eqs. 24-26 show that the vapor composition C_{OX} is uniquely determined by temperature T_E if the composition of the liquid is held constant at any location in the DECOR cycle. Three conditions for such stable steady-state operation and the associated operating points will be considered:

1. Constant total oxygen and cesium inventories.
2. Constant hot end composition C_{OLE} .
3. Constant cold end composition C_{OLC} .

4.6.4.2 Constant-Inventory Operation

If insufficient oxygen is added to the liquid cesium to form a solid oxide phase, the operating point (liquid and vapor compositions) will be determined by the overall molar quantities of cesium and oxygen in the cyclical system and by the temperatures associated with the heat flow Q . The overall mass fractions of oxygen and cesium in the system are given by the average mass fractions

$$\bar{C}_o = \frac{\int_0^d C_{OL} dx}{d} = 1 - \bar{C}_c \quad (28)$$

When solved simultaneously with Eqs. 9 and 11-19, Eq. 28 results in a unique steady-state operating point. Combined with Eq. 26 for $C_{OX} \ll C_{OLC}$, Eq. 28 gives

$$\bar{C}_o \approx \frac{x_s}{d} C_{OLE} [1 - \exp(-d/x_s)] \quad (29)$$

For sufficient heat flow that $x_s \ll d$, the unique composition at the hot end given by Eq. 29 is

$$C_{OLE} = \frac{d}{x_s} \bar{C}_o \quad (30)$$

which together with Eqs. 25 and 26 gives C_{OLC} , and together with Eq. 17 gives the dependence of the equivalent pressure of oxygen P_{OX} in the external vapor on the DECOR hot end temperature T_E .

While this formally is a stable operating point, the strong dependence of P_{OX} on composition below the liquidus composition $C_{OL} \leq 0.04$ in Eq. 17 makes this type of operation potentially unstable if oxygen is either consumed or evolved during long term converter operation. Because of the oxygen "amplification factor" d/x_s in Eq. 30, the total inventory of oxygen required for this type of operation can be very small. Nevertheless, if constant-inventory operation can be achieved practically, it permits operation over a wide range of compositions if an optimum composition is required.

4.6.4.3 Constant C_{OLE} (Two-Phase) Operation

The liquidus composition (phase boundary) for Cs/O solutions occurs near $C_{OL} \approx 4$ w/o ($X_{OL} \approx 26$ a/o) for vapor conditions approaching optimum converter operation. If sufficient oxygen is added to the cesium in a converter to exceed $C_{OLE} \approx 0.040$ in Eq. 30, the excess oxygen added will precipitate as solid Cs_2O such as to maintain a constant value $C_{OLE} \approx 0.040$ in the liquid. Thereafter, increase or decrease of total oxygen inventory will not change C_{OLE} in the liquid for all values $0.040 \leq C_{OLE} < 0.056$ computed from Eq. 30, i.e. as long as the liquid and solid phases coexist. Accordingly, the equivalent oxygen pressure in the vapor P_{OX} will be dependent only on temperature T_E , as indicated in Eq. 17.

This type of operation is very stable, therefore, but imposes two significant limitations. First the P_{OX} vs T_E obtainable is restricted to that for $C_{OL} \approx 0.040$ which constrains the DECOR design operating point. Second, if too much oxygen is added, the pores of the DECOR structure can become plugged with solid Cs_2O (no liquid), impairing operation.

4.6.4.4 Constant C_{OLC} (Chemical-coexistence) Operation

In practice thus far the condensing Cs/O liquid is in contact with molybdenum at the cold end of the DECOR structure (at $x = d$). Molybdenum reacts there with oxygen and cesium to form cesium molybdate by the chemical reaction

As long as separate solid molybdenum and molybdate phases coexist there, the composition of the Cs/O liquid C_{OLC} there remains independent of oxygen inventory at a given cold end temperature T_C . This results in a constant composition C_{OLE} at the hot end and a constant equivalent oxygen pressure P_{OX} in the vapor at hot end temperature T_E via Eqs. 17 and 26.

In Appendix H, Lamoreaux employs the associated solution thermochemical analysis to estimate the dependence of P_{OX} on T_E for a DECOR with C_{OLC} maintained constant by molybdenum-molybdate coexistence at $T_C = 500$ K. It is shown in Fig. 1 of Appendix H that the experimentally observed $P_{OX}(T_E)$ is consistent with a hot end composition of $X_{OLE} = 24$ a/o ($C_{OLE} = 3.7$ w/o). This is sufficiently near the liquidus phase boundary, however, that it is ambiguous as to whether the vapor composition in the experiment is being controlled by the two-

phase physical process described in Section 4.3 above or by the chemical coexistence process described here, within the analytical and experimental uncertainties. It seems clear, however, that both processes are capable of stabilizing DECOR operation in the range of practically significant operating points.

A potential advantage of chemical-coexistence-stabilized operation is that it does not tend to plug the pores with precipitated Cs_2O as in two-phase-stabilized operation. Another advantage is that the vapor-forming composition C_{OLE} is not constrained to fall on the liquidus phase boundary; i.e. the operating point giving desired oxygen and cesium pressures at a given temperature T_E can be selected by choosing an appropriate coexistence metal at the cold end of the structure. In fact, the DECOR biporous structure itself could be constructed of a metal giving the desired coexistence compound. The thermochemical analysis of such a structure would be much more complex, however, because of the need to consider local chemical equilibrium throughout its temperature gradient.

A potential limitation of this type of stabilized operation is that the dependence of oxygen and cesium pressures in the vapor on the heat rejection temperature T_C is much larger than that of two-phase-stabilized operation which can be nearly independent of T_C , as described in the following section.

4.6.5 System and Converter Design Aspects

4.6.5.1 Temperature Drop Across DECOR

As shown in the preceding section, the composition of the external vapor formed by DECOR is dependent primarily on the hot end temperature T_E for stabilized operation. That temperature depends on the heat flow Q and cold end temperature T_C . In a practical system both Q and T_C generally depend on heat transfer characteristics of the system and/or converter design into which the DECOR structure is integrated. These conditions therefore establish the boundary conditions for solution of Eqs. 11-12, which yield the value of T_E required for determination of vapor composition via Eqs. 12 and 17.

Some approximate algebraic solutions of Eqs. 12 and 17 can be obtained for special cases. For small temperature drops it can be shown from Eqs. 11-12 [Ref. 29] that vapor formation and acceleration require a temperature drop

$$\Delta T_o = Qx_o/K \quad (32)$$

at both ends of the biporous structure within a distance x_o from the surfaces, given by

$$x_o = \frac{(2\pi)^{1/4} R^{3/4} T^{5/4} K^{1/2}}{L (\beta S_p P_{Cs})^{1/2}} \quad (33)$$

In addition, the rapid decrease in oxygen concentration in the liquid within a small distance x_s from the hot surface (given by Eq. 25) increases the cesium activity ϵ . To maintain the cesium pressure required for heat transport, the temperature must decrease across x_s by an amount ΔT_ϵ obtained by differentiation of Eq. 12 with respect to ϵ , giving

$$\Delta T_\epsilon \approx \frac{RT_E^2}{L} \Delta(\ln \epsilon) \quad (34)$$

For two-phase operation, ϵ changes from 1 to 0.32 and Eq. 34 becomes

$$\Delta T_\epsilon \approx 1.3 \times 10^{-4} T_E^2 \quad (35)$$

independent of all other design and operating parameters as long as two-phase operation exists and $d \gg x_s$.

For sufficiently large heat flow Q and small K , vapor heat transport is dominant and Eqs. 9 and 11 give

$$P_v \approx \left[P_E^2 - \frac{300\mu bRT}{D^2\beta L} Qx \right]^{1/2} \quad (36)$$

which together with Eq. 12 gives the temperature distribution in DECOR.

Fig. 4-69 illustrates the various contributions to the temperature drop across DECOR. As the temperature decreases the vapor pressure P_{Cs} falls exponentially until heat conduction by the structure dominates and the temperature profile approaches linearity near the cold end.

Fig. 4-69 Contribution of various heat transfer processes to temperature profile in DECOR. Conditions are the same as in Fig. 4-28.

If the DECOR design is chosen such that the thermal conductivity K is very small, and heat flow Q and thickness d are sufficiently large, Eq. 36 and Fig. 4-69 show that the temperature T_E of the hot end and corresponding cesium and oxygen pressures become nearly independent of the heat sink temperature T_C . This is a significant system design consideration since only the heat supplied to the DECOR needs to be controlled in order to control the cesium and oxygen pressures.

4.6.5.2 Criterion for Vapor Control by DECOR

When a converter is first activated there is a possibility that oxygen exists in several locations inside its vapor envelope. The local Cs/O solution in each of these locations will contribute to the oxygen content of the vapor to a degree dependent on the local temperature. The Cs/O liquid in these regions will creep up the temperature gradient and thereby segregate into a band of compositions constituting a local DECOR-like cycle. During this initial stage of operation, therefore, the oxygen content of the vapor might not be controlled by the temperature of the DECOR porous structure intended as the control element, but uncontrollably by the high temperature at another location. The question arises, therefore, as to which of these multiple DECOR-like cycles in the same envelope will eventually dominate when a steady state is reached.

It should be apparent that the cycle that processes the greatest total mass rate of external vapor G_{vx} will accumulate oxygen at the expense of all other cycles until the others are exhausted. A very important criterion in the design of a controllable DECOR vapor source, therefore, is that the mass rate G_{vx} of vapor from the DECOR structure must be sufficient to dominate over that from other possible regions in the vapor envelope. In particular, the condensed liquid pool at the cold end of the DECOR structure must not creep to a higher temperature region of the envelope at a higher rate than the rate of liquid flow up the DECOR structure to its hot end. A large internal vapor flow rate $G_v \gg G_{vx}$ within the biporous structure can ensure that this criterion is satisfied.

4.6.5.3 Diffusion Effects and Equilibration Times

a. Background

Although the beneficial effects of oxygen in converters has been well known for 25 years, efforts by many competent groups to make these effects practically useful were thwarted by unstable and irreproducible operation. The HET project has identified the primary

origins of this instability and irreproducibility: physical instability of Cs/O solutions arising from segregation by film creep and distillation; and excessive equilibration time arising from diffusion-limited oxygen transport. The Cs/O physical instability was overcome through the development of the DECOR vapor source. This section concerns the excessive diffusion-limited equilibration time, which probably was months or years in converters used in previous Cs/O research. It is essential that these diffusion limitations are considered in any Cs/O system design.

b. Diffusion of Oxygen-Containing Species through Cesium Vapor

The diffusion coefficient for diffusion of oxygen-containing molecules through cesium vapor is given by Eq. 23. The primary oxygen-bearing species is either Cs_2O or CsOH , but the cross section S for their diffusion through cesium vapor is not known. If the conservative assumption is made that $M_{\text{ox}} \approx M_{\text{Cs}}$ and $R_{\text{ox}} \approx R_{\text{Cs}} \approx 2.5 \times 10^{-8} \text{ cm}$,

$$D_v \approx \frac{333}{P_{\text{Cs}}} \text{ cm}^2/\text{sec} \quad (37)$$

for the cesium pressure P_{Cs} in torr.

It is important to recognize that diffusion-limited equilibration in Cs/O systems is dominated by adsorption on the bounding surfaces. This is because there are far more oxygen-containing molecules adsorbed on these surfaces than exist in the enclosed vapor. For example, in a cubic chamber with edge length H and surface adsorption site density σ , the ratio of the number of adsorbed oxygen-containing molecules to the number in the gas phase at partial pressure P_{OX} is

$$\frac{N_{\text{surface}}}{N_{\text{gas}}} = 6kT\sigma/HP_{\text{OX}} \quad (38)$$

For an adsorbed monolayer ($\sigma \approx 4 \times 10^{14} \text{ cm}^{-2}$) inside an $H = 3 \text{ cm}$ cubic chamber, at pressure $P_{\text{OX}} = 10^{-8} \text{ torr}$ that is typical for a Cs/O system at 600 K, Eq. 38 shows that there are 5×10^6 more molecules on the surface than in the gas.

4.6.5.4. Equilibration Times in the Cube

As the simplest case, approximated in the cube, assume that the diffusion is one-dimensional. A source of oxygen-containing molecules at vapor pressure P_{OX} on one side of the cube cavity will cover the opposite side with a monolayer of these molecules in a time (in seconds), using Eq. 37 and the other values used above,

$$\tau = \frac{\sigma}{D_v (\Delta n / \Delta x)} = \frac{\sigma H k T}{D_v P_{\text{OX}}} = 2.3 \times 10^{-4} \frac{P_{\text{Cs}}}{P_{\text{OX}}} \quad (39)$$

For oxygen-containing molecules at $P_{\text{OX}} = 10^{-8}$ torr diffusing through $P_{\text{Cs}} = 1$ torr Cs vapor, Eq. 39 gives $\tau \approx 6$ hours, which is about equal to the e-folding equilibration time after any perturbation of P_{OX} .

When operation of the cube with cesium vapor at 1 torr is first initiated, it is observed that several hours are required to achieve steady-state oxygen pressures. When the electrodes are initially heated, the associated burst of evolved oxygen requires several hours to dissipate and reach steady state. After the tungsten filament on one side of the cube cavity is flashed to high temperatures, it is observed that the local oxygen pressure is depressed severely but recovers to the initial steady-state value within a few hours. This depressed pressure apparently arises from the creation of a fresh tungsten surface on the adjacent surfaces due to evaporation of the tungsten filament. All of these observed effects tend to confirm that equilibration in the cube is diffusion limited.

4.6.5.5. Equilibration Times in More Complex Cs/O Systems

In past work, attempts were made to employ Cs/O sources external to the measurement chamber. In this case the diffusion of oxygen-containing species along the tube or other passages connecting the source and the chamber is a very complex process. Any change at the source end of the tube must be propagated by a continuous succession of adsorption-desorption steps between the very dilute vapor and the passage walls all along the passage length, greatly extending the equilibration time over that in the simple one-dimensional case without sidewalls.

As a crude estimate, the one-dimensional equilibration time of a small cavity through a tubular passage should be increased by about half the ratio of the internal surface area of the tube to its end area. For a tube of diameter D and length L ,

$$\tau_{\text{tube}} \approx \frac{1}{2} \frac{\pi D L}{\pi D^2/4} \tau_{\text{cube}} = \frac{2L}{D} \tau_{\text{cube}} \quad (40)$$

For typical reservoir tubulation values, $D = 0.5$ cm and $L = 3$ cm, Eq. 40 gives $\tau_{\text{tube}} \approx 12 \tau_{\text{cube}} \approx 3$ days.

If the internal surface area in the cavity is much larger than the internal surface area of its tubulation, as it is in a tubulated converter or test chamber, the equilibration time similarly should be increased by the ratio of the cavity (converter) internal surface area A to the end area of the tube between it and the source,

$$\tau_{\text{converter}} \approx \frac{4A}{\pi D^2} \tau_{\text{tube}} \quad (41)$$

If the internal area of the cavity (converter) is $A = 10$ cm², Eq. 41 gives its equilibration time through the $D = 0.5$ cm, $L = 3$ cm tube as $\tau_{\text{converter}} \approx 50 \tau_{\text{tube}} \approx 5$ months.

While these are very crude estimates, they illustrate why early workers required days of equilibration before they fully developed oxygen effects through a tubulation directly into the converter gap. They also illustrate why many investigators in past years either obtained no effects (their contract would run out first), or if they got effects, it was because they inadvertently (and irreproducibly) transferred some condensed oxide into the converter in high pressure excursions during a desperate search for effects.

4.6.5.6. Effect of Diffusion on Transient Oxygen Pressure Measurement

The question naturally arises as to whether diffusion affects oxygen pressure determination by the sputter-desorption-readsorption (SPREE) method. Specifically, does a significant fraction of the oxygen sputtered from the filament return from the surrounding vapor during the readsorption period? If so, this would invalidate the method.

Quantitative insight into this question can be obtained by analogy with a solution for the transient injection of heat into the boundary of a semi-infinite (one-dimensional) solid

(H.S. Carslaw and J.C. Jaeger, 2nd Ed., Eq. 10, p. 76, Clarendon Press, 1959). It can be shown that the decay of oxygen concentration by diffusion following removal of N molecules from a surface during a sputtering pulse of duration Δt is equivalent to the decay from a region of uniform density $n_0 = N/d$ adjacent to the surface, having a thickness

$$d = (\pi D_v \Delta t)^{\frac{1}{2}} \quad (42)$$

For a sputtering pulse $\Delta t = 4 \times 10^{-3}$ seconds in duration ($1/4$ cycle), Eq. 42 with Eq. 37 gives, for $P_{Cs} = 1$ torr cesium pressure, $d = 2.0$ cm. Since this distance would carry the sputtered oxygen throughout a large part of the cube volume, the fraction that would return to the very small area of the filament is entirely negligible.

While Eq. 42 is not strictly valid quantitatively for three-dimensional diffusion, it is adequate to show that transport by diffusion is entirely rapid enough to remove the sputtered oxygen from the vicinity of the filament. This is confirmed by the complete absence of any observable transient after the sputtering pulse.

This very rapid diffusion and equilibration within the vapor, but very slow equilibration within the vapor envelope, may seem to be paradoxical. The difference arises from the fact that, although oxygen diffuses very rapidly through the vapor (at ~ 5 m/sec), its density is very low at the typical $P_{OX} \sim 10^{-8}$ torr; i.e., oxygen adsorbed on a surface on one side of the envelope must be transmitted to the other side via a medium having only $\sim 10^{-6}$ as many molecules in transit as are adsorbed on the walls. This is analogous to the ability of an SST to transport 100 people across the Atlantic in only one hour, but it would require 300 years to transport the entire US population.

This fulfills the requirement of the task to fully develop the physical/analytical model for DECOR.

5.0 SAPPHIRE TUBE COLD SEAL CONVERTER APPLICATIONS

5.1 Principles and Features of the Sapphire Tube Test Vehicle

5.1.1 Purpose

Prior to use of the "cube" test vehicle, test of a converter design aspect or its modification required at least 3-6 months to design, construct, process and test a special converter for this purpose. Use of the "cube" decreased this iterative cycle time to 3-6 weeks, but at the cost of increased complexity and associated failure modes of the demountable and valvable "cube" system with its integral diagnostics. These limitations paced the rate of progress and limited the control of impurities, the range of experimental variables, and the flexibility of testing innovations.

A new test vehicle concept was developed specifically to overcome these limitations. This system can operate with a much greater range of Cs/O variables than the "cube", with much greater visual access to the vapor source and discharge, and with much greater control over impurities. It is revolutionary in its simplicity and low cost compared with all previous cesium vapor systems, and its cycle time can be less than an hour. Because of this simplicity and low cost, concurrent experiments in multiple vehicles are practical.

5.1.2 Construction

Fig. 5-1 shows a double-ended embodiment of the sapphire tube test vehicle, which is useful for experiments requiring flow through or symmetry of the test region. A sapphire tube, available commercially in many sizes and cross section shapes, is mounted in air between two modified O-ring-sealed tubing couplings. These can be maintained near room temperature by cooling water, but for most experimental conditions cooling by heat conduction through their supports is adequate.

The components to be tested in cesium vapor are mounted on removable O-ring-sealed flanges that mate with flanges attached to the tubing couplings at both ends. The lumen of the couplings and tube is connected with a gas handling or vacuum system through tubing attached to the couplings. A porous metal rod (wick) soaked with liquid cesium extends along the wall of the sapphire tube. It can extend the full length of the tube or only from the test region to the ends of the tube if electrical isolation or a fully open tube lumen is required within the test region. A 25-mil diameter Nichrome electrical heater wire is wound with a 1/8-inch pitch around the sapphire tube in the central test region.

Fig. 5-1 Double-ended Sapphire Tube Test Vehicle Showing Movable Component

Fig. 5-2 Partial Pressures in the Test Vehicle shown in Fig. 5-1

5.1.3 Gas-Buffered Operation

In the gas-buffered operating mode [Ref. 30] an inert gas (e.g. argon) is maintained at a constant applied pressure in the tube ends by an external source. As the temperature in the test region is increased by its electrical heater, eventually a temperature is reached where the vapor pressure of cesium exceeds the applied argon pressure. The argon then is expelled from the test region by cesium vapor flow to give a gas-vapor interface at the point where the tube wall temperature precisely equals the cesium condensation temperature. Thereafter the cesium vapor pressure and temperature in the test region between these interfaces are constant and equal to the applied argon pressure and corresponding cesium condensation temperature, respectively, as shown in Fig. 5-2. The temperature falls about linearly, and the partial pressure of cesium falls exponentially, in the end region between the gas-vapor interface and the tube ends. The argon partial pressure rises correspondingly to maintain a constant total (applied) pressure. The cesium partial pressure at the tube ends and in the external tubing is about 10^{-6} torr (at 20°C), regardless of its pressure in the test region (1 torr typically at 275°C).

The size of the cesium vapor test region increases directly with heater power and inversely with applied argon pressure. The extent of the test region is visibly apparent since the end regions are coated with a film of condensed cesium and the test region is film-free. The argon pressure is not strictly zero in the cesium-filled test region because some argon diffuses back into the test region against the cesium vapor outflow. The presence of this small argon background pressure there usually is not significant under test conditions since argon has only about 1/100 the effect on electron transport as the same amount of cesium and about an equal effect on ion transport. Nevertheless, it is worthwhile to define the degree to which the buffer gas is present in the test region and the design factors by which it can be controlled, if necessary.

The actual process at the gas-vapor interface is very complex because cesium is condensing (i.e. precipitating or "raining") there in a gas phase. Condensation products (micro droplets or molecular clusters) and heat of condensation must be transported continuously from that interface. Possibly gravity and micro-turbulence are factors there. Even in an idealized case where such transport complexity is ignored, the boundary condition for argon diffusion into the cesium region is not simply 100% argon at the interface. In fact, in Fig. 5-2 it can be seen that the argon partial pressure actually is nearly zero at the condensation plane.

To obtain a crude estimate of the maximum extent to which back diffusion affects such an idealized representation of the interface, let us make the extreme assumption that the argon partial pressure is indeed 100% at the interface, and estimate the associated maximum possible extent of back diffusion. At such an interface the rate of argon diffusing into the cesium region must equal the rate at which it is carried back out of this region by being entrained in the condensing cesium stream moving outward at velocity v ,

$$D_v \frac{dn}{dx} = -nv \quad (1)$$

where n is the argon atom density at distance x , and D_v is the diffusion coefficient for argon diffusion through cesium vapor, given by Eq. 23 in Section 4.6 as $D_v \approx 500/P_{Cs}$ cm²/sec for P_{Cs} in torr.

The solution of the differential Eq. 1 gives an exponential decrease in argon partial pressure away from the interface into the cesium with an e-folding distance equal to

$$x_o = D_v/v \quad (2)$$

Heat is transferred out of the test region almost entirely by outward vapor flow, but that heat then is conducted almost entirely by the tube wall in the stagnant end region. The stream velocity v is that which transports cesium vapor of density $\rho_v \approx 3.7 \times 10^{-6} P_{Cs}$ g/cm³ and latent heat $L \approx 550$ Joules/gram through a tube lumen area A_t to supply the heat Q conducted by the sapphire tube wall of area A_w over a distance d from the gas-vapor interface to the end of the tube by a temperature drop ΔT ,

$$Q = KA_w \Delta T/d = \rho_v v L A_t \quad (3)$$

Eqs. 2 and 3 combine to give the distance of appreciable penetration of argon into the cesium vapor as being much less than

$$x_o \approx 1.0 A_t/Q \quad (4)$$

independent of pressure P_{Cs} . For the 1/2-inch diameter x 1 mm wall thickness sapphire tube, described below, having $d \approx 3$ cm distance between the gas-vapor interface at 275°C and tube end at about 100°C ($K \approx 0.25$ w/cm-°C), Eq. 4 gives $x_o \approx 2$ mm = 75 mils. Since this is much smaller than the

distance cesium vapor penetrates into the argon region, the argon partial pressure is a tiny fraction of the total pressure at the interface and decreases further by an order of magnitude for each ½ cm distance into the cesium region of the presently used tube. Indeed, it would be difficult to detect its presence beyond a centimeter from the interface.

Nevertheless, it is apparent from Eq. 4 that the vapor flow area A_t and total heat transport Q must be chosen properly to achieve any required degree of "sharpness" of the vapor-gas interface in future designs. If the experiment requires operation in mixed Cs/Ar vapor, as in advanced converter operating modes, the applied argon partial pressure is maintained higher than the cesium vapor pressure, as shown in Fig. 5-2. In this case, the cesium partial pressure is established by the local wick temperature, which can be measured by a thermocouple attached externally with refractory cement to the sapphire tube in the test region next to the wick.

5.1.4 Vacuum Operation

In the vacuum operating mode of the sapphire tube test vehicle, the ends of the sapphire tube are maintained at high vacuum, i.e. at much lower pressure than the cesium vapor pressure in the test region. A major advantage of this type of operation is that a very low level of impurity gases can be maintained in the test region since evolved gases are continuously swept into the end regions where they can be continuously removed.

The basis of this type of operation is readily derived if Poiseuille's law for the flow resistance through a tube of inner diameter D_t is substituted for that of a porous medium, as in Eq. 9 of Section 4.6. Eq. 36 of Section 4.6 thereupon becomes, for vapor pressure $P_v = 0$ at the end of the tube, $x = d$,

$$Q = \frac{\pi}{256} \frac{L D_t^4 P_{Cs}^2}{\mu R T d} \quad (5)$$

Eq. 5 gives the heater power Q required to maintain a cesium vapor pressure P_{Cs} in the test region. Eq. 5 is valid only for the portion of the end region in which heat transport by vapor flow is much greater than that conducted by the tube, so that d here is somewhat smaller than the length of the end region. A full solution of Eq. 11 in Section 4.6 is required for a more accurate description of the actual pressure and temperature distribution in this case, an example of which is shown in Fig. 4-4 of Section 4.6. X
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5.1.5 Features

In addition to its extreme simplicity of construction, the sapphire tube test vehicle also is extremely easy and versatile to use. A variety of experimental test assemblies can be mounted on flanges and inserted into the test region where they are highly visible, for continuous observation of electrode surfaces and discharge configuration during operation, and for optical pyrometry. As shown in Fig. 5-1, this can include components that are movable during operation through a sliding and rotating O-ring seal in the cold flanges. The test region can be brought to steady operation at 1 torr cesium pressure within 5-10 minutes from a cold start. The cesium pressure can be changed in a few seconds by changing the buffer gas pressure or the heater power.

Furthermore, modifications to test assemblies can be made quickly and conveniently. If a change is needed, the test region is cooled in a few minutes by switching off its heater and bringing the argon buffer gas to atmospheric pressure. Thereafter, the flange can be unbolted and the test assembly removed while a rapid outflow of gas from the lumen is maintained to prevent air from entering the cesium-containing tube. After the test assembly is modified and cleaned, it can be reinserted against argon outflow, its flange bolted and be under test again in cesium vapor within 5-10 minutes.

The operating limits of the sapphire tube test vehicle have not been explored. The extreme strength, thermal shock resistance and chemical inertness of sapphire suggest that the walls of the test region could be operated well over 1000°C (without a wick in that region), and cesium vapor pressures well above one atmosphere (670°C wick temperature) could be maintained, if required.

The following sections describe specific experiments performed in sapphire tube test vehicles in both gas-buffered and vacuum operating modes.

5.2 Electro-Magnetic Vapor Pump

5.2.1 Purpose

Although the vapor from cesium/oxygen solutions (Cs/O) has been found to greatly improve the performance of thermionic energy converters, it can be difficult to transport the vapor into the interelectrode space by gaseous diffusion in practical converters, as discussed in Section 4.6.5.5

It was proposed, therefore, to circulate the Cs/O vapor through the interelectrode space by forced convection arising from the magnetic pumping force that occurs naturally in

cylindrical converters. In one concept, shown in Fig. 5-3, a porous metal plug soaked with Cs/O liquid is located in the coldest region of the converter envelope. The $J \times B$ force on the plasma causes the equilibrium vapor above the Cs/O to be circulated down the interelectrode space and back through slots within the collector without a change of phase.

Fig. 5-4 illustrates the origin and magnitude of the magnetically-induced pressure drop from one end of the converter to the other. If the rate of circulation is much greater than the rate of removal of any Cs/O vapor component along the circuit, the composition of the Cs/O vapor must become essentially constant at steady state. The theoretical expression for the pressure drop ΔP generated by a uniform current density J over the emitter length L is [31]: $\Delta P(\text{torr}) = 4.7 \times 10^{-5} (JL)^2$, with JL in A/cm. The corresponding values are shown in Fig. 5-5 for various J and L . For a 5 cm long converter with an emission current density of 10 amp/cm², the magnetically-induced pressure drop is $\Delta P = 0.1$ torr. This is sufficient to circulate Cs/O vapor about once per second through the converter if four 0.5 x 2 mm slots are provided in the collector. This rate is probably far greater than necessary to maintain a uniform equilibrium composition in the gap.

5.2.2 Electromagnetic Vapor Pump Experiment

A proof-of-principle experiment was designed to verify and measure the pressure change induced by the application of a magnetic field across a cesium discharge in a gas-buffered sapphire tube. As shown in Fig. 5-6, the discharge could be ignited in the test region between a directly-heated Mo ribbon emitter and a collector (wick) made of porous stainless steel rods soaked with liquid cesium. Fig. 5-7 shows photographs of the experiment.

A permanent U-shaped magnet could be swung into position to generate a magnetic field perpendicular to both discharge and tube axis. A capacitance pressure gauge with a sensitivity of 0.001 torr was used to register the pressure at either end of the tube.

Fig. 5-8 helps illustrate the method used to measure ΔP , developed by the electromagnetic pump (EMP).

Fig. 5-3 Circulated Vapor Converter (CVC) Concept

Fig. 5-4 Self-induced Electromagnetic Pumping of Converter Plasma

Fig. 5-5 Self-pumping pressure in a cylindrical converter of length L

Fig. 5-6 Schematic of Proof-of-Principle demonstration of electro-magnetic pumping

Fig. 5-7 Experimental set-up for electro-magnetic pumping demonstration

Fig. 5-8 Sketch of Fig. 5-6 showing the respective volumes

With Valve A shut and Valve C open, the pressure change at the gauge was observed when the EMP was activated. Since the volume of gas on the gauge side of the pump is much larger than that on the other side, the pressure rise on the gauge side arising from gas displacement is much less than the decrease on the other side. With the following definitions:

- V_1 = volume AB
- V_2 = volume BC
- V_3 = remaining volume (including gauge)
- ΔP_i = pressure change in V_i ($i = 1, 2, 3$)
- T_i = average temperature in V_i

and the following equalities:

$T_1 = T_2$, $V_1 = V_2$, and $\Delta P_2 = \Delta P_3$, it is easily shown that

$$\Delta P = \left(2 + \frac{T_1}{T_3} \frac{V_3}{V_1} \right) \Delta P_3$$

V_3/V_1 was determined by expansion to be 2.2. An experiment was run at a total current I of 4A, magnetic field $B = 1060$ gauss, interelectrode spacing $L = 0.63$ cm, emitter area $A = 0.79$ cm², $T_1 = 410$ K, $T_3 = 300$ K and gave a $\Delta P_{\text{obs}} = 0.18$ torr. The theoretical value $\Delta P = 7.5 \times 10^{-5} IBL/A$ being 0.25 torr, the agreement is good, considering the non-ideality of the pump and discharge geometries. Thus, the experiment confirmed the validity of the electromagnetic vapor pump

approach. However, this type of pump was not used in the circulating vapor experiment (Section 4.5) because it was found that the DECOR vapor source itself develops sufficient ΔP for that experiment.

5.3 DECOR Scoping Experiments

5.3.1 Purpose

The DECOR embodiments tested in other tasks of the HET-IV program consisted of a biporous platinum-black compact, either in the form of a free-standing pellet or of a compact-filled tube or cartridge. Although these embodiments verified the basic operating principle and enabled stable Cs/O vapor control, they had features that made their integration into practical systems difficult: the Pt-black compact was fragile and unstable mechanically; the properties of the compact were difficult to characterize quantitatively for reproducibility and for representation in a physical/analytical model; the internal and external flow paths were poorly defined for design purposes; platinum is expensive; the cartridge embodiment could accumulate impurity gases such as hydrogen; and, it is difficult to incorporate either of these embodiments into a cylindrical thermionic converter such as to minimize diffusion limitations.

The purpose of this series of experiments was to use this new cold seal method to test and characterize a form of DECOR that overcomes these difficulties. This task, therefore, constitutes a mockup and verification of a DECOR circulating Cs/O vapor source that can be integrated into the practical cylindrical converter design described in Section 5.4

5.3.2 Free-Standing Screen-Wick DECOR Test Assembly

Fig. 5-9 shows the DECOR configuration that was tested in a single-ended sapphire tube test vehicle. The single-ended embodiment was chosen for these tests because two DECORS would have been required in a double-ended embodiment. As described in Section 4.6.4.2, such operation would not be stable because one DECOR would gradually deplete oxygen from the other, causing a drift in the operating point. Furthermore, this configuration constitutes a mockup of operation under conditions occurring when the DECOR is mounted in the emitter lead region of a cylindrical thermionic converter, as described in the next Section 5.4

The choice of this specific DECOR configuration arose from the need to overcome the practical difficulties associated with the Pt-black compacts listed in Section 5.3.1. The metal screen wick is much more durable and stable mechanically, and can be quantitatively characterized

Fig. 5-9 Sapphire Tube Test Vehicle with DECOR Cs/O Vapor Source and SPREE Cs/O Detection Probe

and reproduced with much greater precision. Furthermore, nothing in the DECOR physical model suggests that the vapor flow path cannot be entirely external to the liquid-bearing wick; i.e., the wick need not be bi-porous. Similarly, nothing in the model depends specifically on the properties of platinum. In fact, coexistence of a cesium/oxygen compound of the wick metal with the wick can potentially stabilize DECOR operation, as described in Section 4.6.4.4. Nickel is known to be metallurgically stable in contact with liquid cesium and is inexpensive. Also, operation with a getter or vacuum at the cold end eliminates accumulation of impurity gases there.

As shown in Fig. 5-9, a 1/2-inch diameter x 4 1/2-inch long x 1 mm (40 mil) thick wall sapphire tube with one closed end is mounted in a 1/2-inch brass O-ring compression fitting, as described for the double-ended embodiment in Section 5.1.2. A wick consisting of 5 turns of 100x100 mesh Ni-200 screen of 2-mil wire, vacuum outgassed at 900°C. This screen-wick was spaced from the tube wall by a similar 5-turn wick located within the fitting (heat sink). The remainder of the wick extended without touching 1.7 inches into the tube. A 5-mil type-K thermocouple was spot-welded to the free end of the wick with its leads extending through 2-hole 40-mil diameter alumina tubing to vacuum feedthroughs in the 1 1/8-inch Varian UHV flange attached to the fitting. A tube heater consisting of 16 turns of 25-mil diameter Nichrome wire was double-wound onto the end of the tube beyond the end of the wick. A 10-mil type-K thermocouple was cemented onto the flat end of the tube using refractory cement (Saureisen Insoluble). The tube-supporting fitting was clamped in an aluminum heat sink which could be rotated around the 1/4-inch diameter evacuation tubing via an O-ring compression coupling. This assembly, shown in Fig. 5-10, is a highly versatile chamber for experiments in Cs/O vapor whose orientation to gravity can be altered easily over all angles during operation.

For the present experiments a thermionic diode probe for emission and vapor composition measurements was mounted on a 9-pin vacuum feedthrough attached to a mating Varian UHV flange. The emitter consisted of a 5-mil diameter tungsten wire loop extending 1/8-inch from the end of 1/8-inch diameter 4-hole alumina tubing. The ends of the emitter were spot-welded to 30-mil diameter nickel wire leads recessed 1/8-inch into the tubing holes. The collector consisted of a 0.16-inch square x 32 mil thick molybdenum plate spot-welded to 20-mil type-K thermocouple wires extending through the remaining tubing holes. The emitter was accurately spaced 20-mils from the collector. The collector supporting leads thus served both for measuring its temperature and for carrying the diode current.

Fig. 5-10

Photographs of sapphire test tube with DECOR (top) and SPREE detector (middle) with a close-up view of emitter and collector (bottom)

When fully inserted into the sapphire tube assembly, the diode probe was located about midway in the test region between the wick and the closed end of the tube. Six turns of 5-mil diameter tungsten wire were double-wound on the probe tubing within $\frac{3}{8}$ -inch of the end of the wick, with 30 mil molybdenum leads sheathed in alumina tubing bound to the probe tubing. This heater had two functions: it maintained the probe above the cesium condensation temperature to prevent liquid cesium short circuit of the diode; and it radiantly heated the end of the wick to maintain the DECOR cycle.

A $\frac{1}{8}$ -inch wide x 10-mil thick vacuum outgassed titanium ribbon loop was mounted on feedthrough pins concentric with and just inside the probe mounting flange. This ribbon, when heated directly with electric current, maintained the sealing gasket and feedthrough above the local cesium condensation temperature, and acted as a bulk getter to remove all reactive gases expelled from the test region by the DECOR cycle.

Initial processing of the assembled test vehicle involved outgassing the emitter and wick heaters at 1500°C, and the wick end, diode, getter and tube test region at 300°C until the evacuating turbopump approached its base pressure near 1×10^{-6} torr. The test vehicle was then filled with argon at one-atmosphere pressure, charged directly with 0.5 gram of liquid cesium in its closed end in the argon glove box (< 1 ppm oxygen) and evacuated again with the turbopump.

5.3.3 Exploratory Tests

The test vehicle was first operated with the closed end of the tube down so as to locate the liquid cesium charge there. Upon initial heating of the test vehicle the turbopump pressure rose at first to 5×10^{-6} torr, but within a few minutes returned to 2×10^{-6} torr or less, where it remained throughout subsequent tests (i.e. at about the room temperature vapor pressure of cesium). When isolated from the pump the pressure at the tubulation outlet would rise slightly but would remain constant near 1×10^{-6} torr thereafter. All subsequent tests described here were performed in the vacuum mode of DECOR operation, i.e. with the pressure at the cold end of the wick near these pressures.

The liquid cesium was distilled from the tube end into the wick by maintaining the tube end hotter than the wick. It was found necessary to heat the wick end to nearly the same temperature as the tube end for the wick to wet sufficiently to transfer the entire cesium charge into

the wick without dripping back. Subsequently, the tube was rotated into a horizontal position to minimize gravitational effects in all subsequent tests.

After the cesium was transferred into the wick it was apparent that a thin deposit in the form of a few specks and spots had remained behind in the previously clear test region. This was suspected to be cesium oxide from the oxygen impurity in the commercially purchased ampules of cesium, and from oxygen absorbed in the glove box and during the outgas upon initial heating described above. After the DECOR cycle was initiated by heating the wick end to about 525°K, these deposits gradually disappeared, presumably being scavenged and deposited in the wick end by the circulating cesium vapor.

The hypothesis that the deposits were Cs_2O was confirmed by using the SPREE method of diode operation to measure the equivalent oxygen pressure in the test region vs the local tube wall temperature there. As can be seen in Fig. 5-11, the measured equivalent oxygen pressures approached those of Cs_2O at the wall temperature during this scavenging period, well within the uncertainties in the analytical estimates of Cs_2O pressure and in the accuracy of the SPREE measurements. Conversely, this agreement tends to verify the accuracy and validity of both the thermochemical model and the SPREE measurements over the entire range of oxygen pressures relevant to optimum Cs/O converter operation. Furthermore, the data in Fig. 5-11 indicate that extremely low impurity levels are maintained by DECOR in the test region of the sapphire tube. Hydrogen pressures greater than 10^{-8} torr, for example, would have formed CsOH with much higher pressures than the values observed at the lowest wall temperatures.

A considerable amount of exploratory experimentation was performed to develop physical understanding of the unusual mode of DECOR operation observed with this configuration. The primary cycle with the free-standing wick here is the same as with the biporous DECOR structures: heat supplied to the free end of the wick vaporizes cesium, the cesium vapor flows through the wick lumen to condense in the wick at its cold end, and the liquid condensate flows back to the free end through the wick by capillary action. Because of the low vapor pressure of cesium oxide, oxygen accumulates at the temperature-controlled free end, as described quantitatively in Section 4.6. The hot end of the wick must be free-standing; otherwise, the highly mobile Cs/O will creep along anything touching the end to deposit the oxygen in an uncontrolled location at higher temperature.

Lamoreaux's calculational results for Cs-O added for comparison.

Fig. 5-11 SPREE equivalent oxygen pressures measured in sapphire tube with cesium oxide deposits on wall of test section.

The unusual aspect of DECOR operation in the configuration shown in Fig. 5-6 is that a liquid Cs/O film exists on the sapphire tube wall immediately adjacent to the wick and participates in the cycle. Initially, it was expected that this film would be maintained by condensation of vapor from the wick onto the colder tube wall and that this nearly pure cesium would accumulate on the wall and flow back to the wick at its cold base as on the cold floor of the cup in the pellet DECOR configuration (Fig. 4-66). It was observed, however, that the film on the wall opposite the free end of the wick was black, indicating a high oxygen content there rather than the very low content expected for a condensate. It became apparent, therefore, that the observed operation corresponded to two parallel DECOR cycles: in one cycle loop the Cs/O liquid wicked up the temperature gradient in the wick; in the other cycle loop the Cs/O liquid crept up the temperature gradient on the sapphire tube wall. Since adjacent areas of wick and wall shared the same vapor, at any location where the wall film existed the wall and wick temperatures and Cs/O film compositions must be identical.

This situation is represented schematically in Fig. 5-12. For simplicity of illustration of the process, it is assumed here that the heat supplied to the wick is negligible compared with the heat conducted down the tube wall. Accordingly, the wall temperature profile is nearly parabolic in the region of the tube heater (test region) and linear in the end region. The temperature of the wick is nearly constant, however, since heat supplied to its free end by its heater is transported along the wick almost entirely by vapor. At some point A along the wick, however, the local wick temperature starts to exceed the local wall temperature. An appreciable temperature difference cannot develop, however, because vapor from the wick would deposit cesium and heat on the wall beyond point A which is at the edge of the visible film on the wall. The converse is also true, i.e. a film creeping up the wall cannot proceed beyond this point because it would transfer cesium and heat to the wick. In summary, the temperature of the wick and wall must be equal in the region where the wall film exists.

As can be seen in Fig. 5-12, as the temperature of the wick end is increased by its heater, the film edge on the wall approaches the free end of the wick. Similarly, as the tube temperature is increased by its heater, the film edge recedes from the wick end location. This is precisely what is observed experimentally. It should be possible to analytically model this complex heat transport process and obtain the dependence of the wick end temperature on the wick and tube heater powers and on their thermal conductances.

Fig. 5-12 Schematic drawing of heat transfer elements explaining the observed movement of Cs/O film edge position A along sapphire tube with changes in heat power.

In spite of the complexity of this process, this DECOR embodiment maintains the pressure and composition of the vapor in the test section very constant in time and can be reproducibly adjustable by varying the tube and wick heaters. It was found via SPREE measurements with the diode probe that the equivalent cesium and oxygen pressures were nearly independent of the tube temperature for constant wick end temperature. They were strongly and reproducibly dependent on the wick end temperature, however.

An attempt was made to map the pressure and composition of the Cs/O vapor in this system. It was found, however, that the observed oxygen pressures were much too low to correspond to the tube temperature in the test region and much too high to correspond to the measured wick-end temperature. Close examination of the wick indicated that portions of the wick end had dried out. With no liquid present in those regions the temperature there could have risen well above the temperature at the wetted region where the thermocouple was located. This would explain the observed much higher oxygen pressure from those dried-out regions.

In fact, this suggests that wick operation could be physically unstable at its free end. If one region of the wick end is hotter than the others there, it will evaporate cesium more rapidly and more oxide will be precipitated there. If this inhibits flow into that region, that region will become hotter, leading to more precipitation until it dries out. It appears, therefore, that the wick must be modified to suppress temperature gradients and dry-out around its free end.

It can be concluded that the objectives of this task have been met. This DECOR configuration has been shown to be capable of maintaining and controlling circulated Cs/O vapor stably in the practical pressure and composition range, but that thermal conductance must be added to the wick end to ensure that it does not dry out and overheat locally.

5.4 Simulated Cold Seal Cylindrical Converter

5.4.1 Purpose

As described in Section 5.3.1, experiments on the free-standing screen-wick established that this more practical DECOR configuration permits formation and control of circulated Cs/O vapor in the regime for optimum converter operation. The objective of this task was to integrate this new DECOR configuration into the practical cylindrical converter configuration.

Two especially significant DECOR/converter interface design issues remain to be evaluated experimentally, however. One of these is the heat transfer issue relative to providing the

stable and appropriate heat supply required for operation of DECOR. The other issue is the extent to which diffusion inhibits or delays transport of oxygen along the necessarily long path from the DECOR throughout the interelectrode gap in a cylindrical converter. The heat required for operation of the sleeve-like configuration of the free-standing screen-wick described in Section 5.3 is inherently provided by radiant heat from the emitter when it is integrated into the emitter lead end of a cylindrical converter. This radiant heat transfer is a difficult design problem, however. The multiplicity of paths for radiation "piping" along the various gaps and the effective radiant emissivities of the various surfaces in the Cs/O system, including the oxide-laden wick end, are poorly defined.

Most important in this respect is the possibility for unstable (possibly oscillatory) operation. This arises because of the feedback coupling of radiant heat from the emitter, and associated Cs/O pressure from the DECOR, with the resulting large changes in emission cooling resulting from changes in the Cs/O pressure, compounded by the time lag arising from the diffusion delay. Since analytical design anticipation of this complex time-dependent problem probably is not possible with the existing data base, it is best to establish the design principles with its simulation in an experimental mock-up prior to constructing and testing a fixed-parameter prototypic converter.

The mock-up described below draws directly on the experience already obtained with the DECOR embodiment tested in the sapphire tube by adapting this same test configuration to include cylindrical converter electrodes. This is especially appropriate since this cold-seal configuration inherently facilitates iterative testing of design changes that must accompany the required experimental exploration and design innovation.

5.4.2 Mock-Up Design

Fig. 5-13 illustrates the primary features of the DECOR-equipped cylindrical converter mock-up that is recommended as the initial configuration in an iterative design and test series. The cold-seal fitting, mount and free-standing screen-wick of the sapphire tube DECOR scoping experiments (Section 5.3) are employed in the mock-up. The sapphire tube, however, is replaced with a nickel collector-envelope which can be operated in air at the required collector temperatures. Forced air convection from a simple ducted fan will be adequate for its cooling. The attached electrical heater is convenient for shim temperature control and is useful also for calorimetry in efficiency measurements.

Fig. 5-13 Mock-up cylindrical converter with cold-seal DECOR Cs/O vapor source (mounted as in Fig. 5-10).

For high temperature operation ($\geq 1350\text{ K} = 2000^\circ\text{F}$), the emitter is a refractory metal tube (tungsten, molybdenum, or W-or Re-coated Mo) mounted on a flange containing feed-throughs for the emitter thermocouples and potential probe. The electron-bombardment emitter heater is mounted on a separate flange with its feed-throughs. Electrical isolation of the emitter and collector output flanges is provided by the sealing gasket between them and insulated clamping screws. These flanges are water-cooled by attached copper tubing which also serves as the high-current output leads. The vacuum maintained for vacuum-mode operation of DECOR is entirely adequate for operation of the EB-heater.

For low temperature operation ($\leq 1350^\circ\text{K}$), such as would be possible with advanced electrodes and plasma modes, the emitter can be superalloy steel heated by a commercially available cartridge resistance heater. The required number and configuration of radiant heat shields between the emitter and the wick should be determined experimentally to give optimum converter output characteristics in the operating region of greatest interest for practical application.

This cold seal simulated cylindrical converter meets the requirements of this task.

6.0 ADDITIONAL HARDWARE

6.1 Alkali Additive Converter Test Stand

A new test stand was built to operate either a variable-spacing planar converter or a fixed spacing cube converter, and to supply either of them with three different alkali vapor sources: Cs, Rb and K.

Fig. 6-1 shows a schematic of the plumbing required to achieve that goal. Three calibrated reservoirs, identical to those used in HET-III, each containing one of the three alkali metals, are connected to a manifold through their own high temperature valves. An oven surrounds this plumbing, but each reservoir is outside the oven and has its own separate heater. (To transfer each alkali at a reasonable rate, Cs and Rb would have to be at $\sim 250^\circ\text{C}$, and K at $\sim 330^\circ\text{C}$.)

The planar converter mount is identical to the one built in HET-III.

To process the converter and to operate it, two separate vacuum systems are supplied with the test stand. Fig. 6-2 shows schematics of the vacuum systems. The water-cooled bell jar housing the converter is pumped by a V250 turbo pump, while the converter is pumped down/outgassed through a V60 turbo pump. Various gas inlets allow backfilling selected sections with Ar, or for the converter adding measured amounts of oxygen.

Fig. 6-1 Plumbing for the 3-alkali converter test stand

Fig. 6-2 Vacuum systems for the 3-alkali converter test stand

Various temperature regulators and heating power supplies are provided to operate the converter electrodes, the various reservoirs and the plumbing oven. A PC-based data acquisition system is used to monitor various parameters and record J-V characteristics.

Fig. 6-3a shows the converter vacuum system and 6-3b is a general view of the finished test stand.

Fig. 6-3a (bottom) Converter Pumping Hardware

Fig. 6-3b (top) Finished Test Stand

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Appendix A

Diffusion of C₂H₅I in Xe

The diffusion coefficient of a gas impurity 1 in gas 2 is given as:

$$\text{as } D = \frac{8 (2kT/\pi)^{1/2} (1/m_1 + 1/m_2)^{1/2}}{3\pi n_2 (d_1 + d_2)^2}$$

where m and d are, respectively, the mass and diameter of each molecule, k the Boltzman constant, and

$$n_2 = \frac{P_2}{kT}$$

In MKS units, $m_1 (\text{Xe}) = 0.132/N_A \text{ kg}$, $N_A = 6 \times 10^{23}$

$$m_2 (\text{C}_2\text{H}_5\text{I}) = 0.156/N_A \text{ kg}$$

$$P_2 (\text{Xe}) = 133 \text{ Pa (1 torr)}$$

At room temperature

$$n_2 = 3.2 \times 10^{22} \text{ m}^{-3}$$

$$d_1 \sim d_2 \sim 5\text{\AA} = 5 \times 10^{-10} \text{ m}$$

The diffusion coefficient is

$$D = 3.9 \times 10^{-3} \text{ m}^2\text{s}^{-1}$$

Assuming all C₂H₅I to be concentrated in one corner in 10 seconds the diffusion front will move by

$$z = 2.3 (Dt)^{1/2} = 0.46 \text{ m,}$$

which is longer than the maximum linear dimension of the apparatus.

Appendix B

Operating Instructions for Vacuum Systems

1.0 TOFMS STAND

1.1 TOFMS Pumping

Turn on backing pump and push START on both V250 turbo controllers. In about 10 minutes the turbos should reach the following rotation speeds:

V250DP 48KRPM

V250 56KRPM

1.2 TOFMS Pressure Measurements

Only two gauges installed so far, both Bayard-Alpert types (hot filament). BA1 reads pressure in ionizer-Brubaker lens-ion trap region; BA2 in flight tube (with the multi-channel plate detectors). The readings can be displayed sequentially by pushing CHAN on the gauge reader.

To get a reading though the filament must be ON, which is done by pushing EMIS. The display shows --- for a few seconds, then the pressure appears. The display will be E09 if the pressure is higher than 1×10^{-3} torr, and the filament is then automatically turned off.

BA1 is used to read He pressure around the ion trap. However, a substantial correction needs to be applied to the pressure increase when He is injected: a pressure increase of 1×10^{-5} torr actually corresponds to an added He pressure of 6.5×10^{-5} torr.

1.3 TOFMS Safety Circuit

It is designed to turn off all TOFMS power supplies if one of three potentially damaging conditions occur:

- Loss of primary water flow = Flow switch in primary water supply for the M&W cooler opens.
- Pressure from BA1 too high = Above Setpoint #1 entered in the gauge reader.
Currently set at 3×10^{-4} torr. Opens a switch.
- Pressure from BA2 too high = Above Setpoint #2, currently set at 5×10^{-6} torr.
Opens a switch.

(When the gauge readings are below the setpoints, the indications SETPT 1 & 2 are lit in red at the gauge reader.)

For the setpoints to be activated, the BA gauges must be turned on. In other words, the TOFMS supplies cannot be operated without gauge readings. If any of these switches are open, the corresponding light on the safety panel comes on, and the power to all TOFMS supplies is turned off.

When the condition that tripped the safety is fixed, the light will come off, but to restore the power to the TOFMS one must flip the RESET switch.

1.4 TOFMS Venting

In addition to the various functions already mentioned, the safety panel provides for inert gas venting of the TOFMS. To start the venting procedure, push both STOP keys on the turbo controllers. Venting will start 5 seconds later at the V250. When the vent valve opens, the noise from the backing pump becomes much more noticeable: at this point, switch backing pump off.

With the switch below the VENTING COMPLETE light in the upward position, venting will proceed until the pressure in the ionizer region reaches 1 atm, at which point the VENTING COMPLETE light will come on.

To continue flushing the TOFMS with argon (to prevent air from getting in), flip switch downward to CONTINUOUS.

2.0 CUBE PUMPING

2.1 Cube Pumping

Turn on (or plug in) backing pump, open gate valve by flipping ELECTROVALVE switch and push START in V60 controller.

2.2 Pressure Readings

A convection gauge (TC1) reads from atmosphere to 1×10^{-4} torr, a cold cathode gauge (CC1) reads below 1×10^{-3} torr.

To go from one to the other, push CHAN repeatedly to display the appropriate channel. (Since there are currently no other thermocouple gauges installed, TC2-3 and 4 indicate EO3).

To get a reading from CC1, one must start the discharge by pushing EMIS. To make sure that the discharge is easily ignited, it is better to try to get a reading from CC1 when TC1 indicates around 1×10^{-2} torr.

2.3 Cube Backfilling

After closing the butterfly valve close to the spool, purge the Ar inlet line twice into the turbo. To backfill, reopen the butterfly valve, close the electrovalve and let Ar in, making sure that the relief valve is letting some Ar out during the backfilling.

2.4 Turbo Pump Venting

Depress STOP on controller and turn off (or unplug) backing pump. Venting starts in 5 seconds.

3.0 BELL JAR PUMPING

3.1 Pumping

Roughing is done through the pump-out fitting left of the gate valve handle: connect a turbo cart and pump down, as usual.

When vacuum is good enough and most of the outgassing has been done, open gate valve to the ion pump. It may be necessary for a while to take the ion pump off the PROTECTED mode. This is accomplished by pressing START/PROT key.

3.2 Safety

Protection is provided against:

- Loss of water flow.
- Belljar pressure too high. (When ion pump is in PROTECTED mode, threshold is 100 mA or $\sim 5 \times 10^{-5}$ torr.)

3.3 Warning

It is essential to raise the temperature of the coolant from 2°C to ~18°C prior to opening the bell jar. Otherwise, excessive moisture condensation will take place on the coolant lines while the bell jar is exposed to air, which will severely affect the following bell jar pump-down and might even saturate the ion pump.

Appendix C

Thermodynamic Instability of Cs_2O in the Presence of H_2

In the presence of hydrogen it is likely that Cs_2O would spontaneously form CsOH which is a very stable species. This can be verified by simple thermodynamic calculations.

From the reaction

comes

$$\Delta G_{\text{React}} = \Delta G_{\text{CsOH}}^{f(600)} - \Delta G_{\text{Cs}_2\text{O}}^{f(600)}$$

Using available thermodynamic values of ΔH_f° , C_p° and S° from National Bureau of Standards for CsOH

$$\begin{aligned} \Delta H(600) &= -59 + 600 \cdot 0.01188 \frac{dT}{T} = -59 + 3.59 \\ &= -55.41 \text{ Kcal/mole} \\ &= -2.41 \text{ eV} \end{aligned}$$

and

$$\begin{aligned} \Delta S(600) &= 0.06088 + \frac{600}{298} \cdot 0.01188 \frac{dT}{T} = 0.06088 + 0.01188 \ln \frac{600}{298} \\ &= 0.0691 \frac{\text{Kcal}^\circ}{\text{mole} \cdot \text{K}} \\ &= 3 \times 10^{-3} \text{ eV/K} \end{aligned}$$

gives

$$\Delta G^f_{\text{CsOH}}(600) = -55.41 - 41.46 = -96.87 \text{ Kcal/mole}$$

For ΔG^F Cs_2O (600) we use the value extrapolated by Flotow, et al,² -27 Kcal/mole.

Assuming equilibrium for the above reaction, the following applies:

$$\frac{P_{\text{CsOH}}}{P_{\text{Cs}_2\text{O}}} = \frac{P_{\text{H}_2}^{1/2}}{P_{\text{Cs}}} \exp \left(\frac{-\Delta G_R}{RT} \right) \approx \frac{P_{\text{H}_2}^{1/2}}{P_{\text{Cs}}} (2 \times 10^{25})$$

So, at $P_{\text{Cs}} = 1$ torr and $P_{\text{H}_2} = 1 \times 10^{-8}$ torr, the ratio of CsOH to Cs_2O pressures is $\sim 5 \times 10^{22}$.

² H.E. Flotow, et al, J. Chem. Thermodynamics, 6, 135 (1974)

Appendix D

Beam Attenuation by Expansion

From the kinetic theory of gases, the flux of atoms Γ effusing from a small hole of diameter d into a solid angle $d\omega$ is

$$\Gamma = \frac{nv}{4} \frac{1}{\pi} \cos\theta \, d\omega$$

If D is the diameter of the first ionizer aperture, located at a distance x from the small hole, the solid angle is

$$d\omega = \frac{\pi D^2}{4} \frac{1}{x^2} = \frac{\pi D^2}{4x^2}.$$

With $\cos\theta \approx 1$,

$$\Gamma = \frac{D^2}{4x^2} nv = \frac{nv}{16} \left(\frac{D}{x} \right)^2.$$

Thus, the number of atoms/sec flowing through an aperture of diameter d that also flows through an ionizer aperture of diameter D is

$$G = \frac{\pi d^2}{4} \Gamma = \frac{\pi d^2}{4} \frac{D^2}{x^2} \frac{nv}{16}.$$

Defining n_i as the effective gas density at the ionizer

$$G = n_i v \frac{\pi D^2}{4}$$

and the attenuation factor is

$$\alpha = \frac{n_i}{n} = \frac{1}{16} \left(\frac{d}{x} \right)^2.$$

This means that if our CUBE pressure is 1 torr, we will have a density equivalent pressure at the ionizer of

$$1 \text{ torr} \times \frac{1}{16} \left(\frac{d}{x} \right)^2 = 8 \times 10^{-7} \text{ torr}.$$

for $d = 0.01$ in and $x = 2.8$ in.

Appendix E

Equilibrium Pressure of the Dimer Cs_2

From the equilibrium

comes a relationship between pressures in torr

$$760 P_{\text{Cs}_2} = P_{\text{Cs}}^2 \exp \left(- \frac{\Delta G_F}{R_T} \right)$$

where ΔG_F is the Gibbs energy of formation at temperature T and $R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$.

Combining the expansion for ΔG_F given in Pankratz.³

$$\Delta G_F = 25,667 + 5.366 T \ln T - 9.6 \times 10^{-5} T^2 \\ + 48,450/T - 59.334 T \text{ in cal. mol}^{-1}$$

and

$$P_{\text{Cs}_2} = 2.45 \times 10^8 T_{\text{Cs}}^{-1/2} \exp (- 8910/T_{\text{Cs}}),$$

leads to

$$\text{Log } P_{\text{Cs}_2} = 3.317 \text{ Log } P_{\text{Cs}} - 7.513$$

where all pressures are in torr.

³ L.B. Pankratz, "Thermodynamic Properties of Elements and Oxides," Bur. of Mines Bull. 3673, 125 (1983).

Appendix F

Electron Reflection at Converter Electrodes

1.0 Background

Although prospects for developing a practical Cs/O vapor source now are very good, it should be recognized that perfecting and fully developing the Cs/O vapor source alone will not improve converter performance beyond that which corresponds to a back voltage ("barrier index") of 1.9 - 2.0 eV. It is appropriate now to seek the basic origin of this heretofore enigmatic "barrier" and to eliminate or suppress it.

The viewpoint taken thus far in thermionic technology is that the back voltage $V_B = 2.1 - 2.2$ eV that characterizes cesium vapor converter performance consists of the sum of an arc drop of about 0.5 eV and a collector work function of 1.6 - 1.7 eV. This is compatible both with the arc drop obtained from interelectrode plasma theory, and with independently-observed work functions for clean surfaces immersed in pure cesium vapor. With the addition of oxygen to the surfaces or to the vapor, work functions as low as 1.1 eV are observed outside the converter, leading to the expectation that converter performance should be improved to $V_B \approx 1.6$ eV. Since performance no better than 1.9 - 2.0 eV is actually obtained using oxygen, however, this performance limitation is anomalous. The cause of the 0.3 - 0.4 eV discrepancy has been the subject of much work and speculation for many years, but primarily has been assumed to result from an inability to achieve a collector function of less than about 1.5 eV under converter operating conditions.

An alternative viewpoint is that the collector work function in Cs/O converters already is about 1.1 eV, but that an unidentified (rogue) process causes the arc drop to be 0.3 - 0.4 eV greater in Cs/O converters than expected from known plasma processes. An abundance of evidence now indicates that the rogue process arises from increased electron reflection by very low work function surfaces with coadsorbed cesium and oxygen. Furthermore, it seems likely now that this process can be suppressed by properly chosen surface preparation.

2.0 Evidence of Severe Electron Reflection Effects

It has been recognized for many years that electron reflection is a necessary consequence of electron emission and collection at electrode surfaces. Because of the abrupt and large change in potential energy of an electron as it passes through a surface, the Schroedinger equation describing the

electron wave function requires that a portion R of the electron current be reflected (back scattered). This is mathematically equivalent to the reflection of a portion R of light waves incident on a dielectric (e.g. glass) surface upon an abrupt change in dielectric constant. This reflection coefficient R depends on a variety of factors including angle of incidence, interference (resonance) effects, abruptness of change in potential energy (or dielectric constant) and, in the case of electrons, availability of energy states in the electrode at the incident energy. The ability to suppress troublesome light reflection in optical systems is evident in view of the very effective anti-reflection coatings widely applied to optical elements. A similar ability to suppress electron reflection from electrodes should be achievable.

The second law of thermodynamics requires that the reflection coefficient for electron emission be exactly equal to that for electron collection. Otherwise power could be generated by electron flow between two electrodes at the same temperature. The full form of the Richardson-Dushman equation for electron emission from a surface with work function ϕ at temperature T is

$$J_s = (1 - R) AT^2 \exp(-\phi/kT) \quad (1)$$

Ordinarily the reflection coefficient R is neglected since it is small for most clean metallic electrode surfaces and is simply incorporated in the constant A as a deviation from the theoretical value of $120 \text{ amp/cm}^2 - \text{K}^2$. Nevertheless, R can significantly affect emission from metal surfaces with high bare work functions or adsorbed layers, as shown in Figs. 1-4. In fact, Fig. 1 shows that the experimentally observed reflection coefficient approaches unity, i.e. total reflection, at zero electron kinetic energy for both polycrystalline Pt and W(110). This results in a severe distortion of the energy distribution of emitted electrons and a ~4-fold reduction in the total electron emission current as shown in Fig. 2. Incorporating this into A in Eq. 1 (if the effect of reflection is neglected by setting $R = 0$) reduces A from 120 to 30, or incorporating it into ϕ reduces ϕ by 0.24 eV from its true physical value. Fig. 3 shows that R can be very different for low and high work function faces of tungsten.

Unfortunately, there are no comparable measurements of electron reflection coefficient R for surfaces under thermionic converter operating conditions, i.e. at high temperatures in cesium vapor with adsorbed cesium and oxygen. Some few data exist for surfaces with adsorbed Cs and oxygen

measured in high vacuum near room temperature, however. Fig. 4 and Table 1 show that the observed reflection coefficient R is near 30% for most polycrystalline metal surfaces with adsorbed cesium at the average energy of electrons arriving at the collector from the ignited converter plasma ($2kT_{ec} \approx 0.4$ eV), and for work functions 1.5 - 1.7 eV typical for cesium-only collectors.⁴ It is apparent that R increases as the work function is lowered by Cs adsorption. It is apparent also in Fig. 4 that the energy dependence of R with adsorbed Cs is found to be the reverse of that found in Fig. 1 for bare metals. Special attention should be given to the exceptionally low $R < 7\%$ reported for Pt-black in Fig. 4 and Table 1, which will be utilized in a later section of this Note.

Fig. 5 shows the reflection coefficient measured for bare iridium, for Ir with adsorbed Cs, and for Ir with adsorbed Cs and oxygen. While these data do not extend into the low energy region of interest here, they do show an increase in the low-energy electron reflection coefficient from the vicinity of 20% for surfaces with adsorbed Cs to the vicinity of 60-80% for coadsorbed Cs/O. In addition, these measurements were made at room temperature with "saturated" (monolayer) Cs coverage, whereas the minimum work function occurs in the sub-monolayer region.

It should be noted here that all the values of R shown were measured at normal incidence. There is good reason to believe that values of R for small angles of incidence, appropriate for most of the electrons collected from the plasma, may be substantially greater.

3.0 Effect on Converter Performance of Electron Reflection at the Collector

In summary, the foregoing available data show that electron reflection from Cs-covered surfaces may be in the $R = 30$ -50% range, and that surfaces with coadsorbed Cs/O may have $R = 60$ -80%. Figs. 6-8 show the effect on converter performance of electron reflection at the collector computed using the TECMDL physical/analytical model of the thermionic converter.

In applying TECMDL to this problem, it was concluded that the temperature of the reflected electrons must equal the collector temperature because:

1. The incident electrons interact strongly with the collector electrons via the image force during the entire time that the electrons acquire and then lose their kinetic energy in twice traversing the image barrier, which constitutes most of the work function.

⁴ Subsequent measurements gave $R = 40$ -50% for Cs-covered W(110), Ref. 4.

2. The incident electrons are reflected primarily at the last layer of surface atoms which are immersed in the very high density conduction electron gas in the collector.

Accordingly, the reflected electrons are equivalent to an electron emission from the collector of magnitude $J_c = RJ_{ec}$, where J_{ec} is the electron current from the plasma that is incident on the collector. As a result, the reflected electrons do not change the current through the plasma and therefore have virtually no effect on the transport processes giving rise to the current attenuation voltage V_a . Their effect almost totally is to increase the arc potential drop V_d through two processes:

1. The cold reflected electrons must be heated to the temperature of the electrons in the adjacent plasma, requiring an additional arc drop.
2. The height of the collector sheath must be lowered in order to re-collect the reflected electron current, adding to the arc drop.

TECMDL indicates that these effects are of comparable magnitude and, as can be seen in Fig. 6, together can add more than 0.3 eV to the arc drop V_d and back voltage V_B . This is much greater than the $\lesssim 0.1$ eV increase in V_B previously ascribed to increased V_a by current loss due to electron reflection.

For more than about 50% electron reflection a negative sheath occurs at the collector that tends to prevent reflected electrons from returning to the plasma. If the reflection is perfectly specular and elastic, all reflected electrons return to the plasma, corresponding to the upper branch of the curves in Fig. 6. If the reflection is diffuse and/or inelastic, few reflected electrons reach the plasma and the effect of reflection is suppressed, as in the lower branch.

Fig. 7 gives the computed J-V characteristics corresponding to the example in Fig. 6, but with a collector work function $\phi_c = 1.5$ eV typical of Cs-only adsorption. For this case the data given in the previous section indicate that a reflection coefficient R of at least 25% is appropriate, resulting in a back voltage near $V_B = 2.1$ eV. Surface conditions giving higher values of R result in values of V_B up to 2.5 eV for the diffuse reflection case shown. Complete elimination of reflection, $R = 0$, would reduce V_B only to 2.0 eV. This corresponds to the full range of performance observed for Cs-only converters.

Oxygen added to the converter causes the two compensating effects illustrated in Fig. 8: the work function is reduced to as low as $\phi_c = 1.1$ eV, but the reflection coefficient is increased to 60% or higher. As a result, V_B is decreased only to about 1.9 eV. Suppression of reflection, $R \rightarrow 0$, would reduce V_B to near 1.6 eV, as indeed is reported in the Russian data for oxygen-ion-implanted electrodes (Ref. 6).

4.0 Effect on Converter Performance of Electron Reflection at the Emitter

One effect of the electron reflection coefficient at the emitter is given by Eq. 1. The increase in attenuation V_a (and therefore also V_B) by reduction of J_s (i.e. $kT_E \ln(1-R)$) is less than 0.1 eV.

This could be more than compensated, however, by the reduction in both V_a and arc drop V_d that would result from an electron reflection coefficient that increases rapidly with electron energy in the 0.5 eV region, as in Fig. 4. Such a surface would preferentially reflect the hot electrons back-scattered from the ignited plasma. The return of these back-scattered electrons to the emitter is the major origin of the arc drop V_d and attenuation V_a . These effects can be evaluated using TECMDL, but have not been investigated quantitatively yet.

5.0 Basic Description of Electron Reflection

5.1 Prior Work

Although much data and analytical investigation of electron reflection from surfaces exist in the literature, almost all of it is concerned with electron energies corresponding to electron wave lengths approaching or less than the interatomic spacing at the surface ($\leq 5\text{\AA}$) (the wave length is $\lambda_e = 19/E^{1/2}$ Angstrom units, for energy E in eV). This is because the diffraction effects that occur at those energies are useful in exploring the surface structure via LEED (Low Energy Electron Diffraction) apparatus. At the energies of most interest in thermionics (0.3 eV), however, the wave length is about 30-40 $\text{\AA}$, which is much greater than the surface atomic structural dimensions, and therefore reflection at these energies is insensitive to surface atomic structure. Furthermore, it becomes very difficult experimentally in LEED apparatus to form and direct a monoenergetic electron beam at these very low energies.

It is inappropriate here to attempt a detailed review or description of the basic electron reflection process at very low energies. However, a few aspects will be described that permit enlightened speculation on methods for suppression of the offending effects in converters.

5.2 Wave-Mechanical Reflection of Electrons at Surfaces

The most elementary process that can be considered quantitatively is the reflection of the electron wave by the change in potential energy at a surface. Rigorously done, this would require employing a detailed three-dimensional analytical model of the surface atomic structure, including the potential and associated wave functions for the various species of adsorbed atoms and for the electrode surface and interior structure.. Such *ab initio* numerical computations now are feasible using modern computational methods and equipment. It is useful, however, to explore a much simpler one-dimensional model to define intuitive aspects that might be lost in a rigorous numerical computation. The simple model might approximate some surface situations, but it will be totally inappropriate for others.

A model for the electron potential energy that might represent surfaces with an adsorbed layer is shown in Fig. 9. It combines the potential energy arising from the image force U_i with the potential energy change upon traversing the dipole layer formed by the polarized adsorbed monolayer, U_d ,

$$U = U_i + U_d \quad (2)$$

The image potential energy is accurately described by

$$U_i = -e^2/4x \quad \text{for } x \geq x_o = e^2/4\phi_o \quad (3)$$

where e is the electronic charge, x is the distance of the electron from the surface and ϕ_o is the work function of the bare surface. The average electron potential energy upon traversing an adsorbed dipole layer that lowers the work function from ϕ_o to ϕ is given by

$$U_d = \frac{\phi_o - \phi}{R_i - x_o} (R_i - x) \quad \text{for } x_o < x < R_i \quad (4)$$

where R_i is the thickness of the dipole layer. This results in a potential well of depth

$$V_o = \frac{e^2}{4R_i} - \phi \quad (5)$$

and average width of about

$$b \approx R_i - x_o \quad (6)$$

For polycrystalline tungsten $\phi_o \approx 4.6$ eV ($x_o \approx 0.8$ Å), and for adsorbed cesium $R_i \approx 1.8$ Å, whereupon Eqs. 5 and 6 give $V_o \approx 0.5$ eV for $\phi = 1.5$ eV and $V_o \approx 0.9$ eV for $\phi = 1.1$ eV, with $b \approx 1.0$ Å.

Detailed wave-mechanical solutions for various one-dimensional potential energy models, including use of the image potential, have been reported elsewhere (Ref. 7). Unfortunately, all the numerical results reported there are useless since all the potential distribution examples examined are non-physical. It is possible to modify their square potential well solution to describe the example in Fig. 10, which is a crude approximation of the physical model represented by Eqs. 2-6 and shown in Fig. 9. The reflection coefficient for electrons with kinetic energy E incident on the potential distribution given in Fig. 10 is

$$R = \frac{S_{1+}^2 + S_{2+}^2}{S_{1-}^2 + S_{2-}^2} \quad (7)$$

where

$$S_{1\pm} = \left([E(E + \phi)]^{\frac{1}{2}} \mp [E + \phi + V_o] \right) \tan(b/\lambda_e) \quad (8)$$

$$S_{2\pm} = \pm (E + \phi + V_o)^{\frac{1}{2}} [(E + \phi)^{\frac{1}{2}} \mp E^{\frac{1}{2}}] \quad (9)$$

and the electron wavelength λ_e is given by

$$\lambda_e = h/[2m(E + \phi + V_o)]^{\frac{1}{2}} \quad (10)$$

This solution is consistent with that for a symmetrical square well ($\phi = 0$) given in Ref. 8 only if $\tan(b/\lambda_e)$ in Eq. 8 is replaced by $\sin(b/\lambda_e)$. No effort was made to resolve this inconsistency since the width b of the well is always much smaller than the electron wavelength λ_e in the present case, i.e., $b/\lambda_e \ll 1$, whereupon $\tan(b/\lambda_e) \approx \sin(b/\lambda_e) \approx b/\lambda_e$ in Eq. 8. In fact, $(b/\lambda_e)^2$ is so small that $S_1 \ll S_2$, whereupon Eq. 7 becomes

$$R = \left[\frac{(1 + \phi/E)^{1/2} - 1}{(1 + \phi/E)^{1/2} + 1} \right]^2 \quad \text{for } b \ll \lambda_e \quad (11)$$

This simple model suggests, therefore, that one-dimensional wave-mechanical reflection is primarily independent of the depth and width of the potential well formed by an adsorbed dipole layer and is primarily dependent only on the ratio of the work function ϕ to the incident kinetic energy E of the electron. Indeed, Eq. 11 describes the experimentally observed R for Pt and W(110) surprisingly well for this simple model, as shown in Fig. 1, when there is no adsorbed layer. Elementary wave-mechanical reflection appears not to be the dominant mechanism for electrons incident on surfaces with adsorbed layers since the energy dependence in Fig. 4, and the dependence on work function in Fig. 5 and Table 1, are opposite from those given by Eq. 11. A much more rigorous *ab initio* analysis is required to describe the details of electron "scattering" from the atomic structure of the surface and its adsorbed layer.

5.3 Angle of Incidence

It is conceivable that part of the failure of a one-dimensional model to describe electron reflection from a surface with an adsorbed layer arises from the existence of a strong dependence of R on the angle of incidence of the electron. The data shown in Figs. 1-5 all are for normal incidence of an electron beam that is nearly monoenergetic parallel to the beam but that has a Maxwellian energy distribution transverse to the beam, i.e. the beam approaches a full Maxwellian distribution at low incident energies. The data, therefore, can poorly represent the true energy dependence of R in this region of greatest importance here. Furthermore, it is likely that the structure of the surface becomes more important in the reflection process at small angles of incidence and a one-dimensional representation becomes even less appropriate.

It is worth noting by analogy that the reflection coefficient for light approaches unity (total reflection) at small incident angles, which is the basis of fiber optics. Also, it should be recognized that most of the electrons in a Maxwellian distribution are incident on the surface at small angles; e.g. 64% of such electrons are incident at angles less than 45 degrees. Clearly, data and theory are needed for small angles of incidence on surfaces with coadsorbed Cs/O, or for a full Maxwellian distribution at all electron temperatures of interest.

5.4 Degeneracy Energy vs. Fermi Energy

In the approximation of Fig. 9 shown in Fig. 10, it is assumed that the electron energy level in the metal that is appropriate for wave-mechanical computation of the reflection coefficient is the Fermi energy, i.e. that the end-state potential energy of the incident electrons in Fig. 10 is the work function ϕ . This seems appropriate since this is the level from which kinetic energy is referred in the energy distribution of emitted electrons which must have the same reflection coefficient as for incident electrons.

Yet the Schroedinger equation for the electron wave function would formally include the potential energy of electrons in the metal, i.e., the degeneracy energy μ , which is near 10 eV in tungsten. Accordingly, if $\mu + \phi$ replaces ϕ in Eqs. 8-10, the term in b/λ_e might not be negligible in Eq. 8 and the conclusions reached in Section 3.1 would have to be re-examined. The choice between ϕ and $\phi + \mu$ in Eq. 11, requiring detailed consideration of both statistical mechanics and wave mechanics, has not been undertaken.

5.5 Availability of Energy States

When the incident electron traverses the surface there is an abundance of available free electron energy states for it to enter in a metal electrode. The only forbidden states are at the Bragg angles which represent only a very small portion of the total solid angle.

The Cs/O surfaces having the lowest work functions (1.0 - 1.1 eV), however, are described as multilayers having a semiconductor rather than a metallic band structure (Ref. 9). In this event it is possible that these layers might have a negative electron affinity, i.e. that the vacuum level near which most incident electrons arrive falls within a forbidden band of energies in the multilayer, as shown in Fig. 11. With few available end states in the layer, most incident electrons would not be collected.

The availability of states could be assessed by measuring the dependence of the kinetic energy and yield of photoelectrons from the collector surface.

6.0 Suppression of Electron Reflection

The experimental data in Section 2.0 and the implication of their effect on converter performance in Figs. 6-8 suggest that electron reflection is the rogue process giving rise to the long-standing performance "barrier" encountered in thermionic energy conversion. While better understanding of the basic origin of the reflection might suggest additional means of suppressing it, at least one potentially effective approach for its suppression is recognized.

If the electrons are incident on a surface having a dendritic or other highly developed structure instead of a plane surface, two concurrent processes are introduced that should substantially suppress reflection. In one of these processes, illustrated in Fig. 12, electrons that would be incident at angles outside of the capture cone of a smooth surface (containing angles having low probability of reflection near normal incidence) would fall within the capture cone of the dendrite walls. In the other process illustrated, those electrons reflected from the dendrites undergo n multiple reflections in the structure, decreasing the effective reflection coefficient to R^n .

It should be evident that these processes can be effective only if the dimensions of the surface structure is much less than the Debye length in the plasma. Otherwise, a thin plasma sheath would cover all structures, giving a reflection coefficient equivalent to that for a plane surface. Since the Debye length for the plasma adjacent to the collector typically is about one micron, a surface with a submicron developed structure is required.

A variety of means for producing such a structure has been defined:

1. Coating the surface with a very thin layer of adherent submicron diameter particles.

Platinum black is made up of such particles; indeed, Table 1 shows that a surface coated with Pt-black has an exceptionally low electron reflection coefficient. Carbon black also consists of submicron diameter particles, and work in Sweden has reported $V_B = 1.6$ eV using a collector coated with carbon black.

2. Erosion of the surface by a high energy ion beam. Work at the USSR Sukhumi laboratory reported $V_B = 1.6 - 1.7$ eV using electrode surfaces bombarded with 100 KeV oxygen ions (Ref. 6).

3. Deposition of the surface by sputtering. Submicron dendritic structures are produced by magnetron sputter deposition.
4. Electrodeposition. Under conditions that usually are avoided in commercial electroplating practice, submicron dendritic structures can be formed.
5. Chemical vapor deposition. Dendritic structures can be formed during CVD under unusual conditions.
6. Ion milling, etching, and other micro-forming processes. Formation of precise structures on surfaces by a variety of processes are under development by the semiconductor device industry for VLSI applications, and these are now entering the submicron region.

7.0 DOE Project

An attempt to verify and employ the Sukhumi results is being undertaken by RAI under a US DOE grant. Thus far, converter performance improvement has not been achieved by the Russian group attempting to verify the Sukhumi results, but the ion implantation conditions used to produce the electrodes in Sukhumi were not reproduced. In the remaining months of the project the Russians are rigorously reproducing the Sukhumi ion implantation conditions and testing the resulting electrode in a converter. Also, Rasor Associates has produced submicron structures by magnetron sputter deposition for comparison of their electron collection properties with planar surfaces.

8.0 Maintenance of Sub-Micron Collector Structure

Concern has been expressed that it might not be possible to maintain a reflection-suppressing sub-micron structure under converter operating conditions. In particular, the use of oxygen in the converter to obtain enhanced electrode properties opens the possibility of mass transport from emitter to the collector by oxygen to the extent that the structure would be covered in a short time by emitter vaporization products.

First consider the essential magnitude of the mass transport be expected. The worst case assumption is that all oxygen atoms arriving at the emitter result in deposition of oxide molecules on the collector; e.g. three oxygen atoms arriving at the emitter deposit one WO_3 molecule on the collector. Experience with DECOR in the cube indicates that an oxygen arrival rate equivalent to about 10^{-8} torr of O_2 is adequate to maintain the desired Cs/O adsorbed layer on the electrodes.

If it is assumed that each oxygen atom in the oxide molecule occupies an oxygen adsorption site ($\sim 7 \times 10^{-16} \text{ cm}^2$), and that the thickness of each molecular layer is about the oxide unit cell length ($\sim 2 \times 10^{-8} \text{ cm}$), then the thickness of the oxide layer deposited on the collector would increase at a rate of $6 \mu\text{m/yr}$. In the oxygen pressure range $10^{-10} < p < 10^{-4} \text{ torr}$ it has been shown (Ref. 10) that the maximum rate of tungsten oxide evaporation is about 10^{-2} that for atomic oxygen evaporation. Also, since the atom mean free path in $\sim 1 \text{ torr}$ cesium vapor is about one tenth the interelectrode spacing, the oxide transport rate is reduced proportionately. Accordingly, these factors combine to give a $0.006 \mu\text{m/yr}$ oxide deposition rate, which would have negligible effect on the topography of $0.1\text{-}1 \mu\text{m}$ developed surface structures.

Three other processes can significantly alter this estimate. First, the effect of sticking coefficient of the oxide on a surface with a Cs/O adsorbed layer could reduce the deposition rate further by more than an order of magnitude. Second, the presence of hydrogen could, via the water cycle, result in oxygen being returned from the collector to the emitter at an arrival rate approaching that corresponding to the H_2 pressure between the electrodes. For this effect to be negligible, therefore, the hydrogen pressure would have to be much less than 10^{-8} torr . Third, if the emitter material contains a sufficient amount of impurities that are sufficiently mobile and form sufficiently volatile species at the emitter surface, these evolved impurities could form a thicker layer on the collector than that estimated for the oxide. If the total impurity in a 1 mm thick emitter is less than 100 parts per million, this could not significantly affect the surface topography. Diffusion from the fuel through the emitter could be a potent source of impurities, however, if the thermochemistry and diffusion rate permit it to be significant.

It is worthwhile to identify processes by which emitter evaporation products can be prevented from depositing on the collector or their deposition tolerated. First, for deposition products such as tungsten (resulting e.g. from the water cycle), a trace element can be added to the vapor to react with the deposit to form a volatile compound. The volatile compound decomposes pyrolytically on the hot emitter to return the deposited element (W) to the emitter and to release the trace element, completing the perpetual cycle. The partial pressure of the trace element required to prevent accumulation of a deposit is only about the same as the partial pressure of the vapor transporting the deposit (e.g. the oxide pressure or the hydrogen pressure). This is a thermochemically complex process, but it is used successfully to prevent evaporated tungsten from blackening the bulb in halogen lamps, in which a halogen is used as the trace element in the filling gas.

The complexity is increased in the converter by the effect on the chemistry that occurs in the hot cesium vapor arc plasma ($\sim 3300^\circ\text{K}$). This arc-thermochemical transport process is ideal for treatment by the methods developed by Dr. A.A. Sobelev at the Institute of Physics and Power Engineering in Obninsk, Russia, who is available very cost-effectively at the present time. A bonus in this process is the maintenance of an atomically clean surface having potentially a very low thermal emissivity.

For electrically conducting and adherent deposits (again, e.g. tungsten from the water cycle), it is possible that the deposit itself can maintain the submicron structure continuously by forming dendrites on the collector. In particular, if the surface is prepared with an initial submicron dendritic structure, the ends of the dendrites facing the emitter receive a much higher rate of deposition than the base of the dendrites which are shielded from the emitter. This tends to extend and preserve the initial dendritic structure. This effect can be enhanced by having the exposed crystal faces of the initial dendrites be those for which surface diffusion of the deposits tends to maintain a uniform layer of deposits by epitaxy, thereby preserving the initial topography. One way to accomplish this is to grow the initial dendritic layer by the same deposition process as occurs in the converter (e.g. by the water cycle), only accelerated through use of higher temperatures and pressures.

Appendix F. References:

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10. N.S. Rasor, "Physical-Analytical Model for Cesium/Oxygen Coadsorption on Tungsten," Proc. 27th IECEC, San Diego, August 1992, Vol. 3, p. 529 (Figs. 3, 4, 6 and 8).

Fig. 1 Dependence of reflection coefficient R on energy of incident electrons for polycrystalline Pt and W(110) in vacuum (Ref. 1) compared with values computed using Eq. 11 with $\phi = 6.0$ and 5.4 eV respectively.

Fig. 2 Modification of emitted electron energy distribution by energy-dependent electron reflection given in Fig. 1b (Ref. 1):

Fig. 3 Observed dependence of transmission coefficient ($1-R$) on crystal face of tungsten (work function for W(110) is near 5.4 eV, and for W(100) is near 4.3 eV)(Ref. 2).

Fig. 4 Electron reflection coefficient for surfaces with near-monolayer of adsorbed cesium (Ref. 3).

TABLE I. Summary of measured reflection coefficients for several target materials at various degrees of cesium coverage. Ref. 3

Target material	Low work function eV	$\Delta\phi$ (High w.f.- low w.f.)	Measured reflection coefficient-% at various primary energies								Min ref
			0.05 eV	0.1	0.5	1	2	3	4	5	
Advance	3.14	0.006 eV	11.5%	14.0	30.0	39.0	45.0	48.2	50.7	52.0	10.0
	2.02	0.025	19.5	19.0	33.0	43.0	49.9	53.5	56.2	57.3	18.7
	1.59	0.016	18.3	19.3	33.5	43.3	51.3	55.7	59.4	60.5	18.3
101 Stainless steel	1.50	0.007	16.3	18.6	34.8	43.8	51.2	55.8	60.2	64.4	16.0
Inconel	1.59	0.008	16.0	18.8	35.5	45.3	52.8	57.0	60.7	64.5	15.0
Monel	1.55	0.005	16.4	18.7	35.5	45.2	52.0	55.7	59.1	62.5	15.8
Molybdenum	3.48	0.042	12.7	11.4	16.5	31.5	43.3	52.9	58.0	58.2	10.8
	2.94	0.044-0.10		19.8	26.6	34.0	46.3	55.0	58.6	58.2	19.0
	1.68	0.043-0.097		28.9	30.2	41.0	50.3	57.8	63.7	65.7	24.7
Tungsten	3.56	0.038		13.8	27.7	39.5	48.8	55.1	59.3	60.3	13.7
	1.53	0.015	20.0	20.5	30.2	37.2	53.2	62.1	68.5	72.8	20.0
Tantalum	1.57	0.020	12.1	14.5	32.8	42.6	53.0	60.6	64.8	67.0	12.0
Copper	3.71	0.034		16.0	30.7	39.8	48.0	49.2	49.8	50.0	16.0
Copper	3.68	0.043		15.0	30.9	40.1	46.8	49.5	50.0	50.0	14.7
	1.63	0.014	15.5	18.8	36.7	43.7	49.4	53.5	57.4	60.7	15.5
Silver plate	3.15	0.011	9.7	12.0	27.4	36.5	44.4	47.9	49.8	50.3	9.3
	1.44	0.015	18.4	20.8	38.0	47.0	54.9	58.6	62.0	65.4	18.4
Platinum	1.63	0.006	12.0	12.5	20.7	28.8	41.1	48.3	53.2	57.4	11.8
Platinum black	1.76	0.034	6.0	5.8	6.9	8.1	8.0	7.4	6.7	6.1	5.7

Fig. 5 Effect of adsorbed cesium and coadsorbed Cs/O on electron reflection coefficient (Ref. 5).

Fig. 6 Effect of electron reflection at the collector on thermionic converter performance (computed by J.B. McVey using TECMDL).

Fig. 7 Effect of electron reflection at the collector on output characteristics for cesium-only converters (computed by J.B. McVey using TECMDL).

Fig. 8 Effect of electron reflection at the collector on output characteristics for Cs/O converters (computed by J.B. McVey using TECMDL).

Fig. 9 Electron potential energy near the surface of a metal with and without an adsorbed dipole layer. Scaled for tungsten with Cs/O layer: $\phi_0 = 4.6 \text{ eV}$, $\mu = 9 \text{ eV}$, $\phi \approx V_0 \approx 1 \text{ eV}$, $R_1 = 1.8 \text{ Å}$.

Fig. 10 Square well approximation of electron potential energy U shown in Fig. 9.

Fig. 11 Collector surface having negative electron affinity.

Fig. 12 Suppression of electron reflection by sub-micron development of electrode surface.

**THE CESIUM-OXYGEN SYSTEM:
COMPUTER PROGRAMS FOR
CALCULATING CESIUM AND OXYGEN
PRESSURES AND THE EFFECTS OF
H₂O AND CO₂ IMPURITIES**

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ABSTRACT

This report discusses a group of computer programs based on the Regular Associated Solution theory that calculate partial and total equivalent Cs and O₂ pressures in equilibrium with liquid Cs-O solutions. Additional programs estimate of the effects of H₂O and CO₂ impurities on the partial and total equivalent pressures. Calculated results are presented for the composition range from Cs to Cs₂O.

The programs FIT and OUT calculate Cs and O₂ pressures of pure Cs-O solutions as functions of composition and temperature. The program CEQ uses O₂ pressures and Cs activities to calculate equilibrium gas phase compositions and total equivalent Cs and O₂ pressures. EQPTOP calculates Cs and O₂ partial pressures from equilibrium values of the respective equivalent pressures.

The programs OUTH and CEQH predict trends in Cs and O₂ equivalent pressures as functions of the H₂O impurity level in the Cs-O solutions. OUTC and CEQC deal with the effects of CO₂ impurity.

The existing calibration data for the programs are limited in both range and accuracy. At the present time, results for temperatures below 773 K are extrapolations of unknown accuracy. The programs have been designed to incorporate new experimental data to enable better predictions of Cs and O₂ pressures.

THE REGULAR ASSOCIATED SOLUTION THEORY

Schmid¹ described the Regular Associated Solution (RAS) treatment of strongly interacting metal-oxygen systems. Basically, the RAS assumes that the effective concentrations of the elemental constituents (metal and O) in the solution are decreased by their association into a complex species. In the Cs-O system, the postulated reaction is

with the equilibrium constant, K,

$$K = \frac{x(\text{Cs}_2\text{O})\lambda(\text{Cs}_2\text{O})}{[x(\text{Cs})\lambda(\text{Cs})]^2[x(\text{O})\lambda(\text{O})]} \quad (2)$$

where x is the mole fraction and λ is the activity coefficient of the species present in solution after association. Cs, O, and Cs₂O are hypothetical species used to derive the effect of association on activities. The bulk mole fractions concentrations of the real components Cs and O in solution, ignoring association, are described by the terms $X(\text{Cs})$ and $X(\text{O})$, and for these concentrations there will be another set of activity coefficients, which will be termed $L(\text{Cs})$ and $L(\text{O})$.

The activities of O and Cs are given by the relationship

$$a(\text{A}) = X(\text{A})L(\text{A}) = x(\text{A})\lambda(\text{A}) \quad (3)$$

and where A represents Cs or O.

The present study uses the activity coefficient expansion of Wilson² rather than Schmid's 3rd-order Margules expansion. The Wilson expansion fits the limited available data with only eight adjustable parameters and is readily generalized to multicomponent solutions.³ The Margules expansion, which has more adjustable parameters, may provide a superior fit to the data if and when accurate data are available over wider ranges of compositions and temperatures.

Wilson's equations for a solution of m components are

$$\frac{g^E}{RT} = - \sum_{i=1}^m x_i \ln \left[\sum_{j=1}^m x_j \Lambda_{ij} \right] \quad (4)$$

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp - \left[\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right] \quad (5)$$

$$\Lambda_{ji} = \frac{v_i}{v_j} \exp - \left[\frac{\lambda_{ij} - \lambda_{jj}}{RT} \right] \quad (6)$$

In these equations, g^E is the excess Gibbs energy of mixing, v_i is the molal volume of pure component i , Λ_{ij} is the parameter for the interaction of component i with component j , and λ_{ij} is the pairwise interaction energy between component i and component j .

The activity coefficient for component k is given by

$$\ln \gamma_k = - \ln \left[\sum_{j=1}^m x_j \Lambda_{kj} \right] + 1 - \sum_{i=1}^m \frac{x_i \Lambda_{ik}}{\sum_{j=1}^m x_j \Lambda_{ij}} \quad (7)$$

For the solution of Cs(l), Cs₂O(l), and O(l), the parameters to be fitted to the data are XAF(1)= λ_{11} , XAF(2)= λ_{12} , XAF(3)= λ_{13} , XAF(4)= λ_{22} , XAF(5)= λ_{23} , XAF(6)= λ_{33} , and XAF(7) and XAF(8), where

$$\ln K = \text{XAF}(1) / T + \text{XAF}(8) \quad (8)$$

COMPUTER PROGRAMS

All the programs discussed in this report were written in standard FORTRAN 77 and compiled using Microsoft® FORTRAN Version 5.1. The program versions included with this report supersede all previous versions.

Four programs apply to pure Cs-O solutions. FIT derives RAS parameters to fit the experimental data on the Cs-O system. OUT uses these parameters to calculate Cs activities and O₂ partial pressures at chosen temperatures and at compositions from pure Cs to Cs₂O. CEQ calculates the equilibrium partial pressures of all Cs- and O- containing gas species at the predicted partial pressures of Cs and O₂ and sums these pressures to find the total equivalent pressures of Cs and O₂. The individual programs produce computer files that can be used as input to subsequent programs or for exporting to spreadsheets or plotting programs.

EQPTOP calculates Cs and O₂ partial pressures from experimental values of the Cs and O₂ total equivalent pressures.

Two programs, OUTH and CEQH, apply to Cs-O solutions that contain H₂O as an impurity component. Similar programs, OUTC and CEQC, are for solutions containing CO₂ as an impurity.

The programs are provided on two 3.5" floppy disks. Batch files (INSTALL.BAT) have been written on each disk to facilitate the installation process. To install on drive C, insert Disk 1 in floppy drive A or B and type A: (or B:). AT the new drive prompt, type INSTALL. After Disk 1 is finished, insert Disk 2 and again type INSTALL.

The files in the directories on the floppy disks are copied to similarly named subdirectories of the directory \EQCES on the hard disk. This avoids problems that could be caused by slightly different subroutines with the same name in the different programs. The subdirectory names correspond to the programs FIT, OUT, CEQ, EQPTOP, OUTH, CEQH, OUTC, AND CEQC.

As discussed below, batch files are included to facilitate the sequential use of programs in the different subdirectories.

PURE Cs-O SOLUTIONS

FIT

FIT derives the parameters for applying the RAS to the Cs-O system. The subroutines and other files pertinent to FIT are listed in Table 1. FIT and its required files are in the subdirectory C:\EQCES\FIT. Calculations should begin in this subdirectory. At the conclusion of FIT, typing CONT copies the output file FIT1 and transfers control to the subdirectory OUT.

Input and output files

The input files for FIT are FIT.DAT and a data point file, ***.DAT, whose name is specified at run time (ALL.DAT in the present case). FIT.DAT contains initial estimates of the eight fitting parameters, XAF(1) through XAF(8). ***.DAT contains the experimental data points that are fitted by the program. The file entry formats for these files are shown in Tables 2 and 3. The points in the ALL.DAT file used to derive the results in the present study are listed in Table 4.

Experimental data for fitting the Cs-O system are quite limited and of uncertain accuracy. The data used are of four types: (1) $\ln P(O_2)$ values at 773, 873, and 973 K for $x(Cs) = .832$ to $x(Cs) = .967$, and a value derived by Gibbs-Duhem integration for the composition Cs_2O at 773 K; (2) the Gibbs energy of $Cs_2O(l)$ at 773 and 973 K; (3) the Gibbs energy for the equilibrium between $Cs_2O(s)$ and Cs-rich liquidus at 437K, and (4) $\ln a(Cs)$ values. Type (1) data were taken from Knights and Phillipps (K+P).⁴ Type (2) data uses the thermodynamic data reviewed by Lamoreaux and Hildenbrand⁵ for $Cs_2O(l)$ in the relationship

$$\Delta \frac{G}{RT} = \Delta \frac{G_f^\circ}{RT} (Cs_2O, l) - \Delta \frac{G_f^\circ}{RT} (O, l) - 2 [\ln (x(Cs)\lambda(Cs)) - \ln [x(O)\lambda(O)]] \quad (9)$$

where the Gibbs energy of formation of $O(l)$ is given by the relationship of Schmid

$$\Delta \frac{G_f^\circ}{RT} (O, l) = \frac{-318.588}{T(K)} + 3.78074 \quad (10)$$

The third type of data uses a point from the approximate liquidus line of K+P, specifically $x_{Cs} = 0.76$ at 437 K in the relationship

$$Cs_2O(l) = \frac{2}{N(Cs)} Cs_{N(Cs)} O_{1-N(Cs)} + \left[\frac{3 N(Cs) - 2}{2 N(Cs)} \right] O_2(g) \quad (11)$$

After some algebra this leads to the expression

$$0 = \Delta G_f^\circ(O,l) - \Delta G_f^\circ(Cs_2O,s) + 2 \ln [x(Cs)\lambda(Cs)] + \ln [x(o)\lambda(o)] \quad (12)$$

The only point available for the fourth type of data is the value $\ln a(Cs) = -7.29$ at 773 for the composition Cs_2O derived by K+P by Gibbs-Duhem integration. This point was repeated in the entries in ALL.DAT to give it more weight in the fitting.

OUT

OUT uses the XAF parameters derived by FIT to calculate Cs activities and O_2 partial pressures at chosen temperatures and liquid phase compositions. The subroutines and associated files for OUT are listed Table 5. At the conclusion of running OUT, typing CONT copies the file CEQ.DAT and transfers control to the subdirectory CEQ.

Input and output files

OUT has two input files. FIT1.DAT, produced by FIT, contains the XAF fitting parameters. The entry formats for FIT1.DAT are identical to those of FIT.DAT shown in Table 2. The values of the entries used in the present study are listed in Table 6. OUT.DAT is the listing of temperatures and pressures for which calculated Cs activities and O_2 partial pressures are desired. OUT.DAT file entries are described in Table 7.

OUT produces the file CEQ.DAT. Program CEQ reads CEQ.DAT and calculates the partial pressures of all gaseous species and the total equivalent pressures of Cs and O_2 .

CEQ

CEQ is an adaptation of the author's complex equilibrium program that calculates the partial pressures of Cs- and O-containing species in equilibrium with the previously calculated Cs and O_2 pressures. The total amounts of Cs and O in all the gaseous species are summed and expressed as equivalent pressures of $Cs(g)$ and $O_2(g)$. The equivalent pressures of Cs and O are defined as

$$P(\text{eq}, \text{Cs}) = \sum_{i=1}^n p(i) a(i) \quad (13)$$

and

$$P(\text{eq}, \text{O}_2) = \sum_{i=1}^n \frac{p(i) b(i)}{2} \quad (14)$$

where species i is $\text{Cs}_{a(i)}\text{O}_{b(i)}$ with the partial pressure p_i and n is the number of gas phase species.

CEQ subroutines and associated files are listed in Table 8.

Input and output files

The input file is CEQ.DAT, produced by OUT. The file entries are listed in Table 9.

CEQ produces several output files.

PCS.*** and PO2.*** are files containing the total equivalent Cs and O₂ pressures, arranged to be imported into a spreadsheet or graphics program. The top row identifies the temperature of the equivalent pressures listed in the corresponding columns. In the succeeding rows, the first column identifies the value of $x(\text{O}) = [1 - x(\text{Cs})]$ in the Cs-O solution. The remaining columns contain the base 10 logarithms of the equivalent Cs or O₂ pressures. The columns are each 13 characters wide and are comma delimited, with the first column blank. Different graphics programs require different suffixes on the file names to be read as comma delimited files. Therefore, the user must type this in at the prompt. Two examples are given in the menu: csv for EXCEL and SIGMA PLOT, and prn for CHARISMA (a plotting program).

EQP.DAT lists the equivalent pressure in atm, torr, and log₁₀ torr units.

SPECIES.DAT lists the individual partial pressures of vapor phase species for each of the temperature and composition points.

Entering 1 at the program prompt produces the only the files EQP.DAT, PCS.***, PO2.***, and EQP.DAT. Entering 2 produces these and SPECIES.DAT.

RESULTS

The fitting parameters in Table 6, derived from the data shown in Table 4, were used to calculate the total equivalent Cs and O₂ pressures shown in Figures 1 and 2 for the composition range $x(\text{O}) = 0$ to $x(\text{O}) = .33333$ at temperatures from 437 to 773 K.

The activities for temperatures below 773 K are extrapolations of the limited experimental data. The O₂ activity data of K+P cover only the composition range from $x(\text{O}) = .0333$ to $x(\text{O}) = .168$ and temperatures from 773 to 973K and exhibit moderate scatter. The 773K point for the composition Cs₂O was derived by a graphical Gibbs-Duhem integration, and the Cs-O liquidus is not known accurately. The calculated pressures at temperatures below 773 K should be regarded as indicative of trends rather than quantitatively accurate data. New data points in this region are needed to improve the reliability of the calculated pressures.

EQPTOP

EQPTOP calculates the partial pressures of Cs(g) and O₂(g), and the activity of Cs, from experimental values of the Cs and O₂ equivalent pressures measured over a Cs-O mixture at temperature T. Both equivalent pressures must be known to find the partial pressures.

The vapor phase is assumed to contain the following gases: Cs, O₂, O, Cs₂, CsO, CsO₂, Cs₂O, and Cs₂O₂. The applicable chemical equations and equilibrium constants are:

$$K_1 = p(\text{Cs}_2\text{O}) / [p(\text{Cs})^2 p(\text{O}_2)^{1/2}] \quad (16)$$

$$K_2 = p(\text{CsO}) / [p(\text{Cs}) p(\text{O}_2)^{1/2}] \quad (18)$$

$$K_3 = p(\text{Cs}_2\text{O}_2) / [p(\text{Cs})^2 p(\text{O}_2)] \quad (20)$$

$$K_4 = p(\text{Cs}_2) / p(\text{Cs})^2 \quad (22)$$

$$K_5 = p(\text{CsO}_2) / [p(\text{Cs})p(\text{O}_2)] \quad (24)$$

$$K_6 = p(\text{O}) / p(\text{O}_2)^{1/2} \quad (26)$$

$$K_7 = p^\circ(\text{Cs}) \quad (28)$$

The equilibrium constants are calculated by EQPTOP using thermodynamic data in the file CS.DAT.

The equivalent pressures PEQCS and PEQO2 are

$$\text{PEQCS} = p(\text{Cs}) + 2p(\text{Cs}_2\text{O}) + p(\text{CsO}) + 2p(\text{Cs}_2\text{O}_2) + 2p(\text{Cs}_2) + p(\text{CsO}_2) \quad (29)$$

and

$$\text{PEQO2} = p(\text{O}_2) + 1/2 p(\text{Cs}_2\text{O}) + 1/2 p(\text{CsO}) + p(\text{Cs}_2\text{O}_2) + p(\text{CsO}_2) + 1/2 p(\text{O}) \quad (30)$$

Using Equations 15 through 28, PEQCS and PEQO2 can then be expressed as functions of K_1 - K_6 , $p(\text{Cs})$, and $p(\text{O}_2)$.

EQPTOP then finds the values of $p(\text{Cs})$ and $p(\text{O}_2)$ by a double successive approximation. First, the value of $p(\text{Cs})$ over pure Cs(l) is calculated using Equation 28. The value of $p(\text{O}_2)$ is then found that makes the right hand side of Equation 30 equal to PEQO2 for this value of $p(\text{Cs})$. This value of $p(\text{O}_2)$ is then used to find a new value of $p(\text{Cs})$ that makes the two sides of Equation 29 equal. The process is repeated until stable values of $p(\text{Cs})$ and $p(\text{O}_2)$ are obtained. The convergence properties of the program appear to be very good.

The activity of Cs is simply $p(\text{Cs})/p^\circ(\text{Cs})$.

EQPTOP is in the subdirectory C:\EQCES\EQPTOP. Input to the program is interactive and straightforward. Any number of points may be calculated at the input temperature. The program must be restarted for calculations at a different temperature. The results are printed to the computer screen and also to the file EQPTOP.OUT.

EFFECTS OF H₂O IMPURITY

H₂O is reacts with the Cs-O solutions to form CsOH by the reactions

and

At 523 K, the equilibrium constant for Reaction 31 is 3×10^{23} and that of Reaction 32 is 3×10^{18} ; therefore, all the water is assumed to be converted into CsOH.

Two programs, OUTH and CEQH, are used. OUTH calculates the activities of Cs(l), CsOH(l), and the partial pressure of O₂(g), and outputs these to the file CEQH.DAT, which is then used in the program CEQH.

OUTH

Program OUTH uses the RAS formalism to calculate results at a single temperature and up to 10 H₂O concentrations. OUTH subroutines and associated files are listed in Table 10. OUTH is in the subdirectory C:\EQCES\OUTH, in which calculations should begin. After running OUTH, type CONT to copy CEQH.DAT and transfer control to the subdirectory C:\EQCES\CEQH.

H₂O is treated as an impurity component of the Cs-O solutions. The stoichiometries of the solutions are expressed as the Cs-O ratios ignoring H₂O plus the mole fractions of H₂O impurity. Because of mass balance considerations, moles of water in the solution cannot exceed the moles of O exclusive of water.

The treatment of H₂O as an impurity in Cs-O solutions uses the RAS with species 1 = Cs, species 2 = O, species 3 = Cs₂O, and species 4 = CsOH. The activity coefficients of the species are calculated using the Wilson³ formalism with 4 components. The programs use the true mole fractions of Cs, O, Cs₂O, and CsOH, calculated as shown in Table 11, in the their internal calculations.

Experimental data for fitting the interaction coefficients for the species CsOH are not available. Because H₂O is a minor impurity, the coefficients of interaction among the species Cs, O, and Cs₂O are considered as unchanged from the Cs-O case. Interaction

coefficients for H_2O with the other solution species are estimated as follows. CsOH is considered similar to Cs_2O , but its interaction coefficients differ from those involving Cs_2O by a factor f . Thus, $\text{XAF}(1,4) = f[\text{XAF}(1,3)]$, $\text{XAF}(2,4) = f[\text{XAF}(2,3)]$, $\text{XAF}(3,4) = f[\text{XAF}(3,3)]$, and $\text{XAF}(4,4) = f^2[\text{XAF}(3,3)]$. If accurate data for the effect of H_2O on the equivalent pressures of Cs and O over the solutions can be obtained, appropriate values of f can be established. In the absence of this data, the effects of H_2O can be calculated using estimated f values.

Input and output files

Similar to OUT , the input files for OUTH are OUTH.DAT and FITH.DAT . OUTH.DAT is described in Table 12. The format of FITH.DAT is similar to that of FIT.DAT (Table 2), except that 12 rather than 8 parameters are required. The FITH values used in the calculations are shown in Table 13.

CEQH

CEQH is a modification of CEQ that calculates partial pressures and total equivalent Cs , O_2 , and H_2 pressures. CEQH is located in the subdirectory $\text{C:\EQCES\CEQH}$. Subroutines for this program are listed in Table 14. In CEQH , the partial pressures of Cs(g) and CsOH(g) are regarded as constants as found from the equation $p(i) = p^\circ(i) a(i)$, where $p^\circ(i)$ is the equilibrium vapor pressure of pure component i as calculated from the thermodynamic data, and $a(i)$ is the activity of i calculated by OUTH . The partial pressure of O_2 is also a constant in the calculations. CEQH is applied at one temperature and many values of the H_2O content.

Input and output files

The input files for CEQH are CS.DAT , which contains thermodynamic data for the gas species (including H_2O , CsOH , and $\text{Cs}_2(\text{OH})_2$), and CEQH.DAT . The file entries for CEQH.DAT are shown in Table 15.

The output files produced by CEQH have been described previously except for PH2.XXX , which is similar to PO2.XXX and PCS.XXX and contains the equivalent pressures of H_2 set up to be exported to a graphics program.

THERMODYNAMIC DATA FOR CsOH

Converting the CsOH activities into pressures requires thermodynamic data for CsOH(l), CsOH(g), and Cs₂(OH)₂(g). Both the JANAF⁶ and the Glushko⁷ tables have listings for CsOH(s, l, and g) and for the dimer, Cs₂(OH)₂(g). The heat of formation of the solid, and the transition and fusion data, are based on fairly reliable experimental results. The heat capacity of solid and liquid were estimated. The entropy and Gibbs energy functions of the gaseous species were calculated from measured and estimated spectroscopic data. Agreement between the two tables is good for the monomer and poor for the dimer.

The vapor pressures of condensed CsOH have been measured by Konings and Cordfunke⁸ by the transpiration method and by Blackburn and Johnson⁹ by quadrupole mass spectrometry. The transpiration studies determined the apparent vapor pressure, equal to $P(\text{monomer}) + 2P(\text{dimer})$. The mass spectrometry determined the pressures of both monomer and dimer. The transpiration studies gave total pressures about twice as large as those found by mass spectrometry.

The data presented in Table 16 were derived from the JANAF thermal functions, with the enthalpies of formation of the gas phase species derived from the mass spectrometric studies. Blackburn and Johnson are unclear as to the precise data used to calculate values of the enthalpy of vaporization at 298 K; the values of $\Delta H^\circ_{f,298K} = -264.72$ kJ mol⁻¹ for the monomer and -677.81 kJ mol⁻¹ for the dimer reproduce their pressures within a factor of 2 over the range of the mass spectrometric studies. These data have been incorporated into CEQH, which calculates gas phase pressures for Cs-O systems containing water impurity.

RESULTS

The equivalent pressures presented in Figures 3a through 3e, 4a, and 4b were calculated using the three sets of estimated CsOH interaction coefficients presented in Table 2 at the temperature 523.15 K. The sets correspond to (1) $f = 0$ (all CsOH coefficients set equal to zero); (2) $f = 1$ (CsOH coefficients considered the same as corresponding Cs₂O coefficients); and (3) $f = 0.5$. The indicated liquidus values were taken from the estimated curves of K+P for pure Cs-O solutions.

The calculations assumed that the hydroxide was soluble in the oxide melt at all the compositions shown in the figures. This may not be true at all hydroxide compositions at temperatures below the hydroxide melting point, where the Gibbs energy of melting of the

hydroxide is a component of the solubility relationship. Pure CsOH melts at 588 K with an enthalpy of fusion of 4.56 kJ;⁶ the entropy of fusion is thus 7.76 J mol⁻¹K⁻¹. Below 588 K, there is the possibility that solid CsOH can be in equilibrium with the Cs-O solution. However, calculations assuming ideal solution behavior of CsOH(l) (that is, no attractive forces between Cs-O and CsOH) indicate that the solubility of CsOH in Cs-O remains above $x(\text{CsOH}) = 0.4$ at temperatures as low as 300K. The equation for the ideal solution equilibrium is

$$\Delta H^\circ_{\text{fus}} - \Delta S^\circ_{\text{fus}} = -RT \ln x(\text{CsOH}) \quad (33)$$

The interactions between the other species in the Cs-O system are attractive and would increase the solubility in the melt. On this basis, it can be concluded that at equilibrium CsOH(s) will dissolve completely at the temperatures and composition ranges covered in the calculations.

Figures 3a, for $x(\text{O}) \leq 0.02$, and 3b, for $x(\text{O}) \leq 0.2$, are for the case in which $f = 0$. Figures 3c and 3d show the O₂ equivalent pressures calculated with $f = 1$, and Figure 3d and 3e show the results for $f = 0.5$. The equivalent O₂ pressures are increased most for the assumption that the CsOH coefficients are zero and least by the assuming that CsOH interacts in solution as does Cs₂O. The effects are most pronounced at low O₂ concentrations.

As discussed above, the results of Figures 3a-3d assume that CsOH are based upon CsOH uniformly distributed in the liquid Cs-O solution. However, Cs-O solution production by reaction of Cs and O₂ at relatively low temperatures may lead to local compositions in which Cs₂O(s) is formed. If this is so, CsOH(s) can occur as a separate surface phase on the Cs₂O(s). If the temperature of the Cs-O mixture is then raised, equivalent O₂ vaporization pressures may be high because of the transient presence of small volumes containing high concentrations of CsOH.

Figures 4a and 4b show the equivalent Cs pressures calculated for $f = 0$ (where the effects are greatest). The equivalent Cs pressures are only slightly affected by the choice of CsOH interaction coefficients. The effect of H₂O is small except near the composition Cs₂O.

EFFECTS OF CO₂ IMPURITY

The treatment of CO₂ impurity is similar to that for H₂O. CO₂ is assumed to exist in solution as the species Cs₂CO₃. The net reactions for producing Cs₂CO₃ are

and

At 523 K, the equilibrium constant for Equation 34 is 4×10^{35} and that of Equation 35 is 3×10^{32} .

OUTC

The program OUTC uses the Regular Associated Solution formalism with species 4 = Cs₂CO₃. The activity coefficients of the species are calculated using the Wilson formalism. OUTC calculates values of the activity of Cs(l) and Cs₂CO₃(l) and the partial pressure of O₂(g).

Calculations should begin in the subdirectory C:\EQCES\OUTC. After running OUTC, typing CONT copies CEQC.DAT and transfers control to the subdirectory C:\EQCES\CEQC.

Table 17 lists the subroutines and associated files for OUTC. The partial pressure and activity data are then used in the program CEQC to calculate partial pressures and total equivalent Cs and O₂ pressures.

CO₂ is treated as an impurity component of the Cs-O solutions. The stoichiometries of the solutions are expressed as the Cs-O ratios exclusive of CO₂ plus the mole fractions of CO₂ impurity. The programs use the true mole fractions of Cs, O, Cs₂O, and Cs₂CO₃, calculated as shown in Table 18, in their internal calculations.

Input and output files

The input and output files are similar to those for OUTH. Table 19 lists the entries for the file OUTC.DAT. Entries for FITC.DAT are identical to those for FITH.DAT.

CEQC

CEQC is a modification of CEQ that calculates partial pressures and total equivalent Cs, O₂, and C pressures. In CEQC, the partial pressures of Cs(g) and Cs₂CO₃(g) are constants found from the relationship $p(i) = p^\circ(i) a(i)$, where $p^\circ(i)$ is the equilibrium vapor pressure of pure component i as calculated from the thermodynamic data, and $a(i)$ is the activity of i calculated by OUTC. The partial pressure of O₂ is also constant in the calculations. CEQC is applied at one temperature and many values of the CO₂ content.

CEQC is contained in the subdirectory C:\EQCES\CEQC. Table 20 lists the subroutines and associated files for CEQC.

Input and output files

The input and output files are similar to those for CEQH.

THERMODYNAMIC DATA FOR Cs₂CO₃

Kubaschewski and Allcock¹⁰ list the enthalpy of formation, the entropy at 298K, and the heat capacities for solid Cs₂CO₃. Data for the supercooled liquid were estimated from data for the other alkali carbonates.

Gorokhov¹¹ studied the vaporization of Cs₂CO₃ by mass spectrometry and estimated thermodynamic data for molecular Cs₂CO₃ using estimated values of the entropy and heat capacities. In contrast to the other alkali carbonates, Cs₂CO₃ vaporizes to form a substantial amount of gaseous Cs₂CO₃ as well as decomposition products.

Table 21 presents thermodynamic data for solid and gaseous Cs₂CO₃ derived from these sources. The melting temperature and enthalpy of fusion were estimated as 1020K and 20.92 kJ mol⁻¹ in analogy with available fusion data for alkali carbonates. The entropy of fusion is $\Delta H^\circ_{\text{fus}}/T_{\text{fus}}$.

RESULTS

As for CsOH, the interaction coefficients of Cs_2CO_3 must be estimated. The O_2 equivalent pressure results presented in Figures 5a and 5b are for the most pronounced case, with $f = 0$, whereas those for $f = 1$ are shown in Figures 5c and 5d. It can be seen that impurity CO_2 has very little effect on the O_2 equivalent pressure at 523 K. The corresponding equivalent Cs pressures are shown in Figures 6a through 6d.

The effects of CO_2 on the equivalent pressures contrast with those for H_2O because Cs_2CO_3 has much lower vaporization/decomposition pressures than the components of the Cs-O solution. At 523.15 K, the vapor pressure of $\text{Cs}_2\text{CO}_3(\text{g})$ over pure $\text{Cs}_2\text{CO}_3(\text{c})$ is 9.0×10^{22} atm. Effectively, CO_2 ties up O in a less volatile form. Because the O activity is lowered, the Cs activity is raised relative to the pure solution. In contrast, the vapor pressure of $\text{CsOH}(\text{g})$ over pure CsOH at 523 K is calculated as 5×10^{-9} atm or 4×10^{-6} torr, roughly comparable to that of Cs_2O over condensed Cs_2O .

As for CsOH, the Gibbs energy of fusion can lead to limitations on Cs_2CO_3 solubility at temperatures below its melting point. Assuming ideal solution behavior, the solubility limit for Cs_2CO_3 in Cs-O solutions is $x(\text{Cs}_2\text{CO}_3) = 0.10$ at 523 K and 0.02 at 400 K. The solubilities would be increased by the attractive forces between Cs-O species and Cs_2CO_3 in real solutions. The solubility of $\text{Cs}_2\text{CO}_3(\text{s})$ in the Cs-O melt may thus be below the higher values shown in Figures 5b and 5d.

CONCLUSIONS AND RECOMMENDATIONS

The goal of this study has been to predict the gas phase compositions and pressures in equilibrium with Cs-O solutions and Cs-O solutions containing impurity H₂O or CO₂. The accompanying computer programs use the Regular Associated Solution theory, calibrated using the limited amount of available data, to make these predictions. The user should note that the experimental data covers only O₂ activity values for the temperature range 773 to 973 K and the composition range $x(O) = 0.033$ to $x(O) = 0.168$, with an estimated Cs activity value at the composition Cs₂O at 773 K derived by a Gibbs-Duhem method. Partial and total equivalent O₂ pressures calculated outside these experimental limits are essentially extrapolations of data that themselves exhibit a moderate amount of scatter.

The figures presented in this report show calculated values of the total equivalent Cs and O₂ pressures in equilibrium with Cs-O compositions from 0 to .33333 mole fraction O and at temperatures from 437 to 773 K. The values are uncertain, because of the limitations of the experimental data upon which they are based. However, the estimated values and the trends of the equivalent pressures with temperature and composition should be helpful in planning future studies.

The effects of H₂O and CO₂ contamination of the Cs-O solutions have been studied by the Regular Associated Solution programs using estimated interaction coefficients for the solution species CsOH and Cs₂CO₃. H₂O increases, whereas CO₂ decreases, the equivalent O₂ pressure. The effect of the impurities on equivalent Cs pressures is small.

The most critically needed studies at this time are new experimental data on Cs and O₂ pressures as functions of temperature and composition. Further progress in this area does not require significant refinement or extension of the accompanying computer programs, which have been designed to facilitate the inclusion of new data.

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Table 1

SUBROUTINES AND ASSOCIATED FILES FOR FIT

SUBROUTINES

FIT.FOR
 XATT.FOR
 FUNC.FOR
 XFIND.FOR
 GIBBS.FOR
 XCALC.FOR
 DUMPER.FOR
 POWELL.FOR*
 LINMIN.FOR*
 MNBRAK.FOR*
 BRENT.FOR*
 F1DIM.FOR*
 ZBRAC.FOR*
 ZBRENT.FOR*

INCLUDE FILES

COMMON.FI
 DEFLT.FI

V.FI

INPUT FILES

***.DAT
 FIT.DAT

Data points to be fitted
 First estimates of XAF parameters

OUTPUT FILES

FIT1.DAT
 FITOUT.DAT

Best fit XAF parameters
 Comparison of data points with
 calculated data points

*Routines taken from *Numerical Recipes*.¹ ZBRENT has been converted into a subroutine to facilitate separate compilation and the transfer of the large number of variables involved in its use.

-
1. W. H. Press, B. P. Flannery, S. A. Teukovsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986). These copyrighted routines are included on the floppy disks with the knowledge that Rasor Associates is an authorized user.

Table 2

FIT.DAT FILE ENTRIES

Entry	Quantities	Format
1	XAF(1)*	FP
2	XAF(2)*	FP
3	XAF(3)= λ_{11}	FP
4	XAF(4)= λ_{12}	FP
5	XAF(5)= λ_{13}	FP
6	XAF(6)= λ_{22}	FP
7	XAF(7)= λ_{23}	FP
8	XAF(8)= λ_{33}	FP

* $\ln K = \text{XAF}(1)/T + \text{XAF}(2)$

Table 3

***.DAT FILE ENTRIES

Entry	Quantities	Format
1	NTOL	FP
2	NTEMP	I

*****REPEAT ENTRIES 3-5 FOR EACH TEMPERATURE*****

3	T(K)	FP
4	NPTS	I

*****REPEAT ENTRY 5 NPTS TIMES*****

5	NMATCH, N(Cs), F[N(Cs)]	I,FP,FP
---	-------------------------	---------

NOTE: if a point is to be fitted for more than 1 quantity, such as $\ln P(\text{O}_2)$ and the Gibbs energy at the composition Cs_2O , separate entries must be made for each fitting quantity. Data are entered in unformatted, comma delimited form.

I=Integer number, FP=floating point number.

NTOL = tolerance for fitting routine, typically 1×10^{-4} .

NTEMP = number of temperatures for which data are entered.

NPTS = number of entries at temperature T.

NMATCH = type of data. NMATCH = 1 for data to be fitted to $\ln P(\text{O}_2)$; NMATCH = 2 for data to be fitted to ΔG_f of $\text{Cs}_2\text{O}(\text{l})$; NMATCH = 3 for data to be fitted to points on Cs_2O liquidus; NMATCH = 4 for data to be fitted to $\ln a(\text{Cs})$.

N(Cs) = bulk mole fraction of Cs in solution.

F[N(Cs)] = $\ln P(\text{O}_2)$ for NMATCH = 1, $\ln a(\text{Cs})$ for NMATCH = 4, otherwise F[N(Cs)] = 0.

XAF(i) = fitting parameter value.

Table 4

ALL.DAT FILE USED IN CALCULATIONS

1.E-4
4
973.15
1,.9667,-66.08
1,.9535,-64.84
1,.9210,-62.86
1,.8760,-61.18
1,8320,-60.05
2,.666667,0.
773.15
11
1,.9667,-88.62
1,.9535,-87.32
1,.9210,-84.41
1,.8760,-82.22
1,.8320,-80.74
1,.666667,-46.26
4,.666667,-7.29*
4,.666667,-7.29*
4,.666667,-7.29*
4,.666667,-7.29*
2,.666667,0.
873.15
6
1,.9667,-76.061
1,.9535,-74.65
1,.9210,-72.40
1,.8760,-70.49
1,.8320,-69.21
2,.666667,0.
437.
1
3,.7600,0.

* This point was weighted to improve agreement of Cs activity with value derived graphically by Knights and Phillipps.⁴

Table 5

SUBROUTINES AND ASSOCIATED FILES FOR OUT

SUBROUTINES

OUT.FOR
GIBBS.FOR
ACTIVITY.FOR
XATT.FOR
XFIN.D.FOR
DUMP2.FOR

INCLUDE FILES

COMMON.FI
DEFLT.FI
V.FI

INPUT FILES

OUT.DAT
FIT1.DAT

T,X(Cs) values to be calculated
XAF parameters

OUTPUT FILES

CEQ.DAT

T, x(Cs) values and corresponding
a(Cs) and lnP(O₂) (atm) values.

Table 6

FIT1.DAT FILE ENTRIES DERIVED FROM TABLE 3 DATA

+.35512340D+05
-.47090345D+01
-.14811183D+05
+.64789477D+04
-.46743933D+03
-.19303060D+05
-.20984678D+04
+.19324027D+04

Table 7

OUT.DAT FILE ENTRIES

Entry	Quantities	Format
1	NTEMP (≤ 10)	I
2	T(J), J=1, NTEMP	FP, comma delimited, all on 1 line
3	NPTS (≤ 50)	I
*****REPEAT LINE 4 NPTS TIMES*****		
	x(Cs) FP	

Table 8

SUBROUTINES AND ASSOCIATED FILES FOR CEQ

SUBROUTINES

CEQ.FOR
 INDCAV.FOR
 GIBBS1.FOR
 FSTCAV.FOR
 SRTCAV.FOR
 BASIS.FOR
 EQSCAV.FOR
 DMPCAV.FOR

INCLUDE FILES

DEFT.FI
 CSTRG.FI
 CINT.FI
 CFLT.FI

INPUT FILES

CS.DAT
 CEQ.DAT

Thermodynamic data
 Data on T, x(Cs) points

OUTPUT FILES

SPECIES.OUT
 EQP.OUT
 PCS.***
 PO2.***

Listing of partial pressures for
 all gas species at T, x(Cs) points
 Listing of equivalent Cs and O₂
 pressures at T, x(Cs) points
 Graphics program input of
 equivalent Cs pressures.
 Graphics program input of
 equivalent O₂ pressures

Table 9

CEQ.DAT FILE ENTRIES

Entry	Quantities	Format
1.	NTEMP, NPTS	2I2
*****REPEAT LINE 2 NTEMP TIMES*****		
2.	T(j)	FP
*****REPEAT LINE 3 NPTS TIMES*****		
3.	x(Cs)	FP
*****LINE 4 IS REPEATED NTEMP x NPTS TIMES		
4.	a(Cs), ln P(O ₂) (atm)	FP,FP Aranged as NPTS entries at T(1), etc.

Table 10

SUBROUTINES AND ASSOCIATED FILES FOR OUTH

SUBROUTINES

OUTH.FOR
 DUMP2.FOR
 XFIND.FOR
 XCALC.FOR
 XATT.FOR
 GIBBS.FOR
 ZBRAC.FOR
 ZBRENT.FOR

INCLUDE FILES

COMMON.FI
 DEFLT.FI
 V.FI
 F.FI

INPUT FILES

OUTH.DAT
 FITH.DAT

T, X(Cs) values to be calculated
 XAF parameters

OUTPUT FILES

CEQH.DAT

T, x(Cs) values and corresponding
 a(Cs) and lnP(O₂) (atm) values.

Table 11

STOICHIOMETRIC RELATIONSHIPS FOR Cs-O-H SOLUTIONS

In the pure Cs-O solution, there are $x^{\circ}(\text{Cs})$ moles Cs and $x^{\circ}(\text{O})$ moles O, with $x^{\circ}(\text{Cs}) + x^{\circ}(\text{O}) = 1$. A solution containing H_2O is made by mixing $x(\text{H}_2\text{O})$ moles of H_2O with $[1-x(\text{H}_2\text{O})]$ moles of the pure Cs-O solution.

In the new solution, the moles of the elements are

$$N(\text{Cs}) = x^{\circ}(\text{Cs}) [1-x(\text{H}_2\text{O})] \quad (1)$$

$$N(\text{O}) = x^{\circ}(\text{O}) [1-x(\text{H}_2\text{O})] + x(\text{H}_2\text{O}) \quad (2)$$

and

$$N(\text{H}) = 2 x(\text{H}_2\text{O}) \quad (3)$$

It is assumed that enough O is present to react with all the H to form CsOH and that enough Cs is present to react with all the H to form CsOH and all the remaining O to form Cs_2O . Mathematically, these conditions are

$$N(\text{O}) \geq N(\text{H}) \quad (4)$$

and

$$N(\text{Cs}) \geq N(\text{H}) + 2 [N(\text{O}) - n(\text{H})] \quad (5)$$

Actually, the Equation 4 condition used in OUTH is that $N(\text{O}) > N(\text{H})$. The reason for this is that some small amount of O must be present in the solution for an equilibrium to be established.

All the H is assumed to be present as CsOH. Therefore, the number of moles of CsOH is

$$n(\text{CsOH}) = N_{\text{H}} \quad (6)$$

which leaves $(N_{\text{Cs}} - N_{\text{H}})$ moles Cs and $(N_{\text{O}} - N_{\text{H}})$ moles O.

The remaining O is, in the first approximation, present as Cs_2O . Thus,

$$n(\text{Cs}_2\text{O}) = (N_{\text{O}} - N_{\text{H}}) \quad (7)$$

which leaves $[N_{\text{Cs}} - N_{\text{H}} - (N_{\text{O}} - N_{\text{H}})] = (N_{\text{Cs}} - N_{\text{O}})$ moles of Cs. Hence,

$$n(\text{Cs}) = N_{\text{Cs}} - N_{\text{O}} \quad (8)$$

The amount of O in solution is determined by the program using the equilibrium constant K as described in the text. Mole fractions are calculated from the resulting mole numbers.

Table 12

OUTH.DAT FILE ENTRIES		
Entry	Quantities	Format
1	NH ₂ O (≤ 10)	I
2	ENH ₂ O(J), J=1, NTEMP	FP, comma delimited, all on 1 line
3	NPTS (≤ 50)	I
*****REPEAT LINE 4 NPTS TIMES*****		
	4 x(Cs) FP	

Table 13

FITH.DAT (AND FITC.DAT) FILE ENTRIES

Quantities	Values		
	<u>f=0</u>	<u>f=1</u>	<u>f=0.5</u>
XAF(1)	+.35512340D+5	+.35512340D+5	+.35512340D+5
XAF(2)	-.47090345D+1	-.47090345D+1	-.47090345D+1
XAF(3)=XAF°(3) [†]	-.14811183D+5	-.14811183D+5	-.14811183D+5
XAF(4)=XAF°(4)	+.64789477D+4	+.64789477D+4	+.64789477D+4
XAF(5)=XAF°(5)	-.46743933D+3	-.46743933D+3	-.46743933D+3
XAF(6)=f[XAF°(5)]	.0	-.46743933D+3	-.23371967D+3
XAF(7)=XAF°(6)	-.19303060D+5	-.19303060D+5	-.19303060D+5
XAF(8)=XAF°(7)	-.20984678D+4	-.20984678D+4	-.20984678D+4
XAF(9)=f[XAF°(7)]	.0	-.20984678D+4	-.10492339D+4
XAF(10)=XAF°(8)	+.19324027D+4	+.19324027D+4	+.19324027D+4
XAF(11)=f[XAF°(8)]	.0	+.19324027D+4	+.96620000D+3
XAF(12)=f ² [XAF°(8)]	.0	+.19324027D+4	+.48310000D+03

$\ln K = \text{XAF}(1)/T + \text{XAF}(2)$; $\text{XAF}(3)=\lambda_{11}$; $\text{XAF}(4)=\lambda_{12}$; $\text{XAF}(5)=\lambda_{13}$; $\text{XAF}(6)=\lambda_{14}$;
 $\text{XAF}(7)=\lambda_{22}$; $\text{XAF}(8)=\lambda_{23}$; $\text{XAF}(9)=\lambda_{24}$; $\text{XAF}(10)=\lambda_{33}$; $\text{XAF}(11)=\lambda_{34}$; $\text{XAF}(12)=\lambda_{44}$.
[†]XAF°(i) is the coefficient i in the file FIT.DAT for pure Cs-O solutions.

Table 14

SUBROUTINES AND ASSOCIATED FILES FOR CEQH

SUBROUTINES

CEQH.FOR
INDCAV.FOR
GIBBS1.FOR
FSTCAV.FOR
SRTCAV.FOR
BASIS.FOR
EQSCAV.FOR
DMPH.FOR

INCLUDE FILES

DEFT.FI
CSTRG.FI
CINT.FI
CFLT.FI

INPUT FILES

CS.DAT
CEQH.DAT

Thermodynamic data
Data on T, x(Cs) points

OUTPUT FILES

SPECIES.OUT
EQP.OUT
PCS.***
PO2.***
PH2.***

Listing of partial pressures for
all gas species at T, x(Cs) points
Listing of equivalent Cs, O₂, and H₂
pressures at T, x(Cs), x(H) points
Graphics program input of
equivalent Cs pressures.
Graphics program input of
equivalent O₂ pressures
Graphics program input of
equivalent H₂ pressures

Table 15
CEQHL DAT FILE ENTRIES

Entry	Quantities	Format
1.	T, NH ₂ O, NPTS	D13.7, 2I2
*****REPEAT LINE 2 NH ₂ O TIMES*****		
2.	ENH ₂ O(J)	FP
*****REPEAT LINE 3 NH ₂ O x NPTS TIMES*****		
3.	x(Cs),x(O),a(Cs),lnP(O ₂)(atm), lnP(H ₂)(atm)	5D13.7

Table 16
THERMODYNAMIC DATA FOR CESIUM HYDROXIDE

<u>CsOH(l)</u>	$-[(G^\circ - H^\circ_{298})/RT] = 24.565 - 9.3445D-2 T + 2.9608D-4 T^2$ $- 3.8844D-7 T^3 + 1.92926D-10 T^4 \quad (298-600K)$ $-[(G^\circ - H^\circ_{298})/RT] = 13.477 - 4.2710D-3 T + 2.5767D-5 T^2$ $- 2.2521D-8 T^3 + 6.8200d-12 T^4 \quad (600-1000K)$ $\Delta H^\circ_{f,298K}/R = -48.826 \text{ kK}$
<u>CsOH(g)</u>	$-[(G^\circ - H^\circ_{298})/RT] = 36.671 - 5.42540D-2 T + 1.70011D-4 T^2$ $- 2.19301D-7 T^3 + 1.07234D-10 T^4 \quad (298-600K)$ $-[(G^\circ - H^\circ_{298})/RT] = 29.352 + 1.47700D-3 T + 7.8240D-6 T^2$ $- 6.6910D-9 T^3 + 1.85600D-12 T^4 \quad (600-1000K)$ $\Delta H^\circ_{f,298K}/R = -30.545 \text{ kK}$
<u>Cs₂(OH)₂(g)</u>	$-[(G^\circ - H^\circ_{298})/RT] = 52.335 - 7.97300d-2 T + 2.45322d-4 T^2$ $- 3.07239d-7 T^3 + 1.46734d-10 T^4 \quad (298-600K)$ $-[(G^\circ - H^\circ_{298})/RT] = 41.753 - 3.53000d-4 T + 1.81160d-5 T^2$ $- 1.43670d-8 T^3 + 3.90700d-12 T^4 \quad (600-1000K)$ $\Delta H^\circ_{f,298K}/R = -78.935 \text{ kK}$

* Dividing $\Delta H^\circ_{f,298K}$ by R yields the dimensional unit kK (kiloKelvins).

Table 17

SUBROUTINES AND ASSOCIATED FILES FOR OUTC

SUBROUTINES

OUTC.FOR
DUMPC.FOR
XFIND.FOR
XCALC.FOR
XATT.FOR
GIBBS.FOR
ZBRAC.FOR
ZBRENT.FOR

INCLUDE FILES

COMMON.FI
DEFLT.FI
V.FI
F.FI

INPUT FILES

OUTC.DAT
FITC.DAT

T, x(Cs) points for calculations
XAF parameters

OUTPUT FILES

CEQC.DAT

T, x(Cs), x(c) values and
corresponding
a(Cs), lnP(O₂) (atm) values.

Table 18

STOICHIOMETRIC RELATIONSHIPS FOR Cs-O-C SOLUTIONS

In the pure Cs-O solution, there are $x^{\circ}(\text{Cs})$ moles Cs and $x^{\circ}(\text{O})$ moles O, with $x^{\circ}(\text{Cs}) + x^{\circ}(\text{O}) = 1$. A solution containing CO_2 is made by mixing $x(\text{CO}_2)$ moles of CO_2 with $[1-x(\text{CO}_2)]$ moles of the pure Cs-O solution.

In the new solution, the moles of the elements are

$$N(\text{Cs}) = x^{\circ}(\text{Cs}) [1-x(\text{CO}_2)] \quad (1)$$

$$N(\text{O}) = x^{\circ}(\text{O}) [1-x(\text{CO}_2)] + 2 x(\text{CO}_2) \quad (2)$$

and

$$N(\text{C}) = x(\text{CO}_2) \quad (3)$$

It is assumed that enough O is present to react with all the H to form Cs_2CO_3 and that enough Cs is present to react with all the C to form Cs_2CO_3 and all the remaining O to form Cs_2O . Mathematically, these conditions are

$$N(\text{O}) \geq 3N(\text{C}) \quad (4)$$

and

$$N(\text{Cs}) \geq 2N(\text{O}) - 4 N(\text{C}) \quad (5)$$

Actually, the Equation 4 condition used in OUTC is that $N(\text{O}) > 3 N(\text{C})$. The reason for this is that some small amount of O must be present in the solution for an equilibrium to be established.

All the C is assumed to be present as Cs_2CO_3 . Therefore, the number of moles of Cs_2CO_3 is

$$n(\text{Cs}_2\text{CO}_3) = N(\text{C}) \quad (6)$$

which leaves $[N(\text{Cs}) - 2N(\text{C})]$ moles Cs and $[N(\text{O}) - 3 N(\text{C})]$ moles O.

The remaining O is, in the first approximation, present as Cs_2O . Thus,

$$n(\text{Cs}_2\text{O}) = [N(\text{O}) - 3 N(\text{C})] \quad (7)$$

which in turn leaves $[N(\text{Cs}) - 2N(\text{O}) + 4 N(\text{C})]$ moles of Cs. Hence,

$$n(\text{Cs}) = N(\text{Cs}) - 2N(\text{O}) + 4 N(\text{C}) \quad (8)$$

The amount of O in solution is determined by the program using the equilibrium constant K as described in the text. Mole fractions are calculated from the resulting mole numbers.

Table 19

OUTC.DAT FILE ENTRIES

Entry	Quantities	Format
1	NCO2 (≤ 10)	I
2	ENCO2(J), J=1, NTEMP	FP, comma delimited
3	NPTS (≤ 50)	I
*****REPEAT LINE 4 NPTS TIMES*****		
4	x(Cs)	FP

Table 20

SUBROUTINES AND ASSOCIATED FILES FOR CEQC

SUBROUTINES

CEQC.FOR
 INDCAV.FOR
 GIBBS1.FOR
 FSTCAV.FOR
 SRTCAV.FOR
 BASIS.FOR
 EQSCAV.FOR
 DMPC.FOR

INCLUDE FILES

DEFT.FI
 CSTRG.FI
 CINT.FI
 CFLT.FI

INPUT FILES

CS.DAT
 CEQC.DAT

Thermodynamic data
 Data on T, x(Cs) points

OUTPUT FILES

SPECIES.OUT

Listing of partial pressures for
 all gas species at T, x(Cs), x(C)
 points

EQP.OUT

Listing of equivalent Cs, O₂, and H₂
 pressures at T, x(Cs), x(C) points

PCS.***

Graphics program input of
 equivalent Cs pressures.

PO2.***

Graphics program input of
 equivalent O₂ pressures

PC.***

Graphics program input of
 equivalent H₂ pressures

FITC.DAT and CEQC file entries are similar to those of FITH and CEQH.

Table 21

THERMODYNAMIC DATA FOR CESIUM CARBONATE*

$$\begin{aligned} \underline{\text{Cs}_2\text{CO}_3(\text{s})} \quad & -[(G^\circ - H^\circ_{298})/RT] = 38.671 - 1.25575\text{D-}1 \text{ T} + 3.87731\text{D-}4 \text{ T}^2 \\ & \quad - 4.89222\text{D-}7 \text{ T}^3 + 2.35538\text{D-}10 \text{ T}^4 \quad (298\text{-}600\text{K}) \\ & -[(G^\circ - H^\circ_{298})/RT] = 22.187 - 9.6900\text{d-}4 \text{ T} + 2.82270\text{D-}5 \text{ T}^2 \\ & \quad - 2.21900\text{D-}8 \text{ T}^3 + 6.08300\text{D-}12 \text{ T}^4 \quad (600\text{-}1000\text{K}) \\ & \Delta H^\circ_{f,298\text{K}}/R = -137.984 \text{ kK} \end{aligned}$$

$$\begin{aligned} \underline{\text{Cs}_2\text{CO}_3(\text{g})} \quad & -[(G^\circ - H^\circ_{298})/RT] = 60.579 - 1.16843\text{D-}1 \text{ T} + 3.61983\text{D-}4 \text{ T}^2 \\ & \quad - 4.59853\text{D-}7 \text{ T}^3 + 2.22879\text{D-}10 \text{ T}^4 \quad (298\text{-}600\text{K}) \\ & -[(G^\circ - H^\circ_{298})/RT] = 45.537 - 2.16400\text{D-}3 \text{ T} + 2.81280\text{D-}5 \text{ T}^2 \\ & \quad - 2.22570\text{D-}8 \text{ T}^3 + 6.06900\text{D-}12 \text{ T}^4 \quad (600\text{-}1000\text{K}) \\ & \Delta H^\circ_{f,298\text{K}}/R = -98.329 \text{ kK} \end{aligned}$$

$$\underline{\text{Gibbs Energy of Fusion}} \quad \Delta G^\circ_{\text{fus}}/RT = 2516/T - 2.466$$

* Dividing $\Delta H^\circ_{f,298\text{K}}$ by R yields the dimensional unit kK (kiloKelvins).

Figure 1 Equivalent O_2 Pressure Of Cs-O Solutions

- -- Approximate Liquidus Composition

Figure 2 Equivalent Cs Pressure of Cs-O Solutions
 • -- Approximate Liquidus Composition

Figure 3a Effect of H_2O Impurity on O_2 Equivalent Pressure

Case 1: $f = 0$

Figure 3b Effect of H_2O Impurity on O_2 Equivalent Pressure
Case 1: $f = 0$

Figure 3c Effect of H_2O Impurity on O_2 Equivalent Pressure
Case 2: $f = 1$

Figure 3d Effect of H_2O Impurity on O_2 Equivalent Pressure
Case 2 $f = 1$

Figure 3e Effect of H_2O Impurity on O_2 Equivalent Pressures
Case 3: $f = 0.5$

Figure 3f Effect of H_2O Impurity on O_2 Equivalent Pressure
Case 3: $f = 0.5$

Figure 4a Effect of H₂O Impurity on Cs Equivalent Pressure
Case 1: $f = 0$

Figure 4b Effect of H_2O Impurity on Cs Equivalent Pressure
Case 1: $f = 0$

Figure 5a Effect of CO_2 Impurity on O_2 Equivalent Pressure
Case 1: $f = 0$

Figure 5b Effect of CO_2 Impurity on O_2 Equivalent Pressure
Case 1: $f = 0$

Figure 5c Effect of CO_2 Impurity on O_2 Equivalent Pressure
Case 2: $f = 1$

Figure 5d Effect of CO_2 Impurity on O_2 Equivalent Pressure
Case 2: $f = 1$

Figure 6a Effect of CO_2 Impurity on Cs Equivalent Pressure
Case 1: $f = 0$

Figure 6b Effect of CO_2 Impurity on Cs Equivalent Pressure
Case 1: $f = 0$

Appendix H

ANALYSIS OF THE DECOR TEST VEHICLE RESULTS

By:
Robert H. Lamoreaux

BACKGROUND

The DECOR test vehicle has provided a 1000-hour stable source of Cs vapor containing a small controlled amount of oxygen for use in thermionic energy converters. The present study presents an analysis of the physical and chemical processes taking place in the DECOR device with the aim of designing advanced prototypes.

THE DECOR DEVICE

In the DECOR device, Cs/O liquid is contained in an outer Mo sleeve. Near the top of the device, Cs/O vapor can evaporate through a Pt mesh at a temperature set by heating coils. The base of the device is an unheated heat sink. A temperature gradient therefore develops between the device top and bottom. Cs/O vapor evaporated from the top travels through a Mo tube and condenses at the bottom. The space within the sleeve between the base and the top is filled with sintered Pt black, which "wicks" the liquid Cs/O from the base region to the Pt mesh at the top. The equivalent Cs and O₂ pressures vaporizing from the hot end have been measured to be steady over periods of about 1000 hours.

The purpose of this investigation was to determine how the DECOR device leads to stable Cs/O gas mixtures containing very small amounts of O. Several approaches were considered. A diffusion-controlled steady state was postulated and studied in detail. However, a simpler, equilibrium-based analysis ultimately proved successful in explaining the experimental results.

Previous studies developed computer programs for calculating the activity of O in Cs/O liquid mixtures in the composition region from $x(\text{O}) = 0$ to $x(\text{O}) = 1/3$. These programs, based on the Regular Associated Solution model, predict that the vapor over Cs/O liquids in this composition/temperature regime are significantly enriched in Cs.

In the DECOR device, this tendency to enrich the vapor in Cs leads to O accumulating in the high temperature zone, with the liquid in the low temperature region having a very low O content. In the absence of other controlling mechanisms, the oxygen content of the high temperature surface will tend to increase toward those of the Cs/Cs₂O

2-phase region. However, the observed Cs and O₂ pressures have more Cs and less O₂ than for this 2-phase region.

Conservation of mass in the cyclic vaporization-condensation process requires that the vaporizing composition equal that of the condensing composition; that is, the vaporizing composition and the low-temperature, Cs-rich liquid must end up with the same Cs/O ratio.

The steady-state mechanism may be either kinetic- or equilibrium-driven. In the former case, diffusion processes, primarily in the high temperature end of the device, would ultimately lead to the steady-state. Calculating this state is impossible with presently-known data. However, further analysis indicates that a simple equilibrium process is responsible for the observed pressures.

The tubing used in the DECOR device is made from Mo, which reacts with Cs and O₂ to form cesium molybdate, Cs₂MoO₄(s), by the overall reaction

which has the equilibrium constant at temperature T of

$$K = \frac{a(\text{Cs}_2\text{MoO}_4)}{a(\text{Mo})a(\text{Cs})^2a(\text{O}_2)^2} \quad (2)$$

The activities of pure solid Mo and Cs₂MoO₄ are unity. Rearranging,

$$a(\text{O}_2)^2 = \frac{1}{K a(\text{Cs})^2} \quad (3)$$

Since the steady-state vapor is observed to be essentially Cs(g) with a very small amount of oxygen, the activity of Cs in the liquid with the same composition is (as easily calculated with the Regular Associated Solution theory) essentially unity. Therefore,

$$a(\text{O}_2)^2 = \frac{1}{K} \quad (4)$$

This implies that the activity of O₂ (which equals its pressure) is fixed by the equilibrium in Reaction 1.

A complex equilibrium computer program was used to find the partial pressure of O₂ resulting from Reaction 1 at 500 K. The pressure was 2.6×10^{-69} atm or 2.0×10^{-67} torr. (Note: this is the O₂ potential and not its concentration in solution. Oxygen is

strongly associated and its activity in solution is many orders of magnitude less than its composition.)

The programs OUT and CEQ, previously reported, were then used to find the Cs/O vaporizing composition yielding this oxygen activity at 580 K, $x(\text{O}) = 0.24$. The oxygen and Cs pressures vaporizing from this composition, calculated at temperatures from 520 to 580 K, are shown in Figures 1 and 2. (Strictly speaking, the correct composition should have been determined at each temperature. However, because the activity data available for parameterizing the Regular Associated Solution equations are limited to the temperature range 773K to 973 K and compositions with $x(\text{O}) < 0.17$, the results of this study are only approximate and there is little point in pursuing such details.)

The agreement between the calculated and experimental values of the Cs and O₂ equivalent pressures is surprisingly good, and can be taken as evidence that Reaction 1 is controlling the steady-state oxygen content of the low-temperature Cs solution and, therefore, the vaporizing composition. If the liquid Cs should contain oxygen at another level, Reaction 5 will take place in the direction that restores the steady-state level.

The experimental value of the equivalent O₂ pressure found for a DECOR bottom temperature of 420 K is higher than would be expected on the basis of this analysis. However, this pressure, which is lower by an order of magnitude than for the points with a bottom temperature of 500 K, may be influenced by a very small amount of impurity (CsOH).

The effects of adsorbed water

Water strongly adsorbs on Pt black powder, most of which is made by precipitation from aqueous solution. Water reacts with metallic Cs by the reaction

The CsOH produced by Reaction 5 will concentrate at the hot end of the DECOR source, as will Cs₂O (that is, oxygen dissolved in the solution). CsOH is also more volatile than Cs₂O, the main oxygen-containing gas species in the vaporization process.

Figure 3 contains the data of Figure 1 for the equivalent O₂ calculated for a Cs/O solution with $x(\text{O}) = 0.24$ and observed over in the DECOR device with a bottom temperature of 500K. The top solid line is the equivalent O₂ pressure found with high

free H_2 , and the dashed line is calculated for a solution containing H_2O at an impurity level of $x(H_2O) = 0.01$. The agreement is good at 580 K; at the lower temperature, the effect correlated with H_2 is greater, roughly comparable to $x(H_2O) = .025$. In either case, small amounts of H_2O adsorbed on the Pt black can lead to high levels of the equivalent O_2 pressure.

Recommendations

The DECOR device could be modified to include a Mo powder (or a mix of Mo and Cs_2MoO_4 powders) in the low-temperature Cs reservoir to facilitate achievement of equilibrium and provide a controlled source of Cs and O for greater long-term stability.

Pt black can be purified by heating under a high vacuum at 600K, which may cause some sintering. After purification, the powder needs to be handled in a very good glove box or it will pick up water, H_2 and O_2 . Elimination of H_2O from the device can be facilitated by adding a small amount of Cs, equilibrating, heating, and removing the Cs, $CsOH$, and H_2 under vacuum.

Figure 1 Experimental and calculated equivalent oxygen pressures for a 500K DECOR bottom temperature. Solid line--experiment. Dashed line--Calculated for $X(O) = 0.24$.

Figure 2 Experimental and calculated equivalent Cs pressures for a 500 K DECOR bottom temperature. Solid line--experiment. Dashed line--calculated for $x(O) = 0.24$.

Figure 3 Experimental and calculated equivalent oxygen pressures for a 500 K DECOR bottom temperature. Lower group: Solid line--Experiment. Dashed line--Calculated for $x(O) = 0.24$. Upper group: Solid line--Experimental with high free hydrogen. Short dashes--Calculated for $x(O) = 0.24$, $x(H_2O) = 0.01$. Long dashes--Calculated for $x(O) = 0.24$, $x(H_2O) = 0.025$.

RASOR ASSOCIATES, INC.

HIGH EFFICIENCY THERMIONICS PROGRAM

HET-IV FINAL REPORT

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Vol. 2

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Westinghouse Electric Corporation
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**Materials Technology
Alternate Technologies Materials Engineering**

TITLE: Improved Stable Thermionic Converter Performance Through the Use of a Compact Porous Nickel Cesium-Oxygen Reservoir (U)

AUTHOR: D. R. Riley and C. S. Murray

DATE: DEC 5 1995

Abstract:

Stable oxygenated thermionic converter performance was observed for 360 hours in a cube converter. The cube converter consisted of a tungsten coated emitter, molybdenum collector and a porous oxidized nickel reservoir. The oxide film grown on the surface of the nickel pellet prior to converter operation provided a sufficient source of oxygen to sustain oxygenated performance. The impurities in the system caused a growth to form on the nickel pellet and a coating to form on the body and surface of the collector. This contamination could have been from the formation of carbon monoxide gas, which is known to increase the collector work function. After an extensive bakeout procedure prior to the redistillation of cesium into the converter to reduce contamination gas levels to below 10^{-8} Torr (especially carbon monoxide), the performance of the converter was stable and reproducible. Performance parameters (i.e., power density) were dependent on emitter, collector, reservoir and cube temperatures; impurity levels; and concentration of cesium and oxygen.

Summary:

One of the major objectives of the Bettis thermionic development program was to establish high efficiency, high power density thermionic performance through the use of an oxygenated cesium source. The Converter Advancement Program (CAP) was established at Bettis in May 1995 in order to transfer the knowledge gained in oxygenated cesium thermionic converter performance in the physical understanding experiments performed at Rasor Associates Inc. (RAI) to Bettis. The programs intent was to be a long-term, in-house initiative to both understand and control the cesium and oxygen vapor chemistry within an experimental converter with a goal of establishing reliable, reproducible converter operation. In order to meet this objective, several steps were taken:

- 1) A physical understanding experiment (PUE) cube converter was obtained from RAI and an existing converter test stand in the Advanced Energy Conversion Laboratory (AECL) was modified to allow cube installation. The cube converter (further to be specified as CAP-1) is a six-sided 304 stainless steel cube with demountable emitter, collector and reservoir flanges. In addition, CAP-1 contained an oxygen detector and a sapphire viewing window.
- 2) An appropriate reservoir material that could supply a reliable source of oxygen, while retaining its mechanical integrity, was developed. The RAI physical understanding experiments used porous platinum black pellets to wick the liquid oxygenated cesium mixture and showed extremely poor mechanical and thermal stability. Therefore, it was decided to use

an oxidized porous nickel reservoir as the cesium and oxygen source; this proved to be a reliable and stable source of oxygen, as nickel is chemically inert yet its oxide is not stable and will readily give up oxygen to liquid cesium.

- 3) The cesium contained in the external reservoir was carefully purified before distilling into the internal reservoir located in the cube. This was accomplished by exposing the cesium, at temperature, to an activated getter material. The purity of the cesium was verified using a residual gas analyzer (RGA).

After completion of the above tasks, two series of experiments were performed. In the first series of tests, the converter, which has an oriented tungsten emitter and a molybdenum collector, initially exhibited good performance followed by a degradation in electrical performance after approximately 10 hours with a subsequent increase in performance between 40 and 270 hours. After 270 hours, the electrical performance degraded due to the loss of cesium, with termination of the experiment after 400 hours. Residual gas analysis of the cube atmosphere showed a large amount of carbon monoxide contamination. At an emitter temperature of 1800K (2780°F), a collector temperature of 800K (980°F) and a reservoir temperature of 528K (491°F), the power density and barrier index were measured to be 4.0 W/cm² and 1.92 eV, respectively. These measured values result in a calculated electrode efficiency of 17.2% (using a correlated emissivity value of 0.16).

Before distilling cesium a second time, additional bakeout of both CAP-1 and the associated plumbing were performed. After reducing the carbon monoxide and other impurity gases (e.g., carbon dioxide, methane, water vapor, hydrogen, etc.) partial pressures to less than 10⁻⁸ Torr by additional bakeout for 400 hours, the emitter temperature was increased to 1950K (3050°F) for the final 24 hours of bakeout; the system then was prepared for a second cesium distillation.

After the second cesium distillation, stable converter performance for 360 hours was observed. Several system shutdowns, due to power failures in the laboratory, did not adversely affect the operation of the converter as depicted by the power density and efficiency returning to the values before the power outage. However, these power failures and continued operation at high temperature did cause the emitter heat shield to sag and come into contact with the emitter body resulting in the termination of the testing. At an emitter temperature of 1800K (2780°F), a collector temperature of 800K (980°F), a reservoir temperature of approximately 568K (563°F) and a gap spacing of 27 mils; the power density and barrier index were measured to be 5.8 W/cm² and 1.83 eV, respectively after 150 hours of operation. These measured values result in a calculated electrode efficiency of 20.2%. After 350 hours of operation, at the same temperatures, the power density and the barrier index were measured to be 6.6 W/cm² and 1.93 eV, respectively. These measured values result in a calculated electrode efficiency of 18.9%.

1.0 BACKGROUND

The Converter Advancement Program (CAP) was established in May 1995 and was intended to be a long-term, in-house initiative to both understand and control the vapor chemistry within an experimental thermionic converter with an objective of establishing reliable, reproducible converter operation. The program had the following objectives: 1) transfer to Bettis the Physical Understanding Experiment (PUE) technology utilized in the High Efficiency Thermionics (HET) programmatic experiments conducted at Rasor Associates, Inc. (RAI), 2) integrate PUE converter testing into the Advanced Energy Conversion Laboratory (AECL), 3) advance the current experimental design and utility of the cube converter to probe oxygen vapor chemistry, 4) develop a stable, reliable cesium/oxygen source, 5) advance the state-of-the-art performance of

thermionic converters, and 6) transfer knowledge gained from the experimental planar converters to prototypic cylindrical converters.

A concerted effort was initiated to bring on-line an operating cube converter, CAP-1, in the AECL by mid July, 1995. This involved assembling a cube converter with a chemically vapor deposited tungsten coating on molybdenum emitter, molybdenum collector and cesium/oxygen reservoir; modifying a test stand to accommodate a new converter geometry consisting of the converter, cesium pipeline tubulation, getter material, external cesium reservoir, and environmental heater; fabricating, testing and analyzing a new cesium reservoir material; and modifying the data acquisition system.

On July 17, 1995, the first J-V curve was acquired for an operating cube converter at Bettis. Experiments continued on the converter until September 8, 1995, when operation of the converter was terminated due to the failure of the emitter heat shield. Repairs to CAP-1 were not made due to NR redirection from thermionics research to thermophotovoltaic research.

The cube converter was operated after two separate cesium loadings, with the latter resulting in stable electrical operation for the duration of the experiment. During the second period of operation, the cube displayed excellent performance for 360 hours with a power density as high as 6.6 W/cm^2 , a barrier index as low as 1.75 eV and a calculated electrode efficiency of 20%, performance that is equal to or exceeds the best experimental thermionic converters anywhere in the world.

2.0 EXPERIMENTAL SETUP

The experimental setup (Figure 1) consisted of the vacuum system, data acquisition system, getter material, residual gas analyzer, and cube converter. Each of these areas are discussed in detail below. In addition, the preparation of the porous oxidized nickel pellet and the cesium distillation processes are outlined.

2.1 Vacuum System

The vacuum system consisted of two separate vacuum envelopes, each having the necessary pumps and plumbing to obtain background pressures in the low 10^{-8} Torr range. Figure 1 is a schematic representation of the main vacuum system. This system is the housing for the CAP-1 converter valving and environmental heater and is necessary to protect the heater elements from embrittlement which occurs in air at high temperature. The bell jar is water cooled and connected to a collar that contains 20 feedthroughs used for power, cooling, thermocouples, and connection to the cube vacuum system. A 250 l/s turbomolecular pump and a 40 cfm foreline pump are connected to the system through a electropneumatic swing gate valve. The valve closes automatically during a power outage to maintain the vacuum in the system. The pressure is monitored with a combination of thermocouple gauge and cold cathode ionization gauge.

Attached to the main vacuum system is the cube vacuum system which independently evacuates the volume of the cube converter and associated valving. In-line between the cube and the 250 l/s turbomolecular pump are two additional pieces of equipment. There is a cold cathode ionization gauge which is used to monitor cube pressure and a residual gas analyzer (RGA) used to monitor impurity gases in the cube. Details of the RGA are discussed in section 2.4.

Figure 2 shows the components that are contained in the belljar of the main vacuum system, which include the environmental heater, external cesium reservoir, gettering material, and three high temperature valves (cesium, pump out, and isolation valves).

2.2 Data Acquisition System

The data acquisition system is controlled via a Hewlett Packard Vectra 486/66XM computer and consists of an HP 3852A data acquisition and control system (DACS). The DACS contains both a low speed multiplexer (HP44708A), used to measure the thermocouple voltages and high speed multiplexer (HP44711B) used for the current versus voltage sweeps. The user operates in a window associated with the HP basic software.

The power rack contains the necessary DC power supplies for the system heaters. The parameters for the system heaters are listed in Table 1. Each heater is controlled by an output signal from a temperature controller that receives its input signals from the appropriate thermocouples mounted on the system. The getter and environmental heater have no temperature control. The desired temperatures are set from the HP basic control window and the controllers automatically adjust power until the desired temperatures are reached.

The current versus voltage sweeps are generated by applying one period of a 60 Hz signal to the collector. A stepdown transformer is used to transform the 120 VAC line voltage to 10 VAC, thus allowing higher currents to flow through the converter. The amplitude of the applied sinewave is controlled by a variac transformer. In addition, a potentiometer is connected in series to allow a variable load resistance.

2.3 Gettering Material and Operation

The pipeline tubulation contained a commercial getter used to remove gaseous impurities from the cesium; while the cesium is purchased as 99.999% pure of metal constituents, it can contain high levels of gaseous components. The getter material is a non-evaporable alloy of Zr/V/Fe (70%/24.6%/5.4%, respectively). To activate the getter, that is to make the surface of the material capable of capturing impurity molecules, the oxide film covering the surface of the getter first must be removed. This was accomplished by heating the getter under vacuum at 875K (1110°F) for 24 hours. After activation, the getter is capable of removing the following impurity gases: hydrogen, oxygen, carbon monoxide, carbon dioxide, nitrogen, methane and water. Once the getter was activated, the cesium in the external reservoir was purified by heating the cesium to 550K (536°F) while the getter was heated to 600K (621°F). The valve to the external cesium reservoir then was opened allowing for interaction between the getter and cesium vapor. Prolonged exposure of the vapor to the getter removed the gaseous impurities from the cesium.

2.4 Residual Gas Analyzer

A residual gas analyzer (RGA) was utilized to probe the gaseous species generated during experimental operations. The RGA chosen was a small mass spectrometer analyzer containing an array of nine quadrupoles (16 rods) built by Ferran Scientific. In this geometry, the quadrupoles can share adjacent rods; therefore, the size of this "micropole" analyzer is very small. Additionally, the path length of the analyzer is only one centimeter; allowing, the device to operate at pressures up to ten millitorr. The micropole analyzer was connected on the cube vacuum system (Figure 1); therefore, monitoring of the residual gases generated by the cesium, getter, and converter could be completed. The RGA is capable of

monitoring and acquiring pressure data as a function of time for up to eight different gaseous species during operation.

2.5 Cube Converter

Converter components were constructed and supplied to Bettis by RAI. Included as part of the converter were the stainless-steel cube, emitter with a CVD (chemical vapor deposition) coating of tungsten on molybdenum, emitter filament assembly, electropolished molybdenum collector, collector heating and cooling assembly, cesium/oxygen reservoir cup, reservoir heating and cooling assembly, sapphire window, and oxygen detector. Figure 3 illustrates both a photograph and schematic of the cube converter. Additionally, the pipeline tubulation was constructed at RAI and contained the external cesium reservoir, heater and valve, the getter and heater for extracting impurity gases, the pump out and isolation valves, and the structure to support the converter in the test stand (Figure 2). An environmental heater used to provide isothermal heating to the cube and tubulation also was provided to Bettis.

The converter components were cleaned with isopropanol prior to assembly. Each of the converter components attached to the six-sided stainless steel cube with copper conflat gaskets. The emitter and collector were attached to the cube with surfaces parallel at a gap spacing of 27 mils (this corresponded to the closest possible proximity physically attainable for this emitter-collector pair). The cesium/oxygen reservoir was connected to the cube below the emitter-collector pair to provide in-line vapor transport to the interelectrode gap. The sapphire window was oriented on the cube to permit visual inspection of the inside of the converter assembly during operation. The oxygen detector was mounted above the emitter-collector pair but was not operated during these experiments.

Prior to the installation of the pipeline tubulation into the test stand, cesium was loaded into the external cesium reservoir. The tubulation was taken into an inert atmosphere glovebox and the external cesium reservoir was detached. Approximately three grams of cesium was decanted into the reservoir which then was reattached to the tubulation. With the cesium valve closed to inhibit exposure of cesium to the atmosphere, the tubulation was removed from the glovebox. The pipeline tubulation was then mounted into the base of the test stand, the vacuum hardware attached to the pipeline flange, and the converter affixed to the tubulation.

2.6 Nickel Reservoir Material

Previous experiments conducted at RAI utilized a platinum black porous reservoir material in the converter as the source of oxygen and to contain cesium. Platinum black, by definition, is finely divided platinum powder with adsorbed oxygen on its surface. When cesium is distilled into the converter, it collects in the porous structure, assuming the cesium reservoir is maintained as the coldest region in the converter. During operation of the converter, the cesium scrubs the oxygen from the surface of the platinum. As the cesium and oxygen arrive at the top of the reservoir they evaporate based on the temperature of the platinum structure.

Platinum black was selected as the reservoir material because it was available with high surface area and because its adsorbed oxygen which could be scrubbed by cesium. However, platinum black is dimensionally unstable and sinters under its own weight at converter operating temperatures. Several alternative materials were investigated as potential reservoir structures. Porous yttria, alumina, scandia, molybdenum and nickel were

tested; yttria, alumina and scandia became discolored and embrittled in the presence of liquid cesium, while molybdenum and nickel maintained their structural integrity. The high integrity of molybdenum and nickel in the presence of liquid cesium is to be expected based upon the fact that both of these metals are virtually insoluble in liquid cesium. Porous nickel was selected because it has a lower thermal conductivity and does not form compounds with cesium such as cesium molybdate. In fact, nickel oxide should be readily reduced by liquid cesium.

A 23.5% dense (geometric density) porous nickel sample was supplied by Astro Met, Inc. Microstructural analysis indicated that the nickel sample had bi-modal porosity with approximately 50-100 μm interconnected pores and approximately 1-3 μm holes as illustrated in Figures 4(a) and 4(b), respectively. Energy dispersive spectroscopy indicated no metal impurities in the nickel.

Following characterization, the 0.35 inch diameter x 0.40 inch height porous nickel sample was annealed in a reducing atmosphere under two psi of argon/3% hydrogen at 773K (930°F) for 30 minutes. In order to provide a source of oxygen for the cesium, a film of nickel oxide was grown on the surface of the nickel as related in Equation 1:

The nickel pellet was oxidized under argon/4% oxygen at 673K (750°F) for 0.75 hours. Thermogravimetric analysis (TGA) indicated this level of oxidation corresponded to six atomic percent oxygen for 0.5 grams of cesium, assuming that 100% of the oxide film was reduced by the cesium during converter operation as shown in Equation 2:

The formation energy of NiO is 20 kCal less negative than Cs_2O at 550K (530°F); therefore, there is a significant thermodynamic driving force for cesium to reduce NiO to nickel to form cesium oxide compounds.

2.7 Calibrated Cesium Distillation

A four-point resistivity technique was used to measure accurately the quantity of cesium transferred during the distillation of cesium from the external cesium reservoir to the cesium reservoir cup in the converter. The quantity of cesium in the external cesium reservoir can be measured by passing current through two wires connected to either end of the external cesium reservoir, and measuring the voltage between two wires connected in between the current leads (Figure 2). The external reservoir was a stainless steel tube connected to the pipeline tubulation through the cesium valve. The electrical resistance of the tube is proportional to the geometry of the stainless steel tube (length and cross-sectional area) and to the combined electrical resistivities of the stainless steel and cesium liquid. The measured resistance along the length of the tube increases as the liquid cesium level decreases, which is proportional to the amount of cesium being transferred to the internal cesium reservoir. Figure 5 is a plot of the mass of cesium transferred as a function of time, which shows a transfer rate of cesium from the external reservoir to the internal reservoir of 13.4 mg/min.

3.0 EXPERIMENTAL RESULTS AND DISCUSSIONS

The experimental results consist of three operating periods. The first period includes initial operation of CAP-1 for 400 hours until cesium was lost from the CAP-1 volume with concurrent performance degradation. The second period consisted of additional bakeout and monitoring with the RGA of CAP-1 and the associated plumbing. The third period was a second distillation of cesium into CAP-1, with 360 hours of operation. The test was terminated because of the slippage of the emitter heat shield.

3.1 Experiments Following First Cesium Distillation

An existing test stand in the AECL, that was assembled for testing planar converters, was slightly modified for testing CAP-1. Once the modifications were complete, the valving, environmental heater and CAP-1 were installed in the main vacuum system. The necessary heater, cooling water, and thermocouple connections were made to the cube and the bell jar was placed onto the test stand. The cube and main vacuum systems were evacuated to 10^{-8} to 10^{-6} Torr. A quantity of 0.5 grams of cesium was distilled from the external cesium reservoir to the internal cesium reservoir. During this cesium transfer, the temperature of the emitter was 850K (1070°F), the collector was 600K (620°F), the internal cesium reservoir was 410K (280°F) and the external cesium reservoir was 500K (440°F) (the pump out valve remained closed during this procedure to inhibit cesium from escaping into the cube pumping system). Once 0.5 grams was transferred, the cube valve was closed and by visual inspection it could be seen that the distilled cesium had condensed in the internal cesium reservoir.

On July 17, 1995, initial operation of the converter resulted in promising results with a measured power density of 4.9 W/cm^2 and a barrier index of 1.85 eV, resulting in a calculated electrode efficiency of 18.9%. Subsequent operation of the CAP converter resulted in unstable performance and degradation after 270 hours of operation. During this operating period several experiments were performed and the following sequential observations were made:

- in addition to the emitter, collector, and reservoir temperatures affecting the performance of the converter, the temperature of the cube and cube components affect the performance parameters;
- the outside of the nickel pellet was gold in color while the top middle region was black, as though cesium was preferentially evaporating from the top center of the pellet due to the temperature gradient;
- shortly after the initial operation of the cube, a black mass developed on the top of the nickel pellet;
- the collector surface and the body of the collector became coated with a black substance;
- the performance of the cube substantially decreased.

Due to the above observations, it was decided to open the isolation valve to perform mass spectroscopy experiments on the gases in the cube envelope. The RGA indicated a large carbon monoxide peak (28 amu) and a slight increase from baseline of the carbon dioxide (44 amu) and methane (16 amu) peaks. From the discoloration on the collector and the

mass spectroscopy results, we speculate that carbon could be the main contaminant that lead to the performance degradation. Since it is known that carbon impurities precipitate from nickel at 588K (600°F) in the form of graphite, this graphite on the nickel surface could react with oxygen in the gas phase to form CO and the CO could subsequently be reduced on colder surfaces to result in carbon deposition.

After 270 hours, three mass spectroscopy experiments had been completed, and performance had degraded by 20%. Testing was terminated after a total of 402 hours because cesium was lost from the converter envelope (the gold color on the pellet vanished) and performance had decreased by 90%. The cesium likely escaped from the cube during the mass spectroscopy experiments when the isolation valve was opened and during converter operation through the isolation valve seat (previous experiments at RAI indicated that the Stellite seat on the valve was suspect to cracking when over-tightened).

The unstable performance during operation of this period makes analysis of the cube data difficult; therefore analysis of performance of the cube is detailed in the section outlining the second distillation. However, Figure 6 shows a comparison of current versus voltage curves after 250 hours of operation and after 400 hours of operation (loss of cesium). As can be seen, performance degraded substantially and testing was terminated.

3.2 Intermediate System Bakeout Procedures

After the first cesium distillation experiments were terminated, vigorous efforts were taken to reduce the amount of gaseous impurities in the system. To meet this end, additional bakeout of the cube components (i.e., emitter, collector, etc.), valving pipeline and vacuum plumbing were performed. Mass spectroscopy experiments were carried out on the gases evolving from these hardware components as they were heated to remove impurity gases (i.e., hydrogen, carbon monoxide, carbon dioxide, oxygen and methane). The emitter was maintained at 2730°F (24 hours at 3090°F), the collector was maintained at 1020°F (24 hours at 1290°F) and the nickel reservoir was maintained at 570°F (24 hours at 750°F) for 400 hours; the background pressures of all residual gases dropped to below 2×10^{-8} Torr. After a second activation of the getter, the cesium in the external cesium reservoir was purified for a second time with no indication of impurity gases from the residual gas analyzer with partial pressures less than 2×10^{-8} Torr. A second distillation of 0.5 grams of cesium from the external cesium reservoir into the internal cesium reservoir was completed following the procedure described above (Figure 5).

3.3 Experiments Following Second Cesium Distillation

Following the redistillation of the cesium into the cube, the isolation valve was closed. Subsequent "burpings" of the cube to monitor impurity gases were not performed during the second set of experiments. The converter operated for an additional 360 hours before testing was terminated due to slippage of the emitter heat shield. The following observations were made during this period of CAP-1 operation:

- stable performance was observed throughout the entire 360 hours of operation;
- the system suffered several thermal shocks due to power failures in the cooling system and power controllers, during which the converter components cooled down rapidly to room temperature; however, each time the performance returned to its pre-shock level;

- the molybdenum emitter heat shield slowly cracked around its circumference about one inch from the emitter surface; as it broke during a period of about two weeks, the shield slowly dropped down and covered the black body hole used to make temperature measurements on the emitter;
- there was no additional growth on the top of the nickel pellet; possibly indicating that all of the impurities that led to the initial growth had segregated during the first series of experiments;
- the collector surface appeared to be cleaner than at the end of the first series of experiments; this may be due to ion bombardment during operation.

Figures 7-14 are experimental results of CAP-1 after the second distillation of cesium into the converter. Figures 7-9 are cesium temperature families after 150 hours of operation for current versus voltage, power density and efficiency, respectively, at cesium reservoir temperatures of 528K (491°F), 538K (509°F), 548K (527°F), and 558K (545°F). It should be noted that the thermocouple is located in the bottom of the reservoir cup (Figure 3) and could be quite lower than the temperature at the top of the nickel pellet. Figures 10-12 are similar cesium families after 350 hours of operation, just prior to failure of the emitter heat shield. Table 2 summarizes the conditions for Figures 7-12. The emitter temperature for both sets of data was 1800K (2780°F). As indicated in Table 2, the barrier index is generally higher after 350 hours when compared to the 150 hour data, although the power density is also higher (6.7 W/cm² compared to 5.8 W/cm²). The higher barrier indices result in lower calculated electrode efficiencies. This increase in the barrier index could be due to the increased cube temperature, which may be resulting in outgassing of condensed contaminants from the cube walls and a subsequent increase in the collector work function. The cube temperature is the average of four thermocouple readings from Type K thermocouples mounted at different locations on the external faces of the cube. Unfortunately, the emitter heat shield failed before parametrics could be performed to narrow the causes of this phenomenon.

Figures 13 and 14 are the measured power density and calculated electrode efficiency, respectively, versus the cesium reservoir temperature for the 360 hour test after the second cesium distillation. The power density data shown in Figure 13, shows a very distinct trend of higher power density as the cesium reservoir temperature is increased, with a slight asymptotic behavior as the temperature approaches 580K (584°F). This trend is a little surprising because the interelectrode gap is approximately 27 mils (it might be slightly larger due to different thermal expansion of the cube components) and at 580K (584°F), which corresponds to a cesium vapor pressure of 2.2 Torr, the Pd factor is 59.4 mil-Torr. The Pd factor is a measure of how effectively electrons can flow from the emitter to the collector and optimum values for cesium only converters are typically between 20-30 mil-Torr). The increased power density could be due to the increased vapor pressure of oxygen resulting in a higher emitter bare work function and increased emission current. When compared to Figure 14, a plot of the efficiency versus cesium reservoir temperature, a maxima occurs at a temperature of approximately 551K (532°F); this corresponds to a cesium vapor pressure of 1 Torr. This temperature results in a Pd factor of 27 mil-Torr which is in the range of optimized cesium only converters. Therefore, the increased cesium vapor pressure might be increasing the arc drop, which would show up as an increase in the barrier index.

Figure 15 is an efficiency versus power density plot under similar conditions for both the first and second cesium distillations. As illustrated in Figure 15, after additional bakeout of the cube components, both the power density and calculated electrode efficiency increased for

the same operating conditions, which likely is a result of a "cleaner" collector and therefore a lower collector work function.

The final data presented in Figure 16 is the barrier index versus time for both cesium distillations. The initial degradation of performance occurred up to about 40 hours of operation with an increase in the barrier index from 1.85 eV to 2.15 eV. It has been reported in the literature, that carbon monoxide contamination on the order of 10^{-5} Torr can result in increases in the collector work function of 0.29-0.3 eV. After 40 hours the converter seemed to be "self-cleaning" with a steady decrease in the barrier index to 1.92 eV at 270 hours of operation. At this time it is suspected that cesium began leaking from the cube and performance began to decrease with termination occurring after 400 hours. The solid line represents the 400 hours of additional system bakeout. After the second cesium distillation, the barrier index was approximately 1.8 eV and remained at this value until the termination of the testing 360 hours later.

4.0 CONCLUSIONS

Stable oxygenated thermionic converter performance was observed for 360 hours in a cube converter. A porous nickel pellet was used to provide a stable source of cesium and oxygen to the interelectrode gap to increase converter power density and efficiency. The oxide film grown on the surface of the nickel pellet prior to converter operation provided a sufficient source of oxygen to sustain oxygenated performance. The impurities in the system caused a growth to form on the nickel pellet and a coating to form on the body and surface of the collector. After an extensive bakeout procedure prior to the redistillation of cesium into the converter to reduce contamination gas levels to below 10^{-8} Torr (especially carbon monoxide), the performance of the converter was stable and reproducible. During the second period of converter operation, a barrier index was maintained near 1.8 eV, with a calculated electrode efficiency of 20.2% for a measured power density of 5.8 W/cm².

5.0 CHECKS AND REVIEWS

Technical checking and review of this report was accomplished by cognizant management and technical personnel of the Materials Technology and Advanced Technology Applications activities.

6.0 ACKNOWLEDGMENTS

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Executive Summary of WAPD-MT(TME)-475

Purpose: The Converter Advancement Program (CAP) was established in May 1995 and was intended to be an in-house initiative to both understand and control the vapor chemistry within an experimental converter towards establishing reliable, reproducible converter operation.

Results: The experimental results consist of three operating periods. The first period includes initial operation of CAP-1 for 400 hours until cesium was lost from the CAP-1 volume with concurrent performance degradation. The second period consisted of additional bakeout and monitoring with the RGA of CAP-1 and the associated plumbing. The third period was a second distillation of cesium into CAP-1, with 360 hours of operation. The test was terminated because of the slippage of the emitter heat shield.

- The first period exhibited a degradation in performance after approximately 10 hours with a subsequent increase in performance between 40 and 270 hours. After 270 hours, the performance degraded due to the loss of cesium with termination of the experiment after 400 hours. Exposure of the cube vapor space to the RGA showed a large amount of carbon monoxide contamination. At an emitter temperature of 1800K (2780°F), a collector temperature of 800K (980°F) and a reservoir temperature of 528K (491°F), the power density and barrier index were measured to be 4.0 W/cm² and 1.92 eV, respectively. These measured values result in a calculated electrode efficiency of 17.2% (using a correlated emissivity value of 0.16).
- During the second period additional bakeout of both CAP-1 and the associated plumbing were performed. After reducing the carbon monoxide and other impurity gases (e.g., carbon dioxide, methane, water vapor, hydrogen, etc.) partial pressures to less than 10⁻⁸ Torr by additional bakeout for 400 hours, the emitter temperature was increased to 1950K (3050°F) for the final 24 hours of bakeout; the system then was prepared for a second cesium distillation.
- During period three, after the second cesium distillation, stable converter performance for 360 hours was observed. Several system shutdowns, due to power failures in the laboratory, did not adversely affect the operation of the converter as depicted by the power density and efficiency returning to the values before the power outage. However, these power failures and continued operation at high temperature did cause the emitter heat shield to sag and come into contact with the emitter body resulting in the termination of the testing. At an emitter temperature of 1800K (2780°F), a collector temperature of 800K (980°F), a reservoir temperature of approximately 568K (563°F) and a gap spacing of 27 mils; the power density and barrier index were measured to be 5.8 W/cm² and 1.83 eV, respectively after 150 hours of operation. These measured values result in a calculated electrode efficiency of 20.2%. After 350 hours of operation, at the same temperatures, the power density and the barrier index were measured to be 6.6 W/cm² and 1.93 eV, respectively. These measured values result in a calculated electrode efficiency of 18.9%.

Converter Advancement Program Experimental Data (U)

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Table 1

Power Supply Ratings for CAP-1 Component Heaters

Heater Component	Heat Transfer Mechanism	Power Supply Rating
Emitter	Radiation Electron Bombardment	600 W (30 V, 20 A) - AC 1200 W (600 V, 2 A) - DC
Collector	Conduction	540 W (60 V, 9 A) - DC
Internal Cesium Reservoir	Conduction	540 W (60 V, 9 A) - DC
Getter	Conduction	540 W (60 V, 9 A) - DC
Environment	Radiation	960 W (120 V, 8 A) - DC
External Cesium Reservoir	Conduction	540 W (60 V, 9 A) - DC

Table 2

Maximum Output Parameters for 2nd Cesium Distillation in CAP-1

Maximum Output After 150 Hours of Operation						
T_E (K)	T_C (K)	T_{Cs} (K)	T_{cube} (K)	Power Density (W/cm ²)	Efficiency (%)	Barrier Index (eV)
1802	862	528	729	3.6	17.7	1.75
1801	861	538	731	4.5	19.3	1.78
1801	861	548	732	5.2	20.2	1.80
1801	851	558	733	5.7	20.2	1.83
1800	834	567	733	5.8	20.3	1.83
Maximum Output After 350 Hours of Operation						
T_E (K)	T_C (K)	T_{Cs} (K)	T_{cube} (K)	Power Density (W/cm ²)	Efficiency (%)	Barrier Index (eV)
1799	845	528	736	4.0	18.3	1.80
1800	817	538	745	4.9	19.6	1.83
1801	851	548	746	5.7	20.2	1.85
1799	846	558	751	6.4	19.9	1.89
1800	850	568	761	6.6	18.9	1.93
1801	836	578	759	6.7	17.5	1.99

Figure 1

Schematic of the Main Vacuum System

Figure 2

Schematic of CAP-1 Support Hardware

Figure 3

Photograph and Schematic of CAP-1 Showing Emitter, Collector, Nickel Pellet and Oxygen Detector

(a)

(b)

Figure 4

Scanning Electron Micrographs of Nickel Pellet Illustrating Bimodal Porosity at a) 100x Magnification and b) 1000x Magnification

Figure 5

Rate of Cesium Transfer from the External Reservoir to the Internal Reservoir
[$T_{\text{Cext}} = 500\text{K}$ (440°F) and $T_{\text{Cint}} = 410\text{K}$ (280°F)]

Figure 6

Current Versus Voltage for 1st Cesium Distillation Showing Loss of Cesium

Figure 7

Cesium Family of Current Versus Voltage 150 hours After 2nd Cesium Distillation
[$T_e = 1800\text{K}$ (2780°F), $T_c = 860\text{K}$ (1088°F) and $T_{\text{cath}} = 730\text{K}$ (854°F)]

Figure 8

Cesium Family of Power Density Versus Voltage 150 Hours After 2nd Cesium Distillation
[$T_e = 1800\text{K}$ (2780°F), $T_c = 860\text{K}$ (1088°F) and $T_{\text{cube}} = 730\text{K}$ (854°F)]

Figure 9

Cesium Family of Calculated Efficiency Versus Voltage 150 Hours After 2nd Cesium Distillation
[$T_E = 1800\text{K}$ (2780°F), $T_C = 860\text{K}$ (1088°F) and $T_{\text{cube}} = 730\text{K}$ (854°F)]

Figure 10

Cesium Family of Current Versus Voltage 350 hours After 2nd Cesium Distillation
[$T_E = 1800K$ (2780°F), $T_C = 820-875K$ (1016°-1115°F) and $T_{cube} = 760K$ (908°F)]

Figure 11

Cesium Family of Power Density Versus Voltage 350 Hours After 2nd Cesium Distillation
[$T_E = 1800\text{K}$ (2780°F), $T_C = 820\text{--}875\text{K}$ (1016°–1115°F) and $T_{\text{cath}} = 760\text{K}$ (908°F)]

Figure 12

Cesium Family of Calculated Efficiency Versus Voltage 350 Hours After 2nd Cesium Distillation
[$T_E = 1800\text{K}$ (2780°F), $T_C = 820\text{-}875\text{K}$ (1016°-1115°F) and $T_{\text{cubo}} = 760\text{K}$ (908°F)]

Figure 13

Measured Power Density Versus Cesium Reservoir Temperature [2nd Cesium Distillation
 $T_g = 1800\text{K}$ (2780°F), $T_c = 805\text{-}875\text{K}$ ($989^\circ\text{-}1115^\circ\text{F}$) and $T_{\text{cube}} = 725\text{-}765\text{K}$ ($845^\circ\text{-}917^\circ\text{F}$)]

Figure 14

Calculated Efficiency Versus Cesium Reservoir Temperature After 2nd Cesium Distillation
[$T_E = 1800K$ (2780°F), $T_C = 805-875K$ (989°-1115°F) and $T_{cubo} = 725-765K$ (845°-917°F)]

Figure 15

Measured Power Density Versus Calculated Efficiency [$T_s = 1300K$ (2780°F), $T_o = 558K$ (545°F),
 $T_c = 850K$ (1070°F) and $T_{\text{min}} = 73K$ (854°F)]

Figure 16

Measured Barrier Index Versus Time

[$T_F = 1800K$ (2780°F), $T_C = 528K$ (491°F) and $T_C = 800-850K$ (980°-1070°F)]