

 $\sim$ 

by W.B. Notingham underted

#### THERMODYNAMICS OF THERMIONIC ENERGY CONVERSION

# $W. B.$  Nottingham<sup> $\triangle$ </sup>

#### Research Laboratory of Electronics Massachusetts Institute of Technology Cambridge. Massachusetts

#### ABSTRACT

The contribution made to the understanding of thermionic energy conversion through thermodynamics is an example of one of the principal applications of this scientific discipline. First, it shows the broad oulline of possibility and its bounds. It yields numerical results where details are not available. The next step foward the achievement of the practical application of the principle of energy conversion through thermionics demands <sup>a</sup> detailed understanding of many phenomena related to electron physics. A few of these may be enumerated as  $(1)$  properties of the thermionic emitter, (2) properties of the electron collector, and (3) ionization and excitation of gas (cesium) in the interelectrode apace.

Cesium vapor is most helpful as <sup>a</sup> substance in converter technology, since it adsorbs on refractory metal emitters such ag tungsten or rhenium to lower the work-function and thus permits the emission of <sup>a</sup> high electron current density. Cesium is easily ionized by two methods, (1) contact with the heated emitter surface or  $(2)$  collision with high energy electrons. The ions reduce or eliminate the space-charge limitation of the available current. The collector work-function is determined by its temperature, its base material and. most of all, by the adsorbed layer of cesium.

Great names of electron physics are associated with the development of the fundamentals required for the understanding of thermionic energy conversion. These scientists include Richardson, von Laue, Langmuir, Schottky, Franck, Hertz, Fowler, and others. Voltage-current curves demonstrate quantitatively the two principal modes of converter operation which are the "passive" and the "ignited," and provide the experimental data. The analysis of these data depends on the insight furnished through the application of thermodynamics and statistics to this area of research.

 $\Delta$  The preparation and presentation of this paper was made possible in part by the U. S. Army Signal Corps, the Air Force Office of Scientific Research, and the Office of Naval Research.

tthefftt

### GLOSSARY OF SYMBOLS



### THERMODYNAMICS OF THERMIONIC ENERGY CONVERSION

W. B. Nottingham

#### Introduction

One of the earliest experimental demonstrations of the conversion of heat to electricity by means of thermionics was reported by Schottky<sup>1</sup> in 1913, His correct theoretical interpretation of his experiment laid the groundwork in terms of fundamentals of this means of direct energy conversion. Thermodynamics of energy conversion described as <sup>a</sup> heat engine demands <sup>a</sup> difference in temperature. If thermionics is to play <sup>a</sup> major part, an electron emitter at <sup>a</sup> suitably high temperature T, must deliver electrons to a collector maintained at a lower temperature  $T_2$ . This fact dictates that <sup>a</sup> thermionic energy converter contains <sup>a</sup> minimum of three elements: (1) an emitter, (2) an interelectrode space, so that <sup>a</sup> temperature difference (not a temperature gradient, since temperature has no meaning in <sup>a</sup> perfectly evacuated space of finite dimensions) must exist, and (3) an electron collector must recejve the working fluid, namely, the electrons. The recognition that this means of energy conversion involves the elements of <sup>a</sup> heat engine sets the absolute limit of efficiency through the application of the Carnot principle as  $(T_1 - T_2)/T_1$ . Except in so far as thermodynamics served originally in the hands of Richardson<sup>2</sup> to establish the general nature of the thermionic emission process itself, the mechanistic approach to the understanding and development of thermionic energy conversion must be depended upon as contrasted to the more macroscopic approach associated with thermodynamics.

With the advent of quantum statistics, Von Laue<sup>3</sup> and Dushman<sup>4</sup> were among the first to evaluate the universal thermionic constant anticipated by Richardson. Still more details needed for the understanding of the thermionic emission process were supplied by Fowler<sup>5</sup> and Langmuir<sup>6</sup>.

It was Langmuir who introduced In the simplest and clearest possihle form the concept of "motive." Since this concept is essential to all that follows, Langmuir's definition will be quoted. '"The motive is thus defined as <sup>a</sup> scalar quantity whose gradient in any direction and at any point represents the force component per unit charge which must be applied to an electron or an lon to hold it in equilibrium at the given point." Thus the gradient of the motive is the "motive intensity." It is therefore <sup>a</sup> vector which measures the force per unit charge on an electron or an ionat the point in space at which the gradient is taken. This definition is to be contrasted to the definition of the "electric intensity" defined in <sup>a</sup> similar manner but on the basis that the defining charge approaches zero and therefore cannot include the effects of the charge itself which may induce <sup>a</sup> redistribution of charges on neighboring bodies. In its most elementary form this redistribution of charges creates the "mirror-image" force so important to the understanding of thermionic emission. Schottky was one of the first to call attention to the mirror-image force and establish its importance by his experiments. The electron defraction experiments of Davisson and Germer<sup>8</sup> showed that the change in motive between the interior of a conductor and its value at a point approximately  $10^{-9}$  m from the last layer of atoms represents a considerable change in electron potential of the order of 12 to 16 eV. The Fowler application of Fermi statistics<sup>5</sup> showed

 $-4-$ 

that it was not the total change in electron potential that determines thermi onic emission capability at <sup>a</sup> given temperature, but instead that it is the difference in electron energy between the Fermi level in the interior of the conductor and the electron potential just outside as defined above. It is this difference in energy that rightly defines the work-function. The true work-fupction is not defined in terms of the slope of the so-called Richardson plot which displays  $ln (J_0/T^2)$  as a function of  $(1/T)$ . The work-function determined in this manner must be identified as the "Richardson work-function' which often bears little or no relation to the "true work-function." It is only the true work-function that has validity in relation to the thermionic emission process.

It should be evident from these definitions that work-function is not <sup>a</sup> macroscopic quantity that in any individual case can be evaluated by the application of thermodynamics to the material substances involved. Specifically, the true work-function of <sup>a</sup> single crystal of tungsten depends on the detailed structure of the atomic layer across which the thermionic electron escapes. For example, the work-function of the (110) surface of tungsten is not less than 5.3 eV and the work-function associated with the escape of an electron across the (116) surface is less than 4.4 eV. Thus the work required to remove an electron from the interior of <sup>a</sup> tungsten crystal to <sup>a</sup> point just outside <sup>a</sup> specific crystal face bears little or no direct relation to the effective average work-function of 4.6 eV usually associated with tungsten. The quantitative experiments of Taylor and Langmuir<sup>9</sup> established firmly that the adsorption of <sup>a</sup> fractional monatomic layer of atoms such as cesium resulted in the superposition of additional localized forces that act on an

 $-5-$ 

electron as it escapes from <sup>a</sup> surface to reduce the work-function from its hase value of over 4.5 eV to <sup>a</sup> value as low as 1.7 eV. Again, the details of this extremely important reduction in the work required to remove an electron from an emitter depends not only on the materials, namely tungsten and cesium, but on the adsorption properties of individual crystal facets which in turn depend on the temperature of the emitter and the arrival rate of cesium atoms.

This introduction to the complexities of thermionic phenomena should serve to indicate that advances in thermionic energy conversion will depend on the application of basic theories to the interpretation of results obtainable only by experiments and applicable to specimens and structures that can be fabricated as test vehicles used to evaluate factually the basic concepts applicable.

#### General Considerations

Converter technology demands that the emitter be capable of operation in <sup>a</sup> stable manner at relatively high temperature for <sup>a</sup> long period of time. At this stage of the development of this technology, it is impossible to specify with certainty either the material or the physical structure of the emitter which will meet the demands of high-power density and long life in <sup>a</sup> thermionic energy converter. One of the most promising materials for the emitter is tungsten. Rhenium may possibly be even better, but this fact has not been established with certainty. Porous or tubular structures  $^{10}$ designed to supply electrons out of small openings rather than directly from the solid structure may be superior under some circumstances to the solid surface emitter. These are subjects for experimental research that do not lend themselves readily to theoretical analysis.

 $-6-$ 

The essentials of <sup>a</sup> converter are (1) the emitter with <sup>a</sup> sufficiently low work-function to produce an adequate current density at its operating temperature; (2) a collector of these electrons maintained at a sufficiently low temperature so that the back electron emission will not interfere signifi cantly with the current made available at the higher temperature emitter. The power output therefore depends on the product of current and voltage. A converter diode short-circuited may have <sup>a</sup> high current and no voltage whereas <sup>a</sup> converter diode operated at "open-circuit" will have no current and <sup>a</sup> high voltage. Between these two extremes, the maximum power output is obtainable. At maximum power the voltage will be only  $(kT_1/q)$ unless the difference between the emitter and collector work-functions exceedsthis electron-volt equivalent of temperature. The output voltage can never exceed the difference in the emitter and the collector workfunction, specifically,  $V_{\text{out}} \leq (\phi_1 - \phi_2)$ .

#### Systems Considerations

If maximum power were the only consideration, then the above relation would indicate that the lower the work-function of the collector, the more efficient would be the conversion. The need for generation of electrical power in space furnishes one of the strongest incentives to develop an understanding of and a technology related to thermionic energy conversion. It is system considerations then which will dictate the minimum usable collector work-function and not the matter of efficiency per se. The source of the heat will also have an extremely important bearing on the design and constructional features of any practical thermionic energy converter. Sources considered include solar energy, concentrated on the emitter by large

2434 0

 $-7-$ 

reflectors, nuclear energy delivered to the emitter by <sup>a</sup> wide variety of schemes, and heat from the combustion of various fuels, to mention only three of the more important sources under present consideration. It is self-evident that systems considerations, both in terms of heat source and heat removal will be strong determining factors in any practical application of the principles of thermionic energy conversion. Common to all of these, however, is the need for <sup>a</sup> more basic understanding of the electron emission capability of refractory metals in the presence of cesium; the transfer of electrons across from the emitter to the collector through the cesium vapor aided by its ionization and, finally, the control of the collector work-function and its temperature will be important in the creation of an optimum design. In the sections to follow, some of the researches now in progress which contribute important data upon which <sup>a</sup> better understanding of thermionic conversion depends will be reviewed very briefly.

### Thermionic Emission from Tungsten in the Presence of Cesium

The pioneering work of Langmuir and Taylor<sup>9</sup> directed attention to the all-important factor that the work-function of an emitter can be modified by the presence of an adsorbed layer of polarizable atoms. Cesium atoms polarize to give an average dipole moment per funit area in <sup>a</sup> direction that assists electrons to escape from the surface and therefore lowers its workfunction. Various surfaces hold and polarize cesium atoms differently. It is therefore one of the essentials of <sup>a</sup> good emitter that the surface structure on which the cesium atoms are adsorbed shall be electronically as uniform as possible. Such uniformity can be accomplished by the fabrication of the

 $-8-$ 

emitter from <sup>a</sup> single orientation of <sup>a</sup> crystal. From <sup>a</sup> practical point of view this means of obtaining uniformity may not only be difficult but incompatible with other considerations such as adaptability to <sup>a</sup> specific heat source and availability of fabrication techniques. It is therefore one of the objectives of present research to discover the means of design and fabrication of emitters which will have the desired properties and at the same time not present insuperable constructional difficulties. Clearly, as the need arises, difficult experimental problems may be solved, but for the immediate future researches must be carried on within the framework of present technology.

Thermal etching was used by Langmuir and Taylor to try to establish the needed uniformity. The researches of Houston $^{11}$  yielded additional data concerning the average properties of tungsten emitters in the presence of cesium. These data, combined with the Langmuir data by Nottingham<sup>12</sup> to produce the chart,are presented here as Fig. 1. This figure correlates the average emission properties of tungsten in terms of the emitter temperature and the associated cesium condensation temperature. The lines on this chart correspond to the anticipated work-function. If this is known, then the following equation serves to establish the available zerofield thermionic emission capability of the emitter.

$$
J_o = AT^2 e^{-\frac{q\phi_1}{kT}} = AT^2 e^{-\frac{\phi_1}{T}} \qquad |1.
$$

This fundamental equation serves <sup>a</sup> double purpose. Not only does it indicate the anticipated current density but it serves as <sup>a</sup> means of relating an observed average current density  $J_0$  to the work-function of the material that

 $-9-$ 

would be capable of delivering the observed emission. In <sup>a</sup> form ready for direct computation the emitter work-function may be computed as follows

$$
\phi_1 = \nabla (14.0 + 2 \ln T_1 - \ln J_0) \qquad \qquad |2.
$$

Although the chart shown as Fig. <sup>1</sup> was formed as a correlation chart to present all of the then existent data of Langmuir and Taylor<sup>9</sup> and those of Houston<sup>11</sup> in a unified manner, the accuracy of this interpolation and extrapolation has been verified by the research data of Breitwieser $^{13}$ . The Breitwieser results depend largely on the analysis of the voltagecurrent curves taken with a very specialized diode capable of operating ander <sup>a</sup> wide range of emitter temperatures, cesium temperatures, and spacings. The emitter itself was fabricated from <sup>a</sup> tungsten body, largely <sup>a</sup> single crystal, with the exposed surface perpendicular to the (110) direction within the crystal. There is no proof that the actual exposed surface after its polish and thermal treatment is <sup>a</sup> (110) surface. The true nature of the surface cannot be established until the conclusion of the present research. <sup>|</sup>

Attention is called to these results in that they are illustrative of the factual data needed. The base material, in this case tungsten, must be processed according to some well defined method so that its recrystallization and ultimate surface condition may be controlled. Similar data are needed for rhenium, molybdenum, and tantalum, to name only <sup>a</sup> few of the refractory materials that could have utility in their relation to the direct conversion of heat to electricity by thermionics. Such data will undoubtedly become

available as additional researches in this area continue.

Correlated with these studies are those related to the properties of the collector. Its temperature is always lower than that of the emitter, and therefore it is likely to have <sup>a</sup> higher fractional coverage of cesium. Associated with this higher fractional coverage the desired lower collector work-function may be maintained. The collector must be uniform or it will tend to effectively reflect electrons and thus decrease the current capability of the converter.

#### Ionization and Excitation Properties of Cesium

Except in structures that can be created and maintained as extremely close-spaced diodes, the current avallable from an emitter is likely to be strongly space-charge limited. Of all of the materials readily available to assist in the solution of problems related to thermionic energy con~ version, cesium is without question one of the most important. Its vapor pressure is sufficiently high so that the atom concentration in the interelectrode space can be maintained at <sup>a</sup> convenient level and varied over <sup>a</sup> comparatively wide range by controlling the temperature of the cesium supply maintained in the liquid state. A simple formula serves to relate the atom concentration in equilibrium with the liquid cesium. This equation is given as

$$
N_{Cs} = 2.37 \times 10^{33} T_{Cs}^{-\frac{3}{2}} e^{-\frac{8910}{T_{Cs}}} \text{atoms/m}^3
$$
 [3.

It is not <sup>a</sup> theoretical equation based on <sup>a</sup> thermodynamic analysis of the properties of cesium, but it is an equation which represents the available

 $-11-$ 

experimental data over a very wide range in temperature. Even though this equation serves to relate the atom density in equilibrium with the liquid surface, it is not easy to relate that density to the important one existent actually in the interelectrode space of the converter diode. A useful approximation derivable from kinetic theory and based on certain idealizations not always satisfied in practice uses the expression  $(T_{Cs}/T_1)^{1/2}$ as the multiplying factor. More complex relations may be used, but in view of other related uncertainties, this one has proven to be adequate.

Cesium also has the property that it is relatively easy to excite and ionize. The energy level scheme based on the Grotrian<sup>14</sup> data is illustrated graphically by Fig. 2. The corresponding tabular data are given in Appendix 1. Even though these data define accurately the minimum electron energy required to either excite or ionize the cesium atoms, data on the probability of ionization as the electron energy exceeds the minimum are almost nonexistent. Facts of this type cannot be obtained from theory but must be the result of carefully conceived and carefully executed experiments. Such data are needed in order to assist in the interpretation of experimental results obtained in actual converters.

One of the features that characterizes converter performance relates to the fact that evidence has accumulated in many experiments that copious lonization takes place under circumstances in which it is difficult to account for the necessary electron energy. A simple assumption is that ionization takes place as <sup>a</sup> cumulative process involving first the excitation of the / atom and secondly its ionization from the excited state. Because of the lack of well-documented curves giving the probability of excitation and subsequent ionization, this assumed mechanism is purely hypothetical. Others are within the range of possibility; for example, an excited atom might tend to form an excited molecule and this in turn becomes an ion with very little additional energy,or two excited atoms could combine to form an ionized molecule and an electron as proposed by Witting and Gyftopoulos<sup>15</sup>.

Space ionization is very important when the diode is operating in the "ignited" mode, while for operation in the "passive" mode surface ionization may serve to minimize the adverse effect of electron space-charge. Ion production at <sup>a</sup> hot surface in the absence of either an ion-accelerating or ion-retarding field may be computed by the Langmuir-Saha<sup>16</sup> equation. The basis of this equation is dependent on statistical and thermodynamic reasoning and applies specifically to <sup>a</sup> theoretical computation applicable to an isothermal cavity surrounded by walls having <sup>a</sup> work-function equal to the plasma potential relative to the Fermi level of the surrounding material. Experimentally, this is an unrealistic situation since it implies an absence of either an electron- or an ion-rich sheath that generally separates the plasma region from the surface potential. Since the rate of production of ions depends on the arrival rate of all atoms, the surface temperature and its work-function, it is possible to compute <sup>a</sup> line of demarcation as shown on Fig. <sup>1</sup> which acts as <sup>a</sup> separation boundary between the ion-rich and the electron-rich condition at the immediate surface of the emitter. The line shown there by <sup>a</sup> double dot-and-dash shows the relation between cesium temperature and emitter temperature which for tungsten in the presence of cesium yields an electron current density 492 times greater than the anticipated zero-field ion current density. This

 $-13-$ 

number represents the square root of the mass ratio of the cesium atom to the electron. A general equation by which the plasma potential in an isothermal situation may be calculated has been derived by Nottingham<sup>17</sup> and may be expressed as follows

$$
\phi_0 = \nabla \left[ 25.31 + \frac{3}{4} \ln T + \frac{V_i}{2\nabla} - \frac{1}{2} \ln n + \frac{1}{2} \ln (1 - f)^{-1} \right] |4.
$$

Ion production in an ion-accelerating field is subject to <sup>a</sup> Schottky  $effect$ <sup>18</sup> in a manner very analogous to the phenomena associated with electron emission in the presence of an electron-accelerating field. Unless the test vehicle in which the ion production rate is evaluated for comparison with theory is one designed to have very close spacing, the order of 10 microns, space-charge effects and other spurious phenomena can be expected to interfere with experimental evaluation of the statistical theory.

#### Voltage-Current Curves from <sup>a</sup> Research Diode

One of the first steps that must be taken to evaluate <sup>a</sup> thermionic converter design depends on the acquisition of <sup>a</sup> voltage-current curve. For any particular test vehicle, such <sup>a</sup> curve depends on controllable parameters such as emitter temperature, cesium bath temperature, collector temperature and spacing. Uncontrolled parameters often include the detailed surface structure of the emitter and the collector, and the presence of spurious discharges that may possibly be initiated between other elements of the test vehicle such as the surrounding walls, the emitter or collector support, and other elements that may be present in <sup>a</sup> particular device. In

order to acquire information concerning fundamental mechanisms active in determining <sup>a</sup> voltage~current characteristic, it is necessary to devise a test vehicle which minimizes spurious phenomena. Such a test vehicle has been under investigation by Breitwieser<sup>13</sup> and has yielded valuable information. His studies have not been confined to the limited region in the voltage-current curve that corresponds to power conversion. In his studies, the collector potential may be made quite negative with reference to the Fermi level of the emitter. Under this condition at close spacing, the ion-current yield may be observed and thanks to the presence of supporting guard-rings, leakage currents may be minimized. Two typical voltage-current curves are shown in Fig. 3. One applies to the very close spacing of <sup>10</sup> microns and the other to the larger spacing of 460 microns. Data may be analyzed in terms of the Schottky theory as it relates to ion production. Figure <sup>4</sup> is presented as illustrative of these results. At the close spacing of 10 microns, the observed data follow close to the theoretical line associated with that small spacing. At the larger spacings, the figure shows lines of steeper slopes than those observed at close spacing, and these indicate directly that the Schottky theory is not applicable within the range of applied voltage available before sputtering effects and other interferences set in.

The analysis of the ion-current data, combined with possible electron emission from the collector, serves as the means of separating out the electron current itself from the total observed current in the voltage-current characteristics. The plot of the logarithm of the current density as <sup>a</sup> function of the dimensionless parameter  $(V/\nabla)$  yields additional valuable information.

 $-15-$ 

Four lines typical of these results are shown in Fig. 5. This means of displaying the data yields straight lines over the range in current density that corresponds to the Maxwell-Boltzmann electron energy distribution. The theoretical slope of these lines is such that for a shift in  $(V/\nabla)$  of 2.3 the electron current density changes one decade. The observed results yielded this slope quite accurately up to the Maxwell-Boltzmann limit after which the slope became less than that required by theory. This deviation from theory is <sup>a</sup> direct indication of the presence of some space-charge effect. At the very close spacing of 10 microns, the knowledge of the current density at <sup>a</sup> particular value on the Boltzmann line permits the accurate calculation of the effective work-function of the collector as given by the following formula:

$$
\phi_2 = \nabla \ (14.0 + 2 \ ln T_1 - \ln J_v) + V_{app}
$$

Figure <sup>5</sup> would seem to indicate that the collector work-function increases with the spacing even though its temperature and the other controllable parameters, namely, the emitter temperature and the cesium temperature, are held constant. It is our opinion that this displacement of the Boltzmann line is not <sup>a</sup> true indication of <sup>a</sup> change in the collector work~function but simply shows that <sup>a</sup> certain fraction of the electrons. which normally in the absence of collisions with cesium atoms or ions would have crossed the interelectrode space, are turned back in the "electron-retarding' field and thus re-enter the emitter and are lost to the electron collector.

Another interesting point illustrated by the curves of Fig. <sup>5</sup> is that at very close spacings, the apparent saturation current is very close to 0.28  $A/cm^2$ . This value is remarkably close to that expected on the basis of the chart of Fig. 1. Note, however, that the apparent saturation when the spacing is increased to 790 microns is 7 x 10<sup>-2</sup> A/cm<sup>2</sup>. The flatness of this curve indicates two things: first, <sup>a</sup> space-charge effect is limiting the current; secondly, the modulation of the space-charge by the variation of the surface potential of the collector is hardly noticeable. This means that a complex motive diagram must be assumed to exist in the interelectrode space. Quantitative evaluation of the apparent saturation establishes the location of the space-charge minimum relative to the Fermi level of the emitter.

As the applied potential is made slightly positive and the surface potential of the collector is only slightly negative with respect to the Fermi level of the emitter, ignition takes place. Inspection of the motive diagram shown here as Fig. <sup>6</sup> would seem to indicate that this generation of ions near the collector surface is established at <sup>a</sup> very copious rate when the electron energy available barely exceeds 2.6 eV. This is <sup>a</sup> specific example of the transfer from the "passive" mode of diode operation, in which <sup>a</sup> negligible space ionization is taking place, over to the "ignited" mode for which space ionization is dominant.

After ignition, the applied potential may be made less positive and the current observed remains practically equal to the emission capability of the emitter, as illustrated by the dotted line of Fig. 5. Very close to zero applied voltage, it is evident that the current falls very sharply. In spite

 $-17-$ 

of the steepness of this curve, it Is retraceable as long as the minimum current transferred across the diode does not become less than 7.5 x 10<sup>-2</sup> A/cm<sup>2</sup>. The ignited mode is lost when the electron current transmitted across the diode approaches within <sup>5</sup> percent of the current observed while it was still operating in the passive mode.

It has been the objective of this discussion to indicate that valuable information concerning thermionic diode operation can be acquired as the result of the detailed study of the voltage-current curve. To obtain this information, it is necessary to study over <sup>a</sup> very wide range of applied potentials, so that the various components of current can be separated. It is not easy to make this separation In <sup>a</sup> completely unambiguous manner, Small details should not be overlooked since they may have <sup>a</sup> very important bearing on the determination of the real mechanisms controlling the converter performance.

#### Concluding Remarks

It has been the purpose of this discussion to review the more essential factors that control the effectiveness of the application of thermionics to the direct converslon of heat to electricity. Since direct conversion can be thought of broadly as a heat engine having the electrons as the working fluid, the application of thermodynamics to the problem is limited to rather broad generalizations. It Is difficult to establish <sup>a</sup> line of demarcation between the application of thermodynamics on the one hand and the development of the more detailed considerations associated with the application of statistical mechanics. It has been through the latter that the true meaning of "work-function" and its relation to the Langmulr concept of motive that

~]8-

the principal mechanisms involved in energy conversion can be understood and evaluated. Since practical devices can never be constructed strictly according to theory, the performance characteristics as illustrated by voltage-current curves demand the best possible background of thermodynamic and statistical theory to aid in the interpretation. Theory without experimentally determined factual information serves mainly to establish guidelines. It is the factual information concerning emitter materials and properties, collector materials, adsorption and ionization properties of cesium that need to be filled in in order to provide the necessary working information by means of which practical devices can be developed in order to utilize to the best advantage the concept of direct energy conversion through thermionics.

#### References

- 1. W. Schottky, "Über den Austritt von Elektronen aus Gluhdrahten bei verzögernden Potentialen, "Ann. Physik 44, 1011 (1914).
- 2. O. W. Richardson, "Some Applications of the Electron Theory of Matter," Phil. Mag. 23, 594 (1912).
- 3. M. von Laue, "Gluhelektronen," Jahrb. Radioakt. Elektr. 15, 205 (1928). "Die Entropiekonstante von Glühelektronen, "Jahrb. Radioakt. Elektr. 15, 257 (1928). "Die Rolle der Bildkraft in der Thermodynamik der Gluhelektronen," Jahrb. Radioakt. Elektr. 15, 301 (1928).
- 4. S. Dushman, "Electron Emission from Metals as a Function of Temperature, " Phys. Rev. 21, 623 (1923).
- 3 R. H. Fowler, "The Restored Electron Theory of Metals and Thermionic Formulae," Proc. Roy. Soc. (London) A117, 549 (1928). "The Photo-Electric Threshold Frequency and the Thermionic Work-Function," Proc. Roy. Soc. (London) A118, 229 (1928).
- 6. I. Langmuir and K. H. Kingdon, "Thermionic Effects Caused by Vapours of Alkali Metals," Proc. Roy. Soc. (London) A107, <sup>61</sup> (1925).
- 7. W. Schottky, "Uber den Einfluss von Strukturwirkungen, besonders der Thomsonschen Bildkraft, auf die Elektronenemission der Metalle, " Physik. Z. 15, 872 (1914). "Uber kalte und warme Elektronenentladungen," Physik. Z. 14, 63 (1923).
- 8. C. J. Davisson and L. H. Germer, "Reflection and Refraction of Electrons by <sup>a</sup> Crystal of Nickel," Proc. Natl. Acad. Sci. U.S. 14, 619 (1928).
- 9. J. B. Taylor and I. Langmuir, "The Evaporation of Atoms, Ions, and Electrons from Caesium Films on Tungsten." Phys. Rev. 44, 423 (1933).
- 10. D. L. Dresser, "Analysis of Capillary Converter Experimental Results," Thermionic Conversion Specialist Conference, Gatlinburg, Tennessee, October. 1963, p. 134.
- 11. J. M. Houston, "Thermionic Emission of Refractory Metals in Cesium Vapor," Proceedings of the Round-Table Discussion, June 1 and 2, 1961, Power Information Center Report PIC-ELE-TI 3/3, University of Pennsvlvania, Philadelphia, Appendix F-1.
- 12. W. B. Nottingham, "Analysis of Typical Voltage-Current Curves," Proceedings of the Third Government-Industry Thermionic Round-Table Discussions, December <sup>6</sup> and 7, 1961, Power Information Center Report PIC-ELE-TI 209/1, p. 1-1. "Sheath and Plasma Theory of an Isothermal Diode," Thermo Electron Engineering Corporation Report No. 4-62. October. 1962.
- 13, R. Breitwieser, "Cesium Diode Operation in Three Modes," 23rd Annual Conference on Physical Electronics, M.I.T., March, 1963, p. 267. "On the Relation of Ion and Electron Emission to Diode Diagnostics," Thermionic Conversion Specialist Conference, Gatlinburg, Tennessee, October. 1963. p. 17.
- 14. W. Grotrian, "Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei und drei Valenzelektronen, " Struktur der Materie in Einzeldarstellungen VII, M. Born and J. Franck, Eds., Springer Verlag, Berlin, Germany, vol. 2, p. 40; 1928.

W. B. Nottingham, "Energy Levels of the Cesium Atom," Proc. IEEE 51, 1771 (1963).

- 15. H. L. Witting and E. P. Gyftopoulos, "Volume Ionization Processes in Cesium Converters," Thermionic Conversion Specialist Conference, Gatlinburg, Tennessee. October. 1963, p. 72.
- 16. K. H. Kingdon and I. Langmuir, "Thermionic Effects Caused by Vapours of Alkali Metals," Proc. Roy. Soc. (London) A107, <sup>61</sup> (1925).
- 17. W. B. Nottingham, "Sheath and Plasma Theory of an Isothermal Diode,' Thermo Electron Engineering Corporation Report No. 4-62, October, 1962.
- 18. W. B. Nottingham, "Cesium Ion Production in a Strong Ion Accelerating Field," 23rd Annual Conference on Physical Electronics, M.I.T., March, 1963, p. 281. "Voltage-Current Data Interpreted in Relation to Isothermal Diode Theory,'" Thermionic Conversion Specialist Conference, Gatlinburg,

 $\mathbb{Z}$ 

Tennessee, October, 1963, p. 33.

 $-21-$ 

### APPENDIX

# TABLE 1

### PRINCIPAL SERIES



### TABLE 2

### SHARP SERIES



# TABLE <sup>3</sup>





# TABLE 4

# FUNDAMENTAL SERIES



#### FIGURE CAPTIONS

Fig. 1. Emission properties of tungsten. Solid lines: work-function related to emitter temperature and cesium temperature. Dotted lines: current density in A/cm<sup>2</sup>. Double dot-dash line: demarcation between electron-rich sheath on the left and ion-rich sheath on the right as given by Langmuir-Saha equation. Plus-dash line: demarcation between stable and unstable region. To the right of line ions must be returned to the emitter to obtain stable results.

Fig. 2. Grotrian diagram applicable to cesium. Energy levels shown both relative to the ground state and also expressed relative to the ionized state.

Fig. 3. Two voltage-current curves taken by Breitwieser. Emitter temperature 15000K, cesium condensation 5000K. Solid line spacing: 450 microns. Dash line spacing: 10 microns. Note change in voltage scale for ion currents shown negative. Current density anticipated from chart of Fig. 1: i<sub>0</sub>. MBL limit of Maxwell-Boltzmann distribution. Passive mode range d to e: quasi saturation due to limiting barrier. ignition at f. Range g to h: ignited mode before arc mode at i. Ignited mode returned toward passive mode j to k. Line may be retraced if k remains <sup>5</sup> percent above passive mode line.

Fig. 4. Ion currents plotted on the basis of the Schottky mirror-image theory for ion current increase with applied voltage. Six spacings shown from 10 microns to 790 microns.  $(L-S \cdot 2)$ : anticipated ion current based on Langmuir-Saha theory. ISO: random current in isothermal diode. (1): Langmuir-Saha equation with statistical weight of <sup>2</sup> omitted.

Fig. 5. Electron currents plotted according to Maxwell-Boltzmann energy distribution analysis. Emitter 1500°K, cesium 500°K. Limit of Maxwell-Boltzmann range shown by +. Dashed lines: space-charge theory applied to an ion-free electron emitter. Dotted line: return from ignited mode toward passive mode for the spacing 790 microns. ISO: random current density expected in an isothermal diode.

Fig. 6. Hypothetical motive diagrams applicable to spacing of 450 microns, temperatures 1500°K and 500°K. Surface potential of the emitter relative to its Fermi level shown by left-hand dot. Collector surface potentials shown for six different values of applied potential. Collector work-function 1.8 eV. Note intermediate space-charge barriers not easily modulated. Important changes in the collector sheath are shown.



Fig. 1. Emission properties of tungsten. Solid lines: work-function related to emitter temperature and cesium temperature. Dotted lines: current density in A/cm<sup>2</sup>. Double dot-dash line: demarcation between electron-rich sheath on the left and ion-rich sheath on the right as given by Langmuir-Saha equation. Plus-dash line: demarcation between stable and unstable region. To the right of line ions must be returned to the emitter to obtain stable results.



# **GROUND STATE**

Fig. 2. Grotrian diagram applicable to cesium. Energy levels shown both relative to the ground state and also expressed relative to the ionized state.



Fig. 3. Two voltage-current curves taken by Breitwieser. Emitter temperature 15000K, cesium condensation 5000K. Solid line spacing: 450 microns. Dash line spacing: 10 microns. Note change in voltage scale for ion currents shown negative. Current density anticipated from chart of Fig. 1: i. MBL limit of Maxwell-Boltzmann distribution.<br>Passive mode range d to e: quasi saturation due to limiting barrier. Ignition at f. Range g to h: ignited mode before arc mode at i. Ignited mode returned toward passive mode j to k. Line may be retraced if k remains 5 percent above passive mode line.



 $E_{\perp}$ 





Fig. 5. Electron currents plotted according to Maxwell-Boltzmann energy distribution analysis. Emitter 1500°K, cesium 500°K. Limit of Maxwell-Boltzmann range shown by +. Dashed lines: space-charge theory applied to an ion-free electron emitter. Dotted line: return from ignited mode toward passive mode for the spacing 790 microns. ISO: random current density expected in an isothermal diode.

