THE THERMIONIC CONVERSION OF HEAT TO ELECTRICITY by W.B. Nottingham, undated

REPRINTED FROM ADVANCES IN ELECTRON TUBE TECHNIQUES

The Thermionic Conversion of Heat to Electricity*

WAYNE B. NOTTINGHAM

Massachusetts Institute of Technology, Cambridge, Massachusetts

~~Introduction~~

(A) ~~Basically, a thermionic converter~~ is a diode. It has an electron emitter and an electron collector. The emitter must be at a higher temperature than the collector and the net electrical flow corresponds to an electron current flowing from the emitter to the collector. Energy, in the form of heat, is supplied to the emitter and a smaller amount of heat energy must be removed from the collector, either by radiation or by means of a heat sink which can conduct the excess heat away, possibly for use in some other heat conversion device. The difference between the heat supplied and the heat removed is available for the direct conversion of heat to electricity. Electrical power, delivered to an external circuit is the product of the current through the circuit multiplied by the voltage drop across the terminals of the external circuit. Figure 1 .1 is offered as a means of unifying the discussion to follow and point up the interdependence of the various detailed features of the thermionic converter.

The user of the vacuum diode as a heat to power converter must depend on his ability to construct and maintain a diode of ultra-close spacing~~¹~~. (B) At 10μ spacing, reasonable efficiency can be expected. Approximately 20μ marks the upper limit of spacing for which this device can be expected to have any utility. An alternate method for the elimination of the current limitation by space charge is the introduction of an ionized gas. ~~Since cesium vapor is the easiest gas to ionize by electron impact, the cesium diode is recognized as having very great utility likelihood.~~ (C)

The diagram shows cesium to be influential in three different directions. First, it ~~may influence~~ lowers the emitter work-function so as to enhance its electron emission capability at a specified emitter temperature if the cesium pressure is sufficiently high. Second, and in many respects of first importance, is the fact that the cesium ~~can~~ reduces the collector work-function. In most converter designs any reduction in collector work-function is a direct gain in terms of the power available since it reacts directly on the voltage output with no corresponding change in current. The third influence of cesium in a cesium diode relates to the neutralization of electron space charge if there is a means available for its ionization. Because of the low ionization potential of cesium, ionization takes place at heated surfaces. If the work-function of such a surface is greater than 4 V, then the efficiency of ionization approaches 100 per cent. Lower work-function heated surfaces can also produce ions, but their efficiency falls very rapidly as the work-function decreases below 3.89 V. (D) A second means of producing

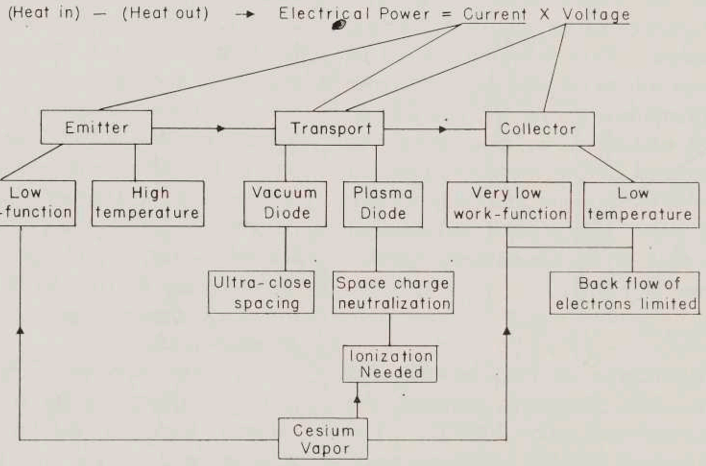


FIG. 1.1

For the interpretation of Fig. 1 .1 we should follow the flow lines both up and down through the diagram. The current available is emitter-controlled. In thermionics, high emitter current density must be associated with a sufficiently low work-function and a sufficiently high operating temperature. Even though the emitter may be capable of high electron emission current density, this current must be transported to the collector for it to be effective. Two important factors influence the transport. These are the space-charge effects in the space between the emitter and the collector, and secondly the surface potential of the collector.

---

*This work has been supported in part by the U.S. Army (Signal Corps), the U.S. Air Force (Office of Scientific Research, Air Research and Development Command) and the U.S. Navy (Office of Naval Research).

cesium ions depends on the presence of moderately high energy electrons. Ionization by direct impact requires electrons with an energy higher than the ionization potential, whereas two-step ionization can take place with lower energy electrons since the first step ~~could~~ can raise the valence electron of the cesium atom to its first excited state and the second impact ~~could~~ can carry it to ionization. If there is a sufficient number of cesium ions present then ion-rich space-charge sheaths form at both the emitter surface and the collector surface. The emitter sheath serves the function of accelerating all of the electrons available at the emitter into the ionized space between the emitter and the collector. Here, if conditions are suitable, plasma oscillations may develop to cause the energy distribution among the electrons to be one characterized by a much higher temperature than that of the electron emitter itself. Thus electron temperatures in the transport space as high as 5000° or 6000°K are considered quite possible. In some diodes, the emitter itself serves as the initial ionization surface, whereas other designs call for the insertion of an auxiliary heated electrode.

It has been the purpose of this introduction to show as briefly as possible the interrelation between the principal elements of a thermionic converter and indicate that in order to overcome the technical disadvantage of the ultra-close spacing associated with the vacuum diode, the introduction of an ionizable gas, and in particular cesium vapor, influences the operation of the diode in a very significant manner. ~~In the immediate future, cesium diode design will proceed~~ principally on the basis of experimental cut-and-try, enlightened by reasonable guesses as to what are the true electronic properties of cesium. Basic research related to these properties is needed, not only to help the device designer to construct more useful thermionic converters, but also to help the design engineer to understand in more detail the properties of the devices created during the interim period required for the acquisition of the fundamental data needed. The later sections of this paper will present information specifically related to the physics associated with various blocks schematically outlined in Fig. 1.

E

~~The emitter~~

F

The electron emitter may receive its heat in any of a number of different ways. For all known emitters, the minimum temperature is approximately 1000°K. The maximum may possibly approach 3000°K. The source of heat must provide a temperature suitable to the material of the emitter.

It is important, at the very outset, to distinguish between the *true work-function* of an emitter and its *Richardson work-function*[2]. True work-function may be defined as the energy difference between the Fermi level of the emitter and the potential energy of an electron at a distance of approximately 10^{-6} cm. from the surface through which the electron escaped. The definition is expressed in this manner for the present purpose since it is assumed that the linear dimensions of emitter inhomogeneity are likely to be significantly greater than 10^{-6} cm. The Richardson work-function may be contrasted to the true work-function in that it is obtained from an analysis of "zero-field" emission data as a function of the temperature. These data, plotted as log (I/T^2) as a function of $(1/T)$ usually yield a straight line and from the slope of this line the Richardson work-function is determined. For example, with tungsten the generally accepted Richardson work-function is 4.52 V, whereas the true work-function of the tungsten depends on the crystallographic direction within the tungsten crystal normal to the emission surface. The total range of true work-function is thought to go from 4.3 V to over 5.3 V. The emission and adsorption properties of tungsten are therefore very sensitive to the surface-exhibited crystallographic orientation and any statement which neglects to take this fact into account is dealing with an empirical result averaged in some unknown manner over the actual surface. These same remarks apply to practically all of the refractory emitters, including tantalum and molybdenum as other examples. The equation which gives the electron emission capability of an emitter in terms of its true work-function is :

$$I = 120\,T^2 \exp\left(\frac{-q\varphi}{kT}\right)\ \text{A/cm}^2 \qquad (1)$$

In this equation, the current density I is determined exclusively by the temperature T and the true work-function φ. The electron charge is q and Boltzmann's constant k. If the actual surface has areas of different true work-function, each of those areas will have an emission capability expressible by this equation if the true work-function is inserted.

It is the true work-function and not the Richardson work-function which determines the ionization capability of a hot surface. Experimental verification of the theory of ionization has been inadequate. The results to date may be summarized merely by the statement that if the true work-function of a given area is a few tenths of an electron volt greater than the ionization potential of cesium, which is 3.89 V, then that part of the surface will be a good ionizer at a sufficiently high temperature. If the work-function is less than the ionization potential by a few tenths of a volt, it will be a relatively poor ionizer. Thus, electron emission goes up very rapidly with the decrease in true work-function, whereas the emitter's ionization capability goes down very rapidly with a decrease in work-function.

The adsorption of a polarizable material has a very profound effect on the true work-function of a surface. Oxygen increases the work-function, whereas barium, thorium and cesium are examples of adsorbable atoms which decrease the work-function. In a suitably high pressure of cesium and with a suitably high temperature of the tungsten surface ($T \gg 3.6\, T_{Cs}$), the work-function of tungsten associated with a 110 direction is the highest of any but as the temperature is lowered, cesium begins to adsorb on the 110 surface to lower its work-function. It then acquires the lowest work-function of all the surfaces through which the electrons are emitted. At still lower temperatures, the other surface directions adsorb cesium and become the best electron emitters. These facts are mentioned by way of illustration to show how important to the understanding of a thermionic converter is precise knowledge with regard to the true work-function of the emitter in the environment in which it is to be used.

Collector properties

Again it is the *true work-function* of the collector that is significant in the thermionic converter. In order to realize good power conversion, the collector work-function must be very low. If this condition is not satisfied the output voltage is no higher than the voltage equivalent of temperature defined by the symbol $\bar{V}$ according to the following equation :

$$\bar{V} = \frac{kT}{q} = \frac{T}{11600} \qquad (2)$$

As the collector work-function is reduced to a value less than that of the emitter, the available output voltage goes up directly. Thus, if the collector work-function can be adjusted by the suitable control of its temperature, and the adsorption on its surface of a polarizable layer such as cesium to obtain a true work-function of 1.2 V, then the output voltage of a converter having an emitter with a 3 V work-function could be as high as 1.8 V. Associated with this desirable, very low work-function surface is the necessity to cool it. Electron emission from the collector corresponds to a current flowing in the reverse direction and therefore it is necessary to maintain the collector at a lower and lower temperature to lower the work-function obtainable.

φs >and given by Eq 1:6

φs >increases

φs >depending on the collector

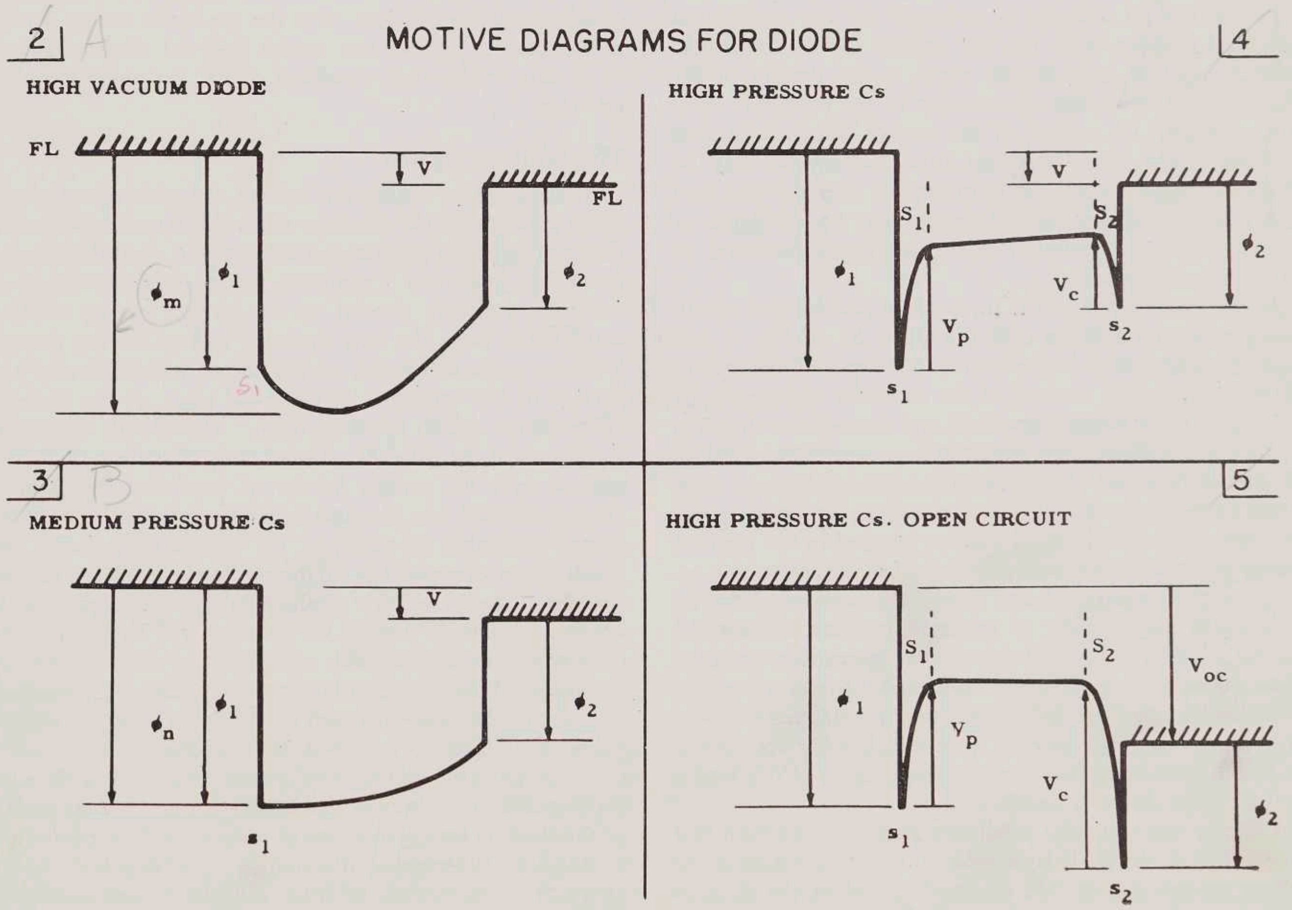
(I)

and potential

Motive diagrams

Before it is possible to discuss some of the problems related to the transfer of electrons from the emitter to the collector, it is necessary to introduce the concept of a "motive diagram". Langmuir defined "motive" in a manner very similar to the conventional expression for the "electrostatic potential". The difference in the definitions is that the motive is defined in terms of the work required to transfer a charged body, specifically an electron or an ion, from one place to another and expressed in terms of the work per unit charge required. The electrostatic definition implies the work per unit charge as the charge approaches zero. The electron motive is the work per unit charge for an electron and thus can include the mirror-image potential and other influences which depend on the presence of the charge itself near a region of great change in physical properties such as the boundary layer of an emitter or a collector. Typical motive diagrams are shown in Figs. 2, 3, 4, and 5.

Figure 2 may be used to define some of the important quantities pertinent to this discussion. Here the emitter and the collector are designated and their Fermi levels indicated by "*FL*". On this motive diagram the difference between the Fermi levels shown as V is directly measurable as the applied voltage difference between them. The true work-function of the emitter φ_1 represents the energy difference between the Fermi level of the emitter and an electron at rest in the immediate neighborhood of the emitter surface that is of the order of 10^{-6} centimeters. The true work-



FIGS. 2, 3, 4 and 5

Fg 1:6

1:6D

End (K)

function of the collector is defined in the same way and is represented by φ_2. If the electron emission is high, then an electron space-charge sheath may be expected to create a space-charge minimum which lies at φ_m with respect to the emitter Fermi level. Electrons emitted within the energy band φ_1 to φ_m are returned to the emitter, whereas those emitted with greater energy than φ_m contribute to the observed diode current.

If cesium atoms are permitted to enter the space between the emitter and the collector, many of them in their random motion will collide with the emitter. If φ_1 is greater than 3.89, most of the atoms that arrive at the surface are ionized and will leave it as though they started at the surface point s_1. Since the ions will have an initial velocity distribution characteristic of the temperature of the emitter, they will occupy ion states within the motive diagram beginning at s_1 and move in states within the space region at energy levels higher than s_1. As long as a net electron space charge exists in front of the emitter area the ions will be accelerated toward the collector but they will not pass all the way to it since the positive surface charge indicated by the motive diagram will bring them to a stop and return them to the emitter. Some ions, even though the mean-free path may be long, will collide with atoms and lose some of their kinetic energy. That will put them in energy levels below s_1 and therefore they will be trapped. As more and more ions are trapped the space-charge minimum will disappear.

As the cesium pressure is increased the ion production will also increase until the ion density in the immediate neighborhood of s_1 is exactly equal to the density of the electrons in transit from the emitter to the collector. The motive field at the surface of the emitter will then be zero and the " zero field " emission from the emitter may be obtained. This situation is illustrated in Fig. 3. The zero field electron emission current density may be calculated by Eq. (1). In this equation T is the emitter temperature, φ_1 its true work-function.

As the cesium pressure is increased a positive ion sheath represented as extending over the space S_1 of Fig. 4 will develop. The change in the motive function from the surface potential to that at the end of the sheath is represented by V_p. In the space region between S_1 and the collector sheath at S_2 we can anticipate that there will be a small rise or fall in the motive function. This change is necessary because some electrons that are emitted over the surface barrier at s_1 will lose energy by collision and become trapped in the electron energy levels below the surface potential of the collector at s_2. This trapped negative charge must be compensated for by ions which are brought to rest and returned toward the emitter. Under the conditions shown, the surface potential of the collector is negative with respect to the motive function at the sheath boundary S_2. In this range the trapped electrons are repelled and the positive ions which enter the sheath at S_2 are accelerated into the collector. Again in this region the net space charge is positive.

If the applied potential V is made more negative than that shown in Fig. 4 then it is possible to set up a condition for which the ion arrival rate is exactly equal to the electron arrival rate. When we assume that there is no electron emission from the collector, then this condition of balancing currents is the " open-circuit " voltage designated as V_{oc} of Fig. 5. Under these conditions there will be nearly twice as much negative charge per unit volume in the space region as there was under the condition illustrated in Fig. 4 because there will be a double stream of electrons across this space. That change will result in a somewhat lower value of V_p to permit more ions to enter the space region for neutralization. Again near the collector a positive ion space charge will develop because the motive function is such as to turn back all electrons with kinetic energy associated with their motion toward the collector which is insufficient to surmount the barrier at s_2. If there were no electron interactions in the space region, then the electron current received at the collector could be computed by means of Eq. (1) by the insertion of φ_{oc} in place of φ_1. A calculation of current density by this formula would in many cases give the minimum current expected at the collector whereas if some electron energy sharing takes place because of their injection into the space by the accelerating potential V_p, then it is possible for more electrons to be received at the surface s_2 than would otherwise have been permitted. In any case the ion current which is accelerated through the collector space-charge sheath S_2 must balance the electron arrival current. It should be clear from this discussion that the open circuit electron arrival current could very well be less than the " saturation " ion current produced at the hot surface emitter. If the cesium density is sufficiently low, then the ion space-charge sheath at the emitter surface can vanish and the electron arrival at s_2 can, under that condition, equal the saturation ion emission.

(4)

5

(M)

The emitter sheath

Although many details are lacking, the general experience in the use of cesium in converter diodes leads to the conclusion that, as the cesium pressure is increased, and a suitable scheme for cesium ionization is available, the space-charge sheath of electrons normally present at the surface of an efficient emitter first traps the ions available and as the ion density increases more and more, an ion sheath is formed near the surface of the emitter[3]. It takes the place of the electron space-charge sheath formerly there. This sheath formation is illustrated by Fig. 4. Under this condition electrons emitted over the surface barrier of true work-function φ_1 become injected into the intermediate space with an average energy somewhat in excess of the motive drop across the sheath, shown here as V_p. If the spacing between the emitter and the collector is very small, then the electrons may be accelerated directly over to the collector and have very little opportunity to interact with each other or with the ions in the space. If the distance between the electrodes, measured in terms of the mean-free path of the electrons in the cesium vapor, is as large as two or three mean-free paths or more, it is thought that plasma oscillations develop and through these oscillations, electron interaction causes a redistribution of the electron energy to arrive at something that approaches a Maxwell–Boltzmann distribution characterized by a temperature comparable with the value of V_p and computed with the aid of Eq. (2). Before this interaction took place,

1:6

> The properties of close-spaced vacuum diodes are discussed in Sect.

^ a process known as "charge-exchange" may contribute to this loss in kinetic energy of the ions. Such losses

is not stable in thermionic (diode operation) the electrons, as they were injected across the emitter sheath, were more or less mono-energetic but upon redistribution, the total energy of an electron group need not change for some of them to have lost energy and others to have gained it. The important feature is that this redistribution of energy results in there being many electrons with sufficient energy to ionize the cesium vapor either by direct impact or by cumulative impact. It is not certain which mechanism is the more important, although ionization by direct impact seems to be adequate. Under these circumstances, the mechanism for the maintenance of a sufficient ion density to neutralize all of the space charge of the electrons in transit may be provided by the electrons themselves. When electron space charge is absent, the presence of a very weak field between the emitter and the collector is sufficient to permit a drift current flow of many amperes per square centimeter.[7]

7 Details concerned with [illegible] formation are given in Sect

Cs

Expand

These phenomena are relatively simple in concept, but difficult to evaluate quantitatively because of the lack of fundamental physical data related not only to the electronic properties of cesium itself in the vapor phase, but to the influence that cesium has as it is adsorbed either on the emitter or the collector, or both.

Summary

In review, I wish to return to Fig. 1 to emphasize the importance of the emitter properties and the transport properties of the interelectrode space in the determination of the current that can flow across the thermionic diode used as the converter of heat to electric power. A better understanding of the lowering of surface work-function by the presence of adsorbed cesium will, through its control of the collector work-function, increase the voltage available in the converter. The voltage output thus depends both on the transport mechanism and the surface potential of the collector relative to its Fermi level. The motive diagrams of Figs. 2–5 serve also as a means of reminding the reader concerning the interplay of all of the factors. Specifically these factors are the true work-function of the emitter, the true work-function of the collector, and the details of space ionization and sheath control.

References

[1] W. B. Nottingham ; *Rep. 20th Ann. Conf. Phys. Electronics, M.I.T.*, p. 58 (1960).

[2] W. B. Nottingham ; " Thermionic Emission ", *Handb. Phys.*, **21**, 145–146 (Springer-Verlag, Berlin 1956).

[3] W. B. Nottingham ; *Rep. 20th Ann. Conf. Phys. Electronics, M.I.T.*, p. 95 (1960).

Printed in England by Metcalfe & Cooper Ltd., 10-24 *Scrutton Street, London, E.C.2*

Thermionic Conversion of Heat to Electricity

W. B. Nottingham, G. Hatsopoulos, E.N. Carabateas

Introduction

Direct conversion of heat to electricity demands a device which accepts heat at its input, rejects excess heat at its output, and generates a driving voltage which can put current through an external load. The thermionic diode is such a device. It has an electron emitter which accepts the heat, delivers electrons for transport through an intervening space to the electron collector. The collector also receives heat which must be discharged by some cooling mechanism.

A diagram which serves to make these statements more graphic is given in Fig. 1. This diagram illustrates the fact that the current flow is predominantly controlled by the properties of the emitter and the transport mechanism. The voltage output also depends directly on the transport mechanism and specifically on the collector work-function. The desired properties are summarized by Fig. 1 in that the emitter should operate at a high temperature and yet have a low work-function. Pure tungsten has a relatively high work-function and yet in the presence of a sufficiently high concentration of cesium vapor, a low work-function can be obtained as a result of adsorption of cesium atoms on the surface.

The transport mechanism in most low-powered diodes is through the evacuated space. A high-powered diode requires a high current density to be transported and ultra-close spacing is therefore demanded. Spacings as close as 10 microns are difficult to maintain for a long period of time and even this spacing is marginal as higher power density is required of the device. The introduction of cesium vapor combined with some method of ionization permits the designer to create a plasma diode. Years of experience with gas discharge phenomena have demonstrated that a plasma is characterized by the fact that equal numbers of positive ions and electrons create a highly conducting mechanism free of space charge limitations. The presence of such a plasma can even operate to accelerate the electrons from the emitter into the plasma space. Under some modes of operation this injection of emitted electrons functions to help maintain the plasma condition. The presence of a high cesium density required to maintain the low work-function of the emitter can inhibit the flow of electrons through the space between the emitter and the collector and therefore even though the space charge is neutralized, it is advantageous to think in terms of emitter-to-collector spacing that is as short as it is practical to construct and preferably not more than 10 to 20 mean free paths of electrons in cesium vapor at these high densities.

Again cesium plays a very important part at the collector surface since its adsorption on the surface operates to create a very low work-function. An objectionable back flow of electrons from the collector would arise unless this low work-function surface is maintained at a sufficiently low temperature. For efficient direct conversion, the collector should be cooled to 900°K (1650°F) or lower.

These introductory remarks are made in order to prepare for a more detailed discussion of each of the three essential components of the thermionic diode energy converter.

The Thermionic Electron Emitter

An efficient converter demands that the emitter be capable of giving out an electron current density of not less than 10 amperes per square centimeter and preferable two or three times this much. Pure tungsten will deliver currents this large if operated at a temperature near 3000°K. Such a high temperature causes the emitter to evaporate at a prohibitively high rate. Fortunately, sufficient cesium will adsorb on a tungsten surface, even at tungsten temperatures ~~of~~ near 2000°K if the cesium pressure is high enough. Adsorbed cesium lowers the tungsten work-function and permits the desired high current densities at far lower temperatures than otherwise. If the true work-function of a surface is known at the operating temperature, then the following equation permits the correct evaluation of the current density available for use in a thermionic converter.

$$I = 120\, T^2 \; e^{-\frac{q\phi}{kT}} \qquad a/cm^2 \qquad (1)$$

This equation shows that the current density I is uniquely determined by the emitter temperature T and the true work-function ϕ. The electron charge is q, Boltzmann's constant is k, and the base of the natural logarithms is e.

The heated emitter serves still another important purpose. Since a small fraction of the cesium atoms that evaporate from the surface continuously come off as positive ions. The ionization potential of cesium defined as the electron energy necessary to remove one of the electrons from a neutral cesium atom is 3.89 volts. The experimental studies of Irving Langmuir and his colleagues have established that nearly every cesium atom that hits a clean tungsten surface maintained at a sufficiently high temperature will leave as a cesium ion because the normal work-function of clean tungsten is well above the ionization potential of the cesium atom. This high efficiency of ionization falls rapidly if the work-function of the heated surface is less than the ionization potential. In spite of this fact a sufficient number of ions can be produced by a tungsten surface of lowered work-function to neutralize the space charge associated with the desired high electron current density. This excess ionization therefore functions to create a very localized region of positive ion space charge at the immediate surface of the emitter.

Electron Transport

In order to discuss electron transport from the emitter to the collector, it is necessary to introduce the concept of the "motive diagram" for a diode. These diagrams can be best understood by our considering first the one appropriate to the vacuum diode. Figure 2 serves this purpose and shows diagramatically the meaning of the true work-function of a surface. The interpretation of the phenomenon of electrical conduction in metals depends the concept derived from the physics of solid substances that there are electronic quantum levels occupied by the valence electrons associated with the atoms composing the structure. All of the low energy quantum states in this structure are occupied and most of the high energy quantum states are not. An intermediate quantum state can always be found which has a probability of occupancy of exactly 50 per cent. It is this quantum state that defines the "Fermi Level" associated with this conductor. All are familiar with the fact that the application of a difference in potential as indicated on a voltmeter will cause a current to flow through a conductor, and yet they may not realize that the applied voltage here indicated is a direct measure of the difference in energy on a potential scale of the Fermi Level at the voltmeter contact points.

It is therefore important in the understanding of a motive diagram that the difference in level indicated by the arrow V is the voltage which would appear as an IR drop over a load resistance connected to a vacuum diode represented by the motive diagram of Fig. 2. Electrons are prevented from flowing freely out of the emitter into the evacuated space by the potential barrier at the surface represented in the diagram by the arrow ϕ_1. It is this potential difference between the Fermi Level of the emitter and its surface potential that is the correct definition of the true work-function of an emitter. By the same definition ϕ_2 is the true work-function of the collector. If the emitter is at a sufficiently high temperature so that in spite of the barrier ϕ_1, electrons are emitted into the evacuated space, the high energy ones that occupy levels in the diagram below ϕ_m can shoot across the evauated space in spite of the presence of the space charge minimum shown in the diagram. Electrons in energy levels between ϕ_1 and ϕ_m are emitted into the vacuum space but are all returned to the emitter and therefore do not contribute to the current of electrons transmitted. By bringing the collector closer and closer to the emitter and maintaining its surface potential as shown to be $V + \phi_2$ negative with respect to the emitter Fermi level, it is theoretically possible to deliver practically all of the thermionic emission to the collector without its being retarded by the space-charge minimum shown.

If cesium is admitted to the diode, and ionization takes places at the heated surface of the emitter, some of these ions will be trapped in the space charge minimum of the motive diagram. When a sufficient number are there to exactly neutralize the space charge, then the diagram takes on the appearance of Fig. 3. This condition happens not to be stable because the slightest excess of positive ions will result in a reduction in the space charge of the electrons since they will then become injected with increased velocity into the diode space. A still greater production will result in a strong ion space charge sheath such as that illustrated in Fig. 4. The drop in potential over this sheath is indicated to be V_p and it takes place over a space shown to be S_1. In general this space is smaller than a mean free path and therefore electrons which have sufficient energy to cross over the surface barrier at s_1 will be injected into the space. The fact that no curvature shows in the motive line between the boundary of the emitter sheath and the boundary of the collector sheath at S_2 is an indication that the space is free of net charge, that is, there are just as many positive charges per unit volume as there are negative charges. The electrons have such a high velocity in their normal motion that a very small accelerating field can result in a rather large drift current. After injection at V_p, the electron energy tends to be randomized and often takes on a distribution energy of the type referred to in the expression "Maxwellian distribution" of high temperature. Measured in terms of the electron energy distribution this temperature may be in excess of 5000°K in spite of the fact that the electrons themselves actually were emitted from a surface at only 2000°K. This apparant anomaly is an indication that they have been injected through a space charge emitter sheath and that they do not have a true temperature in the sense that they are in temperature equilibrium with the cesium atoms. It simply indicates that with this new distribution in energy, the average energy is still comparable with V_p. At the surface of the collector, the higher energy electrons can surmount the collector sheath shown to be V_c and pass over the surface potential of the collector at s_2. A detailed examination of this flow of electricity in at the emitter and out at the collector permits one to explain by this model the observed voltage current curves found in practical diodes.

The final figure in this series shows that as the applied voltage V is increased in the negative direction, a condition occurs which is identified as the "open circuit" voltage V_{oc}. Note that as this applied voltage has increased in this direction most of the change has taken place in the collector sheath and only a very small decrease is observed in the emitter sheath. The reason this is called open circuit voltage is that by increasing the value of V_c the electron arrival rate for those electrons that can surmount the surface barrier at s_2 becomes equal to the ion arrival rate of those positive ions swept out of the plasma region across the boundary at S_2 and into the collector. Thus a balance of the arrival of positive and negative electricity gives zero current and by definition this is the open circuit condition.

Experimental Voltage Current Curves

Figure 6 serves to illustrate in a rather dramatic manner the shift-over associated with the change from the motive diagram of Fig. 2 to that of Fig. 3 or Fig. 4. Here in the lower part of the figure is the power output from a laboratory diode plotted as a function of the voltage output. Note that the power at maximum is only 0.6 milliwatts per square centimeter. The introduction of cesium at a very moderate pressure however resulted in a delivery of 10 times the former electron current with no change in the temperature of the emitter and practically no change in the output voltage. This power of 6 milliwatts per square centimeter is not at all typical of the yield obtainable with a diode operating at a higher temperature and a higher cesium pressure. A thousand times this output has been achieved already.

An observed voltage current curve associated with a moderate cesium pressure and emitter temperature is shown in Fig. 7. The open-circuit voltage is identified at about 4.3 volts and is the cross-over from positive current to negative current and therefore corresponds to the balance of currents as mentioned above. As the surface potential of the collector is made more and more positive than this, more and more electron current can come to the collector until finally when the surface potential of the collector practically coincides with that of the emitter, the drift current saturates and there is no longer an appreciable increase in circuit current. In this example, maximum power will occur at approximately 2.5 volts output with a current value of about 2.5 amperes. Under these experimental conditions this curve is relatively easy to analyze as is shown in Fig. 8. Here an attempt has been made to separate the electron current arriving at the collector from the ion currents arriving there and the solid line with circles is the plot of a logarithm of the current ~~and~~ as a function of the voltage. The fact that this plot follows closely to a straight line permits one to compute the effective electron temperature to be 4800°. ~~The fact~~that this temperature is over twice that of the cathode is illustrated by the fact that a temperature of 2370° would have fallen as shown on the dot-dash line. Clearly this difference is well beyond experimental error, and it is on the basis of this difference that one supports the concept that electrons are injected across an emitter sheath as has been discussed in connection with the motive diagram of Fig. 4.

At higher cesium temperatures the observed curves are less easily analyzed, and yet it has been possible to carry through an interpretative theory which supports the general nature of the motive diagrams presented here as typical of plasma diode operation.

REPRINTED FROM ADVANCES IN ELECTRON TUBE TECHNIQUES

The Thermionic Conversion of Heat to Electricity*

WAYNE B. NOTTINGHAM

Massachusetts Institute of Technology, Cambridge, Massachusetts

Introduction

Basically, a thermionic converter is a diode. It has an electron emitter and an electron collector. The emitter must be at a higher temperature than the collector and the net electrical flow corresponds to an electron current flowing from the emitter to the collector. Energy, in the form of heat, is supplied to the emitter and a smaller amount of heat energy must be removed from the collector, either by radiation or by means of a heat sink which can conduct the excess heat away, possibly for use in some other heat conversion device. The difference between the heat supplied and the heat removed is available for the direct conversion of heat to electricity. Electrical power, delivered to an external circuit is the product of the current through the circuit multiplied by the voltage drop across the terminals of the external circuit. Figure 1 is offered as a means of unifying the discussion to follow and point up the interdependence of the various detailed features of the thermionic converter.

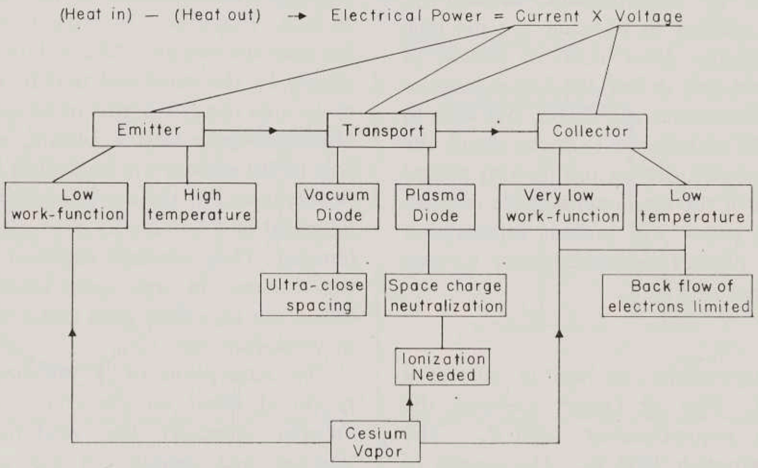


FIG. 1.

For the interpretation of Fig. 1 we should follow the flow lines both up and down through the diagram. The current available is emitter-controlled. In thermionics, high emitter current density must be associated with a sufficiently low work-function and a sufficiently high operating temperature. Even though the emitter may be capable of high electron emission current density, this current must be transported to the collector for it to be effective. Two important factors influence the transport. These are the space-charge effects in the space between the emitter and the collector, and secondly the surface potential of the collector.

The user of the vacuum diode as a heat to power converter must depend on his ability to construct and maintain a diode of ultra-close spacing[1]. At 10μ spacing, reasonable efficiency can be expected. Approximately 20μ marks the upper limit of spacing for which this device can be expected to have any utility. An alternate method for the elimination of the current limitation by space charge is the introduction of an ionized gas. Since cesium vapor is the easiest gas to ionize by electron impact, the cesium diode is recognized as having very great utility likelihood.

The diagram shows cesium to be influential in three different directions. First, it may influence the emitter work-function so as to enhance its electron emission capability at a specified emitter temperature if the cesium pressure is sufficiently high. Second, and in many respects of first importance, is the fact that the cesium can reduce the collector work-function. In most converter designs any reduction in collector work-function is a direct gain in terms of the power available since it reacts directly on the voltage output with no corresponding change in current. The third influence of cesium in a cesium diode relates to the neutralization of electron space charge if there is a means available for its ionization. Because of the low ionization potential of cesium, ionization takes place at heated surfaces. If the work-function of such a surface is greater than 4 V, then the efficiency of ionization approaches 100 per cent. Lower work-function heated surfaces can also produce ions, but their efficiency falls very rapidly as the work-function decreases below 3.89 V. A second means of producing

---

*This work has been supported in part by the U.S. Army (Signal Corps), the U.S. Air Force (Office of Scientific Research, Air Research and Development Command) and the U.S. Navy (Office of Naval Research).

cesium ions depends on the presence of moderately high energy electrons. Ionization by direct impact requires electrons with an energy higher than the ionization potential, whereas two-step ionization can take place with lower energy electrons since the first step could raise the valence electron of the cesium atom to its first excited state and the second impact could carry it to ionization. If there is a sufficient number of cesium ions present then ion-rich space-charge sheaths form at both the emitter surface and the collector surface. The emitter sheath serves the function of accelerating all of the electrons available at the emitter into the ionized space between the emitter and the collector. Here, if conditions are suitable, plasma oscillations may develop to cause the energy distribution among the electrons to be one characterized by a much higher temperature than that of the electron emitter itself. Thus electron temperatures in the transport space as high as 5000° or 6000°K are considered quite possible. In some diodes, the emitter itself serves as the initial ionization surface, whereas other designs call for the insertion of an auxiliary heated electrode.

It has been the purpose of this introduction to show as briefly as possible the interrelation between the principal elements of a thermionic converter and indicate that in order to overcome the technical disadvantage of the ultra-close spacing associated with the vacuum diode, the introduction of an ionizable gas, and in particular cesium vapor, influences the operation of the diode in a very significant manner. In the immediate future, cesium diode design will proceed principally on the basis of experimental cut-and-try, enlightened by reasonable guesses as to what are the true electronic properties of cesium. Basic research related to these properties is needed, not only to help the device designer to construct more useful thermionic converters, but also to help the design engineer to understand in more detail the properties of the devices created during the interim period required for the acquisition of the fundamental data needed. The later sections of this paper will present information specifically related to the physics associated with various blocks schematically outlined in Fig. 1.

The emitter

The electron emitter may receive its heat in any of a number of different ways. For all known emitters, the minimum temperature is approximately 1000°K. The maximum may possibly approach 3000°K. The source of heat must provide a temperature suitable to the material of the emitter.

It is important, at the very outset, to distinguish between the *true work-function* of an emitter and its *Richardson work-function*[2]. True work-function may be defined as the energy difference between the Fermi level of the emitter and the potential energy of an electron at a distance of approximately 10^{-6} cm. from the surface through which the electron escaped. The definition is expressed in this manner for the present purpose since it is assumed that the linear dimensions of emitter inhomogeneity are likely to be significantly greater than 10^{-6} cm. The Richardson work-function may be contrasted to the true work-function in that it is obtained from an analysis of " zero-field " emission data as a function of the temperature. These data, plotted as log (I/T^2) as a function of $(1/T)$ usually yield a straight line and from the slope of this line the Richardson work-function is determined. For example, with tungsten the generally accepted Richardson work-function is 4.52 V, whereas the true work-function of the tungsten depends on the crystallographic direction within the tungsten crystal normal to the emission surface. The total range of true work-function is thought to go from 4.3 V to over 5.3 V. The emission and adsorption properties of tungsten are therefore very sensitive to the surface-exhibited crystallographic orientation and any statement which neglects to take this fact into account is dealing with an empirical result averaged in some unknown manner over the actual surface. These same remarks apply to practically all of the refractory emitters, including tantalum and molybdenum as other examples. The equation which gives the electron emission capability of an emitter in terms of its true work-function is :

$$I = 120\,T^2 \exp\left(\frac{-q\varphi}{kT}\right)\ \mathrm{A/cm^2} \qquad (1)$$

In this equation, the current density I is determined exclusively by the temperature T and the true work-function φ. The electron charge is q and Boltzmann's constant k. If the actual surface has areas of different true work-function, each of those areas will have an emission capability expressible by this equation if the true work-function is inserted.

It is the true work-function and not the Richardson work-function which determines the ionization capability of a hot surface. Experimental verification of the theory of ionization has been inadequate. The results to date may be summarized merely by the statement that if the true work-function of a given area is a few tenths of an electron volt greater than the ionization potential of cesium, which is 3.89 V, then that part of the surface will be a good ionizer at a sufficiently high temperature. If the work-function is less than the ionization potential by a few tenths of a volt, it will be a relatively poor ionizer. Thus, electron emission goes up very rapidly with the decrease in true work-function, whereas the emitter's ionization capability goes down very rapidly with a decrease in work-function.

The adsorption of a polarizable material has a very profound effect on the true work-function of a surface. Oxygen increases the work-function, whereas barium, thorium and cesium are examples of adsorbable atoms which decrease the work-function. In a suitably high pressure of cesium and with a suitably high temperature of the tungsten surface ($T \geqslant 3.6\, T_{Cs}$), the work-function of tungsten associated with a 110 direction is the highest of any but as the temperature is lowered, cesium begins to adsorb on the 110 surface to lower its work-function. It then acquires the lowest work-function of all the surfaces through which the electrons are emitted. At still lower temperatures, the other surface directions adsorb cesium and become the best electron emitters. These facts are mentioned by way of illustration to show how important to the understanding of a thermionic converter is precise knowledge with regard to the true work-function of the emitter in the environment in which it is to be used.

Collector properties

Again it is the *true work-function* of the collector that is significant in the thermionic converter. In order to realize good power conversion, the collector work-function must be very low. If this condition is not satisfied the output voltage is no higher than the voltage equivalent of temperature defined by the symbol $\bar{V}$ according to the following equation :

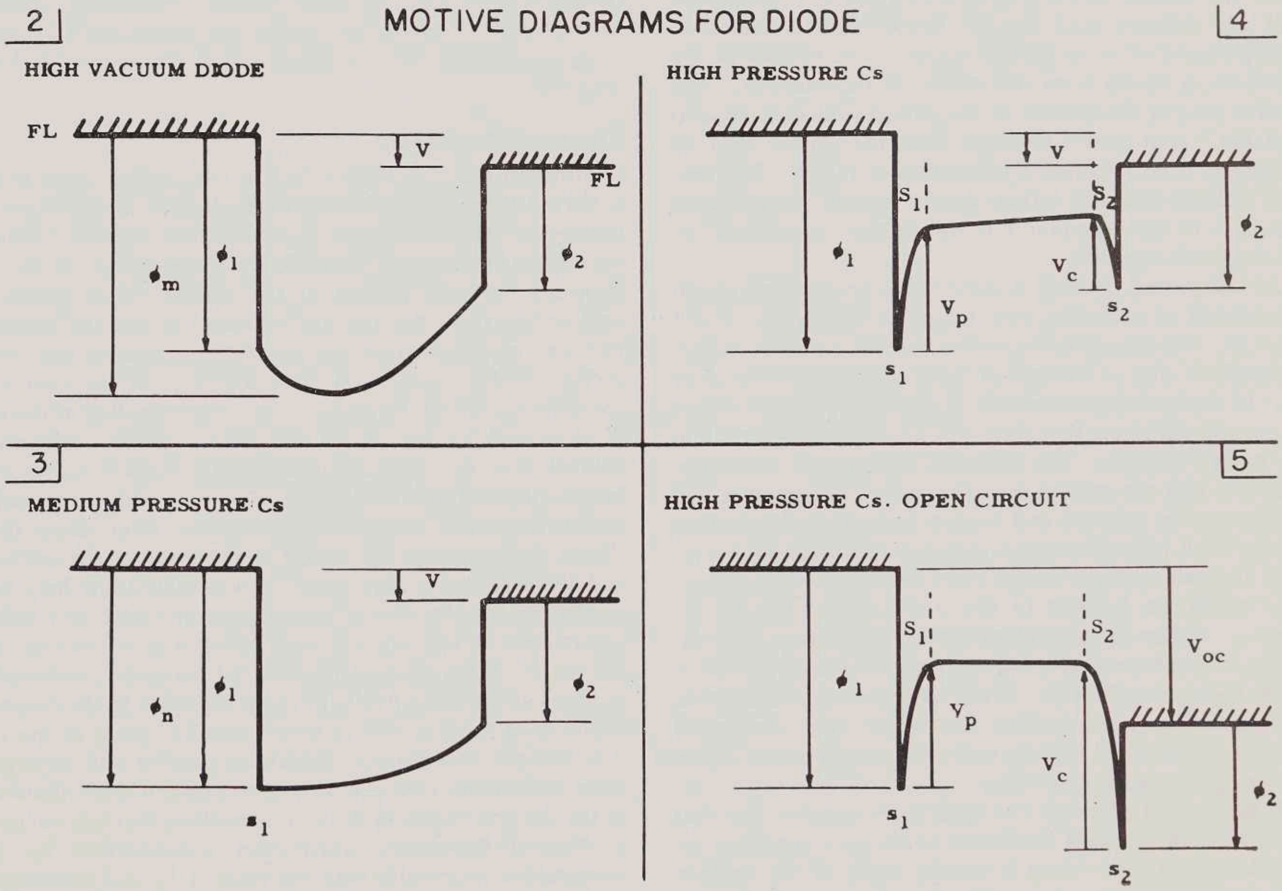
$$\bar{V} = \frac{kT}{q} = \frac{T}{11600} \qquad (2)$$

As the collector work-function is reduced to a value less than that of the emitter, the available output voltage goes up directly. Thus, if the collector work-function can be adjusted by the suitable control of its temperature, and the adsorption on its surface of a polarizable layer such as cesium to obtain a true work-function of 1.2 V, then the output voltage of a converter having an emitter with a 3 V work-function could be as high as 1.8 V. Associated with this desirable, very low work-function surface is the necessity to cool it. Electron emission from the collector corresponds to a current flowing in the reverse direction and therefore it is necessary to maintain the collector at a lower and lower temperature to lower the work-function obtainable.

Motive diagrams

Before it is possible to discuss some of the problems related to the transfer of electrons from the emitter to the collector, it is necessary to introduce the concept of a " motive diagram ". Langmuir defined " motive " in a manner very similar to the conventional expression for the " electrostatic potential ". The difference in the definitions is that the motive is defined in terms of the work required to transfer a charged body, specifically an electron or an ion, from one place to another and expressed in terms of the work per unit charge required. The electrostatic definition implies the work per unit charge as the charge approaches zero. The electron motive is the work per unit charge for an electron and thus can include the mirror-image potential and other influences which depend on the presence of the charge itself near a region of great change in physical properties such as the boundary layer of an emitter or a collector. Typical motive diagrams are shown in Figs. 2, 3, 4, and 5.

Figure 2 may be used to define some of the important quantities pertinent to this discussion. Here the emitter and the collector are designated and their Fermi levels indicated by " *FL* ". On this motive diagram the difference between the Fermi levels shown as V is directly measurable as the applied voltage difference between them. The true work-function of the emitter φ_1 represents the energy difference between the Fermi level of the emitter and an electron at rest in the immediate neighborhood of the emitter surface that is of the order of 10^{-6} centimeters. The true work-



Figs. 2, 3, 4 and 5

function of the collector is defined in the same way and is represented by φ_2. If the electron emission is high, then an electron space-charge sheath may be expected to create a space-charge minimum which lies at φ_m with respect to the emitter Fermi level. Electrons emitted within the energy band φ_1 to φ_m are returned to the emitter, whereas those emitted with greater energy than φ_m contribute to the observed diode current.

If cesium atoms are permitted to enter the space between the emitter and the collector, many of them in their random motion will collide with the emitter. If φ_1 is greater than 3.89, most of the atoms that arrive at the surface are ionized and will leave it as though they started at the surface point s_1. Since the ions will have an initial velocity distribution characteristic of the temperature of the emitter, they will occupy ion states within the motive diagram beginning at s_1 and move in states within the space region at energy levels higher than s_1. As long as a net electron space charge exists in front of the emitter area the ions will be accelerated toward the collector but they will not pass all the way to it since the positive surface charge indicated by the motive diagram will bring them to a stop and return them to the emitter. Some ions, even though the mean-free path may be long, will collide with atoms and lose some of their kinetic energy. That will put them in energy levels below s_1 and therefore they will be trapped. As more and more ions are trapped the space-charge minimum will disappear.

As the cesium pressure is increased the ion production will also increase until the ion density in the immediate neighborhood of s_1 is exactly equal to the density of the electrons in transit from the emitter to the collector. The motive field at the surface of the emitter will then be zero and the " zero field " emission from the emitter may be obtained. This situation is illustrated in Fig. 3. The zero field electron emission current density may be calculated by Eq. (1). In this equation T is the emitter temperature, φ_1 its true work-function.

As the cesium pressure is increased a positive ion sheath represented as extending over the space S_1 of Fig. 4 will develop. The change in the motive function from the surface potential to that at the end of the sheath is represented by V_p. In the space region between S_1 and the collector sheath at S_2 we can anticipate that there will be a small rise or fall in the motive function. This change is necessary because some electrons that are emitted over the surface barrier at s_1 will lose energy by collision and become trapped in the electron energy levels below the surface potential of the collector at s_2. This trapped negative charge must be compensated for by ions which are brought to rest and returned toward the emitter. Under the conditions shown, the surface potential of the collector is negative with respect to the motive function at the sheath boundary S_2. In this range the trapped electrons are repelled and the positive ions which enter the sheath at S_2 are accelerated into the collector. Again in this region the net space charge is positive.

If the applied potential V is made more negative than that shown in Fig. 4 then it is possible to set up a condition for which the ion arrival rate is exactly equal to the electron arrival rate. When we assume that there is no electron emission from the collector, then this condition of balancing currents is the " open-circuit " voltage designated as V_{oc} of Fig. 5. Under these conditions there will be nearly twice as much negative charge per unit volume in the space region as there was under the condition illustrated in Fig. 4 because there will be a double stream of electrons across this space. That change will result in a somewhat lower value of V_p to permit more ions to enter the space region for neutralization. Again near the collector a positive ion space charge will develop because the motive function is such as to turn back all electrons with kinetic energy associated with their motion toward the collector which is insufficient to surmount the barrier at s_2. If there were no electron interactions in the space region, then the electron current received at the collector could be computed by means of Eq. (1) by the insertion of φ_{oc} in place of φ_1. A calculation of current density by this formula would in many cases give the minimum current expected at the collector whereas if some electron energy sharing takes place because of their injection into the space by the accelerating potential V_p, then it is possible for more electrons to be received at the surface s_2 than would otherwise have been permitted. In any case the ion current which is accelerated through the collector space-charge sheath S_2 must balance the electron arrival current. It should be clear from this discussion that the open circuit electron arrival current could very well be less than the " saturation " ion current produced at the hot surface emitter. If the cesium density is sufficiently low, then the ion space-charge sheath at the emitter surface can vanish and the electron arrival at s_2 can, under that condition, equal the saturation ion emission.

The emitter sheath

Although many details are lacking, the general experience in the use of cesium in converter diodes leads to the conclusion that, as the cesium pressure is increased, and a suitable scheme for cesium ionization is available, the space-charge sheath of electrons normally present at the surface of an efficient emitter first traps the ions available and as the ion density increases more and more, an ion sheath is formed near the surface of the emitter[3]. It takes the place of the electron space-charge sheath formerly there. This sheath formation is illustrated by Fig. 4. Under this condition electrons emitted over the surface barrier of true work-function φ_1 become injected into the intermediate space with an average energy somewhat in excess of the motive drop across the sheath, shown here as V_p. If the spacing between the emitter and the collector is very small, then the electrons may be accelerated directly over to the collector and have very little opportunity to interact with each other or with the ions in the space. If the distance between the electrodes, measured in terms of the mean-free path of the electrons in the cesium vapor, is as large as two or three mean-free paths or more, it is thought that plasma oscillations develop and through these oscillations, electron interaction causes a redistribution of the electron energy to arrive at something that approaches a Maxwell–Boltzmann distribution characterized by a temperature comparable with the value of V_p and computed with the aid of Eq. (2). Before this interaction took place, the electrons, as they were injected across the emitter sheath, were more or less mono-energetic but upon redistribution, the total energy of an electron group need not change for some of them to have lost energy and others to have gained it. The important feature is that this redistribution of energy results in there being many electrons with sufficient energy to ionize the cesium vapor either by direct impact or by cumulative impact. It is not certain which mechanism is the more important, although ionization by direct impact seems to be adequate. Under these circumstances, the mechanism for the maintenance of a sufficient ion density to neutralize all of the space charge of the electrons in transit may be provided by the electrons themselves. When electron space charge is absent, the presence of a very weak field between the emitter and the collector is sufficient to permit a drift current flow of many amperes per square centimeter.

These phenomena are relatively simple in concept, but difficult to evaluate quantitatively because of the lack of fundamental physical data related not only to the electronic properties of cesium itself in the vapor phase, but to the influence that cesium has as it is adsorbed either on the emitter or the collector, or both.

Summary

In review, I wish to return to Fig. 1 to emphasize the importance of the emitter properties and the transport properties of the interelectrode space in the determination of the current that can flow across the thermionic diode used as the converter of heat to electric power. A better understanding of the lowering of surface work-function by the presence of adsorbed cesium will, through its control of the collector work-function, increase the voltage available in the converter. The voltage output thus depends both on the transport mechanism and the surface potential of the collector relative to its Fermi level. The motive diagrams of Figs. 2–5 serve also as a means of reminding the reader concerning the interplay of all of the factors. Specifically these factors are the true work-function of the emitter, the true work-function of the collector, and the details of space ionization and sheath control.

References

[1] W. B. Nottingham ; *Rep.* 20*th Ann. Conf. Phys. Electronics, M.I.T.*, p. 58 (1960).

[2] W. B. Nottingham ; " Thermionic Emission ", *Handb. Phys.*, **21**, 145–146 (Springer-Verlag, Berlin 1956).

[3] W. B. Nottingham ; *Rep.* 20*th Ann. Conf. Phys. Electronics, M.I.T.*, p. 95 (1960).

Printed in England by Metcalfe & Cooper Ltd., 10-24 *Scrutton Street, London, E.C.2*