IONIZATION AND RESONANCE POTENTIALS FOR ELECTRONS IN VAPORS OF ARSENIC, RUBIDIUM, AND CÆSIUM.

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When electrons are accelerated in a metallic vapor, at least two types of inelastic impact between an electron and atom occur. The first of these results in an orbital shift of the electrons bound in the atom and the second in the complete removal of an electron or ionization of the atom. The potential differences through which an electron must fall to obtain sufficient velocity or kinetic energy for these two types of collision are known as the resonance and the ionization potentials for the particular metal in question. The resonance and ionization potentials of a series of metals have been determined in this laboratory.[1] The present paper is a report upon the work with arsenic, rubidium and cæsium.

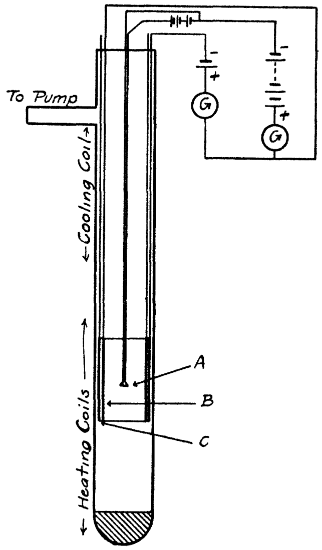

Fig. 1.
Diagram of apparatus used for arsenic.

The arrangement of apparatus for arsenic is shown in Fig. 1. Arsenic was vaporized at the bottom of the pyrex glass tube and the vapor, after passing through the superheated ionization chamber, condensed in the upper half of the tube. The ionization chamber was supported entirely by steel rods running from the top of the tube. The source of electrons was a hot tungsten wire cathode, *A*, of low resistance, coated with lime. Surrounding the cathode was a cylinder of iron net, *B*, and outside and coaxial with this a cylinder of sheet iron, *C*. The apparatus was evacuated by means of a Langmuir and Stimson condensation pump to a gas pressure of about 5.10^{-5} cm. Hg as registered by a McLeod gage. Sufficient vapor was obtained by heating the arsenic to about 400 to 500° C.

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[1] Na, Tate and Foote, J. Wash. Acad. Sci., 7, p. 517, 1917. Cd, Tate and Foote, Bur. Standards Sci. Paper No. 317. Na, Cd, K, Zn, Tate and Foote, Phil. Mag., 36, p. 64; 1918. Mg, Tl, Foote and Mohler, Phil. Mag. (in press).

A trap containing cadmium-tin alloy chips immersed in liquid air was used between the pumps and the ionization tube in order to preclude the possibility of the presence of mercury in the ionization chamber.

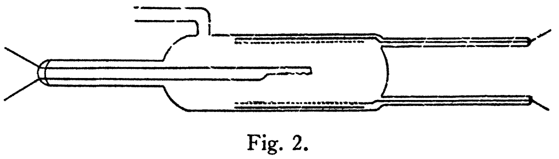

Fig. 2.
Ionization tube used for rubidium and cæsium.

The experimental procedure consisted in applying a constant retarding potential of 0.8 to 1.5 volts between the net and the outside cylinder and measuring both the total current from the hot wire, and that portion of the current which reached the outside cylinder against the retarding field, as functions of a variable accelerating potential applied between the hot wire and net. The apparatus used for rubidium and cæsium is illustrated by Fig. 2. This was constructed of soda glass, as it was found that the heated vapors of these metals do not noticeably attack soda glass while the reaction with lead glass is very pronounced. The net and cylinder were of nickel, and a platinum hot wire coated with lime served as the cathode. A retarding potential of about 0.5 volt was applied between the net and cylinder. Metallic rubidium from Kahlbaum was used and several grams of cæsium were obtained by heating metallic calcium and Kahlbaum cæsium chloride to about 400° C. at a very low pressure. The metal was distilled into a small test-tube, covered with a drop of benzol, and inserted into the pump intake, after which the apparatus was sealed and evacuated. The metal was then redistilled into the ionization chamber. During the observations the

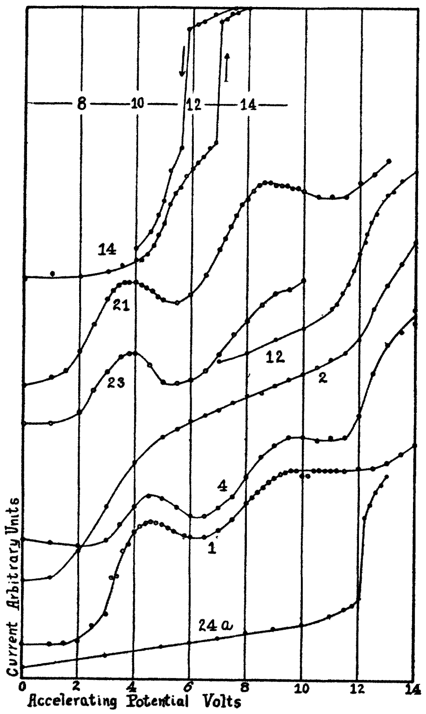

Fig. 3.
Total and partial current curves for arsenic.

entire ionization tube was uniformly heated to about 150° C., and the metal gradually distilled out, condensing in the exhaust tube. When necessary the metal was redistilled back into the ionization tube.

TABLE I.

Ionization and Resonance Potentials for Electrons in Arsenic Vapor. [*Curves 1 to 12; Cadmium-tin alloy trap and liquid-air trap between pump and ionization tube for several hours before and during the time of observation. Curves 21 to 24a: All apparatus reconstructed and both traps used continuously from the time the apparatus was assembled.*]

Curve.	Resonance.			Applied Potential at Ionization.	Initial Potential.	Ionization Potential.[1]	Resonance Potential.[2]	
	a.	*b.*	*c.*				*b–a.*	*c–b.*
1	3.6	8.4	. . .	. . .	. .	. . .	4.8	. .
2	. .	. .	. . .	10.4	1.0	11.4	. .	. .
3	. .	. .	. . .	10.5	1.0	11.5	. .	. .
4	3.8	8.4	12.6	. . .	. .	. . .	4.6	4.2
4*a*	3.8	8.4	12.8	. . .	. .	. . .	4.6	4.4
5	. .	. .	. . .	10.6	1.0	11.6	. .	. .
10	3.6	8.8	. . .	. . .	. .	. . .	5.2	. .
12	. .	. .	. . .	10.6	1.1	11.7	. .	. .
21	2.8	7.7	. . .	. . .	. .	. . .	4.9	. .
22	. .	. .	. . .	10.0	1.8	11.8	. .	. .
23	3.0	7.8	. . .	. . .	. .	. . .	4.8	. .
23*a*	3.2	. .	. . .	. . .	. .	. . .	. .	. .
24	. .	. .	. . .	9.6	1.6	11.2	. .	. .
24*a*	. .	. .	. . .	10.0	1.6	11.6	. .	. .

Fig. 3 represents some of the data obtained for arsenic. A complete analysis of these and other curves is given in Table I. The partial-current curves show pronounced changes in curvature at successive points *a*, *b*, *c*, which differ in potential by a constant amount. This constant difference gives the resonance potential directly, eliminating any consideration of initial velocities. The total-current curves show a rapid increase in slope at a point for which the potential, corrected for the initial velocity (potential) of the electrons as obtained from the partial-current curves, gives the ionization potential. The initial potential is the difference between the resonance potential and the applied potential corresponding to the first point of resonance. A detailed discussion of this method for determining the ionization potential has been given elsewhere.[3] Curve 14, Fig. 3, is of interest as an example of a discontinuous total-current curve. On increasing the accelerating potential the total current increases gradually up to about 13 volts. At this point the current increases discontinuously and upon decreasing the

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[1] Mean ionization potential = 11.5 volts.

[2] Mean resonance potential = 4.7 volts.

[3] Tate and Foote, J. Wash. Acad. Sci., 7, p. 520, 1917.

accelerating potential the current decreases discontinuously at about 12 volts. Similar curves have been obtained for mercury, sodium and rubidium. Curves of this type may be secured when the vapor density and the electronic current are high. In the present instance a measurement of the initial velocity of the electrons was not made but, in general, these discontinuous curves afford as accurate a determination of the ionization potential as those obtained with a smaller vapor density and initial velocity. The discontinuous change occurs considerably above the ionization potential and is probably due to a potential redistribution in the ionization chamber. As the potential is gradually increased the most intense part of the discharge, at least for rubidium, sodium, etc., for which metals the glow discharge is visible, moves suddenly at the point of discontinuity from the hot wire to the net.

The final results with arsenic gave 4.7 volts for the resonance potential and 11.5 volts for the ionization potential. These values are quite similar to the corresponding voltages for mercury, namely, 4.9 volts and 10.3 volts, and for this reason it was at first suspected that mercury from the pumps and gage was present in the ionization chamber. Although both liquid air and cadmium-tin alloy were used as a mercury trap in the first series of experiments here described (curves 1 to 12) the apparatus was entirely reconstructed with every precaution again being taken to avoid contamination by mercury. The results of this second series of experiments (curves 21 to 24*a*) confirmed those of the first series. In work at this laboratory with eleven different metals no trace of mercury has ever been observed, when the metals are volatilizing rapidly, in the characteristic ionization and resonance curves, although heretofore we have never used either cadmium-tin or liquid-air traps. In the case of the gases and non-metallic vapors, however, considerable precaution must be taken to avoid the presence of mercury. It was therefore thought possible that contamination by mercury might still be present and show up prominently in the somewhat non-metallic arsenic vapor. The following experiment was accordingly performed.

It was noted that, contrary to our experience with other metals, no glow discharge could be detected in arsenic at the ionization point. A special discharge tube was constructed for observing the arsenic arc more carefully. A steel disk anode and a tungsten hot-wire cathode were mounted about 1 cm. apart in a glass tube lined with iron net in electrical contact with the hot wire. The tube was mounted in a special electric furnace having a small side opening through which the arc could be viewed. Above the distillation point of arsenic the electron current indicated marked ionization as before at the ionization potential of 11.5 volts. With a current of 30 milliamperes no arc or glow discharge whatever was visible. A few drops of mercury were then placed in the ionization tube. A visible arc was obtained with a current of 0.02 milliampere, and with a current of 20 milliamperes the arc was very intense. Thus the fact that a current of 0.02 milliampere is sufficient to show the presence of mercury as an impurity of arsenic, and that a current of 30 milliamperes in supposedly pure arsenic vapor does not show a trace of any glow whatever, must be taken as a proof of the purity of the vapor. It is of further interest to note that when arsenic is heated with a small amount of mercury the ionization due to the mercury will appear 200° C. below the point where arsenic vaporizes sufficiently to show ionization, and after prolonged heating at 500° C. the mercury is driven out of the tube so that finally the ionization of arsenic alone is observed and the glow discharge disappears.

It has been shown in the earlier papers referred to that for many metals the ionization and resonance potentials are determined by the quantum relation $h\nu = eV$ where h is Planck's constant of action, e the electronic charge, V the resonance or ionization potential, and ν a frequency determinable from spectroscopic data. The value assigned to ν appears to depend upon the column of the periodic table to which the particular metal under consideration belongs. Thus, for Group I. of the periodic table, ν is the frequency of the first line of the principal doublet series for resonance potential and the convergence of this series for ionization potential. For Group II. the resonance potential is determined by the first line of the combination series of single lines $1.5\ S\text{–}mp_2$, and the ionization potential is determined by the convergence of this series. Arsenic is the first metal in Group V. so far investigated. The quantum relation may be written $\lambda = 12334/V$ on substituting the proper values for h and e, where λ is the wave-length in Ångstrom units corresponding to the potential V expressed in volts. Thus, the resonance potential of 4.7 volts and the ionization potential of 11.5 volts correspond to the wave-lengths $\lambda = 2620$ Å. and $\lambda = 1070$ Å., respectively. No series having its first line at $\lambda = 2620$ Å. or its convergence at $\lambda = 1070$ Å. is known for arsenic. In fact, all the series relations so far observed in arsenic have been quite unsatisfactory, which is true also of the other metals in this family. Accordingly, the present work very likely indicates an undiscovered series in arsenic having its first term (or terms if a doublet series) near $\lambda = 2620$ Å. and converging near $\lambda = 1070$ Å., but as to the character of the series nothing can be inferred.

Fig. 4 represents the partial-current curves and Fig. 5 the total-current curves obtained with rubidium. As seen from Table II., the mean value of the resonance potential is 1.6 volts. This value and the first point of resonance collision, *a*, permit the determination of the initial velocities or equivalent potentials shown in column 9. The total-current curves 1, 6, 11, 12 were taken under the same experimental conditions as the partial-current curves 3, 4, 5, so that the initial potential, V_0, to be added to the observed applied potential at ionization to give the ionization potential, is 1.2 volts. Curve 12 corresponds to curve 7 with an initial potential of 1.4 volts, the cathode being operated at a higher temperature when these two curves were obtained. In the case of rubidium and cæsium the total current did not show saturation below the ionization potential, so that the point at which ionization begins is not indicated by as sharp a break as would otherwise occur. The following method for determining the break point proved quite satisfactory.

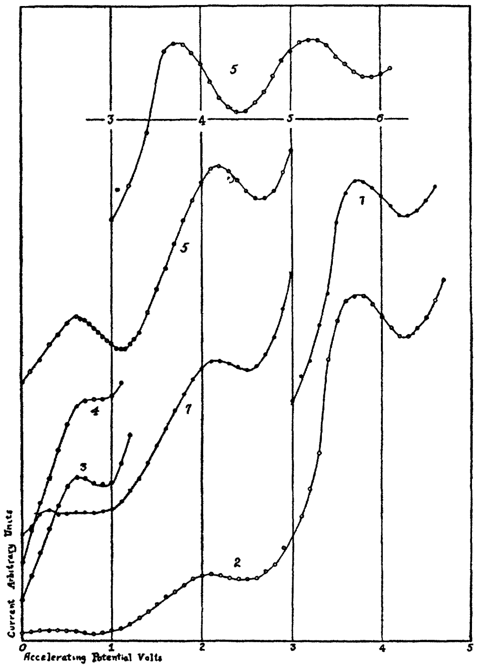

Fig. 4.

Partial-current curves for rubidium.

Langmuir[1] has derived an equation showing the relation between the thermionic current and voltage for the case of a hot wire surrounded by a cylindrical anode. If account is taken of the initial velocity of the

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[1] PHYS. REV., 2, p. 457, 1913.

electrons, an additional constant appears in the equation derived by Langmuir. The kinetic energy of an electron at a distance r from the hot wire is:

$$\tag{1} \tfrac{1}{2}mv^2 = (V + V_0)e,$$

where V_0 is the initial potential and $V = f(r)$ is the applied accelerating potential. Defining i as the thermionic current per unit length of the hot wire, one obtains directly from Poisson's equation:

$$\tag{2} r\frac{d^2V}{dr^2} + \frac{dV}{dr} = i\sqrt{\frac{2m}{e(V + V_0)}},$$

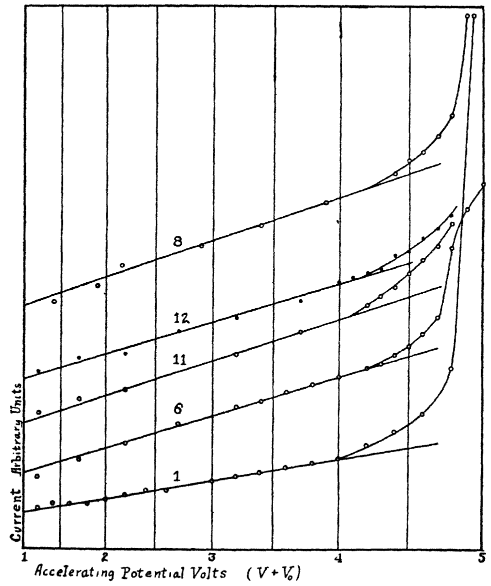

Fig. 5.
Total-current curves for rubidium.

the solution of which may be represented by the following relation where A is a constant for any definite configuration of the ionization chamber and temperature of the hot wire.

$$\tag{3} i = A(V + V_0)^{3/2}.$$

Hence, the relation between i and $(V + V_0)^{3/2}$ is linear for the purely thermionic current below its saturation value. When ionization begins the current increases more rapidly so that the ionization potential is given by the value of $(V + V_0)$ at the point where the curve i plotted against $(V + V_0)^{3/2}$ deviates from a straight line. Fig. 5 represents the total-current curves for rubidium plotted in this manner. The values of the applied potential were corrected by adding the initial potential V_0 as given in Table II. The linear relation is well satisfied except possibly at the lowest potentials. The agreement is even better than might be expected from a more careful consideration of the applicability of equation (3). Strictly considered, this equation should not hold exactly for two reasons: (1) Because of inelastic collision of some of the electrons at the resonance potential, and (2) because of the potential drop along the hot wire. Thus, equation (3) states that when $V = 0$, $i = A V_0^{3/2}$, but, although V_0 is comparable with V, the observed current is practically zero when the applied field is zero. The reason for this is that the electrons with no accelerating field between the hot wire and net fall along the hot wire from points of lower to higher potential or along one of the leading-in wires. A measurable current is observed only when the applied potential is comparable with the electrostatic field along the wire. This fact accounts in part for the high initial velocities observed. Also it may be noted that our method of selecting the point of resonance gives greatest weight to the electrons

TABLE II.

Ionization and Resonance Potentials for Electrons in Rubidium Vapor.

Curve.	Resonance.				Resonance Potential.[1]			Initial Potential.
	a.	*b.*	*c.*	*d.*	*b–a.*	*c–b.*	*d–c.*	
2......	..	1.65	3.35	...	...	1.70	...	1.2
3......	0.4	...	...	...	...	...	...	
4......	.4	...	...	...	...	...	...	
5......	.4	1.85	3.45	4.90	1.45	1.60	1.45	
7......	15	1.70	3.50	...	1.55	1.80	...	1.4
					Mean = 1.6 volts.			
	V_0.	$V+V_0$[2].						
1......	1.2	4.0						
6......	1.2	4.2						
8......	1.4	4.2						
11......	1.2	4.1						
12......	1.2	4.2						

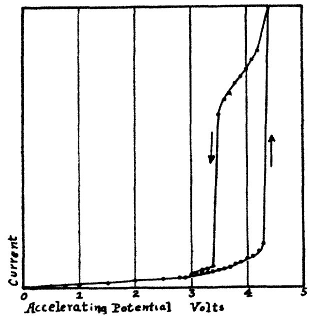

Fig. 6.

"Discontinuous" total-current curve for rubidium.

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[1] Resonance potential = 1.6 volts.

[2] Ionization potential = 4.1 volts.

of highest speed. A point of further interest is that practically the same values for the initial velocity are obtained when the partial-current curves are plotted directly and when they are plotted on the rectified coördinate system used for the total-current curves.

The mean value of the ionization potential of rubidium obtained from the curves shown in Fig. 5 is 4.1 volts. Fig. 6 illustrates a type of discontinuous total-current curve obtained when the density of the rubidium vapor is high.

TABLE III.

Ionization and Resonance Potentials for Electrons in Cæsium Vapor.

Curve.	Resonance.		Resonance Potential.[1]	Initial Potential.
	a.	*b.*		
3	0.60	2.10	1.50	0.88
5	.55	2.00	1.45	.93
7	.50	2.00	1.50	.98
8	.55	2.00	1.45	.93
10	.55	2.00	1.45	.93
11	.55	2.00	1.45	.93
12	.40	1.90	1.50	1.08
14	.40	1.90	1.50	1.08
Mean			1.48	1.0
	$(V+1.0)^{\frac{3}{2}}$.	Ionization Potential.[2]		
1	8.5	4.2		
4	7.7	3.9		
6	7.6	3.9		
9	7.1	3.7		
13	7.4	3.8		

Fig. 7 shows the partial-current curves and Fig. 8 the total-current curves for cæsium vapor. The method of determining the ionization and resonance potentials was that described above for rubidium. The final values, summarized in Table III., are 1.48 volts for the resonance potential and 3.9 volts for the ionization potential.

From the behavior of sodium and potassium one would expect the resonance and ionization potentials of rubidium and cæsium to be determined by the relation $V = 12334/\lambda$ where λ is the first line and convergence wave-length, respectively, of the principal series of doublets for each metal. The following table, to which for completeness have been added the data on the other alkali metals, confirms this fact.

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[1] Resonance potential = 1.48 volts.

[2] Ionization potential = 3.9 volts.

TABLE IV.

Resonance and Ionization Potentials for the Alkali Metals.

Metal.	λ (Å). ($\nu=1.5s-2p$).	Resonance Potential Volts.		λ (Å). ($\nu=1.5\ s$).	Ionization Potential Volts.	
		Computed.	Observed.		Computed.	Observed.
Lithium....	6707.85[1]	1.839	....	2299.67[2]	5.363	....
Sodium.....	5895.94[1] 5889.97[1]	2.092 *2.094*	2.12[3]	2412.63[4]	5.112	5.13[3]
Potassium..	7699.01[1] 7664.94[1]	1.602 *1.609*	1.55[3]	2856.69[5]	4.318	4.1[3]
Rubidium..	7947.64[1] 7800.29[1]	1.552 *1.581*	1.6[6]	2968.40[5]	4.155	4.1[6]
Cæsium....	8943.46[1] 8521.12[1]	1.379 *1.447*	1.48[6]	3184.28[5]	3.873	3.9[6]

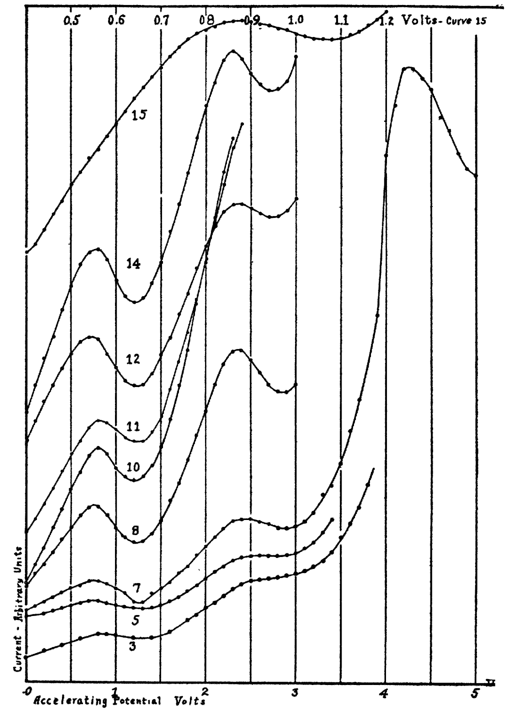

Fig. 7.

Partial-current curves for cæsium.

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[1] Meggers, Bur. Standards Sci. Paper No. 312.

[2] Dunz Tübingen Thesis, 1911.

[3] Tate and Foote, Phil. Mag., 36, p. 75, 1918.

[4] Wood and Fortrat, Astrophys. Jour., 43, p. 73, 1916.

[5] Watts, Phil. Mag., 29, p. 775, 1915.

[6] Foote, Rognley, and Mohler, this paper.

The first pair of doublets in the principal series of both rubidium and cæsium is rather widely separated. In the case of cæsium the separation is equivalent to about 0.07 volt. If resonance collision occurs at both 1.379 and 1.447 volts, corresponding to each member of the cæsium doublet, the partial-current curves should show two sets of maxima differing by 0.07 volt at the first point of resonance, by 0.14 volt at the second point of resonance, etc. None of the curves of Fig. 7 show double maxima and for curve 15, observations were made at every 0.02 volt. It is possible that the presence of double maxima could not be detected on account of the initial velocity distribution from the hot wire. However, it has been found by Foote and Mohler[1] that in the case of thallium the shorter wave-length member of the first doublet of the principal series appears to determine the resonance potential. Hence it seems quite likely that the proper theoretical values for the resonance potentials of rubidium and cæsium are 1.581 and 1.447 volts, respectively. This possibility suggests an analogy to the general behavior of the K

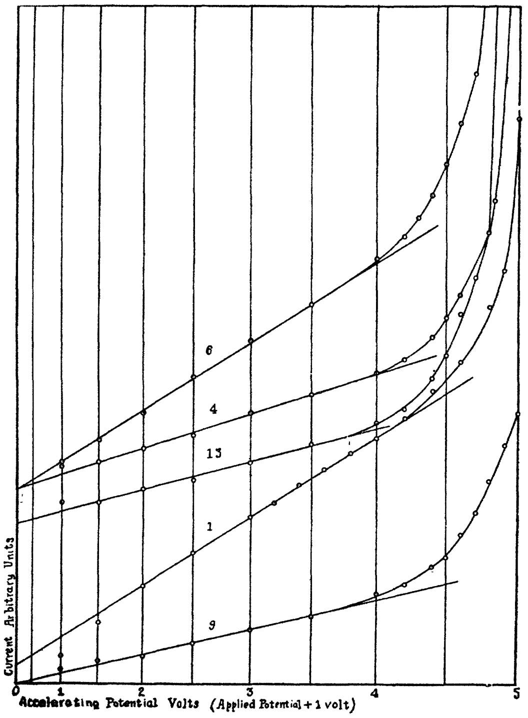

Fig. 8.

Total-current curves for cæsium.

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[1] Phys. Rev., 11, p. 487, 1918.

series in the X-ray spectrum of metals as has been pointed out by Foote and Mohler.[1] The present work indicates that the "single line" spectra of rubidium and cæsium are the doublets $\lambda = 7949$ and 7803 Å. and $\lambda = 8950$ and 8528 Å., respectively. At the ionization potential the principal series, the first subordinate series, and the second subordinate series appear. The following doublets were observed visually in the case of cæsium when the accelerating potential was equal to the ionization potential: Principal series, $m = 3$; first subordinate series, $m = 5, 6, 7, 8, 9, 10$; second subordinate series, $m = 4.5$.

SUMMARY.

Two types of inelastic collision between the electron and atom occur in vapors of arsenic, rubidium and cæsium. The potential differences through which an electron must fall to attain sufficient energy or velocity to produce these collisions are known as the resonance and ionization potentials for the particular metal in question. For rubidium and cæsium the resonance potential is determined by the quantum relation $h\nu = eV$ where ν denotes the frequency corresponding to the first doublet of the principal series. A similar relation holds for the ionization potential where ν denotes the convergence frequency of the principal series. Experimentally determined values of the resonance and ionization potentials for rubidium were 1.6 volts and 4.1 volts, respectively; for cæsium, 1.48 volts and 3.9 volts, respectively; for arsenic, 4.7 volts and 11.5 volts, respectively. By applying the quantum relation to the results obtained with arsenic we are able to predict the presence of an undiscovered spectral series in arsenic having its first term (or terms if a doublet series) near $\lambda = 2620$ Å. and converging near $\lambda = 1070$ Å. A Wehnelt tube discharge in arsenic possesses no luminosity indicating that the important series lines lie in the ultra-violet. At the ionization potential of rubidium and cæsium the principal, first, and second subordinate series appear. No ionization whatever could be detected at the resonance potentials of rubidium, cæsium, and arsenic.

BUREAU OF STANDARDS,
WASHINGTON, D. C.,
August 16, 1918.

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[1] J. Wash. Acad. Sci., Sept. 19, 1918.