A SECOND IONIZATION POTENTIAL IN POTASSIUM VAPOR

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Abstract

The occurrence of a second peak in the photoionization curve of potassium vapor (Lawrence and Edlefsen) suggests that there might be a related peak (or discontinuity) in the curve for ionization by electron impact. The ionization in potassium vapor was investigated by Hertz' method of neutralization of space charge by positive ions. It was found that there was an abrupt increase in gradient of the ionization curve, indicating a second ionization potential at 0.97 ± 0.05 volt above the first one corresponding to the series limit. With mercury vapor, the apparatus indicated the presence of Lawrence's ultraionization potentials in mercury vapor, together with three new ones (10.40, 10.62, 10.88, 11.28, 11.40, 11.77, 12.16, 12.46).

Introduction

CERTAIN peculiarities in the photoionization curve of potassium in the vicinity of the series limit led to these experiments. Lawrence and Edlefsen[1] found that the photoionization of potassium is a maximum at the series limit (2856A), diminishes to a minimum at 2700A, and then rises to a second higher maximum at 2340A. Mohler and Boeckner,[2] however, find that the ionization starts at the series limit and increases steadily. This curve resembles Lawrence's[3] earlier results except for the fact that in the latter case the effect began at 2600A. The peculiar form of the curve obtained by Lawrence and Edlefsen suggests that in ionization by electron impact something of a similar nature might be revealed. The only work which we can find on the ionization potential of potassium by electron impact is that done thirteen years ago by Tate and Foote,[4] who identified roughly the ionization potential with the theoretical value corresponding to the series limit. They were interested only in establishing this approximate identity and made no attempt to study the shape of the ionization curve above the ionization potential. Another result which suggests that a careful study of the ionization curve for potassium might reveal peculiarities is Lawrence's discovery of the ultraionization potentials of mercury vapor (i.e., discontinuities in the ionization curve at 0.20, 0.89, 1.30 and 1.66 volts above the theoretical ionization potential corresponding to the series limit).

Apparatus and Results

The method used for investigating the ionization potential was that originally used by Hertz. An oxide coated platinum filament, F, 11 mm long,

[1] E. O. Lawrence and N. E. Edlefsen, Phys. Rev. **34**, 1056 (1929).
[2] F. L. Mohler and C. Boeckner, Bureau of Standards, Journal of Research **3**, 303 (1929).
[3] E. O. Lawrence, Phil. Mag. **50**, 345 (1925).
[4] J. T. Tate and P. D. Foote, Washington Acad. Sci. Jour. **7**, 517 (1917).

was mounted in a rectangular box of monel metal, B, $25\times30\times15$ mm. A second oxide coated filament, C, was located just outside the box, opposite a small slit 0.6 mm in width. The slit was at right angles to the filament,

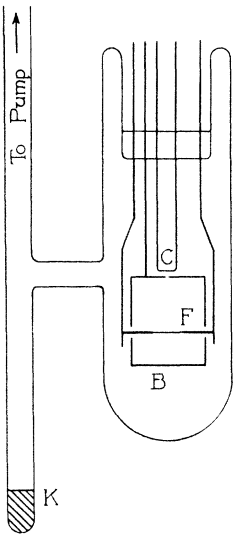

Fig. 1. Diagram of tube.

so that only those electrons coming from a nearly equipotential region of the filament, C, were allowed to enter the box. The potassium was dis-

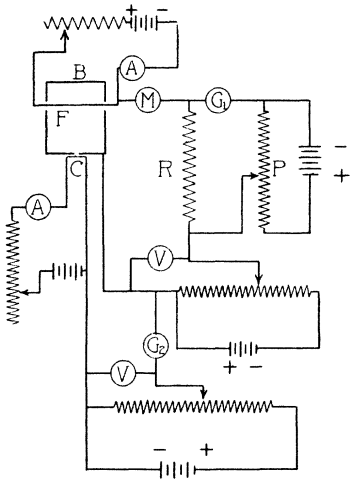

Fig. 2. Arrangement of balancing circuit.

tilled into a side tube, D. The whole of the apparatus, including part of the tube leading to the pump, was surrounded by a furnace, the temperature of which could be controlled.

To measure the change in the space charge limited current from F, caused by ionization inside the box, we used a balance arrangement, shown in Fig. 2. The thermionic current from the filament, F, passed through a resistance R. The voltage drop across R was balanced by an opposing potential from the potentiometer, P, through the galvanometer, G. Any change in the space charge limited current, far too small to be measured

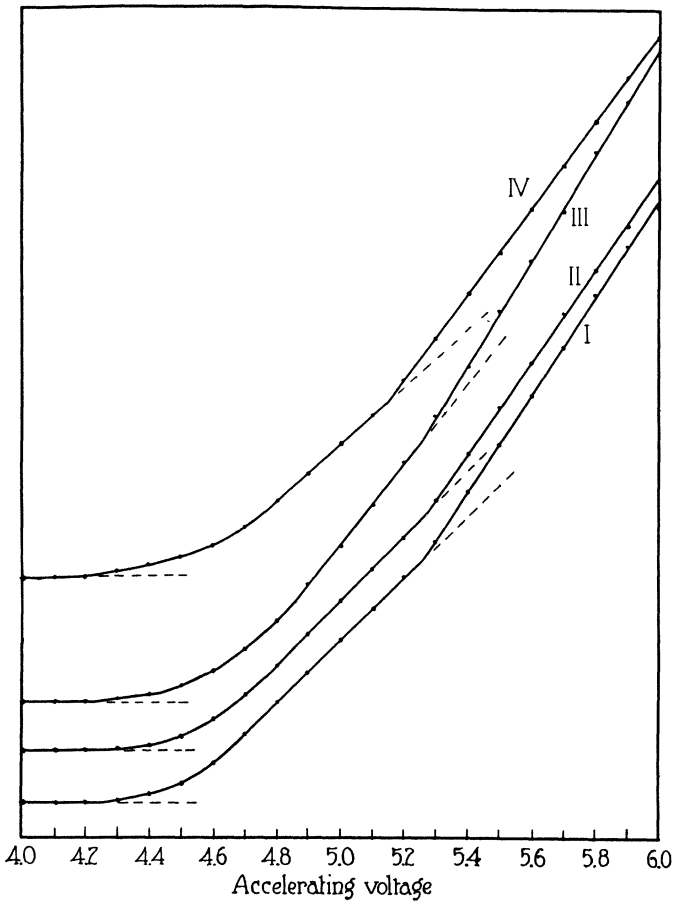

Fig. 3. Ionization curves for K vapor.

Curve:	I	II	III	IV
Temp.:	189	200	197	197°C

accurately on the micro-ammeter, M, could be easily read on the galvanometer. To secure steady conditions, batteries of large capacity were used.

In order that almost every electron from C entering the box should collide with a potassium atom, the apparatus was kept between 180°C and 205°C. This temperature range corresponds to a range of electronic mean free paths from 6 mm to 2 mm, and of vapor pressures from 0.0018 to 0.005 mm of mercury.

Under our final conditions, the space charge limited current from F was independent of the heating current for temperatures well below the rated limit of the filament. The presence of potassium in the apparatus increased the emission from filament C so much that sufficient electrons to cause measurable ionization were given off at a temperature below visible redness. Thus the velocity range of the emitted electrons due to temperature was small.

Some typical curves are shown in Fig. 3. Only relative values of the ionization potentials, of course, are given accurately by this method, since we had no easy way of correcting for the contact differences of potential involved. We have assumed that the initial rise in the curve corresponds to the ionization potential, which from spectroscopic data is 4.32 volts for potassium. All the curves show a second distinct discontinuity nearly one volt above the point at which ionization begins. The average of the separations between the first and second breaks for twenty-three curves is 0.97 ± 0.05 volts. It is interesting to note that just above the first break the curves merge into the horizontal axis asymptotically, making it difficult to determine the exact point at which ionization begins; whereas the second break is very sharp. The sharpness of the second break indicates that the velocity range of the ionizing electrons was small enough to show the true shape of the ionization curve. Thus we conclude that the rounding off of the first break is a true representation showing a slow increase in the ionization probability in the neighborhood of the ionization potential.[5]

As a check on the apparatus we also attempted to verify Lawrence's results on the ultraionization potentials of mercury vapor, before beginning the work on potassium vapor. We found that the discontinuities in mercury vapor were considerably more difficult to reproduce time after time than the single discontinuity in potassium. However, we obtained the following values for the ultraionization potentials of mercury, which are not wholly in agreement with those found by Lawrence.[7]

Lawrence's values	10.40	10.60		11.29		11.70	12.06	
Our values	10.40	10.62	10.88	11.28	11.40	11.77	12.16	12.76

Discussion

We may regard the discontinuity in the ionization curve at 0.97 volts above the first ionization potential as indicating the onset of an additional kind of ionization. This may be considered as a second ionization potential at $4.32+0.97=5.29$ volts. It is tempting to seek a correlation between the

[5] Simultaneously with the measurement of the change in the space charge limited current by galvanometer G_1, the total emission from filament C was measured on galvanometer G_2. We found that the emission from C did not vary over 10 percent over the range of accelerating potentials used in producing the curves. Furthermore, the emission from C was a smooth, almost linear, function of the accelerating potential. Thus the discontinuity in the ionization curves above the ionization potential cannot be due to any abrupt change in the number of electrons entering the box.

[7] E. O. Lawrence, Phys. Rev. **28,** 947 (1926).

second ionization potential by electron impact and the short wave-length peak in Lawrence's work. We should expect to find the onset of a second type of photoionization at 2334A, corresponding to 5.29 volts. However, in Lawrence's experiment, the second type of photoionization begins at 2700A and rises to a maximum at 2340A. Now the second break in our curves corresponds much more closely to the latter value, although we should have expected correlation with the former.

Until recently it was customary[8] to associate the presence of the second ionization potential in photoionization in potassium with an effect on the molecule. Such evidence as we have as to the association in potassium vapor indicates that for every molecule, there are perhaps 5,000 atoms. Therefore, in order to account for the results, it has been suggested that, for light, the molecule has a much larger absorption coefficient than the atom. Since the change in slope at the second ionization potential in our ionization by electron impact curves is of the same order as the change in slope at the first, it would also mean a very large effective cross section for the molecule for electron impact as compared with the atom. Since this line of argument seems to lead to a conclusion which is difficult to believe, we are inclined to associate the second discontinuity with the onset of a second type of ionization in the atom, for which we have no theory.

A close correlation between the effects of light and electron impact is not to be expected. We know, for example, that in the excitation of an atom by light, the fit between the wave-length of the exciting light and the energy changes in the aton must be exact. However, in the case of electron impact, the colliding electron need have only *sufficient* energy. Similarly, in the field of ionization, we could hardly expect an exact parallelism between the effect of light and the effect of electron impact.

[8] E. O. Lawrence, Phil. Mag. **50,** 345 (1925), R. W. Ditchburn and F. L. Arnot, Proc. Roy. Soc. **A123,** 516 (1929).