ACCOMMODATION COEFFICIENTS OF POSITIVE IONS OF ARGON, NEON AND HELIUM

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(Received April 23, 1931)

Abstract

Positive ions of argon, neon and helium produced in a low voltage arc were attracted to a spherical metal collector by regulated potentials up to 140 volts. The resulting heating of the collector was measured by a thermal junction and found to be *considerably less* than the product of the current by the attracting voltage. After taking account of the energy scattering at collisions and of the effect of the secondary electron emission, the following values of the "accommodation coefficients" were obtained: argon 0.75 ± 0.05, neon 0.65 ± 0.05 (both between 21 and 141 volts), and helium 0.35 ± 0.05 between 21 and 51 volts and 0.55 ± 0.05 between 111 and 141 volts.

WHEN an attempt was made to measure the amount of energy ϕ_+ delivered to a metal electrode when a positive ion with no kinetic energy is neutralized at its surface,[1] collisions between the ions and neutral molecules within the sheath, and comparatively large electron currents were thought to be the principal factors complicating the calculation and interpretation of the results. By making measurements of the heat generated when positive ions were drawn to the collector by fields so large that practically no electrons could reach the collector, and by working with such low gas pressures that very few ions would make collisions within the sheath it was later believed possible to make these complicating factors negligibly small. Under these conditions, since the positive ions reaching the collector are believed to start at or near the sheath edge with only a negligibly small velocity,[2] ϕ_+ should be easily obtained from the observed heating of the collector at two different negative potentials, if due allowance were made for the kinetic energy of the ions acquired in passing through the sheath. Thus the heating effect H of a current of magnitude j^+ at a given accelerating potential V with respect to the space potential would be

$$H = j^+(V + \phi_+) \tag{1}$$

and the difference between the heating effects at two different accelerating potentials V_f and V_0 would be given by

$$H_f - H_0 = j_f{}^+(V_f + \phi_+) - j_0{}^+(V_0 + \phi_+) \tag{2}$$

whence

[1] Van Voorhis, Phys. Rev. **30**, 318 (1927).
[2] Tonks and Langmuir, Phys. Rev. **34**, 876 (1929).

$$\phi_+ = \frac{(H_f - H_0) - (j_f{}^+V_f - j_0{}^+V_0)}{j_f{}^+ - j_0{}^+} . \qquad (3)$$

All of the quantities on the right side of Eq. (3) could then be obtained experimentally by means of our apparatus.

However, the results obtained from the application of this line of reasoning led to the surprising discovery that the heat produced by the positive ions striking a collector and being neutralized at its surface, is *much less* than the equivalent of the kinetic energy which they should acquire from the attracting field. Though this deficiency in heating effect has recently been observed by Found[3] and Güntherschulze,[4] they have ascribed it entirely to the effect which a large secondary electron emission would have upon the apparent and true values of the positive ion currents, and thus have assumed that the effect is only apparent and not real.

Careful measurements over a considerable range of accelerating potentials and gas pressures in argon, neon and helium have led us to conclude that the deficiency in heating effect in these gases is entirely too large to be accounted for by secondary electron emission and consequently at least some of the neutral molecules and metastable atoms formed by the neutralization of the positive ions at a metal surface must have left it with energies much larger than would correspond to the temperature of the metal. This means that positive ions with fairly high velocities may be considered as having accommodation coefficients less than unity just as the gas molecules have at much lower velocities or temperatures.[5]

Some of our measurements have been made under gas pressure conditions such that the effects of collisions of ions with gas molecules within the sheath are no longer negligible; but when these results have been corrected by the use of Runge's[6] theoretical values for the scattering of ion energy by collisions with neutral molecules, they become, in general, fairly consistent with those obtained at the lower gas pressures and may therefore be used in testing collision theories.

Experimental Procedure and Calculation of Results

The observations were taken with apparatus of the same type as was described in detail in the earlier paper.[1] A schematic sketch of the parts in the discharge tube and of the electrical connections is given in Fig. 1. A low voltage arc was maintained between the hot tungsten filament F and the anode A by applying a voltage from the battery B_2, this voltage being from 5 to 10 volts higher than the ionizing potential of the gas in use. The collector C was a metal sphere in which was imbedded a very small copper-constantan

[3] Found, Phys. Rev. **34,** 1625 (1929).

[4] Güntherschulze, Zeits. f. Physik **62,** 600 (1930).

[5] Knudsen, Ann. d. Physik **34,** 593 (1911); **46,** 641 (1915); Soddy and Berry, Proc. Roy. Soc. **84,** 576 (1911); Langmuir, J. Am. Chem. Soc. **37,** 425 (1915); Roberts, Proc. Roy. Soc. **129,** 146 (1930).

[6] Runge, Zeits. f. Physik **61,** 174 (1930).

thermocouple. In the measurements with argon and neon the collector was of molybdenum, 3.1 mm in diameter and with helium it was a 3.0 mm platinum sphere.

The gases were carefully purified by arcs between "misch" metal cathodes and iron anodes in glass reservoirs on the vacuum system, before being admitted to the discharge tube. Observations were made on repeated fillings of a given gas until the results from different fillings were quite reproducible, which condition was taken to indicate that no appreciable impurity was coming from the walls or metal parts of the vacuum tight discharge tube.

Of the quantities on the right side of Eq. (3) j_0^+ and j_f^+ were obtained directly from the readings of the Cambridge Universal Test Set used as A_3 in Fig. 1. To obtain V_0 and V_f it was necessary to find V_s, the space potential

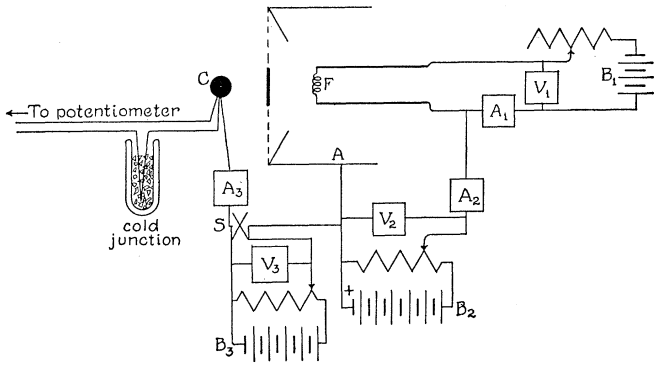

Fig. 1. Schematic sketch of apparatus and arrangement of electrical circuits.

with respect to the anode, by the usual method[7] and add this to the applied potentials as given by V_3 (Fig. 1). The quantity $H_f - H_0$ 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 its potential was changed from V_0 to V_f. Since the temperature, starting at T_0 when $t=0$, approached a final limiting value exponentially,

$$T - T_0 = (T_f - T_0)(1 - e^{-at}) \tag{4}$$

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 (4) that

$$\left(\frac{dT}{dt}\right)_{t=0} = a(T_f - T_0), \text{ where } a = \frac{2.303}{t}\log_{10}\left(\frac{T_f - T_0}{T_f - T}\right) \tag{5}$$

The data for calculating a were obtained by first noting the electromotive force mV_0 of the thermocouple after the potential of the collector had been

[7] 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).

held at V_0 long enough for it to reach a steady temperature. Then simultaneously the collector potential was changed to V_f and two stop watches started. As the temperature of the collector changed, the drum of the potentiometer was slowly turned so as to keep the galvanometer deflection as near zero as possible. At some instant when the deflection was exactly zero one watch was stopped and its time t_1 and the corresponding mV_1 were recorded, after which mV_2 was noted 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_0, record was made of mV_f. From these data two values of a could be calculated and their mean $\bar{a}$ was used in applying Eq. (5).

In Table I are given typical sets of observations and the resulting quantities obtained from various steps in the calculations. To obtain the tempera-

TABLE I. *Typical sets of observations and calculations for the molybdenum collector in argon at 0.1 mm pressure.*

1	2	3	4	5	6	7	8	9
V_0 V_f V_s Volts	j_0^+ j_f^+ m.a.	t_0 t_1 t_2 sec.	mV_0 mV_1 mV_2 mV_f millivolts	T_f-T_0 T_f-T_1 T_f-T_2 °C	a_1 a_2 $\bar{a}$	Q	MH or $\bar{a}(T_f-T_0)Q$ EH milliwatts	MH/EH
20.0	0.354	0	7.653	25.31				
		19.79	7.945	19.77	0.01248	35.97	11.39	
49.9	.430	36.95	8.149	15.93	.01254			0.786
1.5			9.007		.01251		14.49	
49.8	.432	0	8.990	29.10				
		32.70	9.551	18.80	.01338	36.18	14.06	
81.0	.496	60.80	9.875	12.92	.01336			.751
1.5			10.594		.01337		18.73	
81.0	.498	0	10.582	30.18				
		26.57	11.111	20.80	.01401	36.42	15.32	
110.8	.550	50.11	11.445	14.89	.01385			.740
1.5			12.299		.01393		20.70	

ture 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, $mV_T = 0.0400766T + 0.00004344T^2 - 0.00000002244T^3$.

In column 7 the values of Q are the heat capacities in millijoules per degree for the corresponding mean temperatures. In column 8, MH is the measured heating effect in milliwatts obtained from the observations and calculations, whereas EH is the expected heating on the assumption that all of the kinetic energy gained by the ions from the accelerating field would be delivered to the collector in the form of heat, ϕ_+ being neglected for the present. Thus the value of EH is found from the equation

$$EH = j_f^+(V_f + V_s) - j_0^+(V_0 + V_s). \tag{6}$$

In Tables II, III and IV are given the results obtained in argon, neon and

helium respectively. Column 1 of these tables gives the gas pressure and the assumed positive ion mean free path obtained by taking $2^{1/2}$ times the kinetic theory value for the neutral atoms at the temperature in the discharge tube. In column 2 are given the values of the applied potentials (with respect to the space) after slight adjustment to make the voltage intervals exactly 30 volts, the actual intervals used ranging between 29 and 31 volts since the po-

TABLE II. *Results in argon.*

1	2	3	4	5	6	7	8	9	10	11
					Measured heating / Expected heating			If current varies as sheath area		
P / λ	V	m.a.	S/λ (L&B)	S/λ (R&M)	Unmodified	Corrected		m.a.	MH/EH	
						$\phi_+=0$	$\phi_+=V_i-\phi_-$		$\phi_+=0$	$\phi_+=V_i-\phi_-$
0.016 mmHg	20.6	0.106	0.068	same	(0.84^E)	(0.84^E)	(0.76^E)	0.061+	(1.45^E)	(1.31^E)
	50.6	.142	.117	"				.045−		
7.8 mm	80.6	.169	.154	"	.81	.81	.76	.097+	(1.02^F)	(1.96^F)
	110.6	.191	.187	"	.81	.81	.78	.124	($.98^F$)	($.94^F$)
	140.6	.211	.217	"	.80	.80	.78	.146	($.95^F$)	($.92^F$)
								.166		
0.040	20.6	.261	.103	"	.81	.81	.74	.217+	.92	.88
	50.6	.329	.184	"				.044−		
3.15	80.6	.384	.245	"	.80	.80	.76	.285+	.88	.84
	110.6	.431	.297	"	.77	.77	.74	.340	.84	.80
	140.6	.476	.343	"	.76	.77	.74	.387	.83	.80
								.432		
0.10	21.5	.340	.235	"	.77	.77	.71	.277+	.89	.82
	51.5	.416	.411	.410				.063−		
1.26	81.5	.476	.546	.545	.74	.75	.70	.353+	.84	.80
	111.5	.530	.662	.661	.73	.74	.70	.413	.82	.79
	141.5	.580	.766	.765	.72	.75	.72	.467	.81	.78
								.517		
0.25	21.3	.250	.680	.679	.69	.70	.64	.200+	.82	.74
	51.3	.310	1.20	1.18				.050−		
0.505	81.3	.362	1.59	1.55	.68	.71	.66	.260+	.80	.75
	111.3	.409	1.92	1.87	.68	.77	.73	.312	.85	.81
	141.3	.450	2.20	2.14	.67	.77	.74	.359	.96	.92
								.400		
0.50	21.5	.218	1.47	1.44	.69	.77	.70	.172+	1.00	.90
	51.5	.269	2.60	2.53				.046−		
0.253	81.5	.320	3.41	3.32	.64	.78	.72	.223	1.00	.92
	111.5	.373	4.05	3.93	.62	($.87^H$)	($.82^H$)	.274	(1.01^H)	($.94^H$)
	141.5	.424	4.56	4.40	.63	($.92^H$)	($.87^H$)	$.327^I$	(1.00^H)	($.95^H$)
								$.378^I$		

tential change was made by suddenly changing the position of the slider of a slide wire potential divider and the interval could not be exactly duplicated. The values of the measured currents in column 3 are adjusted to correspond to the potentials given in column 2. These adjustments were deemed advisable in order to shorten the calculations involved in the corrections made as explained later, by making it possible to apply these corrections only to the mean values instead of to each individual result which was obtained under

conditions differing only slightly from those of the three to seven other similar results. However, the values of the ratios of the "measured heating" to the "expected heating" given in column 6 are the means of the four to eight

TABLE III. *Results in neon.*

1	2	3	4	5	6	7	8	9	10	11
					Measured heating / Expected heating			If current varies as sheath area		
P / λ	V	m.a.	S/λ (L&B)	S/λ (R&M)	Unmodified	Corrected		m.a.	MH/EH	
						$\phi_+=0$	$\phi_+=V_i-\phi_-$		$\phi_+=0$	$\phi_+=V_i-\phi_-$
0.13 mm Hg	22.5	.166c	.314	same	0.64	0.65	0.52	.130+ .036−	0.76	0.61
	52.5	.216	.538	.537				.180+		
1.68 mm	82.5	.259	.696	.695	.66	.68	.60	.223	.76	.67
	112.5	.298	.830	.828	.67	.70	.64	.262	.77	.71
	142.5	.332	.951	.949	.68	.72	.67	.296	.78	.73
.30	22.0	.427c	.425	.424	.65	.66	.56	.370+ .057−	.73	.62
	52.0	.527	.738	.736				.470+		
.752	82.0	.610	.984	.980	.66	.68	.61	.553	.73	.66
	112.0	.687	1.174	1.160	.65	.67	.63	.630	.72	.66
	142.0	.755	1.35	1.33	.65	.67	.63	.698	.71	.68
.73	21.4	.375	1.08	1.07	.61	.64	.54	.327+ .048	.71	.59
	51.4	.468	1.90	1.85				.420+		
.308	81.4	.548	2.51	2.45	.60	.67	.59	.500	.73	.64
	111.4	.631	3.00	2.92	.59	(.74^H)	(.67^H)	.583	(.79^H)	(.71^H)
	141.4	.718	3.38	3.29	.57	(.74^H)	(.67^H)	.670	(.78^H)	(.71^H)

TABLE IV. *Results in helium.*

1	2	3	4	5	6	7	8	9	10	11
					Measured heating / Expected heating			If current varies as sheath area		
P / λ	V	m.a.	S/λ (L&B)	S/λ (R&M)	Unmodified	Corrected		m.a.	*MH/EH*	
						$\phi_+=0$	$\phi_+=V_i-\phi_-$		$\phi_+=0$	$\phi_+=V_i-\phi_-$
.16 mm Hg	21.4	0.0585e	0.616	0.614	0.36	0.38	0.18	Observed positive ion Currents were quite nearly proportional to calculated sheath areas		
	51.4	.0949	.980	.970						
2.18 mm	81.4	.1248	1.24	1.22	.44	.48	.34			
	111.4	.1540	1.44	1.41	.44	.49	.38			
	141.4	.181	1.61	1.57	.42	.53	.44			
.40	21.7	.128e	1.015	1.003	.36	.40	.22	.089+ .039−	.50	.28
	51.7	.178	1.72	1.68				.139+		
.870	81.7	.220	2.25	2.18	.42	.51	.38	.181	.61	.46
	111.7	.259	2.54	2.47	.43	.54	.44		.64	.52
	141.7	.295	3.09	3.00	.42	(.66^H)	(.57^H)	.220 .256	(.79^H)	(.67^H)
1.0	20.9	.182e	2.08	2.01	.37	(.48^H)	(.25^H)	.117+ .065−	(.64^H)	(.34^H)
	50.9	.244	3.56	3.46				.179+		
.348	80.9	.297	4.48	4.32	.38	(.58^H)	(.43^H)	.232	(.74^H)	(.55^H)
	110.9	.344	5.37	5.12	.40	(.70^H)	(.57^H)	.279	(.88^H)	(.72^H)
	140.9	.386	6.46	6.10	.39	(.82^H)	(.70^H)	.321	(1.00^H)	(.86^H)

ratios calculated from the actual observations and are not modified in any way.

In columns 4 and 5 are given values of the collision numbers or the ratios of the sheath thickness S to the mean free path λ. The sheath thicknesses used in column 4 were obtained on the assumption of no collisions within the sheath, i.e., by means of Langmuir's equation,[8] and Langmuir and Blodgett's[9] tables, for spherical collectors. The collision numbers in column 5 have been obtained by correcting the sheath thickness for the slowing up of the positive ions by the collisions within the sheath, in accordance with some recent unpublished work of H. P. Robertson and P. M. Morse, assuming that the same fractional shrinkage in thickness takes place in the sheath around the spherical collector as would take place in the sheath of an infinite plane,

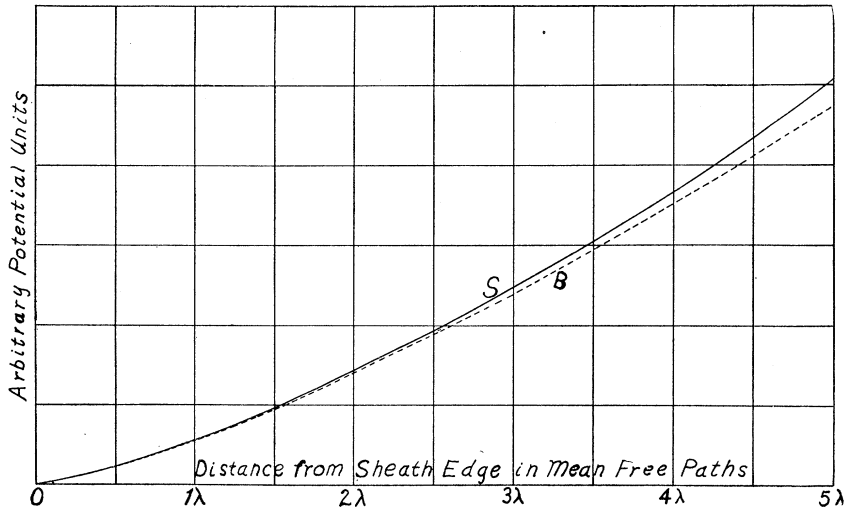

Fig. 2. Potential distribution curves, B from space charge equation (no collisions), and S from assumption of kinetic theory collisions between elastic spheres. For the case of a large plane electrode.

for which case the Robertson and Morse calculations have been made. In Fig. 2[10] the solid line gives the distribution of potential for collision numbers up to five and the dashed line the potential distribution for the same sheath thicknesses if there were no collisions. Thus the difference in abscissas of points having the same ordinate on the two curves gives the shrinkage effect resulting from collisions of ions with neutral molecules within the sheath.

In column 6 are given the mean values of MH/EH obtained in the manner described above in connection with Table I. The values given in column 7 were obtained by correcting for the energy so scattered by collisions of the ions with gas molecules within the sheath that it would not be expected to

[8] Langmuir, Gen. Elec. Rev. **27**, 449 (1924).

[9] Langmuir and Blodgett, Phys. Rev. **24**, 53 (1924).

[10] Published here with the kind permission of Robertson and Morse.

be delivered to the collector. On the assumption of collisions between elastic spheres of equal masses, half of the scattered energy will be delivered to gas molecules on the average, and half will be retained by the ions.[11] All of the energy retained by the ions and part of the energy received by the gas molecules will reach the collector and be delivered in full to it if the accommodation coefficient be unity. However, a part of the energy received by the gas molecules will be so directed as to miss the collector, i.e., if collisions take place at a distance PN, Fig. 3, from the spherical collector no neutral molecules receiving velocities directed at an angle from the normal PN greater

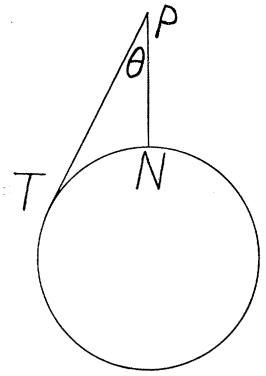

Fig. 3.

than the grazing angle θ will deliver any of their energy to the collector (except as the result of further collisions, and it is assumed that this would just balance the loss of energy from within the grazing angle, resulting from the same cause).

To calculate the fraction of energy, called hereafter $F(E)$, which should not be expected to reach the collector, Runge's[3] theoretical results were used in the following way. Values of $R \sin \theta$ (from Runge's Fig. 3) were plotted as ordinates against θ, R being the energy radius vector and θ the angle with

TABLE V. *Fraction of total energy directed outside of given angles with original direction after from 1 to 5 collisions. (Obtained from Runge's results).*

Angle	Number of collisions 1	2	3	4	5
0°	1.000	1.000	1.000	1.000	1.000
10	.941	.968	.973	.980	.988
20	.780	.874	.905	.932	.944
30	.558	.734	.799	.855	.872
40	.346	.569	.688	.752	.781
50	.176	.410	.531	.636	.674
60	.065	.272	.395	.515	.55
70	.015	.164	.278	.396	.45
80	.002	.089	.190	.290	.35
90	.000	.043	.120	.200	.26

[11] Compton and Langmuir, Rev. of Mod. Phys. **2**, 211 (1930); Runge, reference 6.

the direction of the electric field, i.e., with the direction of the energy at the time of the first collision. We then integrated with a planimeter the areas bounded by the zero ordinate, the curves and the 10° interval abscissa lines and from the integrated values found the $F(E)$ directed outside of given grazing angles after from 1 to 5 collisions. The results thus obtained are given in Table V and plotted in Fig. 4, which has also a plot of the grazing angles from points up to 2 mm distant from our 3.1 mm diameter collector.

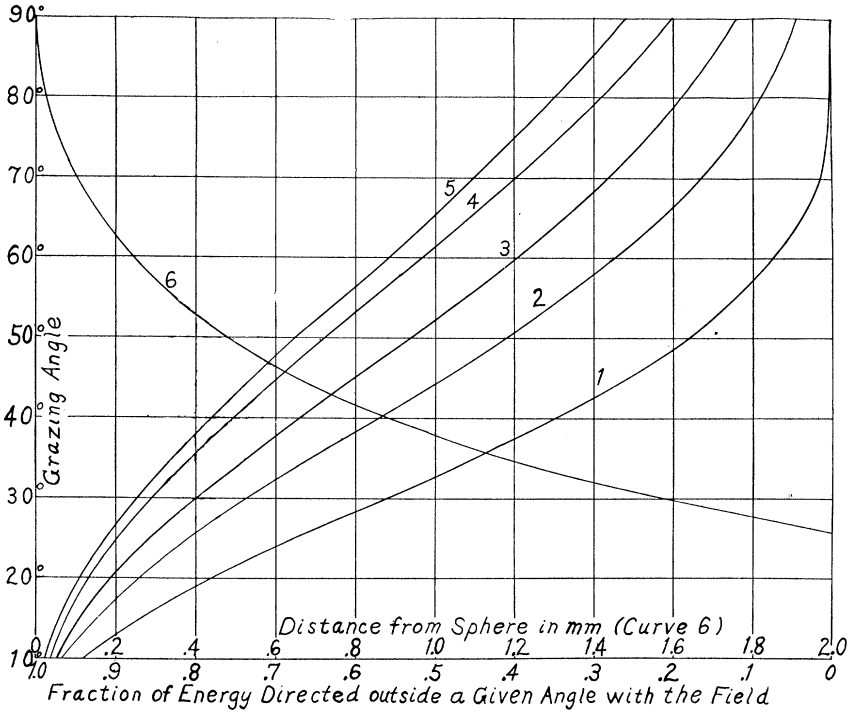

Fig. 4. Curves 1, 2, 3, 4 and 5 show fractions of energy directed outside of given angles with the field direction after from 1 to 5 collisions respectively. Curve 6 is a plot of grazing angle against distance from the 3.1 mm collector.

In applying these results we have followed Runge's assumption that it is legitimate to take account of the scattering of the total energy gained in the whole field between sheath edge and collector by considering piecemeal the energy gained in each λ of distance and the scattering of this energy at subsequent collisions on the way to the collector and then taking the sum of the residual energies at the collector as being the total effective applied potential. Thus, for example, in argon at 0.25 mm pressure (see Table II) with 111.3 volts applied potential the collision number was 1.87 and with 141.3 volts it was 2.14. To calculate the effective potentials (hereafter called EP) it was necessary to obtain from the curves in Fig. 4 the grazing angles recorded in column 2, Table VI, corresponding to the distances from the collector given

in column 1 and the $F(E)$'s directed outside of these grazing angles after collisions, as tabulated in columns 3, 4 and 5 of the same table. Then the potentials with respect to the sheath edge at the various integral λ distances from the collector were obtained from the solid potential distribution curve of Fig. 2, the potentials found being tabulated in columns 6 and 7 of Table IV, whose columns 8 and 9 give the potential differences for the whole λ's and the outside fraction of λ and also, in parentheses, the EP's found by applying the values given in columns 3, 4 and 5 to the potential differences given in 8 and 9 in the following way.

TABLE VI. *Quantities involved in the illustratory example of the calculation of the effective potentials.*

1	2	3	4	5	6	7	8	9
Distance from collector	Grazing angle	Fraction of energy directed outside of grazing angle 1 Col.	2 Col.	3 Col.	Potential relative to sheath edge		Potential difference (Effective P.D.)	
0	90.0°	000	.043	.12	141.3	111.3	[(129.5)	(104.5)]
.14λ	73.2		.137	.25			Total E.P.	
.50λ	59.7	.075					81.1	71.8
.87λ	50.6	.169	.399				(80.4)	(71.2)
1.00λ	48.9	.205	.434		60.2	39.5		39.5
1.14λ	46.8	.224	.457				56.6	(33.3)
1.87λ	38.5	.376				0.0	(46.6)	
2.00λ	37.4	.397			3.6		3.6	
2.14λ	36.2	.422			0.0		(2.5)	

Consider first the potential difference in the first λ distance from the collector. On the assumption that collisions are equally probable all along the path but that all the ions collide once and only once in the distance λ, calculations based on a ten-step division of the first λ for several values of λ, and the resulting potential distributions and energy directions as obtained from the application of the curves in Figs. 2 and 4, showed that the total $F(E)$ received by neutral molecules so directed as to miss the collector is given very accurately by 1/9 the $F(E)$ lost to such molecules at collisions at a point 0.5λ from the collector. Consequently 81.1 $(1-.075/9)$ or 80.4 and 71.8 $(1-0.075/9)$ or 71.2 are the EP differences in the first λ of our examples. For the fractional loss of the energy applied in the second λ, if the $F(E)$ curve for first collision and the potential distribution curve were straight lines we would take 0.5×0.5 the mean of the fractions at λ and 2λ, the one 0.5 factor to give the mean applied potential between λ and 2λ and the other 0.5 factor to take account of the fact that only half of this $F(E)$ is carried by molecules. However, here again ten-step calculations showed that the factor 1/9 should be used instead of 1/8 because of the curvature of the above mentioned curves. For the fractional loss in a given λ of the energy gained outside this λ the fraction $\frac{1}{4}$ was used because the $F(E)$ curves for more than one collision do not differ so greatly from a straight line. Consequently 56.6 $[1-(0.397+0.205)/9]$ $[1-(0.434+0.043)/4]$ or 46.6 was found to be the EP in the second λ of our 141.3 volt case. To obtain the effective part of the potential applied in

the outer fractional λ part of the sheath a slightly different method of calculation was used as will appear from the following examples:

$$3.6\left[1-\frac{0.14}{9}(0.422+0.397)-\frac{0.86}{4}(0.397+0.224)\right]=3.07$$

$$3.07\left(1-\frac{0.457+0.137}{4}\right)\left[1-\frac{0.14}{4}(0.25+0.12)\right]=2.5$$

and

$$39.5\left[1-\frac{0.87}{9}(0.376+0.205)-\frac{0.13}{4}(0.205+0.169)\right]=36.8$$

$$36.8\left[1-\frac{0.87}{4}(0.399+0.043)\right]=33.3$$

Thus the total *EP*'s whose energy may be expected to reach the collector are 129.5 and 104.5 volts instead of the actually applied voltages 141.3 and 111.3 respectively, and the use of the former instead of the latter to calculate the expected heating changed the ratio of *MH* to *EH* from 0.67 to 0.77. By this method of correcting for the amount of energy to be expected to reach the collector all the results tabulated in column 7 of Tables II, III and IV were obtained.

When, instead of using the assumption that $\phi_+=0$, the Schottky[12] assumption that $\phi_+=V_i-\phi_-$, where V_i is the ionizing potential of the gas, is taken into account the results are changed from the values of column 7 to those of column 8 (Tables II, III and IV).

After our experimental tube had been set up and most of the data taken, there came to our attention the work of Oliphant[13] and of Uyterhoeven and Harrington[14] which showed the presence of a fairly large secondary electron emission from negative collectors under conditions somewhat similar to ours. The effect of the secondary electrons would be to make the heating of the collector less than would be expected if all the measured current were carried by positive ions. Since we were not able to measure the secondary emission from the collector directly, although measurements made with an auxiliary Mo plate and Ni collector (added to the discharge tube for this special purpose and not shown in Fig. 1) similar to those used by Uyterhoeven and Harrington[14] showed less than 1 percent secondary emission from the plate under the conditions of our experiments in argon and less than 2 percent in neon (no measurements being made in helium) we have thought it best to show what would be the effect upon our results of secondary electron emissions of about the same magnitude as reported by these investigators. In accordance with Found's suggestion that for different negative collector potentials, other discharge tube conditions remaining the same, the positive ion currents to the collector should be proportional to the sheath areas while the secondary elec-

[12] Schottky, Ann. d. Physik **62,** 143 (1920).
[13] Oliphant, Proc. Roy. Soc. **124A,** 228 (1929); **127A,** 373 (1930).
[14] Uyterhoeven and Harrington, Phys. Rev. **36,** 709 (1930).

tron emission, since chiefly due to metastable atoms, should remain practically constant, we found by the trial and error method, values of positive currents quite accurately proportional to the sheath areas (recalculated for these smaller currents) when we subtracted some certain constant value from our measured collector currents, these constant values being in general fairly reasonable ones for the secondary electron current when compared with Oliphant's,[13] and Uyterhoeven and Harrington's[14] results. In column 9 of Tables II, III and IV are tabulated the current values obtained in this way. The value followed by a negative sign and recorded between the first and second positive values is the assumed value of the secondary electron emission for the given discharge condition, since it was the necessary constant amount to be subtracted from the measured currents to give positive ion currents proportional to the corrected sheath areas. The last two positive ion current values in argon are slightly higher than they should be on this theory but this could be accounted for by the fact that under the existing conditions the secondary electrons would produce an appreciable amount of ionization within the sheath. To obtain results consistent with those for the higher accelerating voltages some of the measured currents in neon and helium for the lowest potentials used (about 21 volts) had to be increased by from 1 to 12 percent, amounts practically the same as those obtained by extrapolating the plots of the logarithm of the current against applied voltage, used in determining space potentials, and thus may be ascribed to the fraction of electrons having random energies greater than about 21 volts. The current values marked with a superscript c in column 3 are the ones so corrected.

The calculations made as for the results given in columns 7 and 8, Tables II, III and IV but using the positive ion currents given in column 9 instead of those given in column 3 led to the ratios of measured heating to expected heating (or accommodation coefficients) given in columns 10 and 11 for $\phi_+ = 0$ and $\phi_+ = V_i - \phi_-$ respectively.

Discussion of Results

Of the results given in columns 7, 8, 10 and 11 of Tables, II, III and IV the ones enclosed in parentheses are probably rather inaccurate, the ones with the superscript E being uncertain because of poor experimental conditions, the ones with superscript F are probably too high because the secondary electron current given by Found's assumption is unreasonably high in this case, and the ones with superscript H being probably too high because an assumption used in determining the fraction of energy not to be expected to reach the collector leads to a value for this fraction which is increasingly too high as the mean free paths become shorter, and the collision number increases. The assumption in question is the one given in parenthesis on page 1603 in connection with Fig. 3. Thus the nearer the point P is to the collector the greater will be the excess of molecules given direction outside of PT when struck by positive ions at P, but which later strike the collector as a result of collisions with other molecules, over those going outward across PT after being given directions inside PT when struck at P, since the distances which

the former must go before getting completely away from the collector are considerably greater than the distances the latter must go to reach it.

A study of the remaining values of the results shows that in helium the "accommodation coefficient" (hereafter referred to as A) increases as the positive ions are given higher velocities. This is in accord with the observations of Kingdon and Langmuir[15] that helium ions penetrate to a considerable depth into the metal which they are bombarding, an effect which would increase with increasing energy of the ions. In argon there appears to be no increase in A with increasing energy of the ions and in neon the effect is only very slight and we have neglected it in determining the mean values given for this gas in Table VII.

TABLE VII. *Summary of mean values of "accommodation coefficients."*

Column	Argon		Neon		Helium	
	Mean	Average variation	Mean	Average variation	21 to 51 V	111 to 141 V
7	0.770	0.023	0.674	0.019	0.40	0.56
8	.725	.029	.591	.038	.20	.47
10	.875	.056	.740	.022	.50	.70
11	.825	.047	.659	.033	.28	.56
Estimate of true value	0.75±0.05		0.65±0.05		0.35±0.05	0.55±0.05

In this table are given the means of the undoubtful values given in columns 7, 8, 10 and 11 of Tables II and III along with the average variations from the means. These average variations from the means are given not because we believe them to be a measure of the absolute accuracy of the results but because they give a concise method of showing the constancy of the results obtained under the four different assumed conditions on which the calculations of the four columns were based.

As judged by constancy, the results in argon would indicate that the actual secondary electron emission from the collector under our experimental conditions in this gas was probably considerably less than the approximately 25 percent given by Found's[3] assumption, and thus are in accord with the finding of only about 1 percent by our direct measurements of the emission from the auxiliary plate. Though the assumption of positive ion currents proportional to sheath areas gives in general reasonable values for the secondary electron currents the following considerations indicate that it is probably only an accident that the assumption does give such results. That the positive ion current is *not* controlled by the sheath area as given by the space charge equation but by a much larger volume, is certain. First, it is easily shown that the electrons, which penetrate within such sheaths surrounding our collector, could produce at most only a very small portion of the positive ions which

[15] Kingdon and Langmuir, Phys. Rev. **22,** 148 (1923).

are actually observed. Second, recent work of Langmuir,[16] and Tonks and Langmuir[2] has shown that, whereas most of the potential drop is within these sheaths, the positive ions which are collected are formed within a much larger volume. Hence there is no reason for believing that positive ion currents should be accurately proportional to such sheath areas, and hence the assumptions which underlie columns 10 and 11 of Tables II, III and IV appear to be unjustified. The values and discussion are included principally to illustrate how moderately large secondary electron currents would affect the results, if present.

Though the actual boundary of the region from which positive ions are drawn to the collector, is shown by the above considerations to be far outside of that given by the space charge equation, the latter value is not far from the boundary of the region into which any appreciable number of external electrons penetrate, and the greater part of the potential drop is between this boundary and the collector. Consequently we believe we are justified in using the space charge equation values for the sheath thicknesses in our calculations of the deflections and energy losses at collisions.

By carefully considering the various factors involved and the effect which changes in the assumed values of ϕ_+ and secondary electron emission have upon the results, we arrived at the estimates given for the true values of A for argon, neon and helium positive ions given at the bottom of Table VII. These values are of the same order of magnitude as the values of A found by Knudsen[5] for cool gases striking a hot filament.

The "Umladung" effect described by Kallmann and Rosen,[17] Penning and Veenemans,[18] and others, i.e., the taking of an electron from a neutral molecule by a positive ion, the now neutralized ion retaining practically all of its kinetic energy and the new ion starting with negligible velocity, would increase the values of A slightly for the conditions giving the larger collision numbers but this effect would probably not be greater than the 0.05 possible error given in our estimates, particularly in argon for in this gas we have values for conditions under which collisions within the sheath are practically negligible.

That the energy given up by positive ions which have been attracted to a metal collector by a field should be less than the total kinetic energy of the ions is to be expected from the explanation of the mechanism of cathode sputtering advanced by Kingdon and Langmuir,[15] and from the observations of Oliphant[13] and others on the reflection of positive ions and metastable atoms, and the probability of the formation of metastables in the neutralization process. If all of the observed deficiency of energy transfer were due to the formation of metastable atoms all of which left the collector with the velocity of the positive ions from which they were formed, this deficiency would give a measure of the production of metastables in the neutralization

[16] Langmuir, Phys. Rev. **33,** 954 (1929).
[17] Kallmann and Rosen, Zeits. f. Physik **61,** 61 (1930); **64,** 806 (1930).
[18] Penning and Veenemans, Zeits. f. Physik **62,** 746 (1930).

process. However, it is very improbable that the conditions are so simple as this.
velocity of the positive ions from which they are formed, this deficiency would give a measure of the production of metastables in the neutralization process. However, it is very improbable that the conditions are so simple as this.

In conclusion we wish to point out that although there is some uncertainty in the exact values of the accommodation coefficients for argon, neon and helium positive ions as found by us, our measurements seem to show conclusively that they are all considerably less than unity and consequently conclusions which have been reached on the tacit assumption of the unity value need revision to take account of the actual, smaller values.

Since the values of the accommodation coefficient found for neutral molecules[5] becomes more nearly unity as the molecular weight increases and since the values found by us for ions are of the same general order of magnitude as those found for the neutral molecules, it is suggested tentatively that the values for mercury and other heavy ions are nearly unity. Also the value of A is likely to depend somewhat upon the factors which affect the surface conditions of the metal such as the gas pressure, purity of the gas, roughness of the surface, and kind of metal.

Our thanks are due Mr. Donald C. Archibald for his help in the experimental work of this paper.