PHOTO-IONIZATION OF A GAS BY A DISCHARGE IN THE SAME GAS[1]

By F. L. Mohler

Abstract

Method. Measurements were made in a tube containing two thermionic units electrically shielded from each other. The first served to give a discharge, the second detected ions produced by the radiation from the first by means of their effect on the space charge.

Results. Relatively little photo-ionization is produced by arc radiation, while spark excitation and soft x-radiation give a strong effect. Curves of photo-effect versus discharge voltage show critical potentials which have been interpreted as follows: Ionization of n_2 rare gas shell—Cs, 13.0; K, 19.0: Spark excitation—Cs, 18.5; K, 21.6; A, 32.2; Ne, 48.0: Double ionization—Cs, 21.5; K, 31.8; A, 34.8; Ne, 54.9: Ionization of n_1 rare gas shell—Cs, 39.0; K, 48.0; A, 39.6. The neon II spectrum is excited at 55 volts.

It was shown that photo-electric emission from the electrodes was at least ten times as great as the photo-electric emission from the gas, while the current change produced by the space charge effect was more than 2400 times the ion current in argon and caesium, the upper limit being quite indefinite.

Introduction

SINCE the first experiments by Davis and Goucher[2] numerous results have been published on the photo-electric effect of radiation from a thermionic discharge as measured by electrodes within the vacuum tube but electrically shielded from the discharge. The method has been particularly useful as a means of locating critical potentials above the first ionization potential. These experiments give no direct evidence as to whether the photo-electrons originate from the metal electrodes or from the gas surrounding them, but undoubtedly both sources contribute to the current when the discharge voltage is high.

In two recent papers,[3] there is described a sensitive method of distinguishing the photo-ionization of a gas from the electron emission from metal electrodes, and measurements are given of the photo-sensitivity of caesium vapor for monochromatic light over the range 3900A to 2500A. The vapor was contained in a two electrode thermionic tube with conditions so adjusted that the current was limited by

[1] Published by permission of the Director, Bureau of Standards, Department of Commerce.

[2] Davis and Goucher, Phys. Rev. **10**, 101 (1917).

[3] Foote and Mohler, Phys. Rev. **26**, 195–207 (1925); Mohler, Foote and Chenault, Phys. Rev. **27**, 37–50 (1926).

electron space charge. Ions produced by radiation neutralized the space charge and caused a change in thermionic current which was enormously greater than the actual ion current. The sensitivity curves showed that the photo-ionization reached a sharp maximum at the limit of the principal series but that, by secondary processes measurable ionization was produced on the red side of the limit when the exciting wave-length coincided with lines of the absorption series from $1s-4p$ to $1s-\infty p$.

The present paper deals with an application of the space charge method for measuring the photo-ionization produced in a gas by the radiation from a thermionic discharge in the same vacuum tube. The results have some bearing on the general theory of discharges in gases, but the method has been used primarily as a tool for measuring critical potentials. To locate excitation stages above the first ionization potential by electrical measurements, it is necessary to find

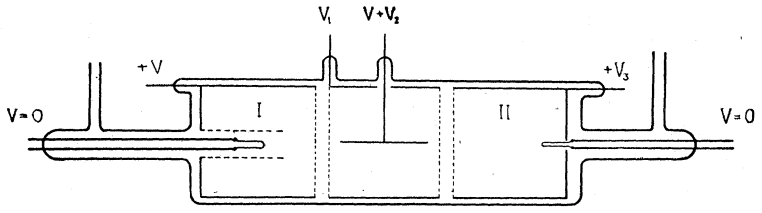

Fig. 1. Double discharge tube. Unit II detects ions produced by radiation from the discharge in I. The manner of applying potentials is indicated.

some effect which is not masked by the copious ionization and radiation produced at low voltage. Measurement of positive ions is entirely unsuited for this purpose and radiation measurements of the usual type have serious limitations. It was hoped that the photo-ionization effect would meet this requirement and the following results show that this is in fact the case. The published curves[3] show that there will be some photo-ionization by arc radiation, but I find that this light is relatively ineffective compared with radiation resulting from double ionization or soft x-ray excitation.

Apparatus and Procedure

The type of discharge tube used is illutrated in Fig. 1. It contains two thermionic units I and II, with screening electrodes between to prevent the passage of electrons and ions from one side to the other. The method of applying potentials is indicated in the diagram. Unit I gives a thermionic discharge at measured current and voltage. $V+V_2$ was usually 100 volts and V_1-6 volts. Unit II is the ion de-

tecting system for measuring the photo-ionization of gas within II by radiation from I. It is designed so that the anode almost completely incloses the fine wire cathode so as to entrap any positive ions and magnify their effect on the space charge.[4] V_3 was usually between 0.5 and 2 volts and was kept constant during each series of experiments. Either tungsten or oxide coated platinum filaments were found suitable. The latter were somewhat less sensitive but more constant than the tungsten.

The observations consisted of measurements of the change in thermionic current in II produced by a discharge in I. To measure this current change, the "dark current" through the galvanometer across II was balanced by a potentiometer circuit and the galvanometer sensitivity increased to the desired amount. Then for each setting of the potential V across I, readings were taken of the discharge current in I and of the deflection of the galvanometer across II with the discharge in I both on and off. In computing results, the difference in these galvanometer deflections divided by the discharge current in I was plotted against the potential V. The initial velocity correction to the applied potential was based on the observed value of the first ionization potential. Removal of the potential $V+V_2$ from the electrode at the middle of the tube permitted ions from the discharge to reach II, and at low pressures accurate measurements of the ionization potential could be made by use of the space charge effect. With gas pressures greater than .01 mm, it was preferable to to measure, by the Lenard method, ions reaching the screening cylinder.

Results

Caesium. The metal was distilled into the body of the tube and the tube maintained at about 160°C, giving a vapor pressure of about .02 mm. Fig. 2 shows some typical curves, taken with nearly constant detecting sensitivity, but with different discharge currents, and Table I gives some data on the curves. Mean values for the critical potentials based on 20 curves are—

$$13.0 \pm .5,\ 18.5 \pm 1,\ 21.5 \pm .5,\ 39.0 \pm 1 \text{ volts.}$$

Uncertainty as to the potential correction is the chief factor in the probable error 0.5. The measurements show that, with discharge currents less than 6×10^{-5}, the photo-current at a given voltage is nearly proportional to the discharge. current With larger currents, the photo-effect above 13 volts increases more nearly as the square

[4] Kingdon, Phys. Rev. **21**, 408 (1923).

of the discharge current. Curves extending over a considerable range of voltage are always distinctly concave to the voltage axis.

TABLE I

Data for curves of Fig. 2.

Curve No.	Maximum discharge current	Maximum current of photo-effect	Maximum volts
I	28×10^{-5}	5.3×10^{-7}	16
II	6×10^{-5}	4.5×10^{-7}	30
III	1.9×10^{-5}	4.8×10^{-7}	46
IV	1.3×10^{-5}	3.3×10^{-7}	46

Potassium. Relatively few curves were obtained with this vapor. The tube was at about 240°C, giving a vapor pressure of the order of .05 mm. The mean values for the critical potentials are

$$19.0\pm1,\ 23.8\pm1,\ 31.8\pm1,\ 48.4\pm1 \text{ volts},$$

the first value being based on published measurements.[5] Curves are similar to the caesium curves, except that the second point is much more pronounced in this case.

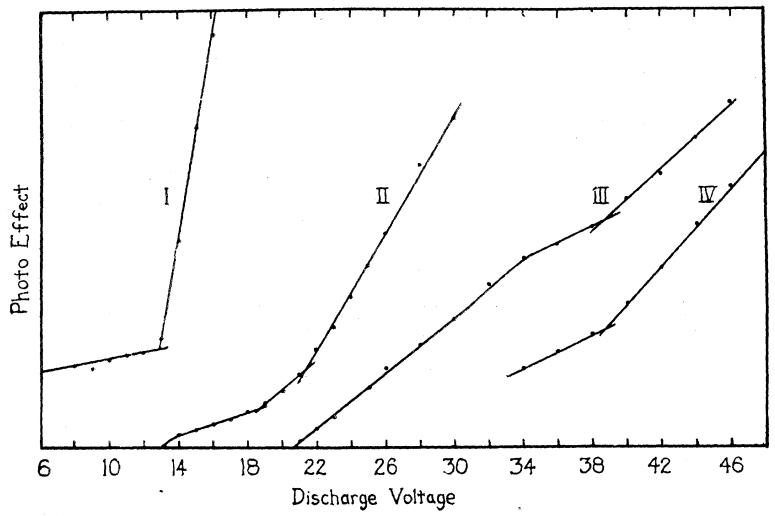

Fig. 2. Photo-ionization of caesium vapor as a function of the discharge voltage. (See Table I.)

Argon. Gas which was known to contain some nitrogen was streamed continuously from a reservoir through a fine capillary tube, hot calcium chips, a liquid air trap, the discharge tube and a second liquid air

[5] Mohler, "Critical Potentials Associated with Excitation of Alkali Spark Spectra," Sci. Paper, Bur. of Stds., No. 505, 1925.

trap. Many curves were obtained with argon in testing out various modifications in the tube design. Fig. 3 gives some typical curves

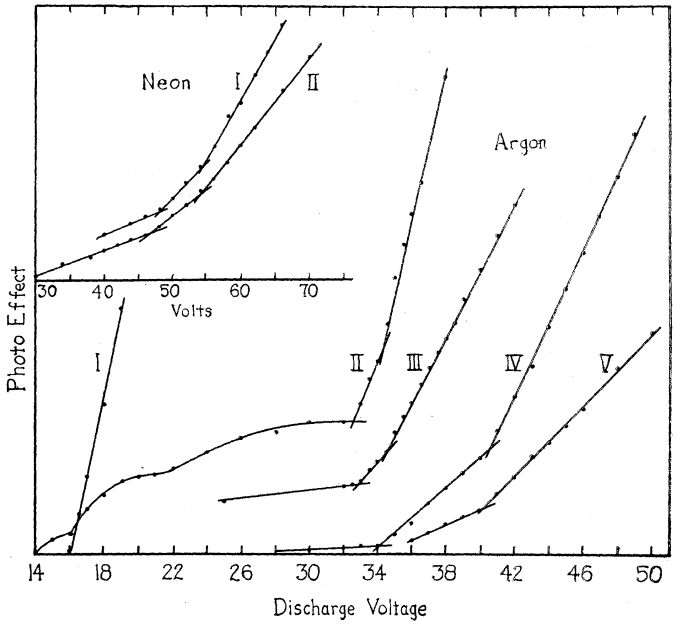

Fig. 3. Photo-ionization of neon and argon as a function of the discharge voltage. (See Table II.)

and Table II gives data relating to them. The mean values of the critical potentials are

$$32.2 \pm .2,\ 34.8 \pm .5,\ 39.6 \pm .5 \text{ volts},$$

the potentials being based on the value 15.4 for the first ionization potential.[6] The sensitivity of ion detection is not the same for the

TABLE II

Data for curves of Fig. 3

Curve No.	Pressure	Maximum discharge current	Maximum photo-current	Maximum volts
Argon I	.01	$.42\times10^{-4}$	Ion current	19
II	.01	8.5×10^{-4}	54×10^{-7}	38
III	.01	$.58\times10^{-4}$	34×10^{-7}	42
IV	.04	2.1×10^{-4}	7.6×10^{-7}	48
V	.04	4.2×10^{-4}	13.3×10^{-7}	50
Neon I	.01	$17.\times10^{-4}$	3.5×10^{-7}	70
II	.01	$18.\times10^{-4}$	2.8×10^{-7}	70

[6] Hertz and Kloppers, Zeits. f. Physik **31**, 463 (1925).

different curves. The effect below 30 volts was relatively large for high discharge currents (curve II), while increased pressure made the change in slope near 40 volts more pronounced (curves IV and V).

Neon. Gas which was known to contain a trace of helium was treated in the same way as the argon. Curves and data are included in Fig. 3 and Table II. The ion detecting sensitivity was much lower for neon than for the other gases and the changes in slope at the critical potentials were less distinct. Mean values for these potentials relative to the spectroscopic value 21.5 volts for the first ionization potential[7] are

48.0 ± 1 and 54.9 ± 1 volts.

The second points falls close to the ionization potential of the helium ion, but spectroscopic results described below show that the potential can safely be ascribed to neon. The curves showed no other critical potentials characteristic of helium.

Spectroscopic observations. A number of spectrograms of thermionic discharges were made to aid in the interpretation of the electrical measurement. A third spectrum of caesium had previously been reported[5] with an excitation potential less than 60 volts. Further photographs of the discharge show a trace of this spectrum at 40 volts with a discharge current of 10^{-2} amps, while with a current of 2×10^{-3} amps the lines were not visible below 55 volts. The spectrum is faint and the threshold potentials could not be located accurately.

Dejardin[8,9] has measured the potentials required to excite the second spectra of the rare gases but his work on neon[9] had not been published at the time my experiments were made. For that reason I have taken a series of spectrograms of the neon discharge. I used a three electrode thermionic tube with the grid and plate at the same potential and photographed the spectrum with a quartz spectrograph. Exposures were made at a series of potentials with currents of a few milli-amperes and a gas pressure of about .05 mm. The second spectrum was absent at 54 volts, distinctly visible at 55 and strongly enhanced in exposures at 58, 60 and 70 volts. The plates show about 25 of the stronger lines of the neon II spectrum[10] with no evidence of any real difference in excitation potentials of the different lines. The strong lines are all between 3700A and 3300A. Discrepancies between

[7] Lyman and Saunders, Nature **116,** 358 (1925).
[8] Dejardin, Ann. d. Physique **11,** 241 (1924).
[9] Dejardin, Comptes Rendus **182,** 452 (1926).
[10] Merton, Proc. Roy. Soc. **89A,** 447 (1913–14);
L. and E. Bloch and Dejardin, Comptes Rendus **180,** 731 (1925).

my results and those of Dejardin[9] will be considered in the following section.

Interpretation of Results

Caesium and potassium. The paper on excitation of alkali spectra[5] gives a basis for the interpretation of the present results, and the correlation is shown in Table III. There is good agreement except in

Table III

Critical potentials of alkalies.

Ref. No.	Caesium Photo-ionization	Caesium Other data[5]	Rubidium Published data[5]	Potassium Photo-ionization	Potassium Published data[5]	Interpretation
1	13.0±.5	14 ±2	16.0±.5	19 ±1	19±1	Ioniz. of n_2 rare gas shell. 2nd spectrum with high current.
2	18.5± 1		21.6±.5	23.8±1	23±1	Ioniz. + ion excitation.
3	21.5±.5	21.5±1	25.2±.1	31.8±1	28±1	Double ioniz. 2nd spectrum with low current.
4	39.0± 1			48.0±1		Ioniz. of n_1 rare gas shell. 3rd spectrum high current.
5		55 ±5				3rd spectrum low current.

Table IV

Critical potentials of rare gases.

Ref. No.	Argon Photo-ionization	Argon Published data	Neon Photo-ionization	Neon Published data	Interpretation
1		15.4[6]		21.5[7]	1st ionization potential
2	(16.8)		(26.5)		Excitation of ion.
3	(19.4)	19.0[8]	(33.4)		Ioniz. of ion. 2nd spectrum with high current.
4	32.2		48.0		Ioniz. + excitation of ion.
5	34.8	34 [8]	54.9	48 [9]	Double ioniz. 2nd spectrum with low current.
6	39.6				Ionization of n_1 shell.
7		70 [8]			Third spectrum with low current.

the case of point 3 of potassium. In all cases the new value is probably to be preferred. The manner in which the excitation of the third caseium spectrum depends on the current indicates that it is a spark spectrum.

Argon and neon. Various observers[8,11] have found that the argon II spectrum is excited near 34 volts with low currents, and near 19

[11] Horton and Davies, Proc. Roy. Soc. **102A**, 131 (1922).

volts with high currents, the difference in the potentials being about equal to the first ionization potential. This clearly indicates that the low current excitation potential measures the work of double ionization. Experiments involving electromagnetic analysis of ions[12] give a much higher value, 45 volts, for the work of double ionization. As other methods fail to show a critical potential at this point, I have interpreted my data on the basis of the spectroscopic results as shown in Table IV. Values in parentheses are ionization and excitation potentials of the ions, computed by subtracting the first ionization potential from the observed higher potentials.

The above described experiments indicate that the neon II spectrum is excited near the higher of the two observed critical potentials, and that all of the stronger lines appear within a volt or two of this potential. The recent results of Dejardin[9] are not in agreement with this. He finds one group of lines (included among the strong lines observed by the author) excited near 48 volts, while a second group (only a few faint lines observed in the present work) appear above 52 volts. For this he used a low pressure discharge concentrated by a magnetic field. With an intense discharge at high pressure the first group appeared between 28 and 30 volts. Since the serious sources or error, space charge, oscillating discharge, and multiple excitation all tend to make observed values too low, I believe that my higher value for the excitation of the first group is nearer the true value, and the neon results in Table II are interpreted on this basis. Dejardin's use of a magnetic field to concentrate the discharge would obviously increase the current density in his experiments and a multiple excitation involving the excitation stage (4) of Table IV would explain this result. My spectrograms give no conclusive evidence for or against the existence of a higher critical potential for Dejardin's second group.

Point (2) of neon can probably be interpreted as measuring the work required to raise an electron in the ion from a 2_2 orbit to a 3 quantum orbit; for the ionization potetial of a 3 quantum state in a hydrogenic ion is 6.0 volts while the ionization potential of this neon level is $33.4-26.5=6.9$ volts. The 3 quantum orbits are probably the final states for the spark lines between 3700 and 3300A. These potential values indicate that the absorption lines of the neon ion with final state 2_2 lie between 465A and 370A, while all other lines of the second spectrum will fall on the long wave-length side of 1800A. These predictions are not in conflict with published results,[13] which

[12] Barton, Phys. Rev. **25,** 469 (1925).

[13] Lyman and Saunders, Proc. Nat. Acad. Sci. **12,** 92 (1926).

mention many lines near 430A, but these unclassified lines may include spectra involving the 2_1 level as well as higher stages of ionization of the level 2_2.

The n_1 levels of the rare gas shell. Tables III and IV identify potentials of potassium and caesium and of argon, as measuring the energy levels of n_1 electrons. There are two reasons for this: first, that other possibilities seem to be excluded, and second, that the magnitudes of the observed potentials are consistent with the general scheme of atomic structure. This is shown in Fig. 4, a Moseley diagram of the beginning of the M series, which includes the observed points, together with

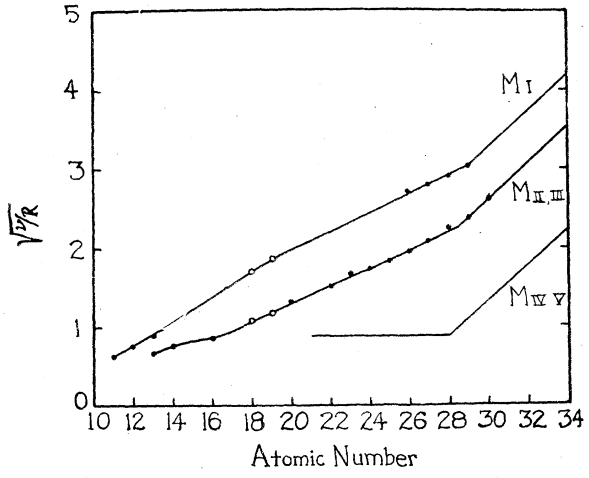

Fig. 4. The beginning of the M series. Dots give limits computed from optical and x-ray data, while circles are based on critical potential values for potassium and argon.

limits computed from optical and x-ray spectra. The 5_1 level of caesium can not be checked in this way but the screening separation of the n_2 and n_1 levels

$$\sqrt{\frac{\nu}{R}(n_1)} - \sqrt{\frac{\nu}{R}(n_2)}$$

is 0.69 for both potassium and caesium. This is definitely larger than the value 0.57 found in the x-ray range between levels of azimuth numbers 1 and 2, but agrees with the values .73 to .64 given by the computed M levels of metals of the iron group (Fig. 4).

Quantitative considerations. In the introduction, I raised the question as to whether photo-ionization contributed appreciably to the total photo-electric effect measured by the usual radiation potential method.

The space charge effect does not give an absolute measure of the photo-ionization. A partial answer to the question is given by the following experiments. The "radiation current" in II (Fig. 1), with other connections as before, but with the filament cold, measures the photo-electrons from the gas, plus photo-electrons from the small area of the cathode and the adjacent screening electrode. With potentials on II reversed, one measures the photo-electrons from the gas plus those from the large area of the cylinder II. The current in the second case was, in order of magnitude, 10 times as large as in the first case in the range of conditions here used. We conclude that, under comparable conditions, photo-electrons from the metal electrodes contribute at least nine tenths of the radiation effect as commonly measured.

The photo-electric current in case one (filament cold and potentials as in Fig. 1) is certainly greater, possibly much greater, than the photo-ionization current alone. Comparison of this current with the current change produced by the space charge effect will at least set a lower limit to the ratio of electron current change to ion current. Measurements in caesium and argon gave ratios of 3800 and 2400 respectively. I have also drawn a measured ion current from the discharge into II and measured the resulting change in thermionic current. The ratio then is much smaller, being about 300 for caesium. The reason for the difference is evident. Ions formed within the cylinder II may circulate many times around the cathode before falling into it.[4] Ions drawn into the space can go directly to the anode in spite of the small retarding field, and then the ratio is, as we should expect, less than the mobility ratio, 500, of electrons as compared with caesium ions.

The current change produced by photo-ions is known to be proportional to the radiation intensity, provided the electron current change is small compared with the dark current.[3] It follows that the effect should here be proportional to the discharge current as long as the current density in the discharge is small enough to avoid secondary effects such as collisions of electrons and ions. We have found that with the caesium such a proportionality held with currents less than 6×10^{-5} amps, but that with higher currents the photo-effect above 13 volts increased at an abnormal rate. This can be correlated with results showing high current excitation of the caesium II spectrum at this potential.[5] Similarly in argon (Fig. 2, curve II), large discharge currents gave an abnormal increase in photo-effect below 30 volts, which is probably related to ion excitation by collisions of electrons and ions.

In all cases the most conspicuous critical potential was that giving double ionization of the n_2 shell. This is probably because the strongest lines of the ion spectrum lie close to the n_2 absorption limit where the absorption coefficient of the gas is high. The radiation resulting from n_1 ionization is probably weakly absorbed, and the intensity must be relatively great. This conclusion is supported by the fact that with argon, increased pressure made the effect above the n_1 critical potential relatively large. The radiation passed through about 10 cm of gas before reaching the detecting chamber so that with the higher pressures the spark lines were reduced by absorption much more than the n_1 spectrum.

BUREAU OF STANDARDS,
DEPARTMENT OF COMMERCE,
April 27, 1926.