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A STUDY OF THE LUMINOUS DISCHARGE IN BROMINE. A POSSIBLE DETERMINATION OF THE IONIZATION POTENTIAL OF BROMINE

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In a recent article[1] the author presented a series of measurements of the potential necessary to maintain luminosity in iodine vapor, and using the theory presented by Gibson and Noyes,[2] a value for the ionization potential of iodine was obtained which agreed within the experimental error with the value obtained by Mohler and Foote.[3] It was pointed out that the conditions obtaining in the luminous discharge in an electronegative gas were modified by the electron affinity of the gas according to the views presented by Gibson and Noyes in an earlier article.[4]

In the present article a study of the luminous discharge in bromine is presented. Due to the shortness of the tubes used, however, the disappearance of the glow was difficult to ascertain on account of the brightness of the filament, and a modification of the method was necessary. Section I will present a brief theoretical discussion, Section II the experimental procedure and Section III the results obtained. Section IV will give a brief discussion of the results, together with the most probable value of the ionization potential of bromine as determined from the results in the previous section.

I. Theoretical Discussion

In the previous article[1] it was suggested that the multiple of the ionization potential obtained as the voltage necessary to maintain luminosity in an electronegative gas should be higher than that in an electropositive gas because the molecules of the gas combine with electrons to give heavy negative ions which would have lower mobilities than the electrons and could not be accelerated sufficiently to produce ionization by collision. The potential gradient should thus be higher and the distance through which an electron must move to be able to produce ionization would be shorter. The multiples of the ionization potential obtained in hydrogen, mercury vapor, iodine vapor and bromine vapor (the gases so far studied) for a tube 1 cm. long were 1 (17 volts), 1 (10.7 volts), 5–6 (50 to 60 volts), and 4–5 (49 to 62 volts), respectively. The values are obtained by interpolation, as tubes of exactly this length were not used. It will be noticed

[1] Noyes, THIS JOURNAL, **45**, 337 (1923).
[2] Gibson and Noyes, *ibid.*, **44**, 2091 (1922).
[3] Mohler and Foote, *Phys. Rev.*, **15**, 321 (1920).
[4] Gibson and Noyes, THIS JOURNAL, **43**, 1255 (1921).

that the multiple in the case of iodine and bromine is considerably higher than in the case of hydrogen and mercury. However, the multiple for bromine is of the same order as that for iodine, in spite of the fact that one would expect bromine to have a greater electron affinity than iodine, from chemical considerations. This result is in agreement with the qualitative experiments of Gibson and Noyes,[4] which showed that the sparking potentials of bromine and iodine were 5 or 6 times those of hydrogen and mercury.

Born[5] gives 84,000 calories (3.64 volts) as the electron affinity of the bromine atom and 77,000 calories (3.33 volts) as the electron affinity of the iodine atom. His values agree well with those of Fajans.[6] The heat of dissociation of iodine as calculated by Lewis and Randall[7] from the data of Starck and Bodenstein[8] is 36,860 calories, while that of bromine calculated by Lewis and Randall[9] from the data of Perman and Atkinson[10] is 52,400 calories. These values correspond to 1.59 and 2.27 volts, respectively.

From the experiments herein described it would seem that diatomic halogen molecules have little or no electron affinity, and that the high potential gradient in the cathode region is due to the combination between halogen atoms and electrons. Since the heat of dissociation of iodine is appreciably lower than that of bromine, there should be a much higher concentration of monatomic iodine in the neighborhood of the filament than there would be of monatomic bromine. The slightly greater electron affinity of bromine atoms would not be enough to counterbalance this factor entirely, and the potential gradient in the case of bromine should, if anything, be slightly less than that for iodine. This conclusion is borne out by the figures presented above.

II. Experimental Procedure

The electrical connections used were the same as for iodine,[1] but it was impossible to note the disappearance of the glow in some cases due to the brightness of the filament. The voltage was, therefore, determined by means of the voltmeter. During the passage of the discharge through the tube, the conductivity of the gas is fairly high. At the moment the glow disappears, however, the resistance becomes very great and the potential suddenly increases. In the connections used the tube is shunted across part of a large resistance, the terminals of which are connected to a 220-volt line. At the moment the discharge disappears the potential drop across the tube and resistance in parallel will suddenly increase compared to the resistance in series and the voltage as read by the voltmeter will suddenly rise. By noting the voltage just prior to the increase,

[5] Born, *Verh. physik. Ges.*, **21**, 679 (1919).

[6] Fajans, *ibid.*, **21**, 714 (1919).

[7] Lewis and Randall, THIS JOURNAL, **36**, 2259 (1914).

[8] Starck and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

[9] Lewis and Randall, THIS JOURNAL, **38**, 2352 (1916).

[10] Perman and Atkinson, *Z. physik. Chem.*, **33**, 215, 577 (1900).

the values of the glow voltage could be obtained. The accuracy of this method was tested in cases in which the glow could be distinguished and the points were found to coincide.

The bromine used was C. P. material and was placed in a bulb containing potassium bromide and immersed in liquid air. The apparatus was then evacuated to a very low pressure for several hours, mercury vapor being excluded by a trap immersed in liquid air. The liquid air was removed from around the bromine bulb and distilled over into another bulb immersed in carbon dioxide snow and ether. The first bulb and the calcium chloride tube through which the bromine was passed were then sealed off. A trace of chlorine might possibly have been formed by the passage of the bromine over the calcium chloride, but since the vapor pressure of chlorine at —80° is very much greater than that of bromine, it would not have condensed. Before any measurements were made, the apparatus was evacuated for several hours with intermittent heating of the filament to a pressure well below 10^{-6} mm. There were no stopcocks in the apparatus.

During the first few runs enormous variations in the values of the glow voltage were obtained. These may possibly have been due to a trace of water vapor or to a trace of chlorine, but constancy was finally obtained after a few weeks. In order to reduce as much as possible errors in reading the voltmeter, the values of the resistance in series and in parallel were changed frequently.

Cuthbertson and Cuthbertson[11] give the vapor pressure of bromine at —80° as 0.13 mm. Their value agrees well with that of Henglein, von Rosenberg and Muchlinski[12] and with that calculated from the formula of Isnardi.[13] This pressure is of the proper order for obtaining the glow discharge, but there are few good fixed points in the neighborhood of —80°, so that it was impossible to vary the pressure of the bromine. The various multiples of the ionization potential were obtained by changing the length of the tube.

III. Results

TABLE I

SUMMARY OF RESULTS

Dimensions of Tubes: No. 1, Length 5 mm., Diam. 21 mm.; No. 2, L. 14 mm., D. 21 mm.; No. 3, L. 2 mm., D. 21 mm.; No. 4, L. 20 mm., D. 21 mm.; No. 5, L. 31 mm., D. 21 mm. No. 6, L. 33 mm., D. 29 mm. Vapor pressure of bromine, 0.13 mm.

Multiple of ionization pot.	Voltage	Tubes	No. of obs.	Multiple of ionization pot.	Voltage	Tubes	No. of obs.
3	37.35 ± 0.42	1 and 3	17	7	87.30 ± 0.49	5	4
4	49.90 ± 0.39	2 and 4	12	8	100.34 ± 1.00	5 and 6	3
5	62.53 ± 0.31	4	7	9	114.03 ± 0.17	6	2
6	74.78 ± 0.24	4	2				

Dividing Col. 2 by Col. 3, the following values for the ionization potential of bromine are obtained: 12.5, 12.5, 12.5, 12.5, 12.5, 12.5, 12.6. This method introduces an error due to the velocity of thermal emission of the electrons, but the correction must be small, of the order of 0.3 volts, and as it would be divided by the corresponding multiple it would be lower than the experimental error. After the various multiples have been subtracted from each other and divided by the proper integer, the following

[11] Cuthbertson and Cuthbertson, *Proc. Roy. Soc.* (London), **85A**, 306 (1911).

[12] Henglein, von Rosenberg and Muchlinski, *Z. Physik*, **11**, 1 (1922).

[13] Isnardi, *Ann. Physik*, **61**. 264 (1920).

values are obtained: 12.6, 12.6, 12.3, 12.5, *13.0*, *13.7*, 12.6, 12.5, 12.5, *12.6*, *12.8*, 12.4, 12.5, 12.6, 12.8, 12.4, *12.6*, *12.9*, *11.9*, *12.8*, *13.4*. The values in italics are obtained by use of the 2 highest multiples. Since the number of observations is small, the absolute values of these 2 voltages are undoubtedly in error by a volt or more. These values are given only half weight in determining the average of all the above determinations. The most probable value of the ionization potential of bromine as determined by the above results is 12.5 ± 0.5 volts.

IV. Discussion of Results

The only value heretofore obtained for a critical potential of bromine is that of Hughes and Dixon[14] who found 10.0 volts. Since this value differs from the one obtained in this article by more than the experimental error, it may be well to search for the reason for the discrepancy. Hughes[15] at a more recent date raises some question as to whether the value of Hughes and Dixon is not a resonance instead of an ionization potential. This seems hardly probable, however, in view of the low value for the resonance potential of iodine found by Mohler and Foote.[3] If the ionization potential corresponds to the equation $Br_2 = Br + Br^+ + \ominus$, then the ionization potential minus the heat of dissociation should give the ionization potential of the atom. The heat of dissociation of bromine[9] corresponds to 2.3 volts, and subtraction of this from 12.5 gives 10.2 ± 0.5 volts as the ionization potential of the atom. This value agrees within the experimental error with that of Hughes and Dixon. It is possible that enough monatomic bromine was present in the experiments of Hughes and Dixon to give the ionization potential of the atom rather than the molecule.

Summary

1. Using a slight modification of the method of Gibson and Noyes, the ionization potential of bromine is found to be 12.5 ± 0.5 volts.

2. The fact that for tubes of a given length approximately the same multiple of the ionization potential of bromine as of iodine was obtained is accounted for by the higher heat of dissociation of bromine, the molecules having little or no electron affinity. The higher electron affinity of bromine would thus be counterbalanced by a lower concentration of the monatomic gas.

3. The facts agree with the work of Gibson and Noyes on the sparking potentials in gases.

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[14] Hughes and Dixon, *Phys. Rev.*, **10**, 495 (1917).

[15] Hughes, *Bull. Nat. Res. Council*, **2**, Part 2, 138 (1921).