The Positive Ion Current at the Cathode in the Glow Discharge

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The positive ion current passing through a perforation in the cathode of a glow discharge tube has been measured with various types of collectors and the factors influencing the ratio of positive ions to total current studied. At pressures above 0.5 mm the positive ion current constitutes but a small fraction of the total current, while at lower pressures it increases inversely with the pressure, reaching approximately half the total current below 0.01 mm. The fraction of the current carried by positive ions is independent of the size and shape of the perforation, of the current passing through the discharge, and of the position of the anode provided it is not within a certain critical distance from the edge of the Crookes dark space; it does, however, vary with the gas, increasing for decreasing molecular weight.

The possible sources of current to the collector are discussed. The method by which the current due to positive ions is separated from that due to metastable molecules is described. The energy of the positive ions passing through the cathode is shown to correspond to an appreciable fraction of the cathode fall of potential.

IN A series of recent experiments on chemical action in the glow discharge (I–X)[1] it has been shown that the rate of reaction in the discharge can be expressed by a simple electrochemical equivalence law somewhat analogous to Faraday's law for electrolytes and also that the molecules formed in the negative glow are carried to the walls largely as positive ions; little or no reaction occurs in the dark spaces. An estimation of the M/N ratio for the positive ions formed in the discharge necessitates a knowledge of the rate of positive ion formation. Two separate methods used for evaluating the rate of ion formation yield M/N ratios similar to those found by Lind[2] for α-particles, provided the positive ion current to the cathode is small compared to the electron current.[3] The present research was undertaken, therefore, to measure the fraction of the current carried to the cathode by positive ions.

Many attempts have been made to analyze the current at the cathode. Aston[4] using a perforated cathode measured the current received by a collector immediately behind the performation. He concluded that as much as half the current might be carried by positive ions, but felt that this conclusion must be accepted with considerable caution, since a negative ion rather than a positive ion current was received by the collector when an appreciable positive charge was applied to it. Guntherschulze[5] from measurements of the power appearing as heat at the cathode infers that the positive ion cur-

[1] A. Keith Brewer, et al., J. Phys. Chem. **33,** 883 (1929) to **36,** 2133 (1932).
[2] S. C. Lind, *Chemical Effect of α-Rays*, A.C.S. Monograph.
[3] A. K. Brewer and P. D. Kueck, J. Phys. Chem. (1932).
[4] F. W. Aston, Proc. Roy. Soc. **A96,** 200 (1919).
[5] Guntherschulze, Zeits. f. Physik **37,** 828 (1926).

rent may exceed the electron current by a factor of ten. Uyterhoeven and Harrington[6] have shown that metastable molecules formed in the discharge exert a prepondering effect over positive ions in the emission of electrons from the cathode. It is now felt that these metastable molecules have largely been responsible for the difficulties involved in measuring the current carried to the cathode by positive ions.

METHOD

The method adopted for this study was a modification of that used by Aston; it consisted of measuring the current passing through a hole pierced in the cathode. There are many difficulties involved in using this method of measurement, most of which can be overcome by a current collector of the proper design. These difficulties are: (1) the discharge is not distributed uniformly over the cathode; (2) the cathode field may be distorted at the perforation; (3) metastable molecules and atoms as well as positive ions will

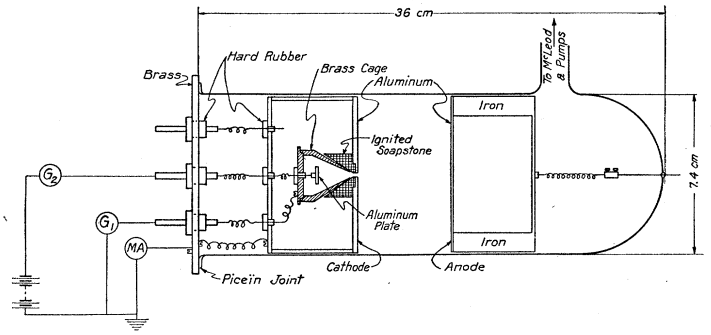

Fig. 1. Apparatus for measuring the positive ion current passing through a perforation in the cathode.

pass through the opening; all are capable of giving off electrons from the collector; (4) the high positive space charge at the opening causes an appreciable electron current to flow from the collecting plate to the cathode even in the absence of applied fields. It is believed that the apparatus as designed overcomes most of these difficulties and that the results give a fair estimation of the positive ion current.

THE APPARATUS

Many types of collectors were tried, including flat plates and a duplicate of that used by Aston. The currents received at the collector varied considerably, depending on the design and dimensions. The apparatus illustrated in Fig. 1 was finally chosen as giving the most reliable results.

The dimensions of the tube are given in the illustrations. The anode was an aluminum plate backed by iron, so its position could be changed by a magnet. The cathode was an aluminum disk covering one end of an enclosed aluminum cylinder 5 cm long and 7.3 cm in diameter. The perforation was a hole 2 mm in diameter placed in the center of the cathode, the cathode wall

[6] Uyterhoeven and Harrington, Phys. Rev. **36,** 709 (1930).

being about 0.5 mm in thickness at this point. The collecting cage was insulated from the cathode by an ignited soapstone block. It was found necessary to have a 5 mm opening in the cage with the soapstone shadowing the cage from the perforation to minimize space charge induced currents between the cage and the cathode. All parts were made tightly fitting to prevent metastable molecules from drifting between the cathode and the cage, thus giving rise to abnormal currents between these points.

The cone shaped cage was superior to the cylindrical type in practice, since it tended to screen the cathode perforation from fields applied to the collecting plate. This prevented a spurious discharge current between the collecting plate and the cathode when a potential was applied to the plate, and also it prevented the number of positive ions entering the cage from being influenced by the plate field.

RESULTS

The effect of pressure

The effect of the pressure in the discharge tube on the positive ion current entering the cage is shown for various gases in Fig. 2.

These data were obtained with no potential applied to either the cage or the plate. In the case of nitrogen the currents to both the cage and the plate are shown. The measured positive ion current in every instance is the sum of these two currents. The corrected positive ion current is the measured current corrected for the fraction of the cathode covered by the discharge at the various pressures. The voltage is the difference in potential between the anode and the cathode; the electrodes were so placed that the positive column was absent.

The currents to the cage and plate are similar for all gases, the only appreciable difference being in magnitude. The cage current, which is larger than the plate current for the higher pressures passes through a maximum and reaches a comparatively small value at low pressures; the current to the plate, however, increased rapidly at the point where the cage current passes through a maximum.

The fraction of the total current carried by the positive ions passing through the perforation is given by the right-hand ordinates. The positive ion current appears to increase with decreasing pressures, the relation between pressure and current being very nearly hyperbolic for every gas except hydrogen. It is of interest to note that when the observed current is corrected for the fraction of the surface covered by the discharge, the positive ion current approaches 50 percent at the lowest pressures for which reliable readings can be taken, about 0.01 mm. At pressures above 0.5 mm the fraction of the total current carried by positive ions in argon, oxygen, and nitrogen is very small, being less than 5 percent. In helium and hydrogen, however, the positive ion current is materially larger.

The effect of pressure on the distribution over the cathode

The positive ion current arriving at various points on the cathode surface as affected by the gas pressure is shown in Fig. 3a. These values given are

for nitrogen and are typical of all gases. The currents passing through holes 2 mm in diameter were measured with plane plate collectors at the cathode center and at 1, 2 and 3 cm from the center. It will be observed that at

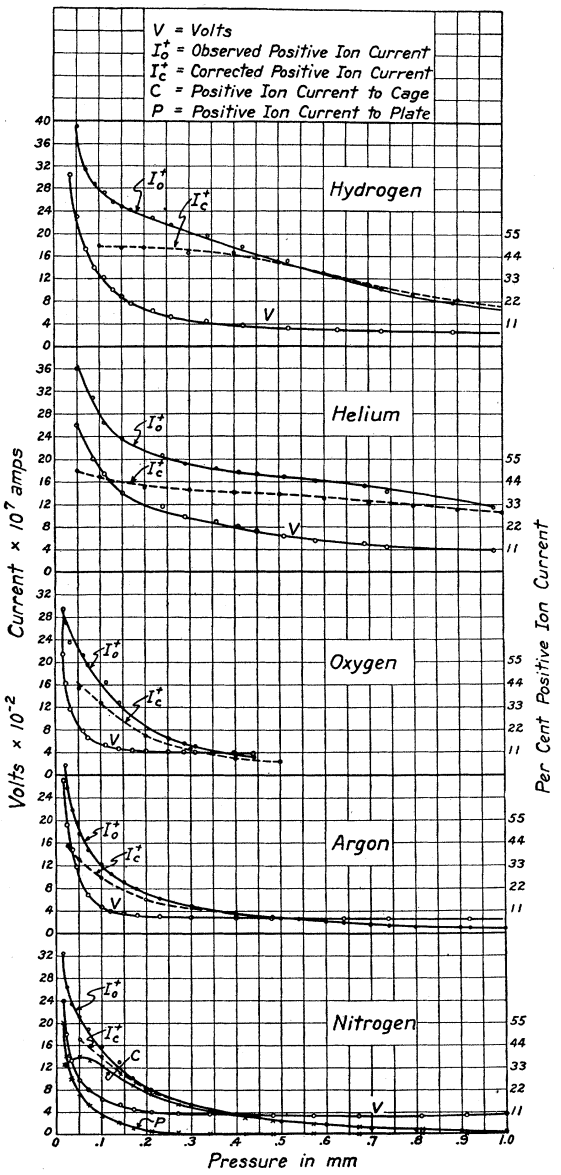

Fig. 2. Curves showing the positive ion current through the cathode perforation and the fraction of the total current carried to the cathode by positive ions.

pressures above 0.3 mm the discharge is quite uniformly distributed over the surface, while at pressures below this point the discharge creeps away from the edge of the cathode and tends to concentrate in two bright sections, one

at the center and the other in the form of a ring at the outer edge of the glowing area.

The effect of the discharge current

The variation of the positive ion current with the current passing the discharge is shown in Fig. 3b. These data are for the current passing through the center perforation in the cathode used in Fig. 3a. The results show the positive ion current to be proportional to the discharge current.

The effect of the cathode potential drop

The correlation between the cathode fall of potential and the positive ion current is illustrated in Fig. 2. In the region where the voltage change with pressure is appreciable, the change is approximately inversely proportional

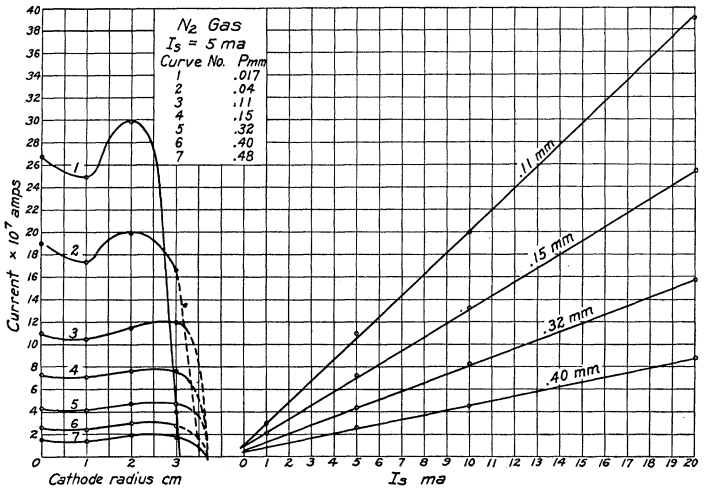

Fig. 3a. The distribution of the positive ion current over the cathode at various discharge pressures.

3b. The dependence of the positive ion current on the total current through the system.

to the pressure. With the possible exception of hydrogen, the positive ion current depends on the pressure in a similar manner.

The effect of area and shape of the perforation

A cathode with an adjustable slit passing through the center was used to test the effect of size of the opening on the positive ion current. The slit was 2.2 cm in length; the areas were varied from 0.007 sq. cm to 0.07 sq. cm, and the pressures from 0.2 mm to 0.5 mm. Over this entire range the positive ion current at each pressure was proportional to the slit area.

The shape of the perforation appears to have little effect on the positive ion current when the distribution of the discharge over the cathode was uniform. Thus round holes gave practically the same current values as did long narrow slits for equivalent areas.

The effect of the anode

The effect of the distance between the anode and cathode on the positive ion current is shown in Fig. 4.

The edge of the dark space is represented by the dotted line at 1 cm. The voltage is the difference in potential between the electrodes. The data show that the position of the anode in the negative glow has no effect on the cathode potential fall, on the current through the system, I_s, or on the positive ion current, I_p, until it approaches within a very short distance from the edge of the dark space. This effective region which determines the characteristics of the discharge is referred to as the vital segment.

The effect of collector potential

The effect of various voltages applied to the plate of the collector illustrated in Fig. 1 is given in Fig. 5.

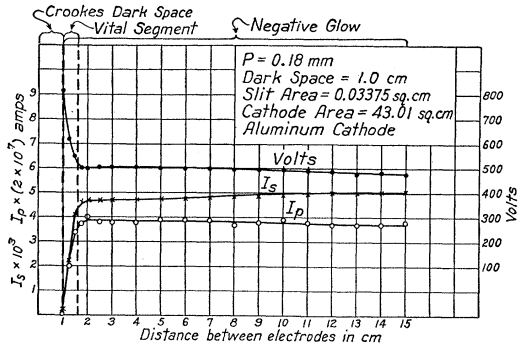

Fig. 4. The effect of the position of the anode on the positive ion current arriving at the cathode.

The results were all very similar in nature so only representative curves are shown. Line 1 shows the effect of potential on the current received by the plate, while line 2 is the current simultaneously received by the cage. Line 3 is the sum of these two currents. It will be seen that the sum of the currents received by the plate and cage is very nearly constant, irrespective of the plate potential. Lines 4, 5, and 6 represent the sums of curves similar to lines 1 and 2 for the pressures indicated.

Line 7 for hydrogen is distinct from those obtained for argon, nitrogen, and oxygen in that it shows a pronounced hump for low applied voltages. The size of the hump decreases with increasing pressure. Similar humps were obtained with helium at the lower pressures.

Line 1 for the current received by the plate is similar to that obtained with a simple plate collector or with a collector of the type used by Aston, the sudden drop for small applied potentials and the negative current for large positive potentials are characteristic of all simple collectors.

The results obtained with a collector of the same type as that shown in Fig. 1, but with a cylindrical rather than a cone shaped cage, were different from those given in Fig. 5 when various accelerating and retarding voltages

were applied to the plate. Two cylinders were used, one with an opening into the cylinder, 2 mm in diameter, the same as the cathode perforation and the other with a 6 mm opening placed symmetrically over the cathode perforation. The walls of the cylinders were machined to a knife edge at the opening in both cases and were insulated from the cathode by a thin sheet of mica. The cylinder with the smaller opening gave unsatisfactory results as the positive space charge due to the ions entering the perforation induced an appreciable electron current from the cage to the cathode. This effect was materially minimized by the 6 mm cage opening. With the larger opening the plate current corresponded exactly to line 1 of Fig. 5. The cage current, however, is illustrated by the dotted line 8, and differs materially from line 2 for the cone shaped cage in that many of the positive ions and metastable molecules that were caught by the cone now go to the cathode and also the number of

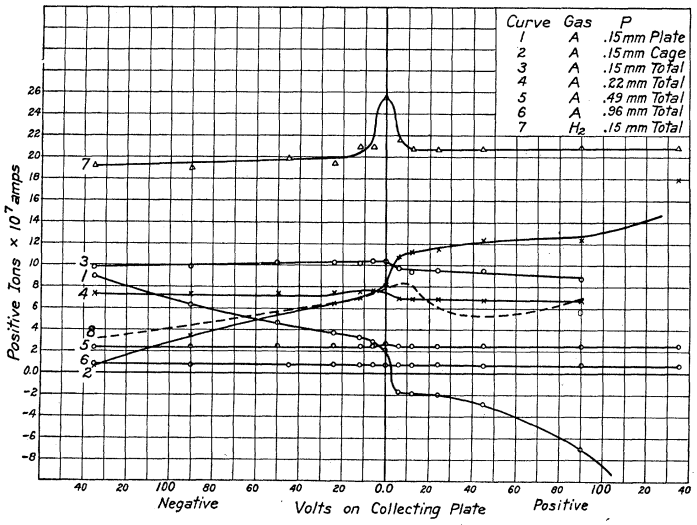

Fig. 5. The effect of plate potentials on the current to the plate and to the cage, and on the total positive ion current passing through the perforation.

positive ions passing through the cathode is doubtlessly materially reduced by the positively charged plate placed immediately over the perforation. Decreasing the distance between the plate and the perforation increased the current from the plate to the cathode, and decreased the current to the cage.

Discussion of Results

The results just presented may be better understood by a consideration of the possible sources of the currents received by the collector cage and plate. The currents received by the collector may be divided into two types; (1) the primary current entering from the discharge, and (2) secondary current arising within the collector. These types may be subdivided as follows:

(1) Primary current
   1. Positive ions from discharge (I^+)
   2. Electrons from discharge (e_c)
      (Dragged in by I^+ or by charge on plate)

(2) Secondary current
1. Secondary electrons ejected by ions (e_{I^+})
2. Secondary electrons ejected by metastable molecules and atoms (e_m)
3. Photoelectrons (e_λ)
4. Ionization by mutual impact of 2 metastables.

The components of the currents received by the plate and cage may now be analyzed as follows:

When plate is negative

Current at the plate
1. I^+
2. e_m from plate
3. e_{I^+} from plate
4. e_λ from plate

Current at cage
1. e_m from plate
2. e_{I^+} from plate
3. e_λ from plate
4. e_c from discharge

When plate is positive

Current at the plate
1. e_m from cage
2. e_λ from cage
3. c_{I^+} from cage
4. e_c from discharge

Current at cage
1. I^+
2. e_m from cage
3. e_λ from cage
4. e_{I^+} from cage

In addition to the above there are two other sources of current that might be registered by the collecting electrodes, namely, an electron current from the plate to the cathode perforation, and an electron current from the cage to the cathode. An example of the plate to cathode current is shown by line 8 in Fig. 5; this did not occur for the cone collector. A cage to cathode current is difficult to avoid but can be reduced by making the cage opening materially larger than the cathode perforation, and also by screening the cage opening from the cathode with some insulating material; a potential on the plate also decreases this current.

A survey of the various currents received by the plate and cage shows that the currents of secondary origin neutralize one another, in that what is lost by one electrode is gained by the other. The sum of the currents to the cage and plate, therefore, represents only the primary currents passing through the cathode perforation, provided no spurious discharges to the cathode occur. Thus it follows that the lines 3, 4, 5, 6, 7, of Fig. 5 represent the current due to the positive ions passing through the orifice minus that due to any electrons that might be dragged along by the inrushing positive ions.

An accurate estimation of the primary electron current passing through the cathode perforation cannot be made from the present data; nevertheless the results indicate it to be small compared with the positive ion current. Since the primary electrons necessarily enter the cage with very low initial energy they should be easily stopped by a negative plate potential; the fact that the total current passing through the perforation remains almost constant irrespective of the potential on the plate indicates a negligible electron current. It may be, however, that the small break in line 7 near zero plate voltage is due to the primary electron current.

The hump in curve 7 is characteristic of all the sum curves, although it is negligible for argon, nitrogen, and oxygen, and small for helium. The presence of the hump results from an abnormal electron current from the cage to the cathode that is apparently due to electrons liberated from the edge of the cage by metastable molecules and atoms and drawn to the cathode by the positive space charge set up by the inrushing ions. This type of discharge is readily checked by a charge on the plate and ordinarily breaks off more readily for positive than for negative potentials.

It is impossible to obtain an accurate estimation of the energy of the positive ions since the data do not distinguish between electrons liberated by the ions and by metastable molecules. The energy of the ions must be an appreciable fraction of the cathode potential drop, however, since the point of crossing of lines similar to 1 and 2 in Fig. 5 moves toward the positive voltages for decreasing pressure, as well as the positive potential at which the plate current became zero increased with a decrease in pressure. In the case of helium the plate did not register a negative current until a stopping potential of one-quarter the cathode potential was reached. This does not mean that the energy of the ions is but one-quarter of the cathode potential drop but rather that at this retarding voltage the positive ion current to the plate is just balanced by the electron current from the cage to the plate. When there is no charge on the plate the positive ions strike the plate at the lower pressures in a well-defined spot about twice the size of the cathode perforation; this is an indication of a fairly homogeneous beam of ions. It seems probable from a survey of the results as a whole that the ions striking the cathode possess an energy near that of the cathode fall. Such an interpretation is not surprising since it has been shown previously that the length of the Crookes dark space is approximately equal to one mean free path for an electron between ionizing collisions.

These results indicate that the current carried to the cathode by positive ions constitutes but a small fraction of the total current passing through the discharge for all pressures above a few millimeters of mercury. The positive ion current, however, is greater in gases of low molecular weight, the currents being roughly proportional to the relative rate of diffusion of ions in the various gases. Since the potential gradient at the junction of the Crookes dark space and the vital segment is small it is not surprising that the cathode potential drop has little or no effect on the values of the positive ion currents; diffusion is evidently the important thing in determining the movement of ions from the negative glow to the cathode. Even in this vital segment of the negative glow the natural tendency is for the ions to be driven further into the glow rather than towards the cathode, since the average electron producing the ionization has an energy component equal to the cathode potential.[7] The studies of chemical action in the discharge show clearly that a majority of the ions formed in the negative glow are neutralized on the walls of the discharge tube[8] rather than at the cathode.

[7] A. K. Brewer and P. D. Kueck, J. Phys. Chem. (1932).
[8] A. K. Brewer and P. D. Kueck, J. Phys. Chem. **35,** 1281 (1931).