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Mass Spectrograph Analysis of Bromine[1]

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An attempt has been made to observe a third isotope of bromine to explain the three periods of the artificial radioactivity induced by slow neutrons. Neither of the expected isotopes is present to more than 1 part in 3000. The relative abundance of the known isotopes was measured. The processes of formation of positive and negative ions of bromine by slow electrons were studied and values were deduced for the heat of dissociation of Br_2 and for the electron affinity of Br.

A. INTRODUCTION

A MASS spectrograph study made by Aston[2] in 1920 showed that bromine is composed for the most part of two isotopes of masses 79 and 81, in approximately equal abundance. This is in accordance with the empirical law that elements of odd atomic number do not as a rule have more than two isotopes. Investigations[3, 4] of the disintegration of bromine by slow neutrons, however, revealed three artificially radioactive products. Two of the reactions were presumably:

$$ {}_{35}\mathrm{Br}^{79}+{}_{0}n^{1}\rightarrow{}_{35}\mathrm{Br}^{80}\rightarrow{}_{36}\mathrm{Kr}^{80}+e^{-} $$

$$ {}_{35}\mathrm{Br}^{81}+{}_{0}n^{1}\rightarrow{}_{35}\mathrm{Br}^{82}\rightarrow{}_{36}\mathrm{Kr}^{82}+e^{-}. $$

All three products were shown by chemical tests to have the properties of bromine. Hence it becomes necessary either to postulate the existence of a third isotope, or to assume that one of the known isotopes is disintegrated in two ways—a phenomenon which has no known parallel. The present investigation was undertaken in the hope of revealing a third isotope. It was expected that the new isotope would have a mass of 77 or 83. An isotope of mass 78, when it took up a neutron, would go into Br^{79} which is stable; hence this would not explain the third radioactive period. Isotopes of masses 80 and 82 are shown to be unstable by the processes of disintegration of the known isotopes 79 and 81.

With the mass spectrograph employed in this study it was possible to make determinations of the relative abundance of the known isotopes. Observations were made also of the processes of formation of both positive and negative ions of bromine by slow electrons.

B. APPARATUS

The apparatus was essentially a Dempster type mass spectrograph. It was constructed in demountable sections so that it could be taken apart conveniently and cleaned.

The ion source was housed in a glass tube as shown in Fig. 1. The ions were produced in the field-free chamber I when slow electrons collided with atoms of the gas. The electrons were emitted from a hot filament F and accelerated by a constant drawing out voltage of 100 volts applied between F and the slit S_1. They were then retarded to the desired energy by a reverse voltage of 0–100 volts applied between the slits S_1 and S_2. The path of the electrons was parallel to the direction of the magnetic field so that the

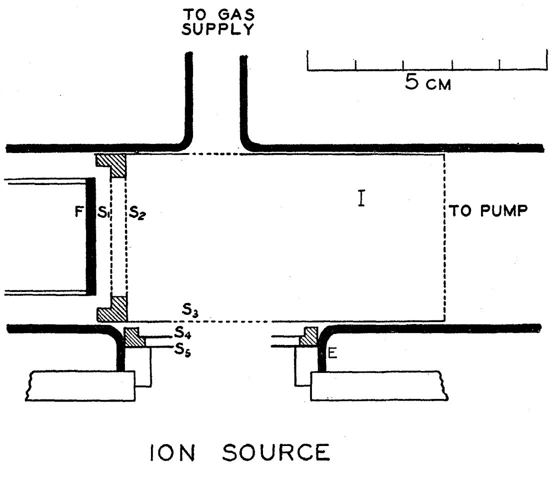

FIG. 1. Ion source.

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[1] Abridged from a thesis presented to the Faculty of Princeton University in candidacy for the degree of Doctor of Philosophy.

[2] Aston, Phil. Mag. **40**, 628 (1920).

[3] Kurtchatow, Myssowsky and Roussinow, Comptes rendus **200**, 1201 (1935).

[4] Rasetti, unpublished.

effect of stray magnetic fields was reduced to a minimum. A short side tube *E* fitted over a circular plate which carried the entrance slit to the magnet space. The ions formed in *I* were drawn out through the slit S_3 by a field of 0–1 volts applied between the slits S_3 and S_4. They were then accelerated into the magnet space by the analyzing voltage of 0–500 volts between slits S_4 and S_5. Both the slit S_5 and the exit slit of the magnet space were 1/10 mm wide. The ionization chamber and the slits were constructed of sheet nichrome.

A magnetic field of 0–6000 gauss was provided by a Pye electromagnet. The pole pieces were of Armco iron and took the form of half-cylinders, 15 cm in diameter and 5 cm long, which were mounted with their flat faces horizontal. The pole faces served as the side walls of the magnet space. The magnet space was enclosed by a brass housing which was made vacuum tight with Apiezon W wax. Baffles were introduced to define the beam and to prevent ions reflected from the walls from reaching the collector. A separate pump lead was provided for the magnet space so that a low pressure could be maintained by a process of differential pumping.

It was found that bromine reacted much more strongly with the iron of the pole faces than with the brass walls, so the poles were removed and plated in a cyanide plating bath, with a thin layer of copper.

Since bromine reacts strongly with stopcock grease and mercury, the supply of bromine was kept in an all-glass gas handling system. A small quantity of liquid bromine supplied the vapor which flowed through a fine capillary leak into the ionization chamber. The pressure behind the leak, and hence the pressure in the ionization chamber could be controlled by varying the temperature of the liquid bromine. After leaving the ionization chamber through the pump leads the gas was frozen in liquid-air traps and thus prevented from reaching the mercury diffusion pumps which maintained the vacuum.

After analysis in the magnetic field, the ions were collected in a Faraday cage and the ion current was measured by an electrometer tube circuit employing a Western Electric D-96475 electrometer tube.

C. Isotopic Constitution of Bromine

A search was made for isotopes in the mass range from 73 to 87, but no new isotopes were found. The positive ion peaks are shown in Fig. 2. The negative ion peaks proved to be somewhat sharper, as may be seen by comparing Fig. 2 with Fig. 3. This is probably due to the fact that dissociation of the Br_2 molecule into a positive ion and a neutral atom involves the production of more kinetic energy than does the dissociation in which a negative ion is produced.

To prove that isotopes of small relative abundance would show up in such a test, runs were taken on the neon isotopes whose relative abundance is well known. The correct relative abundance was obtained within the experimental error, and it was noted in addition that the peaks were all of the same shape regardless of their height.

The amount of a new isotope which would have resulted in a peak definitely resolvable from the background, and hence the degree to which such an isotope is not present, is given for the masses considered, in Table I.

When the apparatus was first set up, before gaseous impurities had been removed, large hydride peaks appeared at masses 80 and 82, as shown by Fig. 4. A peak was observed at mass 83 and was thought at first to be due to a new isotope, but it disappeared with the hydride

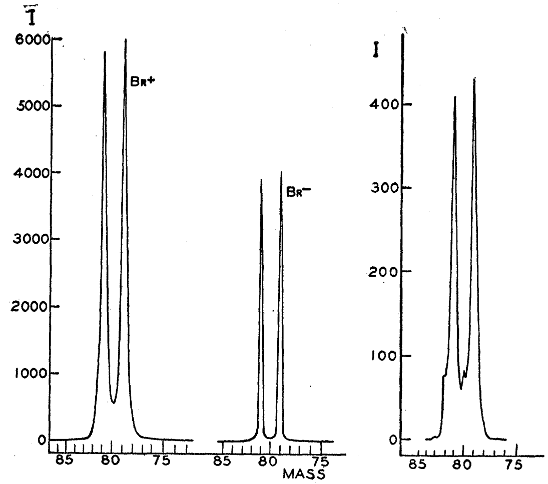

Fig. 2. (left) Positive ion peaks of bromine isotopes.
Fig. 3. (center) Negative ion peaks of bromine isotopes.
Fig. 4. (right) Positive ion peaks of bromine isotopes when hydrides are present.

TABLE I. *The known isotopes of bromine have masses 79 and 81.* The following isotopes do not exist in amounts greater than the abundance ratios indicated.

MASS	PRESENT TO LESS THAN:	MASS	PRESENT TO LESS THAN:
73	1 part in 24,000	82	1 part in 400
74	" 12,000	83	" 3,000
75	" 8,000	84	" 8,000
76	" 6,000	85	" 8,000
77	" 3,000	86	" 12,000
78	" 400	87	" 24,000
80	" 2,000		

peaks. Probably it was due to an H_2Br^+ ion which might be stable in the same manner as is the H_3^+ ion. No negative ions of the bromine hydrides could be detected, so that in general the negative ion peaks provided better material in the search for new isotopes.

The relative abundance of the known isotopes was measured and the ratio

abundance of mass 81/abundance of mass 79

was found to be 0.975±0.025. This value was checked by measurements on the doubly charged positive ions and the negative ions. Assuming that no other isotope is present, this gives for the composition of bromine, 50.6±0.6 percent of mass 79 and 49.4±0.6 percent of mass 81. Combining this with Aston's values of 79.929 ±0.004 and 80.930±0.004 for the masses of the isotopes, we deduce a value for the atomic weight of bromine of 79.92±0.02 on Aston's scale, or 79.90±0.02 on the atomic weight scale. This agrees within the experimental error with the international atomic weight of 79.916.

D. PROCESSES OF IONIZATION IN BROMINE

The heights of the Br^+, Br_2^+ and Br^{++} peaks were studied as functions of the electron energy, and appearance potentials were deduced for all three. Errors due to contact potentials were eliminated by calibrating the electron energy scale from the known ionization potential of argon. The observations are plotted in Fig. 5.

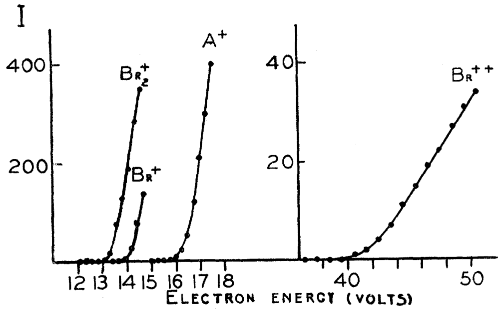

FIG. 5. Curves showing appearance potentials of bromine ions as compared with argon.

Br^+ appears at 13.7±0.5 volts. The ionization potential of atomic bromine is known from spectroscopic data to be 11.80 volts.[5] Subtracting this value from the appearance potential of Br^+, which we assume to be produced by the process $Br_2 \rightarrow Br + Br^+$, we obtain a value of 1.9±0.5 volts for the heat of dissociation of Br_2. This is in good agreement with the value of 1.96 volts quoted in the *International Critical Tables*, indicating that very little kinetic energy is evolved in the dissociation of Br_2 by slow electrons.

Br_2^+ appears at 13.0±0.5 volts which agrees within the experimental error with the value of 12.8 volts obtained by Mackay.[6]

Br^{++} appears at 39.5±1.0 volts. If we assume that this ion is produced by the process $Br_2 \rightarrow Br + Br^{++}$ we must conclude that the ionization potential of Br^+ is $39.5 - 1.9$ (heat of dissociation) $- 11.8$ (ionization potential of Br) $= 26.8$ volts. This disagrees seriously with the spectroscopic value of 19.1 volts obtained by Deb.[7] If Deb's value is correct, either the Br or the Br^{++} must be left in an excited state having an energy of $26.8 - 19.1 = 7.7$ volts. Two levels whose energies agree within the experimental error with this value, exist in the spectrum of neutral atomic bromine, namely a ^4P state at 8.0 volts and a ^2P state at 8.4 volts.

Negative ions, both of Br^- and Br_2^- were found in large quantities, the peaks being of the same order of magnitude as the positive ion peaks. The height of the negative ion peaks is shown as a function of electron energy in Fig. 6. The height of the Br^- peak rises to a sharp maximum at an electron energy of 2.8 volts—an effect similar to that observed by Lozier[8] in the case of O^-. These ions are formed with kinetic energy, as was shown by a definite shift in

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[5] Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932), p. 93.

[6] Mackay, Phys. Rev. **24**, 319 (1924).

[7] Deb, Proc. Roy. Soc. **A127**, 197 (1930).

[8] Lozier, Phys. Rev. **46**, 268 (1934).

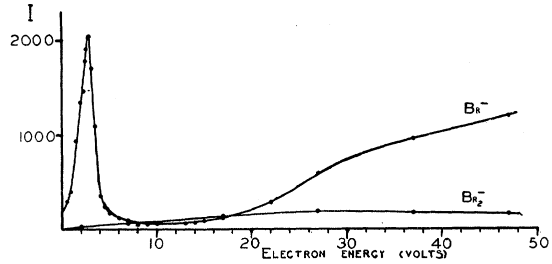

FIG. 6. Height of negative ion peaks as a function of electron energy.

position of the peak with varying electron energy. This kinetic energy was measured by observing the height of the Br^- peak when a retarding voltage was applied between the slits S_3 and S_4 (Fig. 1). The peak disappeared for a retarding voltage of 2.3 volts. We can now deduce the electron affinity of Br from the equation:

Electron energy (2.8 volts) + Electron affinity = Heat of dissociation (1.9 volts) + Kinetic energy (2×2.3 volts).

This gives an electron affinity of 3.8 ± 0.2 volts, which agrees with the values of 3.77 and 3.60 calculated by Sherman[9] and Mayer and Helmholz[10] from the Born-Haber cycle.

The remainder of the curve may be due to the process $Br_2 \rightarrow Br^- + Br^+$. It seems to rise in the neighborhood of the appearance potential of Br^+. The Br_2^- peak is difficult to explain. Since it reaches a maximum at about the same point as the Br^- curve begins to rise it may be involved in the same process. The shape of the Br^- curve above about 10 volts and the whole Br_2^- curve were very sensitive to the operating conditions. For low electron currents (10 microamp.) the height of this region of the Br^- curve becomes small compared with the height of the maximum at 2.8 volts, but as the current is increased to 500 microamp. it becomes several times as high as this maximum. The Br_2^- curve behaves in much the same way and it seems probable that some sort of space charge phenomenon is involved.

E. Conclusion

The relative yields of the three radioactive products of bromine are given by Kurtchatow and her collaborators as approximately 6 : 5 : 1, corresponding to half-lives of 18 minutes, 4.5 hours, and 36 hours. We must conclude, if the third product is due to a third isotope of mass 77 or 83, that its cross section for disintegration by slow neutrons is at least 3000/6 or 500 times as great as that of either of the others. If either of the other periods is due to an isotope of mass 77 or 83, its cross section must be greater than 15,000 times that of one and 2500 times that of the other. Many of the nuclei which present large cross sections to slow neutrons can be represented by $M = 4n + 3$ where M is the mass number and n is an integer. This would suggest that the third isotope, if present, has a mass of 83.

The writer wishes to express his appreciation of many helpful discussions with Professor H. D. Smyth and Professor W. Bleakney.

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[9] Sherman, Chem. Rev. **11**, 93 (1932).

[10] Mayer and Helmholz, Zeits. f. Physik **75**, 19 (1932).