RELATIVE PRODUCTION OF NEGATIVE AND POSITIVE IONS BY ELECTRON COLLISIONS[1]

By F. L. Mohler

Abstract

In the tube used, either positive or negative ions produced by an axial beam of electrons accelerated from a filament by a voltage V, were collected on a concentric cylindrical electrode D by maintaining it at a potential slightly lower or higher than that of the beam, the primary electrons being prevented from reaching D by means of a solenoidal magnetic field of 100 gauss parallel to the axis. While saturation was not always reached, the relative values of the positive and negative ion currents are significant. Contrary to the ordinary theory, the polar compounds *mercuric chloride* and *hydrogen chloride* gave results quite similar to those for the elements *mercury and iodine.* With electron currents of the order of 10^{-6} amp. and pressures of about .001 mm, the negative ion current is in all cases small compared with the positive ion current above the ionization potential. With larger currents the negative current increases sharply at the ionization potential and the ratio to positive current is greater. For vapors other than mercury there are some negative ions produced at all voltages, the negative ion currents each having a maximum at zero and increasing again at certain critical potentials, the voltages being 4 for $HgCl_2$, 6.5 for HCl and 2.4, 4.6, 8.4 for I_2. As far as is known, these potentials are equal to *potentials of inelastic collision.* These experiments give no support to the theory that electron collisions dissociate polar molecules into positive and negative ions. In agreement with the results of the magnetic analysis of positive ions, they indicate that the primary effect of an electron impact is the production of a positive molecule ion. The negative ion curves obtained can be explained by the hypothesis that only slow moving electrons attach themselves to molecules to form ions, but the absence of low voltage negative ions in the case of Hg is not understood.

IT is generally assumed that negative ions are produced by electron collision in two different ways, by an electron attaching itself to a neutral molecule, and by an electron collision splitting the molecule into a positive and negative ion.

Measurements[2] of electron mobility indicate that some normal molecules readily form ions by attachment of electrons, notably chlorine and oxygen, while hydrogen, nitrogen and the rare gases show complete absence of negative ion formation. On the other hand electromagnetic resolution of the ions formed in an electric discharge shows the presence

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Loeb, Phil. Mag. **43**, pp. 229-236 (1922).

of negative ions in other gases including those just excepted.[3] The experiments are not contradictory, however, for Franck and Grotrian[4] have pointed out that atoms or molecules in excited states will have properties entirely different from normal molecules and in some states may well have a strong electron affinity. Mobility measurements are made under conditions insuring almost complete absence of excited molecules while quite the contrary is true in the experiments involving electromagnetic analysis of the ions.

The assumption that electron collisions may dissociate molecules into positive and negative ions is based on the numerical agreement between the computed work required to so dissociate polar molecules and the observed ionization potentials. The hydrogen halides offer the only instance where the data compared are entirely satisfactory and the agreement in these instances is remarkably good. Table I gives some results. It has, however, been questioned whether these data give conclusive proof as to the nature of the ionization process.[5]

TABLE I

Ionization of hydrogen halides.[6]

Halide	Work to separate ions	Observed ionization potentials (Knipping)	(Mackay)	(Foote and Mohler)
H Cl	13.7	13.7	13.8	14.0
H Br	13.1	13.3	13.2	
H I	12.7	12.7	12.8	

The methods of electromagnetic analysis have recently been applied to the low voltage thermionic discharge and important information is being obtained on the minimum potentials required to produce positive ions of known e/m ratio.[7] An inherent limitation of the method makes it difficult, however, to measure the formation of negative ions as a function of the voltage. In the method here described use is made of a magnetic field merely to separate the heavy ions from the electrons.

EXPERIMENTAL METHOD

Fig. 1 indicates diagramatically the arrangement of electrodes in the electron tube used. The filament A and the diaphrams B produce a beam of electrons which passes along the axis of the cylindrical electrode D to the wire gauze electrode C and plate C'. A helix around the entire

[3] J. J. Thompson, "Rays of Positive Electricity" p. 70 et seq.; Smyth, Proc. Roy. Soc. **104A,** 121 (1923).

[4] Franck and Grotrian, Zeits. f. Phys. **4,** 89-90 (1921).

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

[6] Compton and Mohler, "Critical Potentials and Their Interpretation," Bull. Nat. Res. Coun. No. 9, p 112 (1924).

[7] Smyth, J. Frank. Inst. **198,** 795-811 (1924); Phys. Rev. **25,** 452 (1925).

tube gives a magnetic field H of about 100 gauss parallel to the axis and to the electron beam. For ion measurements potentials are applied as indicated in the figure. The electron speed is determined by the variable potential difference V and V_2 is a relatively small potential, usually ± 1 volt, which draws the ions to the receiving electrode. The electrons move in a nearly equipotential region and in the absence of a magnetic field any gas in the tube will tend to scatter them to the side electrode. The current from scattering was found to be large compared with the ion current, a result in accord with published data[8] on scattering and ionization. In argon at 25 volts the probability of scattering is 10 times that of ionization and at 17 volts about 100 times as great. The function of the magnetic field is to prevent this scattered current reaching the side electrode.

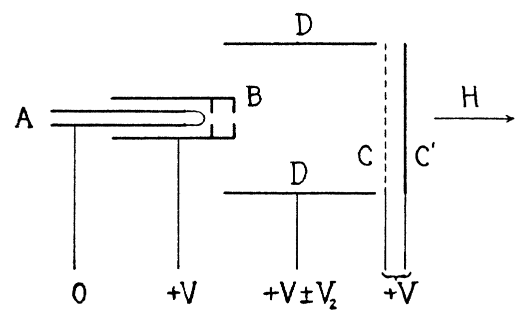

Fig. 1. Arrangement of electrodes and method of applying potentials for measuring either positive or negative ions. The arrow H indicates the direction of the magnetic field.

Electrons[9] having a velocity corresponding to a potential of V volts moving in an equipotential space at right angles to a magnetic field H will describe circles of radius.

$$R = 3.4\sqrt{V}/H.$$

In the form of tube here used an electron moving along the axis is unaffected by the magnetic field but if it is deflected by a single molecular collision through an angle θ it will move in a helix of radius

$$R = (3.4\sqrt{V}/H)\sin\theta.$$

This helix is tangent to the axis so that the electron departs from the axis a maximum distance $2R$. Electrons scattered at 90° reach a distance $6.8\sqrt{V}/H$ from the axis. Ten-volt electrons in a field of 100 gauss will after a single scattering move on helices within .2 cm of the axis.

[8] A. L. Hughes, "Collisions between electrons and molecules," Washington Univ. Studies **11**, 117-152 (1924).

[9] Hull, Phys. Rev. **18**, 34 (1921), gives equations for the motion of electrons in superposed electric and magnetic fields for various electrode shapes. This paper and one by Richardson and Chaudhuri, Phil. Mag. **45**, 337-52 (1923), include some experimental results on the effect of a trace of gas on the motions.

The radius of the cylinder D was about 1.5 cm. An ion of mass 35 relative to hydrogen and with a velocity corresponding to one volt will move on a path with a radius of curvature of about 9 cm. It follows that with the conditions here used the scattering of electrons to the side electrode can be prevented without seriously affecting the motion of the heavy ions.

The magnetic field introduces one complication. Without the field the diaphrams B limit the current to electrons which move along the axis. In the presence of the field electrons move on helices tangent to the axis so that electrons starting at angles of θ between 0° and 90° may be able to pass through the diaphrams. An electron which starts at an angle θ and velocity v, moves along the axis with a speed $v \cos \theta$ and traverses a path of length $1/\cos \theta$ in unit distance along the axis. The stopping potential at a surface normal to the axis will be $V \cos^2 \theta$. Curves of retarding potential between C and C' versus current reaching C' indicate that actually many electrons had large values of θ. The form of the electrodes precludes detailed mathematical analysis but it seems probable that the average value of θ and hence the average length of electron path will vary with the voltage so that quantitative conclusions concerning the production of ions at different voltages cannot be drawn.

To avoid multiple electron collisions and other complicating effects, these experiments were limited to low pressures (less than .01 mm) and small electron currents (between 10^{-5} and 10^{-6} ampere). The positive ion currents were of the order of one percent of the electron current. The construction of the electron tubes was modified in various details during the course of the work but with no important effects on the results.

The tubes showed the following characteristics. The curve of electron current to CC' versus V rose rapidly from near the origin in the first few volts and reached a nearly constant value above 6 or 8 volts. The curve of positive ion current to D as a function of V_2 rose sharply from a point between $+.55$ and zero volts and reached saturation at a negative potential of 2 volts or more. Only at the lowest pressures and currents did the ion current at $V_2 = -1$ approximate the total production of ions. A 50 percent change of the magnetic field in either direction had little effect on the ion current.

Vapor pressures of iodine and mercury were controlled by the temperature of a side tube in which they were contained while the pressure of $HgCl_2$ was determined by the temperature of the main tube. HCl was streamed through a fine capillary tube from a reservoir containing gas at pressures between 76 and 10 cm.

Experimental Results

Figs. 2 to 4 show currents to D as a function of the voltage V applied to the electron current, except that curves marked SP give electron currents reaching C' against a retarding potential between C and C', the potential V being constant. Positive ion currents to D at $V_2 = -1$ volt are indicated by P, negative ion currents with D at $V_2 = +1$ volt, by N. The current per unit electron current would give a curve of different shape in the first few volts. Table II gives data on experimental conditions for these curves. Initial potential corrections were made on the basis of published measurements of ionization potentials. Table III lists the reference values as well as observed values of other potentials relative to these.

Table II

Currents and pressures* for curves of Figs. 2, 3 and 4.*

Vapor	Curve number	Pressure (mm)	Electron current (10^{-6} amp.)	Pos. ion current (10^{-8} amp.)	Neg. ion current (10^{-8} amp.)	Pot. V for current meas.
Hg	PII, NII	.001	.95	2.3	.1	18 volts
	PI, NI	.002	.92	3.7	.6	18
$HgCl_2$	PI, NI	<.003	2.0	3.7	.3	16
	NII	<.003	6.0	....	3.4	16
H Cl	PIV, NIV	.0005	3.2	1.1	.07	18
	PIII, NIII	.001	2.9	2.3	.34	18
	PII, NII, NI	.001	7.5	16	5.5	18
	NV	.002	4.3	(24)	7.7	18
I_2	PIII, NIII	.002?	12.6	2.8	.38	15
	PI, NI	.01	6.9	22	9.5	15
	NII	.01	(3.5)	(120)	....	15

* Values in parentheses are from data not plotted. Pressures are in general not accurate.

Table III

Critical potentials for production of ions.

Vapor	For positive ions	For negative ions
Hg	10.4*	10.4
$HgCl_2$	12.1*	12.1
		4.
HCl	13.8*	13.8
	23.5	6.5
I_2	10.0*	10.0
		2.4
		4.6
		8.4

* These are published values for the first ionization potential (see ref. 5).

The middle section of Fig. 2 gives three curves obtained with mercury vapor at low pressure and with a small electron current. The negative current is practically negligible as compared with the positive. The upper curves of this figure were obtained with the same electron current but higher pressure and show that the negative ion current starts sharply at the ionization potential. With larger currents and pressures the

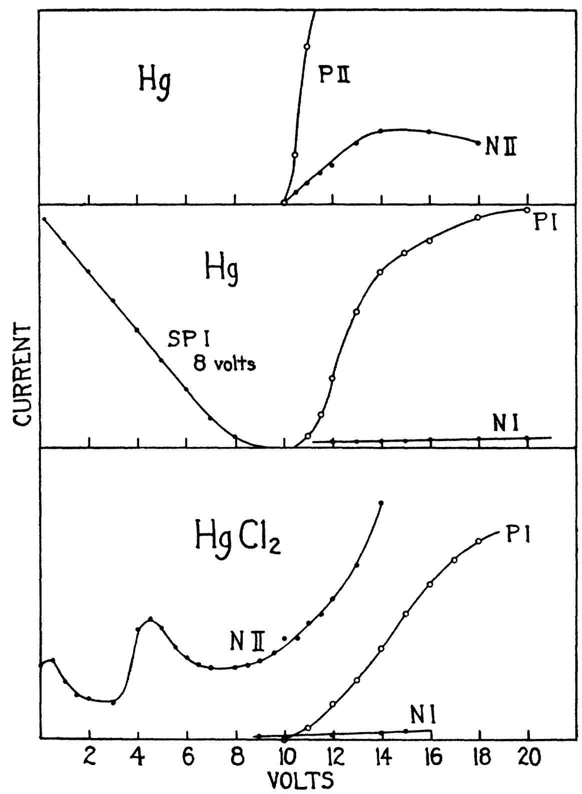

Fig. 2. Ion currents as a function of the potential applied to the electron current. Positive ion curves indicated by *P*, negative by *N*. Curve *SP* shows current against retarding field between *C* and *C'*.

negative ion currents became nearly equal to the positive but under these conditions the ion currents were far from saturated so that there is no reason to believe that the production of ions was equal.

The lower part of Fig. 2 shows ion currents in $HgCl_2$ at 60°C (saturation pressure .003 mm). The chloride was partially dissociated upon evaporation as evidenced by the formation of a film of the less volatile mercurous chloride. Curves PI and NI obtained with low electron current indicate that here too the production of negative ions is small compared with the amount of positive ions above the ionization potential. However, some negative ions were in this case present at all voltages; curve NII shows on a much larger scale the low voltage portion of a negative ion curve. There is a maximum near zero volts and an increase at an applied potential of about 3 volts (corrected value 4 volts).

Fig. 3 gives current voltage curves in hydrogen chloride. This gas is of particular interest in view of the theoretical considerations mentioned above. The liquid air traps used for freezing out mercury prevented

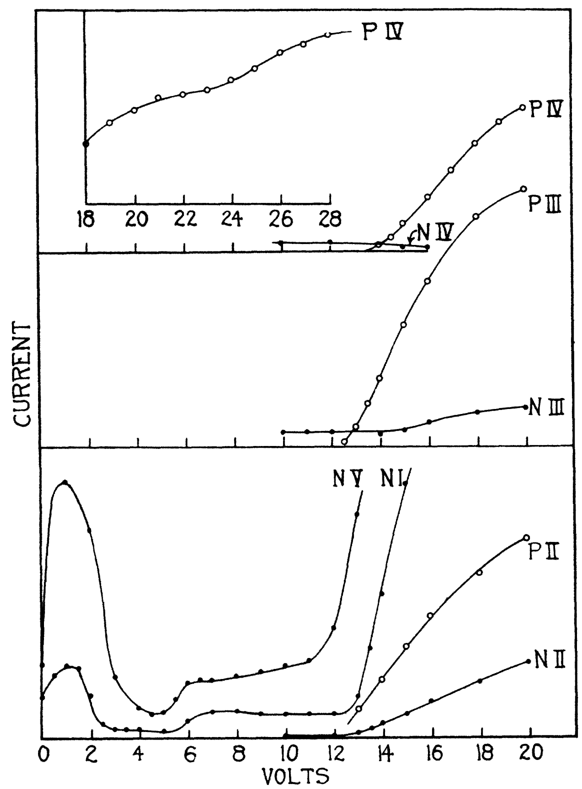

Fig. 3. Positive and negative ion currents in HCl as a function of the applied potential.

the measurement of the pressure under working conditions so that values given in Table II are only rough estimates. Curves PIV, NIV, PIII and NIII, obtained with low pressure and small currents, are, contrary to theory, quite similar to the results obtained in mercury vapor under similar conditions. Above the ionization potential the positive ion current is predominant. The small negative current is, however, measurable at all voltages. The curves in the lower part of the figure were obtained with larger currents and pressures and are similar in general form to those obtained in $HgCl_2$ under like conditions. The ion current *per unit electron current* if plotted would drop sharply from zero volts. There is an increase near 6.5 volts (a large correction has to be added) and another at the first ionization potential. Positive ion currents show a well defined increase at 23.5 volts.

Fig. 4 gives curves obtained with iodine vapor. The upper curves, with the vapor at low pressure, again show the positive ion production pre-

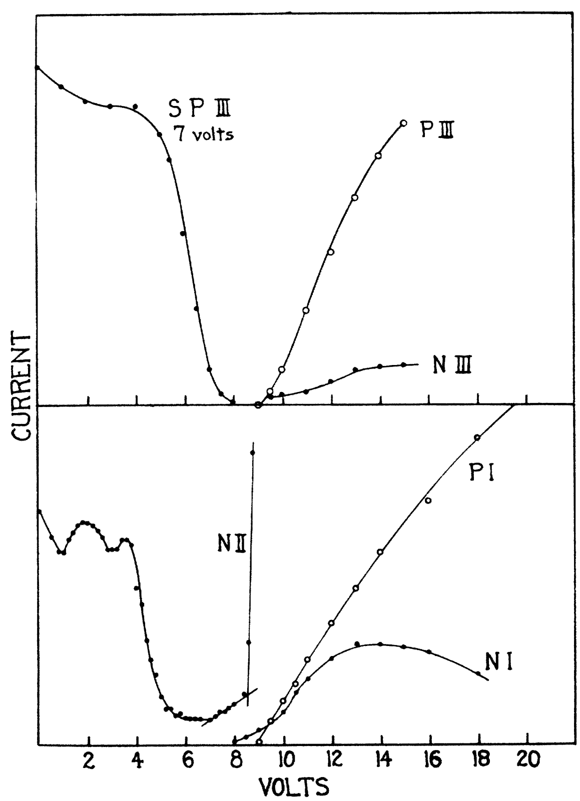

Fig. 4. Positive and negative ion currents in iodine vapor as a function of the applied potential.

dominant. The lower curves taken with much higher pressure show the general features of negative ion curves in the other polyatomic vapors but the critical potentials are in the case of NII exceptionally sharp.

Interpretation of Results

The ion currents above the ionization potential showed the same characteristics in all the gases studied. With low pressures and small electron currents the negative ion currents were negligible compared with the positive. Increasing the pressure or the electron current made the negative ion current relatively larger and it increased sharply at the ionization potential. The increase with electron current was at first more rapid than the first power of the current (pressure and voltage being constant) while the positive current increase was less than that of the electron current because of departure from saturation.

If polar molecules were ionized into positive and negative ions the results with mercury and iodine should be in marked contrast to those with mercuric chloride and hydrogen chloride. With the latter gases the production of positive and negative ions should be exactly equal. The measured currents would not always be equal as the heavier ions would depart more from saturation, but the two currents would approach equality as the pressure and current were reduced. The observed phenomena are quite different and seem to show conclusively that ionization by dissociation is not the primary effect of the electron collision. The negative ion formation above the ionization potential seems to be a secondary effect depending possibly on the amount of excitation as well as on the current. It is not clear why this secondary effect should start exactly at the ionization potential. The theory of Franck and Grotrian[4] indicates that it would start at some lower critical potential.

All the polyatomic vapors, in contrast to mercury, showed a negative ion current at low voltage. The current dropped rapidly from a maximum at zero volts and increased again at well defined critical potentials. The low voltage current was roughly proportional to the electron current in contrast to the condition above the ionization potential. The critical potentials for iodine were determined with fair precision as 2.4, 4.6, 8.4 and 10.0 volts. Iodine gives potentials of inelastic collision at multiples of 2.3 volts and ionization at 10 volts while there is known to be another excitation stage slightly below 10. These potentials apparently agree with the critical points on the ion curve and suggest a simple hypothesis to account for the form of the curve. Assume that only very slow electrons attach themselves to molecules to form negative ions. Then ions will be formed not only near zero volts but also immediately above potentials of inelastic collision, the function of the collision being merely to reduce the speed of the electron. As the potential is increased beyond the critical value electrons will not lose all their speed and the ion production will again decrease. Conditions are different above the ionization potential for there is reason to believe that slow electrons are produced by ionization even though the voltage is far in excess of the critical potential. Potentials of inelastic collision are not known for HCl and $HgCl_2$.

Loeb[10] has shown from analysis of mobility measurements that the probability of electron attachments can be expressed by an equation in which the probability is independent of the electron speed. However, the equation involves the assumption that electron free paths are independent of the speed, which is not strictly true especially at very low speeds. He concludes that the probability of attachment may decrease as the speed increases but that the existence of a "critical potential" for the production of negative ions is excluded. Our results are not inconsistent with this view but many more data are needed before conclusions of any generality can be drawn.

As concerns the process of ionization of polar molecules, while our conclusions are opposed to a commonly accepted theory, they find support in experimental results on positive ray analysis, which show that in general both molecule ions and atom ions are formed in a discharge. J. J. Thompson[11] concludes from data on a great many compounds under different conditions that, with either polar or non-polar molecules, the immediate effect of a collision of a high speed electron is the production of a molecule ion without dissociation. Results with low speed electrons are relatively few and are less conclusive on this point.

Dempster[12] studied ions formed in a thermionic discharge through hydrogen at potentials as low as 90 volts and found that H_2^+ was the primary product of electron collision. Recently Smyth[13] has carried out similar experiments with voltages as low as the ionization potential.[13] Except at very low pressures H^+ and H_3^+ were found, but he gives evidence that they are produced by collisions of H_2^+ with other molecules.

A recent paper[14] on ions formed at low voltage in $HgCl_2$ and HgI_2 is in apparent contradiction to the present results. Cl^- and I^- were found above the first ionization potential, which led them to conclude that the ionization process was of the type $HgCl_2 \rightarrow HgCl^+$ and Cl^-. Positive rays from the chloride discharge contained $HgCl_2^+$, $HgCl^+$, Hg^+ and Hg^{++}. The results are not actually inconsistent with ours for relatively large electron currents are essential in experiments on positive ray analysis and our data show that except with very small currents the production of negative ions is large and increases at the ionization

[10] Loeb, J. Frank. Inst. **197**, 45-55 (1924).

[11] J. J. Thompson, "Rays of Positive Electricity," p. 88 *et seq.*

[12] Dempster, Phys. Rev. **8**, 651-662 (1916).

[13] Smyth, Phys. Rev. **25**, 452-468 (1925). These results indicate that previously published measurements with nitrogen and oxygen as well as hydrogen may have been misinterpreted.

[14] Kondratjeff and Semenoff, Zeits. f. Phys. **22**, 1-8 (1924).

potential. Thermal dissociation will account for the presence of atomic chlorine and iodine.

A preliminary note[15] on ions formed in HCl gives results which are admittedly inconclusive. At 30 volts HCl^+ (or Cl^+), Cl_2^+, H^+ and H_2^+ are found and with decreasing pressure the hydrogen ions become more prominent. The presence of H_2^+ indicates that there was molecular hydrogen in the tube and makes the results ambiguous as regards the process of ionization of HCl.

In view of the conclusion that electron collisions do not dissociate molecules in the process of ionization, the agreement shown in Table I between computed and observed ionization potentials is an unexplained coincidence. This work in no way disproves the theory on which the computations are based. The theory gives the work required to separate a positive and negative ion and experiments show that an electron collision is not effective in producing such a separation but simply removes an electron from the molecule. Strangely enough the binding energy of the electron in the molecule is nearly the same as the binding energy of the positive and negative ion in the ideal polar molecule.[16]

Bureau of Standards,
June 11, 1925.

[15] Barton, abstract in Phys. Rev. **25**, 890 (1925).

[16] I have had the privilege of reading proof of a paper by Barker and Duffendack (Phys. Rev. **26**, 339, 1925) which includes spectroscopic observations indicating that in pure HCl there is no radiation in the range of the quartz spectrograph even at 120 volts. They also show that the thermionic discharge gives no dissociation comparable with the thermal dissociation produced by the hot filament. Their conclusions are quite consistent with those here deduced from an entirely different type of experiment.