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HEATS OF CONDENSATION OF ELECTRONS AND POSITIVE IONS ON MOLYBDENUM IN GAS DISCHARGES

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Abstract

New method for measuring the electronic work function.—A new calorimetric method for measuring the electronic work function of a metal in a gas discharge, has been developed. A small molybdenum sphere was supported in a region of intense gas ionization by three fine wires, two of which formed a thermocouple to measure its temperature, while the third carried the current of the incoming ions. Space potential and mean electronic energies E_- were found by using the sphere as a Langmuir collector. Its rate of heating due to an increment Δj in the electron current reaching it against a small retarding field was measured and equated (with small corrections) to $\Delta j(E_- + \phi_-)$, whence the heat of electron condensation ϕ_- was found.

Values of ϕ_- for molybdenum in argon, hydrogen and nitrogen.—The values of ϕ_- found by this method were: 4.76 volts in argon, 4.04 or 4.35 volts in hydrogen (mixed with argon), and 4.77 or 5.01 volts in nitrogen. The double values follow different treatments of the surface. Owing to uncertainty in the specific heat values of molybdenum these results may be a few percent too high, consequently all the information required for making any necessary corrections from more satisfactory specific heat values has been given.

Measurement and theory of the heating effect on molybdenum due to the neutralization of an argon positive ion at its surface.—By a modification of the method, ϕ_+ for an argon positive ion neutralized at a molybdenum cathode was found to be about one volt. This low value indicates that a large part of the energy of neutralization at the cathode of a discharge tube is lost by the neutralized molecules, probably by radiation, before they make thermal contact with the metal.

Confirmatory evidence for "secondary" electrons.—The presence in a low pressure gas discharge, of the high speed "secondary" electrons discussed by Langmuir, is shown by the good agreement between values of E_- obtained calorimetrically and values calculated from the log j - against-voltage lines of the two groups of electrons, as obtained by Langmuir's methods.

IN RECENT years numerous empirical and theoretical relations have been formulated to describe phenomena of electric discharges in gases, which contain the "work functions" of metals for positive ions and for electrons.[1] The work function ϕ_- for electrons is defined as the work involved when an electron enters or leaves a metal. Similarly the work function ϕ_+ is the energy received by a metal when a positive ion transfers its charge to the metal.

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[1] Güntherschulze, Zeits. f. Physik. **24,** 52 (1924); **31,** 509 (1925); **33,** 810 (1925); **37,** 868 (1926); Penning, Physica, **5,** 217 (1925); de Groot, Physica, **5,** 121, 234 (1925); Compton; Phys. Rev. **21,** 266 (1923); Schottky and von Issendorff, Zeits. f. Physik. **26,** 85 (1924), Seeliger, Phys. Zeits. **27,** 22 (1926).

Values of ϕ_- have been determined (1) by measuring the variation of thermionic emission of electrons with temperature and substituting in Richardson's equation[2]

$$j = A T^{1/2} \epsilon^{-e\phi_-/\kappa T} ;$$

(2) by measuring calorimetrically the heat of evaporation[3] of electrons; or (3) their heat of condensation[4]; (4) by use of Einstein's photoelectric equation[5]; (5) by use of Richardson's equation for the contact difference of potential between metals.[6]

With the single exception of von Issendorff's approximate values of ϕ_- for iron and nickel, in whose determination by method (3) important factors were neglected, all previously published values of ϕ_- have been obtained under conditions which render them of doubtful value in the theory of the gas discharge for one or more of the following reasons: (1) the gas pressure was made as low as possible for the express purpose of eliminating the effect of gas layers on the surface of the metal, as well as other complicating effects; (2) the metal had to be at a high temperature; (3) there was contamination of the cool metal by evaporation from the hot filament as in Cooke and Richardson's[4] determinations; (4) it was impossible to cleanse the surface *in situ*.

There have been no previous measurements of ϕ_+. When this quantity has been used in theoretical equations[7] its value has been calculated from a theoretical relation due to Schottky,[8] which is shown later in the paper to be based on an incomplete analysis of the phenomena involved in neutralization of positive ions at a metal surface.

The present work was undertaken to develop a method for measuring ϕ_- and ϕ_+ with as good precision as possible, for actual electrode surfaces in ionized gases, and to investigate the influence of various gases, electrode materials and surface treatments on these quantities. A preliminary report of some aspects of this work has already been published.[9]

Briefly, the general theory upon which the experimentation was based is as follows. If a Langmuir[10] collector is placed near the anode in a gaseous

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[2] Richardson, Camb. Phil. Soc. Trans. **11**, 286 (1901); Phil. Mag. **201**, 497 (1903); Davisson and Germer, Phys. Rev. **20**, 300 (1922); Dushman, Rowe, Ewald and Kidner, Phys. Rev. **25**, 338 (1925).

[3] Wehnelt and Jentzsch, Verh. d. D. Phys. Ges. **10**, 610 (1908); Ann. d. Phys. **28**, 537 (1909): Cooke and Richardson, Phil. Mag. **25**, 624 (1913); **26**, 472 (1913); Lester, Phil. Mag. **31**, 197 (1916); Davisson and Germer, Ref. 2.

[4] Richardson and Cooke, Phil. Mag. **20**, 173 (1910); **21**, 404 (1911); Schottky and von Issendorff, Zeits. f. Physik. **26**, 85 (1924).

[5] Hughes, Photoelectricity p. 44, 1914; Hagenow, Phys. Rev. **13**, 415 (1919); Kazda, Phys. Rev. **26**, 643 (1925).

[6] Richardson, Phil. Mag. **23**, 264 (1912).

[7] Compton, Phys. Rev. **21**, 266 (1923); Schottky and von Issendorff, Zeits. f. Physik. **26**, 85 (1924).

[8] Schottky, Ann. d. Physik. **62**, 143 (1920).

[9] Compton and Van Voorhis, Proc. Nat. Acad. Sc. **13**, 336 (1927).

[10] Langmuir, Gen. Elec. Rev. **26**, 731 (1923); Science, **58**, 290 (1923); Jour. Frank. Inst. **196**, 751 (1923); Langmuir and Mott-Smith, Gen. Elec. Rev. **27**, 449, 538, 616, 762, 810 (1924).

discharge it will be surrounded by both positive ions and electrons. Now if its potential is maintained at a constant, slightly negative value V_o with respect to the space potential, positive ions will reach it at a constant rate due to their velocity of agitation in the gas, and the small attracting field V_o. Also electrons will reach it at a constant rate against the retarding field V_o because of the Maxwellian distribution of their velocities. Consequently in unit time the collector will receive an amount of heat H_o which is made up of: (1) the heat transfer by radiation H_r; (2) the heat transfer by conduction H_c; (3) the heat contribution of the positive ions due to their average energy of agitation, E_+ in the gas, their acceleration by the field, and their heat of neutralization at the metal surface; and (4) the heat contribution of the electrons due to their energy of agitation E_-, and their heat of condensation into the metal. Thus

$$H_0 = H_r + H_c + j^+(E_+ + V_0 + \phi_+) + j_0^-(E_- + \phi_-). \tag{1}$$

If the potential of the collector is then suddenly changed to a less negative value V_f there will be, immediately after the change, no appreciable variation of H_r and H_c, only a negligibly small change in j^+, but a large change in j^-. Hence

$$H_f = H_r + H_c + j^+(E_+ + V_f + \phi_+) + j_f^-(E_- + \phi_-). \tag{2}$$

Then subtracting Eq. (1) from Eq. (2)

$$H_f - H_0 = j^+(V_f - V_0) + (j_f^- - j_0^-)(E_- + \phi_-). \tag{3}$$

The difference $H_f - H_o$ may be calculated from the heat capacity of the collector and its initial rate of temperature rise when the potential is changed from V_o to V_f. Then ϕ_- may be readily calculated since all of the remaining quantities on the right side of Eq. (3) are measured directly or are easily found by Langmuir's collector methods. In particular

$$E_- = \frac{0.869(V_f - V_0)}{\log_{10} j_f^-/j_0^-}\,. \tag{4}$$

In order to find ϕ_+, much larger potential differences and more negative potentials must be used in order to obtain larger variation of j^+ and to minimize the effect of j^-. Consequently other factors enter in, the full discussion of which will be taken up later.

The general idea of the investigation was therefore to measure the heating effect due to the condensation of known numbers of electrons or ions, measure and make allowance for their initial translational energies in the gas, and thence calculate the respective heats of condensation.

APPARATUS

The discharge tube used in making the observations was constructed as shown in Fig. 1. It was essentially a low voltage arc tube to which was added a small spherical auxiliary electrode C, provided with a thermocouple and located in the axis of the tube and distant about 1 cm from the nearest part *S* of the anode, on the side away from the filament *F*. The anode *A* was made of nickel and consisted of a cylindrical part fitting fairly closely to the walls, a small disk *S*, 1 cm in diameter, supported by two cross wires at the end of the cylinder, and a circular wing *W* placed at such an angle as to shield *C* from the reflected radiation of the 15 mil tungsten wire filament. The disk *S* served to shield *C* from the direct radiation from the filament and to minimize contamination of *C* by evaporated filament material.

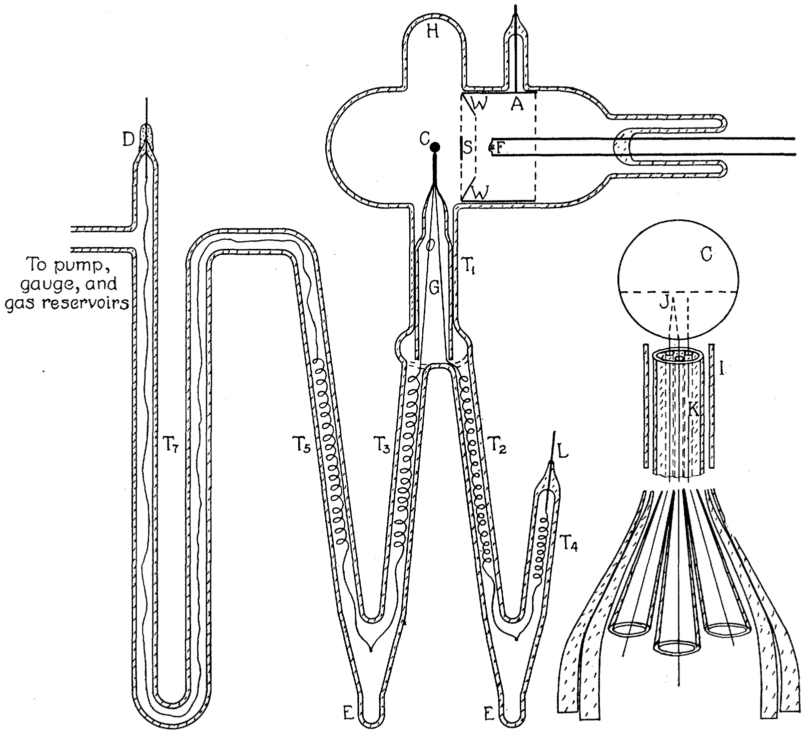

Fig. 1. Arrangement of apparatus and magnified sketch of collector mounting.

The sphere *C* was 3.4 mm in diameter, was made of molybdenum and was formed by drawing an arc between two vertical molybdenum wires in an atmosphere of hydrogen and allowing the arc to run until a bead of the desired size was formed on the upper wire. After this the bead was separated from the wire by grinding in such a way as to give an approximate sphere. Next, to prepare the sphere for mounting, a thin groove was cut nearly half way through it, by means of a thin saw blade and a sludge of fine carborundum in water, while being held firmly by means of two small hemispherical pits directly opposite each other in the leaves of a small steel hinge which was gripped in a vise. Then to free the sphere from hydrogen or any other gases which it might later give out from its interior, it was caged with molybdenum wire on to a disc of molybdenum and the disk heated nearly to the melting point in a vacuum treating bottle, by means of high frequency induction currents. This heated the sphere to almost white heat, at which temperature it was maintained until no further evolution of gas could be detected. After a slight polishing to give a bright clean metal surface the weight of the sphere was accurately determined.

The method of mounting the sphere C is shown in the magnified side sketch in Fig. 1. The sphere was supported by three fine wires about 0.12 mm in diameter, two of which were copper and the third constantan, constituting the leads of the thermojunction J and a current lead. To keep these wires insulated from each other outside of C they were passed through the fine three-channeled glass tube K made by drawing down a larger tube in which had been placed three small thin-walled tubes. Another small thin-walled tube I surrounding K without touching it for at least 2 cm back from the end, and extending up almost to C, served to prevent any chance of electrical contact between any of the leads and whatever metal deposits might later be formed when C was bombarded to free it of gas layers. The lead wires and supporting glass tubes were kept as small as possible in order to minimize the conduction of heat away from the sphere. Good electrical and mechanical contact between C and the lead wires was obtained by placing their ends in the groove and squeezing it shut against them, using again the pitted iron hinge mentioned above, to prevent any considerable distortion of the sphere.

When the sphere had been mounted on its support the whole assembly was placed in a glass tube connected to an evacuating system and the thermocouple leads brought out through a "picein" wax joint. After annealing the thermocouple in vacuum at 500°C for about 60 hours it was calibrated at the steam, tin and sulphur points with the cold junction in an ice bath.

Next, the sphere was put into position in the discharge tube which had previously been connected up to the evacuating system by the connecting tubing shown in Fig. 1. The tube G supporting C fit snugly into the bottom tube T_1 of the discharge tube, and had been adjusted in length so as to bring C at the desired position with respect to S. Holes in the shoulder of G provided for the free passage of gases past it. When G was lowered into place through an opening in H, the previously coiled ends of the leads were guided down into the tubes T_2, T_3 and another similar one behind T_3. Then the ends of these lead wires, and of the ones which had previously been placed as shown in tubes T_4, T_5 and T_6 (behind T_5), were pulled out through the open ends E and melted together with a small reducing flame after which the junctions were drawn back into the tubes by the springs, thus allowing the glass tubes to be closed up. The current lead was brought out through a tungsten seal at L and the thermocouple leads out through small capillaries at D and at the end of the similar tube behind it, De Khotinsky wax being used to make these seals gas tight. This general arrangement was used so as to make it possible to change spheres without much difficulty; to eliminate the thermoelectric effects which might result if segments of tungsten were used to bring the thermocouple leads out through the glass; and to make it possible to keep wax vapors out of the discharge tube, which was done by keeping liquid air around the U tubes T_7. This last precaution was proved to be quite necessary by the very erratic results obtained with an earlier tube having the leads coming out through wax seals in the bulb itself. Mercury vapor was prevented from ever reaching the U tubes by a stopcock and another liquid air trap which was always immersed in liquid air when the stopcock was open.

The discharge tube was surrounded by a tight box of quarter-inch asbestos board in which were placed heating coils so that the tube could be baked to a temperature of about 450°C, this box serving also to prevent temperature fluctuations which might result from air currents in the room during measurements. Care was always taken to keep the room temperature as constant as possible when observations were being made.

The electrical arrangements used are shown in Fig. 2.

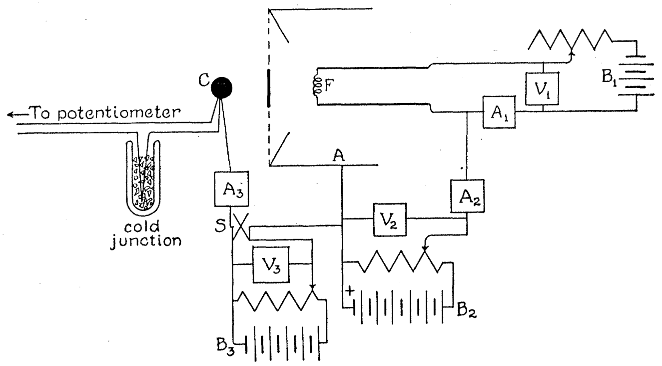

Fig. 2. Arrangement of electrical circuits.

The gases used in the discharge tube while carrying on this investigation were argon, hydrogen and nitrogen. The argon was purified by prolonged arcing between calcium electrodes in a bulb connected to the pumping system. The hydrogen was prepared by the electrolysis of a saturated solution of barium hydroxide and dried with phosphorus pentoxide. Waran's[11] method using ammonia and bromine was used to prepare the nitrogen. When a gas was admitted to the discharge tube it had to pass through both liquid air traps.

METHODS OF OBSERVATION AND CALCULATION

1. *In the determination of* ϕ_-. The quantity (H_f-H_o) of Eq. (3) was obtained from the product of the heat capacity Q of the collecting sphere C and the rate of temperature change dT/dt of C immediately after the change of potential from V_o to V_f. Since the temperature, starting at T_o when $t=0$, approached a final limiting value exponentially,

$$T-T_0=(T_f-T_0)(1-\epsilon^{-at}) \qquad (5)$$

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[11] Waran, Phil. Mag. **42,** 246 (1921).

where T was the temperature at time t, e the Naperian base, and a a constant dependent upon the existing experimental conditions. Then it follows from (5) that

$$\left(\frac{dT}{dt}\right)_{t=0} = a(T_f - T_0)\,, \quad \text{where} \quad a = \frac{2.303}{t}\log_{10}\frac{T_f - T_0}{T_f - T}\,. \tag{6}$$

Consequently to obtain the data necessary to calculate a value of ϕ_- the procedure was as follows. The arc was first allowed to run for an hour or more to insure equilibrium conditions, particularly in regard to temperature. Then, using the sphere C as a Langmuir collector,[10] a set of current measurements was made over a voltage range from negative 30 volts with respect to the anode, to a potential well above that of the space. From this set of measurements could be obtained, by Langmuir's methods, the positive ion current j^+, the space potential V_s and the average energy E_- with which electrons reach the sphere when it is at a negative potential with respect to the space. Then, with the potential V_o of the collector somewhat negative to the space, the system was allowed to stand until the collector reached temperature equilibrium, when the conditions would be those represented in Eq. (1). After recording the current j_o to C, and electromotive force mV_o of the thermocouple, two stop watches were started simultaneously with a change of the sphere potential to some different negative value V_f. Then by slowly turning the drum of the potentiometer, the galvanometer deflection was kept as near zero as possible. At some instant when the deflection was exactly zero, one watch was stopped and the time t_1, and corresponding mV_1, were recorded, after which mV_2 was measured in the same way for time t_2 obtained by means of the second watch. As soon as the temperature became practically constant, which was generally about 5 minutes after t_o, record was made of mV_f. This gave the data for calculating two values of the quantity a, and the mean of the two $\bar{a}$ was used in applying Eq. (6).

In Table I are tabulated typical sets of observations and the resulting quantities obtained from the various steps in the calculating of ϕ_-. In column 2, j_o and j_f are the total collector currents in milliamperes, while j^+ is the positive ion current and is the amount to be added to j_o and j_f to give j_o^- and j_f^-. The value of j^+ was determined in the usual way,[10] *i.e.*, by plotting positive ion currents against applied voltages which were enough negative to the space to prevent any appreciable number of electrons from reaching the collector. This gave a practically straight line with small slope, whose extension gave j^+ at V_o.

To obtain the temperature differences given in column 5 the corresponding millivolt differences obtained from column 4 were divided by the millivolt differences per degree of the electromotive force of the thermocouple at the corresponding temperatures. The temperatures and corresponding millivolt differences per degree were readily determined from two curves obtained by plotting against temperature on a large piece of graph paper, the values of mV and $d(mV)/dT$ calculated at 20° intervals from the calibration equation of the thermocouple, $mV_T = .0400766T + .00004344T^2 - .00000002244T^3$.

For the sake of conserving space, two independent quantities are tabulated in column 8, Q being the heat capacity of the collector in milli-joules per degree, and C^+ the quantity arising out of the term $j^+(V_f - V_o)$ in Eq. (3), which quantity had to be added to the product of the quantity in column 7, times Q, to give $(E_- + \phi_-)$. The values of E_- in column 10 were calculated by means of Eq. (4).

TABLE I

Typical sets of data and quantities obtained in the determination of ϕ_- for molybdenum in pure nitrogen.

The first two sets of observations were taken in close succession about two hours after pure nitrogen had been placed in the arc tube; the third set was one of several similar ones taken after the nitrogen had remained in the tube over night, and the last three were taken in succession after bombarding the collector for 1 minute with a 0.2 milliampere positive ion current under an applied potential of about 550 volts.

1	2	3	4	5	6	7	8	9	10	11
$V_f - V_0$	j_0 j_f j^+	t_0 t_1 t_2 t_f	mV_0 mV_1 mV_2 mV_f	$T_f - T_0$ $T_f - T_1$ $T_f - T_2$	a_1 a_2 $\bar{a}$	$\frac{(T_f - T_0)\bar{a}}{j_f^- - j_0^-}$	Q C^+	$E_- + \phi_-$	E_-	ϕ_-
volts	ma.	sec.	millivolts	°C				volts	volts	volts
	0.390	0	9.135	5.510						
0.632	1.615	24.5	9.255	3.303	.02090	.0937	60.90	5.73	0.93	4.80
	0.034	53.4	9.336	1.814	.02080					
		∞	9.435		.02085		0.02			
	0.395	0	9.095	5.335						
0.613	1.585	23.7	9.209	3.234	.02112	.0944	60.88	5.77	0.92	4.85
	0.034	53.2	9.290	1.744	.02100					
		∞	9.385		.02106		0.02			
	0.395	0	9.220	5.595						
0.652	1.600	20.6	9.325	3.662	.02050	.0951	60.95	5.81	0.98	4.83
	0.037	56.0	9.428	1.775	.02050					
		∞	9.525		.02050		0.02			
	0.475	0	9.130	8.524						
0.679	2.290	26.2	9.325	4.945	.02080	.0970	60.95	5.92	0.90	5.02
	0.035	55.0	9.444	2.763	.02050					
		∞	9.595		.02065		0.01			
	0.505	0	9.085	7.895						
0.631	2.205	35.0	9.305	3.849	.02052	.0958	60.92	5.85	0.89	4.96
	0.035	66.0	9.405	2.013	.02070					
		∞	9.515		.02061		0.01			
	0.500	0	9.032	8.275						
0.630	2.225	24.6	9.208	5.028	.02024	.0961	60.90	5.86	0.87	4.99
	0.035	56.9	9.336	2.676	.01984					
		∞	9.482		.02004		0.01			

The observations for determining ϕ_- in argon were made with the gas pressure about 0.5 mm and a 16 volt 160 milliampere arc running, since under these conditions conveniently large electron currents to the collector could be obtained at potentials well below the space potential, and also the probability that a positive ion would make a collision while passing through the space charge sheath was small, thus practically eliminating any uncertainty which such collisions might introduce in the extrapolated value of j^+. In pure nitrogen the same pressure and a 20 volt 120 milliampere arc were used. It was found that a sufficiently strong low voltage arc could not be easily maintained in pure hydrogen, consequently mixtures containing from 50 to 90 percent of argon were used, and the pressure had to be reduced to about 0.3 mm in order to obtain suitable arc currents (from 40 to 120 milliamperes) with 20 volts across the tube.

When making a series of observations with a given gas, the collector was frequently bombarded with high velocity positive ions for about a minute at a time, in order to change the surface condition, if this could be done, *i.e.*, if the existing surface condition were not the one truly characteristic of the gas. If successive bombardments produced rather variable results contamination of the gas was suspected, whereupon the arc tube was evacuated and refilled with a fresh supply of the pure gas. This process was repeated until bombardment produced no change in results, or only consistent, repeatable changes which will be discussed later. After hydrogen had been used in the tube it was especially difficult to remove the effects of this gas so completely that the characteristic value of ϕ_- in argon or nitrogen could again be obtained, but this could be done by repeated bombardments and flushings with argon.

2. *In the determination of* ϕ_+. In this part of the investigation the arc was maintained in pure argon, since the positive ion currents in nitrogen arcs were found to be much smaller than in argon arcs. To obtain positive ion currents considerably larger than those found under the conditions existing when ϕ_- was investigated, the arc current was increased to about 400 milliamperes by increasing the filament temperature. However, when this was done with the pressure kept at about 0.5 mm the semi-logarithmic plot of the electron current (to C) against the applied voltage indicated the presence of a large number of the high speed "secondary" electrons discussed by Langmuir.[12] To minimize the disturbing effect which these high speed electrons might have upon the experimental results, their concentration was greatly reduced by increasing the pressure to 1.0 mm or more.

At first sight the simplest method of determining ϕ_+ would seem also to be by use of Eqs. (1) and (2), making V_o and V_f sufficiently negative to prevent practically all electrons from reaching the collector and making $(V_f - V_o)$ sufficiently large to give accurately measurable values of $(j_f^+ - j_o^+)$ and of $(dT/dt)_{t=o}$. Under such conditions we have

$$H_f - H_0 = (j_f^+ - j_0^+)(E_+ + \phi_+) + j_f^+ V_f - j_0^+ V_0. \tag{7}$$

This equation would be valid if the positive ions lost no energy at collisions with neutral atoms while passing through the space charge sheath which surrounded the collector. Experimental test of the equation showed that the loss of energy resulting from collisions was an important factor,

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[12] Langmuir, Phys. Rev. **26**, 585 (1925).

for without taking it into account in the calculations, two sets of observations gave for $(E_+ + \phi_+)$ the absurd values of -75 and -55 volts respectively. Though this method could not be used to find ϕ_+ directly, it could be used to obtain the correction which must be made for energy losses at collisions, as will be fully described later.

The procedure actually followed in obtaining data for the calculation of ϕ_+ was based upon the following considerations. When the equilibrium temperature of the collector is followed as its potential is made more and more negative with respect to the space, a potential is found for which the temperature is a minimum. For more negative potentials the increase in heating effect of the positive ions because of both their increasing number and their greater acceleration, overbalances the decrease in heating effect of the electrons due to their decreasing numbers, whereas for less negative potentials the increase in heating effect of the electrons is greater than the decrease in the effect of the positive ions. Consequently there will be, in general, two potentials which will produce the same heating effect at the collector. Calling these potentials with respect to the space, V_o and V_f as before, and representing by $F_o(V_o)$ and $F_f(V_f)$ the respective energies which the positive ions have retained after suffering collisions in passing through the sheath, *i.e.*, the average energies with which they strike the collector under the influence of the respective potentials, the equation which expresses this equality of heating is

$$j_f^+\{F_f(V_f)+E_+ + \phi_+\}+j_f^-(E_- + \phi_-)=j_0^+\{F_0(V_0)+E_+ + \phi_+\}+j_0^-(E_- + \phi_-) \qquad (8)$$

Thus in the method based upon this equation the determination of the rate of temperature change was not involved, and consequently this possible source of considerable error was eliminated.

As a convenient value of V_o, the potential at which equal numbers of positive ions and electrons reached the collector was used since the collector would take up its equilibrium condition for this potential when insulated, as with the switch S open. Consequently the switch needed to be closed only a very short time when determining the potential V_o giving zero current through A_3, or when determining the potential V_f giving a fairly large positive current j_f through A_3 but producing the same temperature in the collector as open circuit. All but the final small adjustments of the potential divider were made with the switch open. In this way the observations could be taken rapidly so that the gradual fluctuations of the room temperature would have no appreciable effect upon the results.

Immediately after a series of the observations just described had been made, a set of current measurements over a wide range of potentials was taken just as was done preliminary to taking data for calculating ϕ_-. From these current measurements were obtained the electron currents at various potentials, and by means of their semi-log plot the average energies of the two groups of electrons as well as the currents at V_o and V_f resulting from each group, were found. To distinguish the two groups of electrons from each other, all quantities involving the faster group will be primed, thus

$j_o^+ = j_o'^- + j_o^-$. The extrapolated semi-log plot of the slower electrons showed that their number was negligibly small at V_f, consequently $j_f^+ = j_f + j_o'^-$. Taking account of the two groups of electrons Eq. (8) takes the form

$$(j_f^+ - j_0^+)(E_+ + \phi_+) = j_0^+ \cdot F_0(V_0) - j_f^+ \cdot F_f(V_f) + j_0^-(E_- + \phi_-) + (j_0'^- - j_f'^-)(E_-' - \phi_-) \tag{9}$$

In order to determine $F_o(V_o)$ and $F_f(V_f)$, the number of collisions made within the sheath and the fraction of energy retained after each collision had to be found. That the sheath thickness when the positive ions made collisions within the sheath, could not be calculated by means of the Langmuir[10, 13] equation for spherical electrodes (which assumes no collisions) was shown by the fact that the results obtained by this method led to widely varying values for the positive ion concentration in the discharge, when based on measurements at different electrode potentials. The sheath thickness was actually found by extending the approximately straight positive ion current-voltage line to the space potential and thus obtaining from the known surface of the collector and the extrapolated value of the positive ion current, the rate at which positive ions crossed unit area in the space. From this rate, the sheath area and thence the thickness of the sheath for any given value of j^+ could be calculated. Since the positive ions in all the cases where these calculations were made had velocities rather large in comparison with those of the neutral gas molecules, their mean free path was taken to be $\sqrt{2}$ times the kinetic theory value for a molecule at the given pressure and temperature.

If y be the fraction of its energy retained by a positive ion after a collision and if, in order to simplify the calculations, it be assumed that the potential drop across the space charge sheath is uniform,[14] it can be shown that as the result of an integral number n of collisions made by a positive ion falling through a potential drop V across the sheath

$$F(V) = \frac{V}{n}\left(y + y^2 + \cdots y^{n-1} + \frac{y^n + 1}{2}\right). \tag{10}$$

If the average number of collisions be a proper fraction f, then $F(V)$ must be obtained from the equation

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[13] Langmuir and Blodgett, Phys. Rev. **24,** 49 (1924).

[14] If V_s represents the potential at the surface of the sheath and V_x that at a point within the sheath a distance x from the surface, instead of $V_x - V_s \propto x$ in accord with the above assumption, probably $V_x - V_s \propto x^b$ approximately, where the exponent b would have a value between 4/3 and 2. The lower limit is the one obtained from the space charge equation, for the case of no collisions or ionization, and the upper limit is obtained from Aston's measurements (Proc. Roy. Soc. London, **A84,** 526 (1911)) of the potential distribution in the abnormal cathode fall space, where the positive ions made numerous collisions and there was probably considerable ionization taking place within the sheath. Though the simplifying assumption is not in exact accord with the actual conditions, from considerations which will be discussed later it is believed that the use of this assumption does not introduce any large error into the results.

$$F(V)=V\left\{1-\frac{f(1-y)}{2}\right\}. \tag{11}$$

To obtain $F(V)$ for a given y and an average number of collisions m, which was a mixed number, the values of $F(V)$ for several integral numbers were calculated from Eq. (10) and from the plotted curve of these values, that for m collisions could be read off directly.

It was evident from the absurd values of $(E_+ + \phi_+)$ obtained from Eq. (7) that the first term on the right side of the equation was small in comparison with the other terms, consequently for a first approximate calculation of y, the equation

$$H_f - H_0 = j_f^+ \cdot F_f(V_f) - j_0^+ \cdot F_0(V_0) \tag{12}$$

could be used. In column 2 of Table II are tabulated the positive ion currents obtained at the potentials given in column 1. These observations were made in argon at a pressure of 1.0 mm and the temperature of the collector ranged from 233° to 243°. Assuming that the temperature in the sheath was the same as that of the collector, the average number of collisions given in column 3 was calculated from sheath thickness, as described. The values

TABLE II

Calculation of y, the fraction of energy retained by a positive ion after a collision.

1	2	3	4	5	6	7	8	9
V_0 V_f	j_0^+ j_f^+	Number of Collisions	Observed H_f-H_0	Calculated values of H_f-H_0			Percent difference in values of a	Weighted estimate of value of y
				For $y=1.0$	For $y=0.8$	For $y=0.75$		
Volts	milliamps.			milliampere-volts				
17.1 32.1	0.402 0.4425	.75 1.20	5.88	7.33	6.14	5.88	7%	
17.05 32.1	0.402 0.441	.77 1.22	5.62	7.30	6.11	5.84	4%	
17.05 32.0	0.400 0.4395	.76 1.21	5.58	7.24	6.06	5.79	1%	0.73
31.8 46.8	0.437 0.473	1.21 1.60	5.65	8.21	6.44	6.02	3%	
31.8 46.8	0.4375 0.474	1.23 1.63	5.80	8.23	6.43	5.99	1%	
31.8 46.7	0.4355 0.470	1.23 1.58	5.75	8.09	6.40	6.00	3%	0.73
46.7 61.5	0.4695 0.5025	1.61 1.94	6.39	8.99	6.67	6.18	4%	
46.3 61.5	0.4705 0.5075	1.64 2.02	6.22	9.45	6.91	6.35	0%	
46.2 61.4	0.4675 0.500	1.61 1.95	6.56	9.10	6.67	6.40	4%	0.75

of $(H_f - H_o)$ recorded in column 4 were calculated by exactly the same method as was used in the determination of ϕ_-. The theoretical values which $(H_f - H_o)$ should have when y is equal to 1.0, 0.8 and 0.75 respectively, were obtained by calculating the value of the right side of Eq. (12) by the method described in the discussion of Eq. (10) and are recorded in columns 5, 6, and 7. A comparison of these values with the observed ones in column 4, taking into account the probable relative accuracies of the values in column 4 as indicated by column 8, led to the estimated values of y for the different voltage intervals, which are recorded in column 9. By extrapolation of the curve of these estimated values of y plotted against the average potentials for which they were calculated, were obtained the proper values of y to be used in obtaining $F_o(V_o)$ and $F_f(V_f)$ in Eq. (9).

Having now described the methods of obtaining all the quantities on the right side of Eq. (9), we pass to an example of the actual calculation of $(E_+ + \phi_+)$ from data obtained by the method outlined in the discussion of Eq. (8). In the first three columns of Table III are tabulated the potentials with respect to the space, and the various current components which had been determined by the method described just previous to the statement of Eq. (9). Column 4 gives the calculated average number of collisions made by the positive ions in passing through the sheath. The algebraic sum of the quantities in columns 5 and 6, which is recorded in column 7 gives the calculated value of the right side of Eq. (9) in milliampere-volts. The value of $(E_+ + \phi_+)$ recorded in column 9 was obtained by dividing this sum by the quantity $(j_f^+ - j_o^+)$ given in column 8. Since $(E_+ + \phi_+)$ was comparatively

TABLE III

Calculation of $(E_+ + \phi_+)$ in argon.

1 V_0 V_f volts	2 $j_0'^-$ j_0^- j_0^+ ma.	3 j_f $j_f'^-$ j_f^+ ma.	4 f_f $f_,$	5 $-j_f^+ \cdot F_f(V_f)$ $+j_0^+ \cdot F_0(V_0)$ ma.-volts	6 7 $j_0^-(E_- + \phi_-)$ $(j_0'^- - j_f'^-)(E_-' + \phi_-)$ ma.-volts	8 Sum of 5 & 6	9 $j_f^+ - j_0^+$ ma.	 $E_+ + \phi_+$ volts
2.634	.0645	.3475	.11	−3.010	1.598			
9.00	.2696	.0036				.037	.0170	2.18
	.3341	.3511	.34	.868	.581			
2.644	.0642	.3465	.10	−3.002	1.595			
8.97	.2690	.0036				.038	.0169	2.25
	.3332	.3501	.33	.867	.578			
2.656	.0639	.3460	.10	−2.992	1.594			
8.95	.2689	.0036				.049	.0168	2.91
	.3328	.3496	.33	.872	.575			
2.661	.0637	.3455	.10	−2.988	1.594			
8.94	.2688	.0037				.051	.0167	3.05
	.3325	.3492	.33	.873	.572			
2.663	.0635	.3445	.09	−2.980	1.589			
8.94	.2680	.0037				.051	.0167	3.05
	.3315	.3482	.32	.872	.570			

small, a second order calculation of y in which the term involving $(E_+ + \phi_+)$ was taken into account, produced only a small change in the value of y, and this in turn led to a negligibly small change in $(E_+ + \phi_+)$.

Determination of $(E_+ + \phi_+)$ in argon was made at the two gas pressures, 1.8 mm and 1.0 mm. The actual procedure followed in making the observations for calculating $(E_+ + \phi_+)$ at a given pressure, consisted of six steps. (A) Four or more sets of observations were made of the potential to give zero current, and of the more negative potential which produced the same heating, and also of the net current at the latter potential. (B) The currents over a large range of voltages were measured, from which measurements were to be obtained: (a) the actual positive ion and electron currents at the potentials observed in step (A); (b) the velocities of agitation in the two groups of electrons, and the fraction of the electron currents due to each group; and (c) the positive ion drift across unit area in the space, which was to be used in calculating the number of collisions within the sheath. (C) The sets of data such as used in Table II for the calculation of y were next taken. (D) Then several sets of observations for obtaining the actual value of ϕ_- under the *existing* conditions were made, since a very slight amount of impurity might affect this value considerably. As soon as possible after (D) steps (A) and (B) were repeated. Though no adjustment of the arc conditions was made during this entire procedure there was a very slow decrease in the arc current, which was probably due to a gradual decrease in the voltage of the filament battery. Consequently a record was kept of the time at which each observation was made, and the arc current was recorded at frequent intervals, so that correction could be made for the change of arc current taking place during the intervals between the taking of the different types of observations. The series of observations above described furnished the data for the calculation of two separate series of values for $(E_+ + \phi_+)$.

TABULATION AND DISCUSSION OF RESULTS

Consideration of the available data on the specific heat of molybdenum. The apparatus had been set up and a series of observations taken before it was discovered that the published measurements of the specific heat of molybdenum are meager and not very consistent. It was deemed advisable, however, to go on with the measurements with the molybdenum collector since the results could easily be corrected, if necessary, when more satisfactory specific heat data became available. In Fig. 3 are shown all of the specific heat values for molybdenum which could be found in the literature, except values for very low temperatures and the values by Wüst for temperatures above 300°C.

The equations of the lines I, II and III are:

$$C_T = 0.0640 + 0.000032T \qquad \text{(I)}$$

$$C_T = 0.0606 + 0.000028T \qquad \text{(II)}$$

$$C_T = 0.0578 + 0.0000257T \qquad \text{(III)}$$

where T is the Centigrade temperature. Eq. (I) was obtained from the straight line which seemed to the author to give the best fit with the experimental data when all values were given equal weight,[15] and was the one used in making all of the original calculations among which were the ones given so far in this paper. When it was learned that Eq. (III),[16] which is based largely on theoretical considerations, was used in the General Electric Company's Research Laboratory, the previously obtained results were recalculated using this equation. Since this recalculation gave values for $(E_+ + \phi_+)$ which seemed to be unreasonable, as will be shown when discussing the results, it seemed probable that Eq. (III) gives too low values of the specific heat. It was deemed advisable to calculate the results also on the basis of an intermediate equation so that when satisfactory specific heat data become available the correct results may be easily obtained by interpolation. Eq. (II) is the intermediate equation used and is one which gives very close agreement between the value of ϕ_- of molybdenum, as determined in argon in this investigation, and the value given by Dushman[17] when the

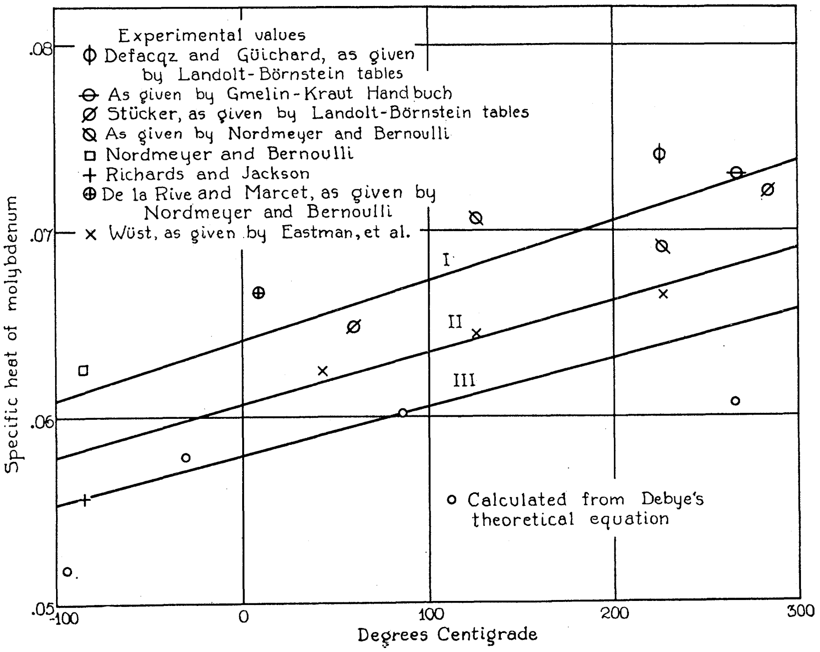

Fig. 3. Specific heat values for molybdenum.

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[15] The measurements of Wüst (Ver. Deutsch. Ing. Forschungarb. No. **204** (1918). cf Eastman, Williams and Young, Jour. Am. Chem. Soc. **46,** 1184 (1924)), were unknown to the author when Eq. (I) was obtained.

[16] We are indebted to Dr. H. A. Jones of the General Electric Company's Research Laboratory for giving us the values obtained from the theoretical calculations, and also the specific heat equation for molybdenum which is used in that Laboratory.

[17] Dushman, Phys. Rev. **21,** 623 (1923).

latter has been adjusted[18] for the temperature (200°C) at which the present measurements were made.

Results for ϕ_-. In the last three columns of Table IV are given the mean values of ϕ_- as calculated when using the specific heat Eqs. (I), (II) and (III) respectively. The average temperatures are given also, since they will be useful if other specific heat data are used to correct these results. Of the two values of ϕ_- obtained with hydrogen present, perhaps one is due to an atomic layer and the other to a molecular layer on the collector. The lower of these two values was usually obtained when there was a large quantity of hydrogen present, and just after the collector had been bombarded with positive ions accelerated by a potential of 500 volts. The higher value was the one which persisted for a long time when the tube was being freed of hydrogen preparatory to taking further readings in argon or nitrogen. It was not found possible to control conditions so that one value could be obtained repeatedly with the complete exclusion of the other. The values would change suddenly from either one to the other when there had been no noticeable change in the experimental conditions. This effect was at first very disconcerting as the results seemed so variable that they did not seem to be reliable, and it was only after a considerable number of values had been obtained none of which came between 4.12 and 4.26 volts that the true state of affairs became apparent.

TABLE IV

Values of ϕ_- for molybdenum.

Gas	Average Temperature	Number of values averaged		ϕ_- in volts	
			I	II	III
Argon	200°C	20	4.76	4.39	4.12
Argon-hydrogen mixture	200°	24	4.35	4.04	3.79
	208°	25	4.04	3.70	3.47
Nitrogen	196°	20	4.77	4.43	4.18
	197°	13	5.01	4.66	4.39

Two values of ϕ_- were obtained also in nitrogen, the lower one of which is seen to be almost identically the same as ϕ_- in argon. The higher value was obtained only after the collector had been bombarded in the regular way by positive ions, the results given in Table I being typical ones for this gas. From the fact that Langmuir[19] found the electron emission from a tungsten filament to be unaffected by the presence of a small amount of

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[18] The temperature adjustments of ϕ_- mentioned here and later, have been made by means of the following equation given by Davisson and Germer[2]

$$\phi_T \text{ (calorimetric)} = \phi_0 + 2kT/e$$

where k is the Boltzmann gas constant, e the charge on an electron and T the absolute temperature.

[19] Langmuir, Phys. Rev. **2**, 450 (1913).

argon, it is not unreasonable to assume that argon does not form such a layer on the surface of the collector as would affect the work function of the metal. If this assumption be true, it would seem to be possible also for nitrogen positive ions and gas molecules to strike a molybdenum surface without forming a layer which would affect ϕ_-, although when the positive ions strike with high velocities such a layer is formed. Consequently nitrogen might affect the value of the work function at the cathode, and yet have no effect upon its value at the anode of a discharge tube.

Except for the uncertainty due to the specific heat values, the results for ϕ_- are believed to be accurate to within about 1 percent. Most of the determinations of any one value were within 1 percent of the mean and only a very few varied from it by as much as 2 percent, even though for every one of the five values the results averaged were obtained at two or more different times between which measurements had been made on one or both of the other gases. Consequently the effects which hydrogen and nitrogen have on the electron work function of molybdenum have been found, even though the actual magnitudes of these effects may still be a little uncertain.

It may not be out of place to note here some values of ϕ_- for molybdenum obtained by other observers using other methods. As adjusted[18] for 200° Lester[3] found 4.35; Stoeckle,[20] 4.70; Dushman,[17] 4.39; and calculations from two sets of slope observations reported by Dushman and collaborators[2] give 4.63 and 4.52 respectively. These values would indicate that the true specific heat line should lie somewhere between I and II in Fig. 3.

Results of ϕ_+ in argon. The three sets of results for $(E_+ + \phi_+)$ as calculated on the basis of the three specific heat equations, are given in Table V. The last set of values has been given triple weight because of more satisfactory experimental conditions and technique. As may be seen in Table III, the quantity from which a value of $(E_+ + \phi_+)$ is ultimately determined is the small difference between two rather large calculated quantities, consequently it is to be expected that the results might vary considerably. However, since

TABLE V

Values of $(E_+ + \phi_+)$ for molybdenum in argon.

Average Temperature	Number of determinations in the series	$(E_+ + \phi_+)$ in volts I	II	III	Weight
223°C	4	−1.8	−9.5	−12.0	1
219°	6	+1.9	−6.4	−10.7	1
231°	5	−1.1	−5.5	− 9.8	1
228°	5	+2.7	−2.0	− 5.9	3
Weighted mean		+1.2	−4.6	− 8.0	
Probable values of ϕ_+ obtained by taking $E_+ = 0.4$ volt.		.8	−5.0	− 8.4	

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[20] Stoeckle, Phys. Rev. **8**, 534 (1916).

it is believed that no large systematic error has entered into the calculations, the errors should be compensating. Though the assumption[14] in regard to the potential distribution in the sheath is not in actual accord with theory and experiment, the error which might enter from this source is believed to be very small owing to the extremely small number of collisions made and the use of a value for the fraction of energy retained after a collision, which was obtained by a short extrapolation to the potential actually used. An error of 1 volt in the determination of the space potential would make a change of only about 0.3 of a volt in the result for $(E_+ + \phi_+)$. Consequently except for the uncertainty arising from the specific heat values used, it is believed that the error in the mean value can not be more than 2 volts, and probably is considerably less than that.

The value of E_+ was not measured, but from Langmuir's[10] observation that E_+ usually has a value between $E_-/3$ and $E_-/2$, 0.4 volt seems to be a reasonable value to use here. Thus the value of ϕ_+ obtained on the basis of the specific heat Eq. (III) has so large a negative value as to be unreasonable. Even the value obtained with Eq. (1) is much lower than would be expected from the theoretical equation $\phi_+ = V_i - \phi_- + L$ proposed by Schottky[8] and later by Compton.[7] According to this equation, at a molybdenum target in argon, $\phi_+ = 15.3 - 4.8 = 10.5$ volts, L in this case being zero since there is no (net) condensation of the gas molecules.

However, as a possible explanation of the fact that ϕ_+ seems to be much lower than would be expected from Schottky's equation, I wish to propose the following view as to the mechanism accompanying the neutralization of an argon positive ion at a metal surface. As the positive ion becomes neutralized at the surface of the metal, its combination with an electron probably occurs before the ion has made actual thermal contact with the metal. Thus the energy of neutralization may be given up by radiation in all directions and the metal would be heated only by the absorbed portion of the radiation which strikes it. On this view

$$\phi_+ = aV_i/2 - \phi_- \tag{13}$$

in which a is the fraction of the incident radiation absorbed by the metal. Thus, by using the value of 0.8 for ϕ_+ we obtain 0.73 for the value of a, which is a very reasonable value when considered in connection with Hulburt's[21] measurements of the reflecting power of molybdenum for ultraviolet light.

If this view of the neutralization mechanism for a *gas* positive ion at a metal surface be correct, it would seem probable that somewhat the same process may take place when *metallic* positive ions condense into the cathode, since all, or at least a part, of the energy of neutralization may be radiated before the atom actually becomes an integral part of the solid or liquid metal. An inference from this would be that the values of ϕ_+ which Güntherschulze[1] has calculated for various metals, are too large.

[21] Hulburt, Astrophys. J. **42**, 205 (1915).

Confirmatory evidence of the pressure of a group of high speed (secondary) electrons in a gaseous discharge at low pressure. The correctness of Langmuir's[12] conclusion that two distinct Maxwellian velocity groups of electrons may be found in a low pressure, high current gas discharge was shown in the following way. With a 400 milliampere arc in argon at about 0.4 mm pressure, observations such as those used to calculate ϕ_- were taken over a rather wide range of voltages. These measurements were used, not to calculate ϕ_-, but to determine the average energy E_- of the electrons reaching the collector at the various voltages, using in these calculations the value of ϕ_- previously determined. In Fig. 4 are plotted the logarithms of the electron currents, against the voltages at which they were obtained, and also the lines H and L showing the average energy of the *secondary* and *ultimate* electrons respectively (which crossed a surface), as well as the contribution of each group to the current at the different voltages. In Table VI the values in the second and third columns were calculated by methods described for the calculations of ϕ_-, *i.e.*, the second column gives the values obtained by multiplying Q by quantities obtained in the same way as those in column 7 of Table I. The

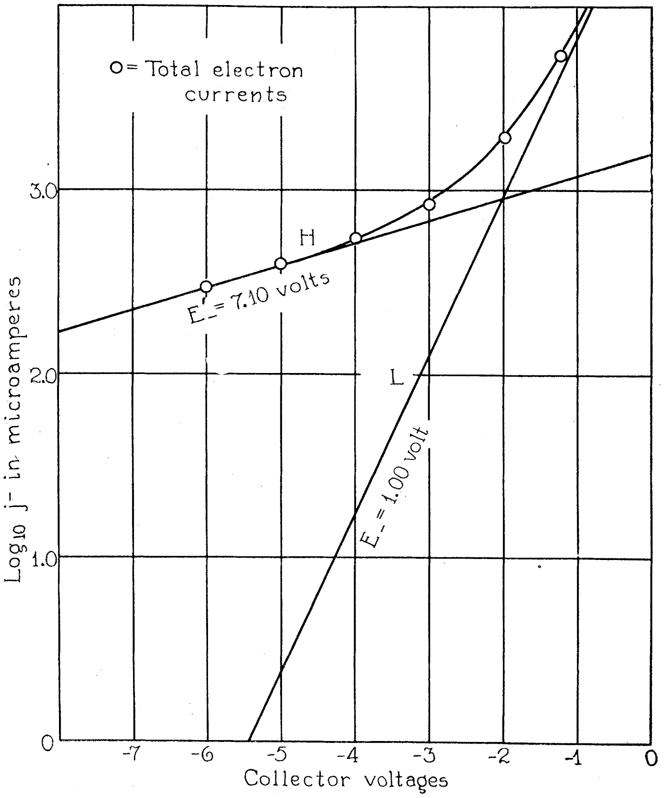

Fig. 4. Variation with collector voltage of the logarithm of the total electron current and of the *secondary* and *ultimate* electron current components.

values in the third column correspond to C^+ of column 8, Table I. The last three columns give respectively the values of E_- as obtained calorimetrically, as calculated from the equations of the lines H and L in Fig. 4, and as calculated by Eq. (4).

Table VI

Confirmatory evidence for the presence of two groups of electrons with widely different Maxwellian velocities.
All values are given in volts.

V_0 V_f	Net heating per electron	Decrease in positive ion energy per electron	$(E_-+\phi_-)$ Total heating per electron	Average energy of the electrons E_-		
				$(E_-+\phi_-)$ minus 4.76	Calculated from group plots in Fig. 4	Calculated by Eq. (4)
−6.00 −5.00	2.49	9.44	11.93	7.17	6.95	6.95
−5.00 −4.00	4.87	6.34	11.21	6.45	6.40	6.48
−4.00 −3.00	5.91	3.40	9.31	4.57	4.58	4.67
−3.00 −2.00	6.17	.90	7.07	2.31	2.25	2.37
−2.00 −1.23	6.12	.20	6.32	1.56	1.42	1.50

It has been suggested that the "high speed" electrons are not real, but only apparent, and that the real explanation of the change in slope in electron current curves like that in Fig. 4, is the occurrence of very high frequency oscillations in the potential of the collector. If such oscillations occur, it is true that they might give such a current-voltage curve, but that they could produce heating effects similar to those of high speed electrons does not seem possible since the mean energy of the incoming electrons is independent of the potential of the collector, provided this is negative as in the present work. The good agreement of the values of electron energies calculated calorimetrically, with those obtained on the assumption of a group of high speed electrons, is thus convincing evidence of the real existence of such high speed electrons. As was mentioned before, the collector was completely shielded from the direct radiation of the filament and consequently from *primary* electrons, so that it gave no evidence of their presence in the discharge.

Further applications of the method. It is planned to extend the measurements by this method to other gases and to other metals. This method should be particularly useful in determining ϕ_- of metals which cannot be investigated thermionically, thus giving a check upon the values obtained by photo-electric methods. Also it is believed that important information may be obtained by using this method in the study of effects due to thin layers of alkali and alkaline earth metals on the electrodes in a gas discharge. A slight modification of the tube will make it possible to measure the contact difference of potential between two metals when under exactly the same conditions as to gas layers, and to measure the effect of such gas layers upon the contact differences of potential.

In conclusion I wish to express my thanks to Professor K. T. Compton who proposed this investigation and who has made many helpful suggestions while it has been in progress.

Palmer Physical Laboratory,
Princeton, New Jersey.
May 28, 1927.