IONIZATION BY COLLISIONS OF THE SECOND KIND IN MIXTURES OF OXYGEN WITH THE RARE GASES

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Abstract

Harnwell's experiments on ionization by collisions of the second kind have been continued. Mixtures of oxygen with argon, neon and helium and incidental effects of water vapor have been studied. Evidence of the following collisions of the second kind was obtained:

(1). $A^+ + O_2 \rightarrow O_2^+ + A$
(2). $A^+ + H_2O \rightarrow H_2O^+ + A$ (very strong)
(3). $H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$
(4). $Ne^+ + O_2 \rightarrow O^+ + O + Ne$
(5). $He^+ + O_2 \rightarrow O^+ + O + He$

The experiments confirm the conclusions of Hogness and Lunn as to the processes of ionization in oxygen but leave the exact value of the first ionizing potential uncertain.

DURING the last year Harnwell[1] published two papers on ionization by collisions of the second kind in mixtures of gases. The present paper describes an extension of his work to include mixtures of oxygen with the rare gases and some incidental effects of water vapor. The object of the work was twofold. In the first place it appeared desirable to study oxygen as a matter of routine so that with Harnwell's results on hydrogen and nitrogen a basis would be laid for experiments on mixtures of these three elementary gases and their compounds. In the second place, there are numerous discrepancies in previous work on oxygen which it was hoped might be cleared up.

A summary of the work on oxygen may be found in Franck and Jordan.[2] Stated briefly the situation is this. The ordinary first ionizing potential of oxygen corresponds to the production of stable O^+_2 but the exact value of the I. P. (ionizing potential) is uncertain, the experimental determinations ranging between 12.6 and 16.1 volts, the values observed by Mackay who was the only observer to find two distinct "breaks" in the ionization curve. There is also a higher I. P. apparently a little above twenty volts which corresponds to a direct production of O^+ ions. Finally there is the spectroscopically determined value of the I. P. of atomic oxygen, 13.6 volts.

It is quite possible, of course, that Mackay was right and that there are two ionizing potentials only a few volts apart and both giving a stable molecular ion. On the other hand, it is now a perfectly familiar idea that molecular ionizing potentials are always difficult to determine exactly experimentally because of the association of vibrational and rotational energy with the electronic energy. There are, therefore, two possibilities with regard to oxygen. First, that there are two ionizing potentials and that all

[1] G. P. Harnwell, Phys. Rev. **29**, 683 and 830 (1927).
[2] Franck and Jordan, Anregung von Quantensprüngen, p. 273.

observers except Mackay have measured an average value. Or second, disregarding Mackay's result, that there is one ionizing potential but its value is uncertain. The first hypothesis seems much the more probable but in either case it was thought that a study of collisions of the second kind in a mixture of oxygen and argon would be interesting since the I. P. of argon is 15.69 as determined spectroscopically. Mixtures with neon were also promising since the I. P. of neon is 21.6 just about the same as that for the production of O^+ ion from diatomic oxygen. Experiments were also done with helium as a matter of routine and some rather striking effects of water vapor were noticed and studied.

Apparatus and Procedure

Experiments were started with the same apparatus which Harnwell had used in the previous year. It seemed, however, to be suffering from age and was unable to give reproducible results. After the loss of a good many weeks a new apparatus was set up. Except for the elimination of one grid and small changes in dimensions it was essentially the same as Harnwell's and it is not necessary to describe it. The procedure was also unchanged. Accelerating fields of forty to sixty volts gave electrons from the filament plenty of energy to produce ions of all kinds in the gas mixture and the relative intensities of the different types of ions were determined by positive-ray analysis and studied as a function of pressure.

Results

It was not found possible to get exactly reproducible quantitative results but by making repeated experiments perfectly definite qualitative results were obtained. Runs were made first with pure oxygen, then with oxygen and argon, then with pure oxygen again and with pure argon. The runs on pure oxygen confirmed Hogness and Lunn's conclusion that the ratio of O_2^+ to O^+ is essentially independent of the pressure, suggesting that

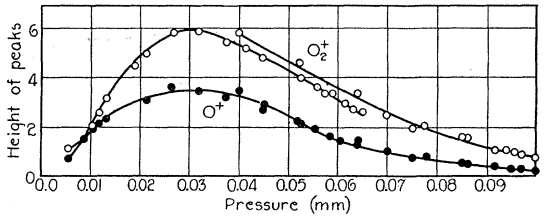

Fig. 1. Pure oxygen. Two overlapping runs. Field accelerating the electrons, $V_1=45$ volts; field to draw out positive ions, $V_2=2$ volts; thermionic current, $i=60$ microamps.

the O^+ is formed directly by electron impact without the need of additional collisions. This is, of course, in contrast to the cases of hydrogen and nitrogen. The relative intensity of O^+ and O_2^+ is much more like that found in

[3] H. D. Smyth, Proc. Roy. Soc. **105A**, 116 (1924).
[4] Hogness and Lunn, Phys. Rev. **27**, 732 (1926).

the early work of Smyth[3] than in Hogness and Lunn's[4] work. Nor is this discrepancy due to impurities as they suggest since both this and the earlier apparatus were capable of resolving N^+, O^+, and H_2O^+.

Pure oxygen. An example of the results in pure oxygen is shown in Fig. 1 where the ordinates are the heights of the "peaks" measured by the electrometer and may be taken as proportional to the numbers of different types of ions coming out of the ionization chamber. The points plotted are from two different runs taken several days apart and over different ranges of pressure. The two runs overlapped in the pressure range from 0.04 to 0.065 mm and the discrepancy between the two sets of points was sufficient in the case of O_2^+ to suggest the drawing of two separate curves. Since the agreement for the O^+ points was much better only one curve was drawn. The general shape and relationship of these two curves was perfectly reproducible but the absolute values of the ordinates were not. The values of thermionic current, voltage, etc., for these runs and later ones are given in the captions of the figures.

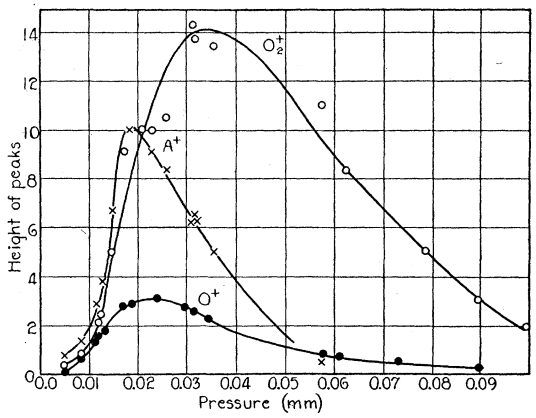

Fig. 2. Equal parts (by volume) of oxygen and argon. $V_1=41$; $V_2=2$; $i=60$.

Argon and oxygen. The striking feature of the runs on argon and oxygen is the increase of the ratio of O_2^+ to O^+ ions. This is illustrated by the curves shown in Fig. 2 and is interpreted as evidence of collisions of the second kind of the following type,

$$A^+ + O_2 \rightarrow O_2^+ + A \qquad (1)$$

In attempting to get a run on pure argon the utmost difficulty was experienced in getting rid of water-vapor ions. When a blank run or one with oxygen or a mixture showed no trace of H_2O^+ a run with the most carefully dried argon gave quantities of it, increasing very strongly with increased pressures. Prolonged baking out of connecting tubing, etc., reduced it but never eliminated it entirely. The curves in Fig. 3 give an example of the situation after drastic attempts at drying. The smallest intensity obtained was roughly one-half of that shown. This continued presence of H_2O^+ ions is interpreted as evidence of the occurrence of the reaction,

$$A^+ + H_2O \rightarrow A + H_2O^+ \quad (2)$$

Furthermore, the smallness of the water "peak" in oxygen even when it was intentionally wet suggests the likelihood of the reaction,

$$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O \quad (3)$$

It was difficult to estimate the amount of water vapor in the tube but it was certainly very small. Speaking qualitatively it appears that the reaction (2) is very probable indeed, more so than any other electron transfer observed either here or in Harnwell's work while (1) is fairly probable and we have no way of estimating the probability of (3).

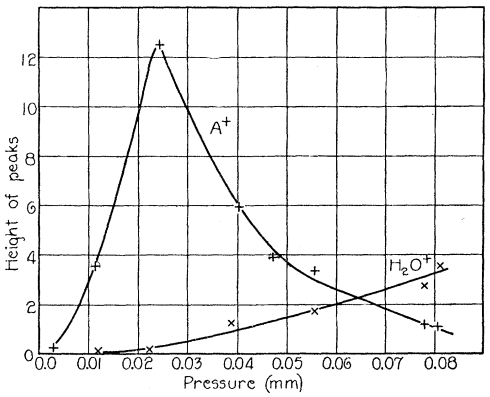

Fig. 3. Carefully dried argon. $V_1=45$; $V_2=2$; $i=60$.

Now the I. P. of water has been determined experimentally three times or more and appears to be definitely within 0.5 volt of 13.0 volts.[5] The difference between this and 15.67 appears too large to account for the strength of the reaction (2) and suggests either that there is another I. P. for H_2O corresponding to the removal of a different electron or that the ionization by a collision of the second kind is accompanied by excitation to a higher vibration state than results from ionization by electron impact. This last hypothesis seems more likely but our knowledge of energy levels is insufficient to test it in this or analogous cases.

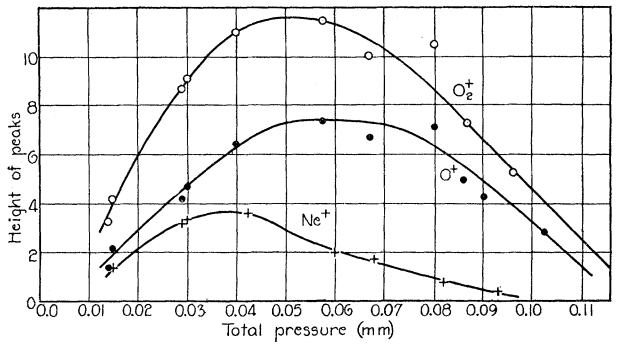

Fig. 4. Equal parts (by volume) of oxygen and neon. $V_1=50$; $V_2=2$; $i=60$.

As to the I. P. of oxygen we can say definitely that it is below that of argon. Judging from the probability of reaction (1) we should say considerably below, perhaps even less than 13 volts which would mean that

[5] Barton and Bartlett, Phys. Rev. **31**, 822 (1928)

that same I. P. was involved in (3) as in (1). This would agree with the results of Hogness and Lunn rather than with those of Smyth and others. However, we cannot be certain that there are not two I. P.'s in this region. Attempts to make critical potential runs with the present apparatus were rather unsatisfactory although they showed that the different types of ions appear in the expected order, first O_2^+ then A^+ and finally O^+.

Neon and oxygen. Since the I. P. of neon is known to be 21.6 volts, very near to that for O^+ it was thought mixing in neon might have a marked effect on the intensity of O^+. That this was the case is evident from Fig. 4 which shows the relative intensity of O^+ very much enhanced. This is interpreted as the result of the reaction

$$Ne^+ + O_2 \rightarrow Ne + O + O^+ \quad (4)$$

which appears to be quite probable.

In the mixtures of neon and oxygen a curious effect was noticed. After oxygen had been in the tube it was found very difficult to get any neon ions, apparently because the electrons never got sufficient velocity to ionize neon. This was in spite of the fact that the applied voltage was more than twice the I. P. It was thought that the violent measures used in trying to get rid of water vapor in the experiments on argon might have distilled some grease from one of the liquid air traps on to the platinum grid in the ionization tube and that a charged layer was being formed. Taking the apparatus down and cleaning it reduced the effect considerably but did not eliminate it. Critical potential runs still showed the peculiar result of approximately correct I. P.'s for oxygen but values 10 to 15 volts too high for neon. Check experiments with argon showed no such effect but it was quite strong in helium. The experiments on which the conclusions as to reaction (4) are based were taken with high (about 50 volts) accelerating potential and there is no reason to suppose that they are at all invalidated by this "layer" effect. It remains as an observation probably of no real importance but not entirely explicable.

Helium and oxygen. The experiments with mixtures of helium and oxygen showed the expected result, that is evidence of the occurrence of the reaction,

$$He^+ + O_2 \rightarrow He + O + O^+ \quad (5)$$

but with smaller probability than (4).

Conclusion

These experiments have confirmed previous conclusions as to the processes of ionization in oxygen and the transfer of electrons by collisions of the second kind. They have brought to light the high probability of the ionization of water vapor by argon ions. But they have not had much success in solving the problem of the correct value or values of the I. P. of oxygen.

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Princeton, N. J.,
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