On the Distribution of Charged Ions in the Path of an Electric Discharge through a Tube Containing Bromine Vapour

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(Received Oct. 20, 1919)

The determination of the electric conditions of vapours and gases in discharge tubes is highly interesting. The distribution of electric intensities along the path of the discharge was already studied by many investigators. H. A. Wilson[1] examined numbers of ions along the path of discharges, but nothing was, so far, known as to the distribution of singly and multiply charged ions separately. Such distribution may be examined indirectly by using a spectroscopic method, and some result thus obtained is given in the following pages.

According to Stark, the emission centres of spectral lines of spark type are doubly or triply charged atomions of elements, and lines of arc type are emitted by atomions which have lost one electron. If we adhere to this view, we can easily determine by using a spectroscope the distribution of charged ions along the path of an electric discharge.

In a preceding paper, the lines of spark and of arc types of bromine are described, and using these data, we will consider the charged states of bromine ions in various parts of a discharge tube containing that vapour.

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1 Phil. Mag. [5], xlix. 505, (1900).

Let us first take the case in which the vapour pressure of bromine is sufficiently low. Starting from the salt cathode, we had streams of cathode rays, the path of which looked pale white. Its spectrum consisted chiefly of lines at $\lambda\lambda$ 578, 524, 533 and a certain number of lines in the blue-violet region, which belong to the lines of the spark type. This shows that bromine atoms are ionized by the impact of cathode rays to the state of doubly or triply charged atomions.

If the diameter of the tube was about a centimeter, the positive column was filled up uniformly with a glow of chamois yellow colour. Its spectrum consisted of a fluted band extending from green to red, and some lines of the pink spectrum of this element. The relative intensities of the band and the line spectra varied with the diameter of the tube; when the tube got wider, the band spectrum was brought up at the expense of the other. The lines of the pink spectrum are chiefly those of the arc type, and this indicates that there are plenty of bromine atomions which have lost a single electron; beside these, there were emission centres of the band spectrum. If we take the view that band spectra are emitted by certain vibrations in molecules, the existence of such a band spectrum seems to suggest that a part of the bromine molecules, when bombarded by electrons, would not be split up into atomions, but vibrations would be called forth in the valency electrons within to make them emit the band spectrum. This explanation seems to be supported by the fact that a weak excitation is favorable for the emission of such a band.

Now, if a constriction was made in a part of the discharge tube, the electric states of bromine in that part would be modified. The current density and the potential gradient would be increased, and a greater energy would be absorbed there. Consequently the process of ionization would proceed deeper inside the atom, and a number of multiply charged atoms would be formed when the energy absorbed by a single molecule exceeded a certain amount. In fact, such a constriction caused the colour of the glow to change to bluish green, the spectrum of which consisted chiefly of lines of the spark type, indicating that atomions which had lost two or more electrons had been produced.

It was sometimes observed that some parts of the surfaces of silver bromide electrodes emitted the green light due to silver. This seems to indicate that, when the discharge was sufficiently strong to remove valency electrons out of surface molecules, positive atomions of silver would have been formed, so that silver would emit its characteristic light.

Next, when the vapour pressure was not low, and the discharge tube had also no constriction, the colour of the glow in the positive column was pink. Its spectrum was made up mainly of lines of the arc type, indicating that the greater majority of the ions produced there were singly charged atomions.

An introduction of a constricted portion in the path of the discharge gave rise to some spark lines, but this was not sufficient to suppress four lines characteristic of the arc type. In other words, if the vapour pressure of bromine was not low enough, the greater part of singly charged atomions remained in that state, even when the ionizing energy was augmented. However, when a spark gap was inserted in the discharge circuit, greater energy would be spent in a single discharge. The process of ionization would consequently proceed further, and some atoms would have been ionized into the state of multiply charged atomions. In the actual experiment this was indicated by the change in the colour of the glow.

The writer's sincere thanks are due to Prof. T. Mizuno for the interest he has taken in this work.