IONIZATION OF MERCURY, SODIUM AND POTASSIUM VAPORS AND THE PRODUCTION OF LOW VOLTAGE ARCS IN THESE VAPORS.

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IT has been well established that when the vapors of a number of the metals are bombarded with electrons that there are at least two critical velocities of the electrons for each vapor: a lower velocity, or "resonance" velocity, produces the single-lined spectrum of the vapor under experimentation, and a higher velocity produces ionization of the vapor and a consequent emission of the complete spectrum. It has further been established that the equation

$$\frac{1}{2}mv^2 = h\nu$$

applies for these two velocities where ν, the frequency, assumes the values corresponding to the first and convergent wave-lengths of one of the optical series of the element.

These phenomena have been explained on the basis of Bohr's atom by assuming that at the "resonance" velocity an electron is knocked from its stationary orbit to the next outer orbit and that in falling back to its original position it radiates its surplus of energy with a frequency corresponding to the first member of the series belonging to this orbit; and that at the ionizing velocity the electron is knocked from its stationary orbit and is completely detached from the atom and in settling back to its normal position radiates the complete spectrum.

It is interesting to compare the results in the permanent gases, H, He, A and N, with those in the metal vapors. There is some evidence that what corresponds to the resonance velocity in vapors is what is found experimentally to be the ionization velocity in some of the gases. Thus for hydrogen the ionization potential instead of being 13.6 volts as called for by the Bohr theory or as might be suspected by analogy from the metal vapors is 10.2 volts which corresponds to the resonance potential in the vapors. That is, if in the equation $Ve = h\nu$ we introduce a value of ν corresponding to the first member of the Lyman series we get 10.2 volts, whereas if we use the value of ν corresponding to the last member, *i. e.*, the convergence frequency, we get 13.6 volts.

There is also some evidence that a similar condition holds for helium. Thus Richardson and Bazzoni[1] have shown that the limit of the helium spectrum lies between 470 A.U. and 420 A.U. If we take the mean of these two values, viz., 445 A.U., and substitute its frequency in the equation $Ve = h\nu$ we obtain a value of V equal to 28 volts. And if we assume that the first optical series of helium is given by the equation

$$\nu = k\left(\frac{1}{1^2} - \frac{1}{m^2}\right)$$

we see that the potential difference corresponding to the first member of the series is .75 of 28 = 21 volts. This is not very different from the observed value of the ionization potential.

The evidence offered by argon and nitrogen although small is worthy of consideration. Lyman[2] has shown that the spectrum of argon ends in the vicinity of 800 A.U. and that of nitrogen in the vicinity of 975 A.U. If the corresponding frequencies be introduced in the equation $Ve = h\nu$ we get 15.5 volts and 12.4 volts respectively. The ionizing potentials for these two elements are 12 volts and 7.5 volts respectively and it is significant that in the case of each element the observed ionization potential is less than that which would be expected from a knowledge of the high frequency limit of its spectrum and an application of the quantum relation $Ve = h\nu$.

An endeavor has been made to explain the low ionization potentials of helium[3] and hydrogen by assuming that as soon as radiation is produced by the collisions of electrons with atoms, this radiation acts photoelectrically on the cathode and liberates electrons with sufficient initial velocity to account for the difference between the observed and theoretical values of the ionization potential. According to the Bohr theory radiation would first occur when the electron is knocked from its stationary orbit to the one next outside of it.

The distinction between the two groups, the vapors and the gases, does not seem to be as rigid as outlined above for it has been shown that under certain conditions mercury vapor[4] is ionized at its resonant potential. And this suggests that possibly the other vapors are capable of a similar action. This paper is a report of some experiments I have performed on potassium and sodium vapors.

For various reasons these elements were studied in an atmosphere of mercury vapor. Although I began the experiments partly with the idea

[1] Richardson and Bazzoni, Phil. Mag., 6, 34, 285, 1917.

[2] Lyman, Astrophysical Journal, 43, 89, 1916.

[3] Van der Bijl, Phys. Rev., 2, 10, 546, 1917.

[4] Hebb, Phys. Rev., 2, 9, 371, 1917 and 2, 11, 170, 1918.

of determining the effects sodium and potassium radiations would have on the mercury vapor I would have extended the experiments to the case of pure sodium and potassium vapors if I had been fortunate in procuring a continuous action low vacuum pump. As the pump was not available that phase of the experiment cannot be reported.

The experimental tube was of the same nature as that used in the study of mercury vapor. It consisted of a glass tube about 2.5 cm. in diameter and 20 cm. in length bent at the center so that when placed horizontally with the bend down a supply of mercury always remained in this depression. The platinum cathode—width 4 mm., length 1.0 cm., thickness .0025 cm.—containing a small patch of CaO was supported at the center of the tube by two iron lead wires. The anode, always capped with platinum, was placed 3 to 4 mm. from the cathode. The ends of the tube were sealed with Khotinsky cement and kept cool by water jackets. The central part of the tube was heated by a gas-heated furnace. The apparatus was connected to a drying tube, a McLeod gauge and the pump. The latter was capable of producing a vacuum of .005 cm. Of course a very pure atmosphere of potassium or sodium and mercury vapors could be obtained by simply heating the central part of the tube. As the vapor pressures of potassium and sodium are small at the temperatures necessarily used with mercury, the major part of the vapor surrounding the anode and cathode was that of mercury. Neither the sodium nor the potassium was distilled before using. It was considered that the necessary purification would take place in the experimental tube and for this reason the mercury was boiled for some time, with the pump running, before observations were made.

The metals, sodium and potassium, were sometimes introduced into the mercury before placing them in the tube and sometimes were placed

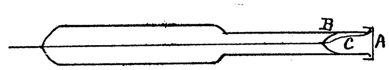

Fig. 1.

pure in a receptacle at the end of the anode. This needs a little explanation. In order to get a greater density of the sodium or potassium vapor it was found necessary to use an anode as shown in Fig. 1.

It was made of glass with a chamber C sealed off at the point B. A platinum wire passed through the anode and made contact with a removable platinum cap A. In the center of A and opposite the center of the cathode there was a small hole. The sodium or potassium was placed in the chamber C and, the platinum cap having been adjusted, the anode was quickly placed into the experimental tube. The mercury was then boiled for some time with the pump running in order to remove impurities. Then when the cathode was heated in close proximity to the cap A the sodium or potassium vapor was forced out through the small hole in A and was very favorably situated with respect to ionization.

Results with Potassium.

It was found that the striking voltage of the arc was lower than the ionization potential, 4.1 volts, and that with favorable density of the potassium vapor it was possible to get the arc to strike as low as 1.5 volts. When the density of the potassium vapor was small, which was usually the case when the potassium was simply dissolved in the mercury and none was placed in the special anode, the arc did not strike as low as when the density was greater nor did the spectrum of potassium usually appear. This was true for potential difference as low as 2.0 volts in rare cases and commonly for potential differences of 3.0 volts or higher. It should be stated that the spectra were observed with the aid of a small direct vision spectroscope so that it is not claimed that the potassium lines were not present but relatively to the mercury lines they must

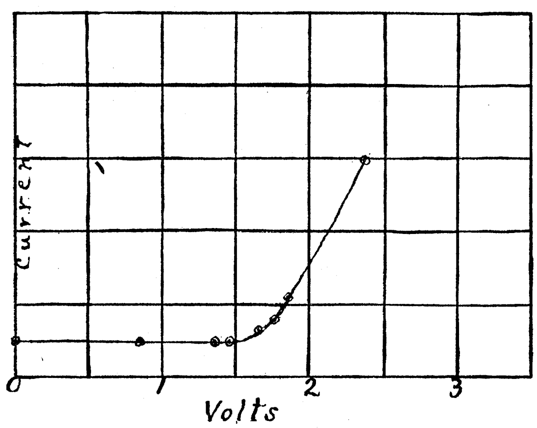

Fig. 2.

have been very weak. This apparently means that the current was carried almost entirely by the mercury vapor. When, however, the arc struck at potential differences lower than 2.0 volts the spectrum of potassium always appeared in strength. But even at these low voltages the mercury spectrum always appeared too.

As I had a low-resistance galvanometer in series with the arc I could make observations on the relation between the current through, and the potential across the arc space. Fig. 2 shows such a current-potential curve. It will be noticed that the curve starts to bend at about 1.5

volts. In this case the potassium had been dissolved in the mercury before introducing it into the tube. A simple anode terminating in a piece of platinum foil was used. At about 2.4 volts the mercury spectrum was showing but no potassium lines could be seen.

I have previously shown that the mercury arc could be made to operate at a potential difference lower than its striking voltage.[1] I have found that in the case of potassium the same thing is true. After the arc struck the voltage nearly always dropped as in the case of mercury and by manipulating the potential across the arc I have had it operating as low as 0.5 volts. It is possible that it could be obtained lower, as no special effort was made to find its minimum value. But a very remarkable thing was that the mercury spectrum still showed at 0.5 volts.

Results with Sodium.

As the melting point of sodium is considerably higher than that of potassium and as its vapor pressure is much lower at the temperatures I was using it did not lend itself well to experimenting in a mercury atmosphere. However, it caused the striking voltage of the arc to fall but not so pronouncedly as in the case of potassium. The lowest I have had the arc strike has been about 2.5 volts, but 3.0 to 3.5 volts was more common. The yellow lines of sodium appeared, but as in the case of potassium the rest of the spectrum was frequently not present. I have not been able to obtain a current-potential curve which broke as low as 2.1 volts—the resonance potential. I do not doubt but that it can be obtained.

Wood and Okano[2] have shown that the spectrum of sodium can be produced at 2.3 volts and that the *D* lines could be obtained with a potential difference as small as 0.5 volts. On several occasions I have had the *D* lines at potential differences lower than 1.0 volt. From a study of the current potential curves for sodium I am of the opinion that the appearance of these lines is not due to ionization. It is of interest to note that the occurrence of the *D* lines below 2.1 volts is similar to the appearance of the single line of mercury below 4.9 volts.[5]

As in the case of mercury and potassium, it was found possible to get the arc to operate at a voltage lower than its striking value and lower than the resonance potential of sodium. In the case of sodium I have had the arc operate as low as 1.4 volts with both the sodium and mercury lines showing.

Discussion of Results.

These results prove that in the case of potassium and probably in the case of sodium ionization can occur at a voltage V given by the equation

[1] Hebb, Phys. Rev., 2, 9, 371, 1917.

[2] Wood and Okano, Phil. Mag., 6, 34, 177, 1917.

$Ve = h\nu$ where ν is the frequency of the first member of the principal series of the element. These elements thus fall in line with mercury and more or less with the cases of hydrogen and helium. The results also appear to throw light on the cause of ionization at the resonance voltage. In the case of mercury it has been suggested that it is the radiation $\lambda = 2{,}536$ A.U. produced by 4.9 volt electrons, which acting photo-electrically causes the ionization. In the cases of sodium and potassium the radiation from the hot cathode should have caused the ionization if the radiations $\lambda = 5{,}890$ for sodium, and $\lambda = 7{,}700$ for potassium were all that was necessary. It thus seems to be certain that the ionizing electron must travel with a velocity corresponding to a fall through its resonant voltage at least before ionization can occur. This does not prove that the ionization is due entirely to collision, but it does seem to prove that collision is necessary and that there is a certain minimum velocity for that collision. That the radiation seems to have a small effect was indicated by former experiments with mercury. Similar experiments were tried with potassium. The light from an arc—the carbons of which had been saturated in potassium chloride—was passed into the experimental tube. No effect could be observed on the ionization potential or on the current through the arc. The galvanometer used was sensitive to about 10^{-5} amperes.

There are several ways by which we might imagine the ionization at the resonance voltage to occur: (1) It may be due to repeated collisions, (2) it may be due to fast electrons liberated from the cathode photo-electrically, (3) it may be due to photo-electric action on the vapor and (4) it may be due to a combination of the above. Cases 2 and 3 seem to be entirely ruled out for sodium, potassium and mercury but as Van der Bijl[3] has pointed out 2 might be effective in the case of helium, and he might have added hydrogen, for 10.2 volt light should liberate electrons from tungsten or platinum with a velocity of approximately 6.0 volts. In a similar manner we can imagine that argon is ionized at 12 volts, for if we take the lower limit of its spectrum to be 800 A.U.—15.5 equivalent volts—it would only mean a difference of 3.5 volts between observed and expected ionization potential. The lower limit of nitrogen's spectrum is 975 Å.U. and this corresponds to a voltage of 12.7. If we take the results of Goucher wihch were apparently obtained with a pure platinum cathode, the long wave-length limit of which is 2910 A.U.—equivalent to 4.3 volts—we find that 7.4 volt light would only produce electrons with an initial velocity of 3.0 volts. This added to 7.4 only gives 10.5 volts which would not be sufficient to produce ionization.[1]

[1] Of course the low ionization potential of argon and nitrogen might be due to the radiation acting on the anode.

Thus while the photo-electric action on the cathode can explain the low ionization for some of the elements it cannot do so for the others. And as pointed out above the photo-electric action on the vapor under experiment does not appear to be able to explain the results. Hence it appears as if the ionization at the resonance voltage was due either to repeated collisions or to a combination of collision and photo-electric effect, but that in either case a minimum velocity of collision was necessary, this minimum velocity corresponding to the resonant voltage. That the single-lined radiation is not able to ionize the vapor under experiment to any appreciable extent is also indicated by the fact that a strong single-lined radiation can be obtained both in mercury and sodium vapor below the resonance voltage, as has been shown by the writer for mercury[5] and by Wood and Okano[6] and the writer for sodium.

Although it requires a minimum potential difference equal to the resonance voltage to start appreciable ionization in the vapors of mercury, sodium and potassium, it does not require this voltage to maintain an arc in these vapors. Both in these experiments and in previous experiments I have had the arc in pure mercury vapor operating as low as 3.0 volts. I have also had the sodium arc operating as low as 1.4 volts and the potassium arc as low as 0.5 volts. Since getting the above results for mercury they have been substantiated by McLennan[1] who states that he has also had a cadmium arc to operate between 2 and 3 volts. As the resonance potential of cadmium is 3.8 volts this is another case where the arc operates lower than the resonance voltage of the vapor. Apparently the same phenomena hold for argon as MacKay and Ferguson[2] state that they have had an arc operating in argon at 4.0 volts. If we consider 12 volts the resonance potential of argon this is considerably below that value.

If we attempt to explain these low arcs on the basis of the photo-electric action of the arc radiation on the cathode, it would appear from the following table that the velocities of emission are sufficiently great with the possible exception of potassium.

Vapor.	Ionization Potential.	Resonance Potential.	Material of Cathode.	Long Wave-length in Eq. Volts.	Max. Vel. in Eq. Volts.
Hg	10.3	4.9	CaO	3.4	6.9
Na	5.1	2.1	"	"	1.7
K	4.1	1.6	"	"	.7
Cd	8.9	3.8	W	4.5	4.3
A	15.5?	12?	"	"	11.0

[1] McLennan, PHYS. REV., 2, 10, 84, 1917.

[2] MacKay and Ferguson, PHYS. REV., 2, 7, 410, 1916.

However, when we consider the magnitude of the arc currrents it does not seem as if the photo-electric action alone was sufficient. Thus in one case with pure mercury vapor the thermionic current was 6×10^{-5} amperes before ionization began at 5.0 volts. After the arc had struck and was operating at 3.7 volts the current was 1800×10^{-5} amperes. After making allowance for the increased electron emission due to the hot point on the cathode this appears to demand entirely too high a photo-electric current from a small cathode.

But still other difficulties exist. It has been shown that an arc will strike as low as about 2.0 volts in an atmosphere of potassium and mercury vapor, and that only the mercury lines are evident. If we assume that some of the potassium vapor ionizes and that the consequent radiation acts on the CaO the 4.1-volt light would liberate electrons from the cathode with a velocity of about 0.7 volts. This added to 2.0 volts would still be insufficient to ionize the mercury vapor. Nor would the action of the 4.1-volt light have any photo-electric effect on the mercury vapor as the long wave-length limit of mercury itself is about 2,800 A.U. The difficulty is still more pronounced in the case where the potassium-mercury arc struck at 1.5 volts and operated as low as 0.5 volts with the mercury spectrum showing. There is, however, the possibility that sufficient potassium adheres to the cool ends of the cathode so that when the potassium vapor ionizes its radiation acts on the solid or liquid potassium and liberates electrons with sufficient velocity to ionize the mercury vapor. The velocity of emission can easily be imagined to be of the right magnitude.

From these experiments and in view of the above considerations it appears to be altogether likely that there are other means of producing ionization and light in these arcs than those considered above. It is possible that the action of the positives is not sufficiently considered and that impacts of the positives on the cathode liberate electrons with an initial velocity as claimed by Tate.[1] Further it seems altogether probable that some of the light of the arc is produced by the positives as Dempster[2] has shown that positives moving with velocities less than that corresponding to 5.0 volts are able to stimulate line spectra. And of course the possibility of chemical action, especially in the case where two metals are employed, is to be considered.

Summary.

It has been shown that: (1) Potassium vapor can be ionized at 1.6 volts, its resonance voltage. (2) Sodium vapor can be ionized at 2.5

[1] Tate, Phys. Rev., 2, 10, 81, 1917.

[2] Dempster, Phys. Rev., 2, 8, 651, 1916.

volts which is very close to the resonance voltage. This result agrees with that found by Wood and Okano. (3) The *D* lines of sodium can be excited at less than 1.0 volt; also in agreement with Wood and Okano. (4) The sodium and potassium arcs in mercury vapor can operate below their resonance potentials and as low as 1.4 volts for sodium and 0.5 volts for potassium. (5) The mercury spectrum can be produced as low as 0.5 volts in an atmosphere of mercury and potassium.

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