GAS PHASE AND SURFACE PHENOMENA OBSERVED WITH A SEEDED PLASMA*

A. C. Pinchak and E. E. Zukoski

Daniel and Florence Guggenheim Jet Propulsion Center
California Institute of Technology
Pasadena, California

This paper describes and discusses some recent experiments conducted with low-temperature seeded plasmas. The plasma was obtained by mixing potassium vapor with arc-heated argon. The experiments indicated two modes of steady, stable current conduction between the electrodes. In the first mode, the effect of gas phase phenomena predominated in fixing the current.

Under certain conditions, a transition to a second mode of operation occurred. In this mode, the current was found to be thermionically limited, and was determined solely by electrode surface effects.

A comparison between the observed voltage-current characteristics and two current conduction theories is presented. Analysis of electrode temperature data indicated that the chief heat transfer mechanism was the penetration of the surface work function barrier as electrons entered or left the surface.

Introduction

Considerable interest has developed during the past few years in the use of cool, seeded plasmas in MHD power generators and plasma accelerators. The present experiments were carried out to determine the influence of some gas phase and surface phenomena in fixing the current-voltage and electrode heat transfer characteristics for such devices.

To keep the experiments as uncomplicated as possible, measurements are made in a simple conduction experiment with no applied magnetic field. The plasma is argon gas seeded with potassium, and the electrodes are tungsten which is allowed to reach high temperatures. The electrodes are arranged coaxially with the gas velocity parallel to the electrode axis. The primary measurements are electrode voltage drop, current, and temperature.

The data are analyzed to determine the dominant phenomena concerning electron emission from high temperature electrodes, gas phase conductivity, and electrode heat transfer.

Apparatus

The apparatus used to supply an ionized gas to a test area is shown schematically in figure 1. A simple arc-jet heater is used to heat the larger portion of the argon gas flow. This main flow is then combined with a smaller, secondary flow of argon which has been passed through a potassium boiler and is saturated with potassium vapor. After mixing, the combined flow is passed through a mixing chamber before entering one of a number of test sections.

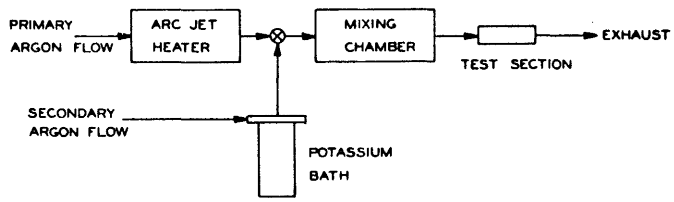

Fig. 1
Schematic Diagram of Experimental Apparatus

The concentration of potassium in the flow which results from the combination of these two streams is fixed by controlling the boiler temperature and secondary argon flow rate. Measurements of the potassium concentration in the resulting stream indicate that the concentration is within 10 per cent of the calculated flow rates.

At the test section entrance, the plasma pressure was maintained at one atmosphere during all the tests and the argon flow rate used during most of the tests discussed here was 2.4 grams/sec. For test section pressure and temperatures used, the mass flow corresponds to a speed of about 400 ft/sec, or a Mach number of about 0.10. The plasma temperature was varied between 1400°K and 2500°K and the potassium seed concentration was set between zero and 1.3 mole per cent. Temperature measurements of the gas at the end of the test section show that the temperature profile there is flat and falls off 5 to 10 per cent as the wall is approached.

The test section used for most of the experiments was a coaxial arrangement shown in detail in figure 2. The inner or axial electrode was made of tungsten wire with a diameter of either 0.04 or 0.08 inches. During a few experiments, two central electrodes were used; by switching one or both into the electric current, the effective electrode surface area could be changed by a factor of two. The outer electrode was a stainless steel cylinder with an inside diameter of 0.370 inches, and was 0.563 inches long; the inner electrode was uninsulated over a similar length. The inner electrode temperature is not controlled independently, but is primarily fixed by a balance between radiant cooling, heat transfer due to the flow of electrons, and forced convection from the gas.

* This work was performed under the auspices of the U. S. Air Force Office of Scientific Research under Contract No. AF 49(638)758.

The coaxial electrode arrangement has the advantage that large current densities can be obtained from the inner electrode with small power requirements, and the arrangement insures that current is conducted through the plasma flow rather than through gas boundary layers or other spurious paths which may develop on the insulator surfaces of two-dimensional electrode configurations. In addition, the potassium concentration and temperature of the gas encountering the inner electrode surface is that of the main flow and has not been changed by contact with the duct walls. The principal disadvantage of this configuration is that the current density, and hence other properties of the flow, change rapidly with distance normal to the axial electrode surface.

The electric circuit used for the tests is shown schematically in figure 2. A variable ballast resistor is used in series with the electrodes and battery to control the current. With this arrangement, the voltage drop across the electrodes is a function of the current and is given by the difference of battery potential and the ballast resistor potential drop.

During the course of the experiments, measurements were made to determine the gas enthalpy, potassium seed fraction, electrode voltage drop, and current temperature and gas temperature. The gas flow and electric instrumentation are conventional; wall temperatures were measured with an optical pyrometer when thermocouples were not applicable. Mean gas flow temperature measurements were obtained by an enthalpy balance which was occasionally checked by use of sodium line reversal measurements. Errors in gas temperature determination are probably less than 5 per cent.

Experimental Results

The experiments indicate that two quite different modes of operation exist for steady current conduction. These two regimes are illustrated by the data of figure 3. In the first, or 'normal', mode, the current is a monotonic function of the applied voltage. However, under certain conditions, the mode of operation can undergo a transition to a second mode in which the current is independent of the applied voltage. Experiments concerning these two modes and the interpretation of the experiments will be discussed separately below.

Normal Mode.

The general features of the voltage-current characteristic and center electrode temperature are illustrated by the examples shown in figures 3, 4, and 5 for the coaxial geometry illustrated in figure 2. For zero current, the inner electrode is always slightly negative (1 volt or less); as the applied voltage is increased, the electron flux from the central electrode increases slowly at first and then more rapidly for higher voltages. For high currents, the curves have very small slopes and are almost flat. The same features are present for negative voltages, and the two branches of the curve are quite similar. The data of figure 5 show that as the temperature of the gas increases, the voltage required to obtain a given current decreases.

For positive voltages, the center electrode temperature drops slightly as current increases, and then may increase slightly for high currents. However, for negative voltages, the temperature increases rapidly and continues to do so. In these experiments, the outer electrode operated at temperatures in the range 800°K to 1300°K.

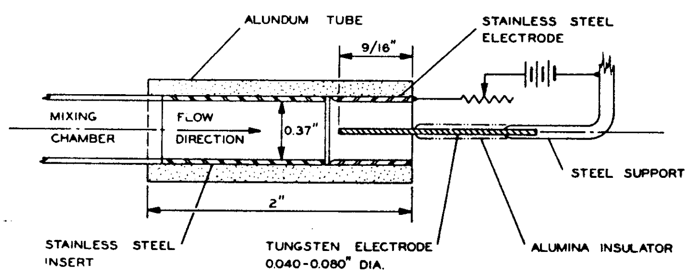

Fig. 2 Coaxial Electrode Configuration

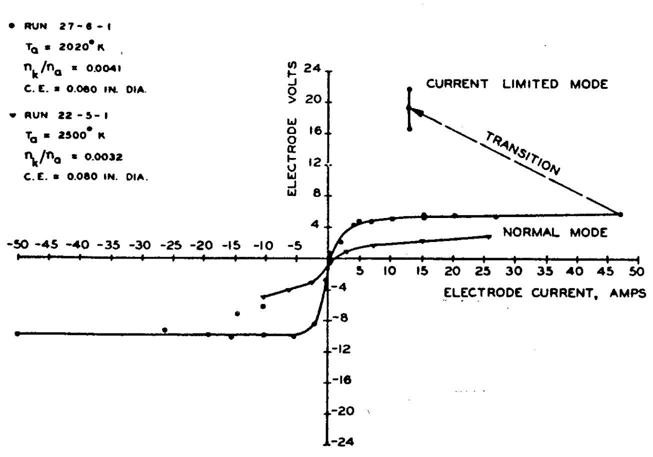

Fig. 3 Typical Voltage-Current Characteristics

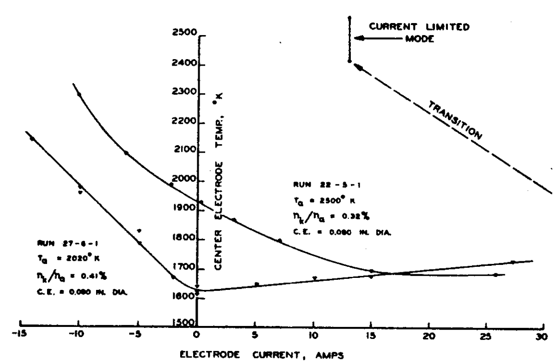

Fig. 4 Center Electrode Temperature vs. Current

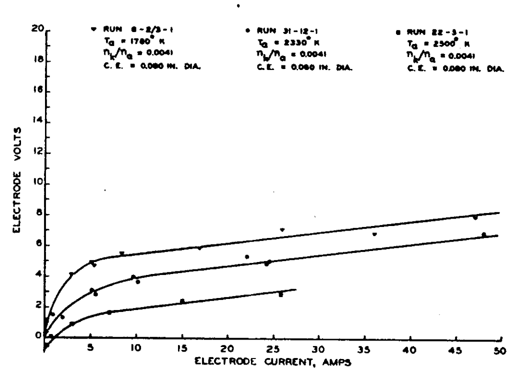

Fig. 5 Current-Voltage Characteristics

In making any interpretation of current-voltage data, such as that presented in figures 3 and 5, one of the primary difficulties is that of distinguishing between voltage drops which occur in the gaseous conductor and voltage drops which occur across sheaths at solid-gas interfaces. This problem is further complicated by the lack of either experimental or theoretical information concerning the electron emission by the thermionic process from electrodes in a potassium-seeded gas. This difficulty was in part removed by making qualitative use of the data obtained by Taylor and Langmuir[1] with cesium vapor.

In the present case, analysis of Taylor and Langmuir's results obtained with cesium and gross extrapolation of the experimental measurements of Killian[2] obtained with potassium suggests that electron emission by a thermionic process is sufficient to furnish current densities of at least 10 amps/cm^2. If this mechanism is responsible for electron emission, then the sheath potentials should be restricted to voltage drops corresponding to a few times the thermal energies of electrons in the gas, and hence should be much less than a volt for most conditions.

The suggestion that electron emission is by the thermionic process and that sheath potentials are small is supported by the small potential observed for the circuit at zero current. A second check is obtained by examination of the voltage changes produced by changing the electrode surface area during a test. It was found that doubling the electrode surface area produced a very small increase ($\Delta v = 0.1$ volts) in voltage for a given current flow. Since large current density changes should have an appreciable effect on sheath potentials and should have little effect on the gas-phase voltage drop, these results indicate that the sheath voltage drop is small compared with the potential applied across the electrodes as long as the applied potential is more than a few volts. Hence, the applied voltage drop is primarily produced by the resistance of the gaseous conductor.

If this conclusion is correct, then the conductivity of the gas can be estimated from the values of current and voltage obtained experimentally. For large current densities, the observed values of conductivity are much larger than calculated equilibrium values. However, as current density approaches zero, the values approach more closely to the theoretical values. Unfortunately, at zero currents where non-equilibrium effects may be negligible, sheath effects are important, and hence conductivity measurements at very small voltages are suspect. To avoid this difficulty, values of V/I obtained for $V \geq 2$ volts were extrapolated to zero current, and estimates of the conductivity of the gas were obtained from the resulting values. This process gives values of conductivity that agree with the theoretical calculated equilibrium values within a factor of four. Examples are shown in Table I.

The dependence of the current-voltage characteristic on potassium seed concentration was determined for a number of gas temperatures and current levels. A typical plot is shown in figure 6; here, ratios of (V/I) normalized by the minimum values are given as a function of the mole fraction of potassium. The minimum value was found to occur for $(n_K/n_A) = 0.003 + 0.0005$ for a wide range of gas temperatures and three different electrode configurations. If we assume that the gas is a pure mixture of argon and potassium and identify the (V/I) ratio with the resistance of the

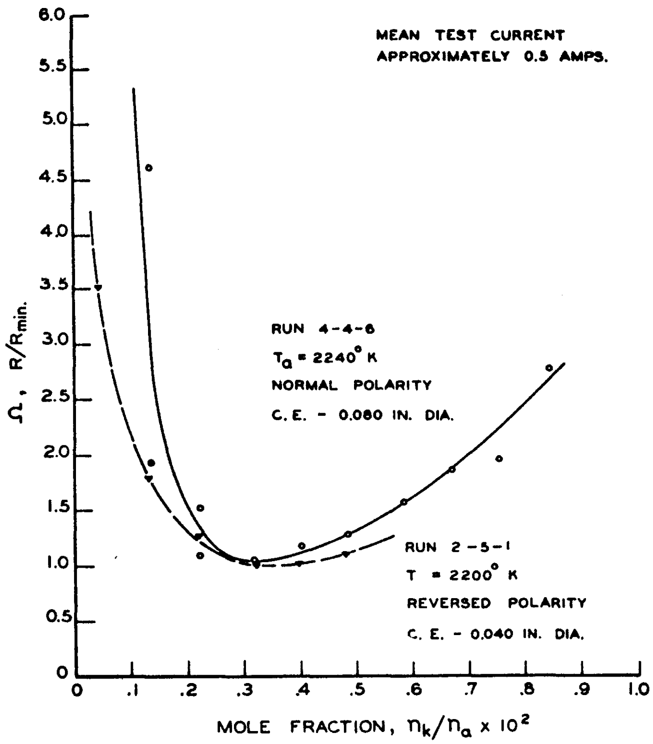

Fig. 6 Non-dimensional Resistance vs. Potassium Mole Fraction

conducting gas element, then the value of n_K/n_A at the minimum should be equal to the ratio of the average value of the momentum cross sections of the electrons in argon to that in potassium, i.e., $\bar{Q}_A/\bar{Q}_K$. The value of this ratio of cross sections is not known well for electrons at a temperature of about 2000°K. Recent estimates of the average cross sections[3] ($\bar{Q}_K = 250 \times 10^{-16}$ cm^2, $\bar{Q}_A = 0.7 \times 10^{-16}$ cm^2) lead to $n_K/n_A \approx 0.0028$, which is very close to the observed value. However, use of other reported values for $\bar{Q}_K$ and $\bar{Q}_A$ gives values of the cross section ratios which range from 0.0007 to 0.02; cf. references 4 and 5. Thus, the interpretation of the observed minimum may be open to some question. Nevertheless, the existence of a well-defined minimum in the conductivity again indicates that in the normal mode, the measured voltage drop across the electrodes is primarily due to gas phase rather than surface phenomena.

The current-voltage characteristic shown in figures 3 and 5 is highly non-linear, and this non-linearity apparently cannot be explained on the basis of changes in sheath potential or other surface phenomena. It remains then to find an explanation based on gas phase phenomena. Two models were investigated; the first, an equilibrium model, depends on the fact that for a seeded plasma, the conductivity is a very sharp function of the gas temperature for certain ranges of the seed concentration and gas temperature. Hence, Joule heating of the gas can produce large changes in conductivity of the gas and thereby produce a non-linear current-voltage characteristic. The second model, that suggested by Kerrebrock[6], is based on the fact that the electron temperature may be considerably greater than the gas temperature when the current density is sufficiently large.

The high electron temperature leads to a high electron density and hence a higher conductivity. Since the magnitude of the non-equilibrium effect depends strongly on current density, a highly non-linear current-voltage characteristic is to be expected.

Current-voltage characteristics calculated by the equilibrium model and for conditions typical of those found in the present experiments are compared in figure 7 with one set of experimental data. For the calculations, it is assumed that the conductivity is an exponential function of the temperature. The equilibrium model predicts that as the current increases the voltage approaches an asymptotic value. The voltage reaches this asymptotic value when the power added to the gas, VI, is about 20 per cent of the enthalpy convected by the gas. In addition, when VI is about 8 per cent of the convected enthalpy, the current-voltage characteristic becomes non-linear.

Comparison of theory and experimental data in figure 7 shows that the equilibrium theory gives the correct general shape of the current-voltage curve, but also shows that non-linearities occur for power addition levels somewhat larger in theory than in experiment, and that the maximum voltage obtained experimentally is between one-half and two-thirds of the predicted value. Thus, although the effects of Joule heating on conductivity are certainly important at high currents, the observed non-linear features which occur at small voltages must be produced by another agency.

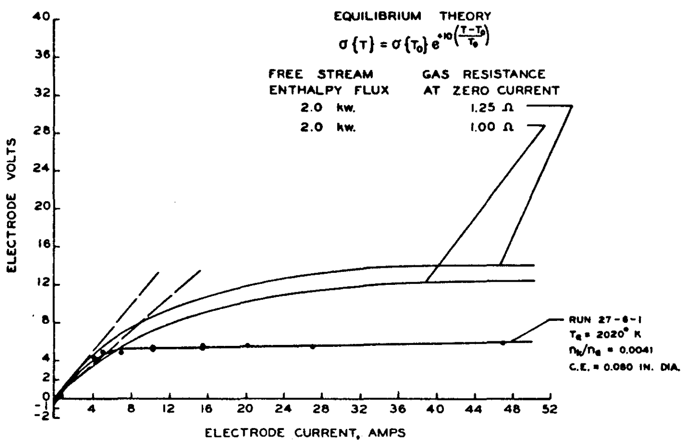

Fig. 7 Voltage-Current Characteristic, Equilibrium Theory

The non-equilibrium theory of Kerrebrock[6] has been applied to the coaxial geometry of the present experiments. One sensitive comparison between this theory and the data is obtained by comparing values of $(d\ln V/d\ln I)$. This is done for a number of temperatures in Table II. It is apparent from these examples that the slope obtained for the low temperature agrees well with the predicted slope, but that the values obtained for higher temperatures do not agree. In addition, the theoretical values have not been corrected for the effects of Joule heating and hence are too high. Thus, the agreement between experiment and the non-equilibrium theory is not very good even at low temperatures.

A more critical check on the two models was attempted by examining the effects of adding nitrogen and helium to the flow. Both gases tend to decrease the conductivity due to their large scattering cross sections; however, nitrogen should have an enhanced effect because it will tend to reduce the electron temperature more than helium. The results for helium indicate that equilibrium changes could produce the observed resistance changes; those for nitrogen, that non-equilibrium or some other effect would be required to explain the results.

However, strong evidence that some non-equilibrium phenomena are present is given by the fact that current densities of 200 amps/cm^2 have been observed at the cathode surface and in the gas, whereas the random electron flux in the gas (computed from equilibrium theory) is only about 7 amps/cm^2 at 2000°K. Hence, some non-equilibrium phenomena must play an important role in fixing the conductivity.

Transition Phenomena.

If the voltage applied across electrodes operating in the normal mode is increased, a limiting value of the current flow is finally reached. At this condition, the current density suddenly decreases and the electrode temperature increases greatly. A further increase in the voltage has little effect on the current density or electrode temperature.

The mechanism for this transition is thought to be as follows. In the normal current mode, the electron flux emitted by thermionic processes from the cathode is greater than the required current flow; a small voltage adjustment in the electrode sheath serves to return a large enough electron flux to the electrode to make the net flux equal to the desired electron current. However, at the transition point, the net current flux is just equal to the thermionic current limit. If an attempt is then made to increase the voltage drop across the electrodes, the current and hence the voltage drop in the gas cannot increase further. As a result, the applied voltage increase must appear as an increase in the potential drop across the sheath. However, as the sheath voltage drop increases, the energy of electrons accelerated by the sheath potential and moving into the gas increases, and consequently, the energy given up by these electrons to the gas near the sheath boundary increases. Finally, the heated gas will return a substantial portion of the energy deposited by the electrons to the electrode by a convection mechanism. Thus, the voltage increase leads to an increase in electrode temperature.

As the electrode temperature increases, the fraction of electrode surface covered by potassium decreases, and therefore, the work function of the surface will increase and the thermionically limited current will decrease. But a decrease in current means that a larger voltage is applied across the electrodes, since the voltage drop across the ballast resistor is decreased. Thus, a larger voltage appears across the sheath, the gas heating is increased, and the current is reduced further. These heating effects are augmented by the reduction in electrode cooling which occurs as the current is reduced and by the rapid rise in the argon cross section for electrons as the electron energy rises above a volt.

The argument suggested here indicates that the current can be decreased suddenly by an appreciable amount. The new equilibrium point will be reached when the increase in energy radiated from the electrode is sufficient to balance the increased convective heat transfer.

If the suggested transition model is correct, current at transition from the normal mode should increase with increasing seed concentration and decreasing electrode temperature. Both trends have been verified experimentally.

Current Limited Mode.

Typical values of voltages and central electrode temperature for the transition condition and for the current limited mode are shown in figures 3 and 4. Data such as this show that in the second mode of current conduction, the current is independent of the voltage, and suggest that it is given by the thermionically limited electron flux from the surface. Thus, the current density is fixed by surface rather than gas phase phenomena.

This contention is supported by comparing the current flux from one central electrode with that obtained from two similar electrodes. Doubling the electrode area doubled the current flux in all cases, as long as both electrodes operated in the second mode.

The effects of changing the concentration of potassium on both normal and transition current are shown schematically in figure 8. In the normal mode, the voltage drop for a given current decreases with increasing seed concentration until the minimum conductivity of the gas is reached, and then the voltage drop increases again as the conductivity decreases. In contrast, both the normal mode current at transition and the second mode current are monotonically increasing functions of concentration.

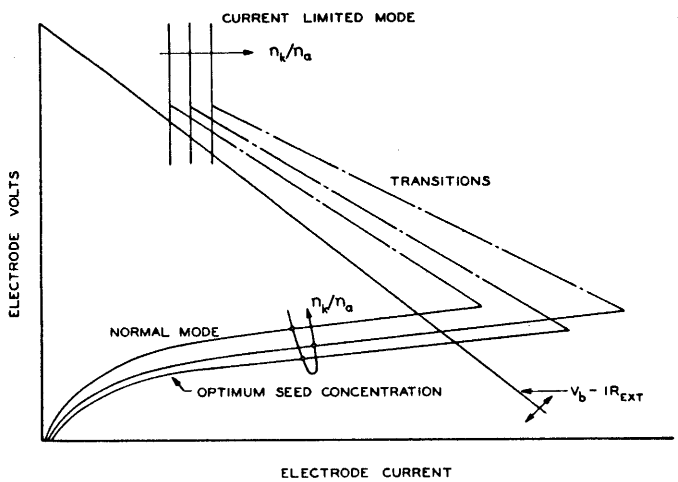

Fig. 8 Schematic Voltage-Current Characteristic

The latter behavior agrees qualitatively with the results of Taylor and Langmuir[1] and the assumption that both of these currents are fixed by surface phenomena. Langmuir showed that for a given electrode temperature the thermionically limited current passing between tungsten electrodes immersed in cesium vapor increased with increasing cesium vapor concentration. This increase was shown to be the result of the increased surface coverage of the electrodes by cesium and the consequent reduction in the surface work function.

Numerical checks of this idea are not possible, since the information concerning a comparable potassium-tungsten system is not available at present. However, the trends presented here are in good qualitative agreement with the results of Langmuir. In addition, typical values of the work function calculated by use of the Dushman equation for normal mode just prior to transition, 2.6 volts, and for the current limited mode, 3.2 volts, are in good qualitative agreement with the suggested reduction in potassium surface coverage during the transition process.

Heat Transfer

Perhaps the most interesting feature of the temperature versus current plots shown in figure 4 is the strong asymmetry of the curves. This asymmetry is the result of the importance of the electron heating or cooling term in the heat balance for electrodes with small sheath potentials.

Consider a metal surface emitting a current density J by a thermionic process and assume that no external potential sheath exists. The electrons which escape from the surface must have energies greater than the surface work function ϕ_w. The mean energy of the escaping electrons with respect to the Fermi energy level in the metal is $[e\phi_w + 2kT_w]$. Each escaping electron is replaced by an electron from the external circuit with a mean energy at the Fermi level. Therefore, for each escaping electron, the metal surface experiences a net energy loss; the cooling effect for a current density, J, is given by $J[\phi_w + 2(kT_w/e)]$. Similarly, if the surface is the anode, the electrons entering the surface arrive with an excess of energy and contribute to anode heating. The heating effect for a current density J is given by $J[\phi_w + 5/2(kT_g/e)]$.

Any real electrode will be surrounded by a potential sheath, which can modify the expressions given here. For example, if the sheath potential, ϕ_s, retards the flux of electrons from the electrode, then ϕ_w is replaced by the sum $(\phi_w + \phi_s)$ in the expressions given above.

In addition to sheath effects, these expressions should also be modified by the addition of a term to account for the flux of ions, ion formation, and recombination of ions at the surface. However, crude estimates indicate that these terms are small for the normal mode case.

For the experiments reported here, the work function term ranges from about 2 volts to 4.4 volts, whereas the value of (kT) in electron volts is about 0.17. Hence, the work function term is the dominant one. The sheath potentials for normal mode operation are thought to be less than two or three times kT. Thus, the range in values for the electron heating or cooling term lies between three and six watts per amp.

The energy balance to the central electrode used in the present experiments can be obtained by taking into account three large terms; convection, electron cooling or heating, and radiation. In addition, ohmic heating and thermal conduction in the electrode must be taken into account.

Estimates of the effects of radiation, conduction, and ohmic heating can be made simply. However, in order to determine the electron cooling term, some knowledge of the work function must be obtained. The convective term also involves several unknown parameters, since the bulk gas temperature and heat transfer coefficient may be greatly affected by the high current densities.

Data have been analyzed in the following manner for the cathode operating in the normal mode. The gas temperature near the cathode was estimated from the equilibrium theory discussed above; a reasonable value of the surface work function was assumed; and the emissivity of a bare tungsten wire was chosen as the emissivity of the electrode. Using these assumptions and the experimental results, it is possible to estimate the heat transfer coefficient:

$$h \equiv [Q_{convective} / A_s(T_g - T_w)] .$$

Typical results are shown in Table III for $\phi_e \equiv [\phi_w + \phi_s + 2kT/e]$ of two and three volts.

The value of h calculated for zero current flow is roughly twice the value obtained for a flat plate. The factor of two is quite reasonable, given the circular cross section of the electrode and its small length-to-diameter ratio, about 6.

For either value of ϕ_e, the heat transfer coefficient increases slowly with current density and is about 2 to $2\frac{1}{2}$ times its original value when current densities of about 30 amps/cm^2 are reached. Slightly higher values of h are obtained for low temperature ($\overline{T}_g \approx 1700°K$) runs.

In the current limited mode, the heat transfer rates are greatly enhanced by the large sheath potentials and consequent heating of the gas near the electrodes. Values of h calculated by the same scheme as above, but for current limited mode data, are some 5 times as high as the zero current values. In this mode, the effects of sheath potentials apparently dominate.

Conclusion

Two modes of steady conduction have been found for current flow between high temperature electrodes in a potassium-seeded argon plasma. In both modes, electron emission from the cathode is apparently by the thermionic process, and steady current densities over 200 amps/cm^2 have been obtained with tungsten electrodes operating at average temperatures of 1700°K.

In the normal mode, current density is less than the thermionic limit and cathode sheath potentials are less than a few (kT_w). In the second mode, current density is equal to the thermionic limit and sheath potentials are much larger than (kT_w).

Heat transfer phenomena are dominated by the electron cooling or heating effects. In the normal mode, the most important term appears to be the energy loss or gain associated with the motion of electrons through the surface work function barrier. In the current limited mode, sheath effects are dominant.

Convective heat transfer rates in the normal mode increase slowly with current density, and appear to be two to three times the zero current values.

Interpretation of current-voltage data indicates that both Joule heating and some non-equilibrium process must be taken into account to explain the high conductivity values observed experimentally.

Table I

Comparison of Conductivity at Low Currents with Equilibrium Theory

Run	22-5-1	25-1-3	8-2/3-1	9-5-3
T_a (°K)	2500	2210	1780	2360
n_K/n_A	.0032	.0041	.0041	.0032
$\sigma\vert_{exp}$ (mho/cm)	0.36	0.10	0.057	0.14
σ_{theory} * (mho/cm)	1.16	0.35	0.016	0.68

* Based on $Q_A = 0.7\times10^{-16}$ cm^2
$Q_K = 250\times10^{-16}$ cm^2

Table II

Comparison of Data with Non-Equilibrium Theory

Run	22-5-1	25-1-3	8-2/3-1
T_a (°K)	2500	2210	1780
n_K/n_A	.0032	.0041	.0041
$\left(\frac{d\log V}{d\log I}\right)_{exp}$	0.53	0.34	0.23
$\left(\frac{d\log V}{d\log I}\right)_{theory}$ *	0.24	0.22	0.16

* Based on J = 10 amp/cm^2

Table III

Reduced Heat Transfer Data

J (amps/cm^2)	0	5.5	10.6	18.1	23.0	29.0
T_{wall} (°K)	1780	1712	1697	1692	1683	1659
T_{gas} (estimated) (°K)	2370	2490	2570	2720	2810	3009
$h\{\phi_e=2\}$ (watts/cm^2 °K)	.027	.028	.037	.045	.047	.047
$h\{\phi_e=3$ volts$\}$ (watts/cm^2 °K)	.027	.035	.049	.063	.068	.068

List of Symbols

A_s	electrode surface area
e	electron charge
h	heat transfer coefficient
I	electrode current
J	current density
k	Boltzmann's constant
°K	degrees Kelvin
n_A	argon atom number density
n_K	potassium atom number density
$\overline{Q}_A$	electron-argon collision cross section
$Q_{convective}$	electrode convective heat transfer rate
$\overline{Q}_K$	electron-potassium collision cross section
T_a	argon gas temperature
T_g	gas temperature
T_w	wall temperature
V	electrode voltage
ϕ_e	effective surface work function potential
ϕ_s	sheath potential
ϕ_w	surface work function potential
σ	electrical conductivity

References

1. Taylor, J. B. and Langmuir, I., "The Evaporation of Atoms, Ions, and Electrons from Caesium Films on Tungsten," Phys. Rev., XLIV, 6, 1933.

2. Killian, T. J., "Thermionic Phenomena Caused by Vapors of Rubidium and Potassium," Phys. Rev., XXVII, 578, 1926.

3. Kerrebrock, J. L., personal communication

4. Brown, Sanborn C., Basic Data of Plasma Physics, Technology Press, M. I. T., and John Wiley and Sons, 1959.

5. Hurwitz, H., Jr., Sutton, G. W., and Tamor, S., "Electron Heating in Magnetohydrodynamic Power Generators," ARS Journal, 1237, 1962.

6. Kerrebrock, J. L., "Non-Equilibrium Effects on Conductivity and Electrode Heat Transfer in Ionized Gases," Technical Note No. 4, Jet Propulsion Center, California Institute of Technology, Nov. 1960 (AFOSR 165).