THE IONIZING POTENTIALS OF GASES.

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INVESTIGATIONS on the least energy required to ionize molecules of a gas by the impact of electrons lead to results which may often be used to test theories of atomic structure. Such experiments are better known as experiments on the ionizing potentials of gases. Of the recent experiments on this subject, the best known are those of Franck and Hertz.[1] During the past year, the results of some of these experiments have been verified and extended by Goucher[2] and Bazzoni.[3] Yet up to the present, the ionizing potentials of only six or seven gases are known. It was thought that a systematic investigation of the ionizing potentials of a number of gases—compounds as well as elements—would prove valuable. It was also thought worth while to measure the ionizing potentials of some gases which have already been investigated to see whether the modifications in the experimental methods lead to appreciable changes in the published constants.

First Method.

In the method used by Franck and Hertz and by Goucher, the electrons are accelerated by an electric field up to a gauze, and a certain proportion of them pass through the interstices into another region where they are subjected to a retarding field. The positive ions produced in this region are driven into an electrode connected with an electrometer. One obvious defect of this method is that, at potentials just above the ionizing potentials, the part of the gas in which ions can be produced is limited to a thin layer close to the gauze, for the electrons are quickly retarded to a speed below which they do not ionize. A method in which all the gas can be ionized, even when the applied potentials are close to the ionizing potentials offers advantages in precision in fixing the ionizing potentials. The apparatus shown in Fig. 1 approximately satisfies this condition. The photo-electrons from a platinum disc *P*, illuminated by ultra-violet light, were accelerated by a suitable electric field towards the hollow platinum cylinder *C*. To prevent any spreading out of the electron stream, a solenoid carrying a current was arranged coaxial with the tube. The

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[1] Franck and Hertz, Verh. d. Deutsch. Phys. Ges., XV., p. 34, 1913.

[2] Goucher, Phys. Rev., VIII., p. 561, Nov., 1916.

[3] Bazzoni, Phil. Mag., XXXII., p. 566, Dec., 1916.

electrons would be compelled to travel in narrow spirals along the lines of magnetic force, and so to keep to the center of the tube. A small field of a volt or two inside the cylinder was sufficient to drive the positive ions produced to the electrode D (a strip of platinum about three mm. wide). The advantage of this form of apparatus was that, once the electrons had passed into the cylinder, their velocity would hardly be affected by the small field inside the cylinder, and consequently they would be available for ionization almost all along their path, in contrast with the conditions obtained with the Franck and Hertz type of apparatus. The curves in Fig. 2 show the way in which the ionization inside the cylinder varies with the potential difference accelerating the electrons from the disc to the cylinder. One curve was obtained with the Gaede mercury pump running continuously, so that the residual gas was mercury vapor at a pressure of about .002 mm. The second curve —showing less ionization—was obtained with air also in the apparatus at a pressure of .0026 mm. The intersection of these curves with the axis takes place at about 9.45 volts. We must, however, take into account the fact that the photo-electrons are emitted with a small velocity from the disc. How much to allow for this velocity of emission is rather difficult to say. Since the line λ 2,537 is by far the strongest line in the ultra-violet spectrum of the mercury arc, we have taken this to be, for our purpose, the shortest line emitted by the mercury lamp. From Richardson's and Compton's curves[1] on the distribution of velocities among the photo-electrons, it is evident that most of the electrons excited by the shorter lines have velocities less than those of the *fastest* electrons produced by λ 2,537. We therefore consider it justifiable to neglect the light of shorter wave-length than λ 2,537. From Richardson and Compton's experiments we know that the long wave-length limit of the photo-electric effect for platinum is λ 2,910. By means of the equation

$$Ve = h\nu - h\nu_0$$

we can get the velocity (measured in equivalent volts) of the fastest electrons due to λ 2,537. Taking $h/e = 4.13 \times 10^{-15}$ (volt-frequency units, Millikan) and

$$\nu = \frac{3 \times 10^{10}}{2537 \times 10^{-8}}, \quad \nu_0 = \frac{3 \times 10^{10}}{2910 \times 10^{-8}},$$

we get $V = .63$ volt. Adding this to the accelerating potential 9.45 volts,

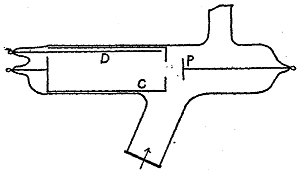

Fig. 1.

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[1] Richardson and Compton, Phil. Mag., XXIV., p. 577, 1912.

we get 10.08 volts, or to the nearest tenth of a volt, 10.1 volts, as the ionizing potential of mercury vapor. (We may note that the straight part of the curve intersects the axis at 10.15 volts. This could be associated with the electrons emerging with practically no initial velocity, though it can be shown that this agreement could only be expected as an approximation.)

To find the ionizing potentials of other gases, the mercury vapor was frozen out of the experimental tube by surrounding a U-tube between the experimental tube and the pump with carbon dioxide snow. It can readily be shown, and verified by experiment, that there is a certain pressure at which the ionization is a maximum, for if the pressure be too low, there will be few molecules available for ionization, and if the pressure be too high, the electrons will be used up before they enter the cylinder.

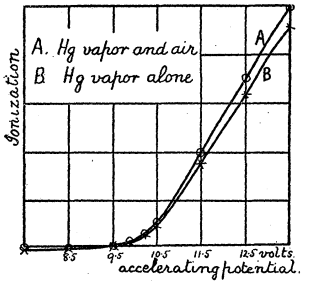

Fig. 2.

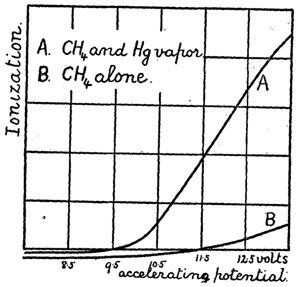

Fig. 3.

On carrying out the experiments, using hydrogen, oxygen, and methane in turn, and choosing the most favorable pressure, it was found that the ionization was surprisingly small in comparison with that in mercury vapor. When investigating the ionizing potential in mercury vapor, a small negative current was obtained for accelerating potentials below the ionizing potential. This did not cause any inconvenience, as the ionization curves were so steep. Fig. 3 shows that the inclination of the ionization curve for methane (the hydrogen and oxygen curves were much the same) was much less than for mercury vapor, and moreover, the negative part of the curve is greater in the absence of mercury vapor. The negative part could not be reduced appreciably either by increasing the magnetic field or by increasing the electric field inside the cylinder. This made it impossible to determine the ionizing potential for gases other than mercury vapor with any accuracy, as there was no definite discontinuity in the curves. The method was therefore of little use, in spite of its attractive features, except for the determination of the ionizing potential of mercury vapor. It served to show that the ionization of mercury vapor by electrons with energy exceeding 10.1 volts is much more intense than that of other gases even when the most favorable pressures are selected. No evidence for ionization by electrons with energies between 4.9 volts and 10 volts was obtained; had the electron current been more intense, it would probably have been observed.

No satisfactory explanation of the negative part of the curves can be given. It was not due to light getting into the cylinder. Some electrons might possibly stick to molecules and become negative ions travelling with the ordinary molecular velocities. For such velocities, however, the electric field inside the cylinder should be ample to prevent any negative ions from reaching the electrode. The electrons may rebound with their full velocities from molecules. Even so, the magnetic field should be sufficient to prevent them reaching the electrode D. If this were the explanation, it would suggest that the collisions with the mercury molecules were non-elastic, while those with the other molecules were elastic, a result not in agreement with Franck and Hertz's experiments.

Second Method.

The method which was finally adopted for the measurement of ionizing potentials was the same in principle as that of Franck and Hertz. A diagram of the apparatus is shown in Fig. 4. It was made entirely of glass and platinum, the amount of metal used being reduced to a minimum. Between what may be called the "experimental tube" and the pump on the one hand and the supply bulb stopcock on the other, traps were provided by which any vapor could be frozen out by liquid air or some other cooling agent. The electrons were emitted from a filament F, about two or three mm. away from the disc D, which was provided with a narrow slit 2 mm. × .5 mm. across the direction of the filament. These electrons were accelerated by an electric field between the filament and the disc. About 5 mm. beyond the disc was an electrode E. To get an ionization curve, E was connected to an electrometer (sensitivity about 1,000 divisions per volt) and the filament F to a positive potential of 3 volts. This prevented any electrons emitted by the filament F from reaching the electrode E. The potential (positive) of D was varied so as to increase the accelerating potential step by step, and the positive charge acquired by E was measured against the accelerating potential. To get a velocity distribution curve, the difference of potential between F and D

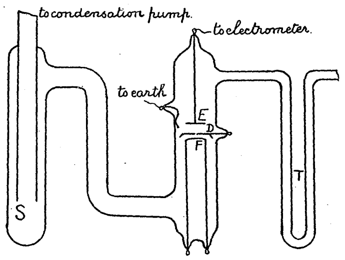

Fig. 4.

was maintained at some suitable value, and the negative charge acquired by E was measured for different retarding potentials between D and E. Fig. 8 is a typical velocity distribution curve. It shows that the "7.46 volt" electrons (electrons produced by an accelerating field of 7.46 volts) have velocities corresponding to values between 10.0 volts and 11.5 volts. (Strictly speaking, the real energy distribution curve, and from it the real velocity distribution curve, is given on differentiating the experimental curve in Fig. 8. As all the information we require can be obtained at a glance from the experimental curves, it was thought unneccessary to differentiate each curve.) When we used apparatus made of glass and brass joined together with sealing wax, the velocity distribution curves were generally very unlike those shown in this paper. The curves seemed to indicate that electrons of all velocities from zero up to a maximum (often considerably less than that corresponding to the applied potential) were present. This may be attributed to the formation of polarization layers on the metal surfaces which have the property of modifying the field in the apparatus very considerably. The state of these polarization layers very probably changes rapidly on passing through an aperture from one side of a plate which receives many electrons to the other side which receives none. There will therefore be strong electric fields in the neighborhood of the aperture which may change the velocity and the direction of motion of the electrons passing through the aperture. This experience leads us to doubt conclusions drawn from experiments in which slow moving electrons are involved, when the experimental apparatus contains brass or such metals joined to glass by sealing wax and with tap grease in close proximity to the place where the electrons are impinging on surfaces. Velocity distribution curves should be taken, as it is unlikely that the actual velocity of the electrons really corresponds to the applied potential. Indeed, with our apparatus, designed to reduce surface polarization effects as much as

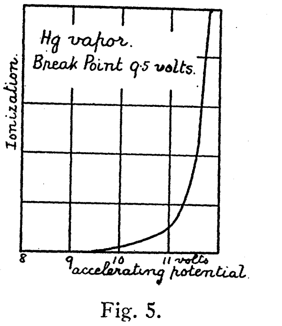

Fig. 5.

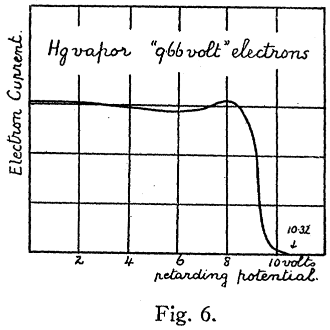

Fig. 6.

possible, we had distinct evidence that with some gases slight surface films were formed.

When working with gases at a pressure of about .01 mm. of mercury, it is difficult to be sure that the gas remains pure, especially if there is a glowing filament in the apparatus. We therefore used the constant flow method of supplying the gas. A supply bulb, of a liter capacity, was filled with gas prepared from pure chemicals and purified according to the usual methods. Between this bulb and the experimental tube was a very fine capillary tube, through which the gas flowed slowly. The gas was removed from the apparatus by a Langmuir condensation pump. By adjusting the pressure in the supply bulb, which determined the rate of flow through the capillary tube, the pressure in the experimental tube could be maintained at any value below .1 mm. Vapors were prevented from entering the experimental tube by cooling the traps T and S on each side of it by liquid air. In some cases, in which liquid air would reduce the pressure of the gas under observation to practically zero, carbon dioxide snow was used.

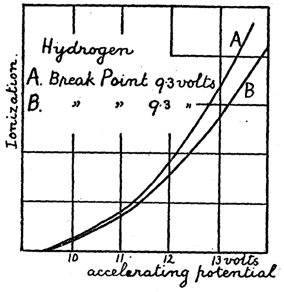

Fig. 7.

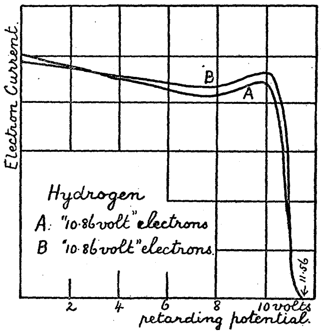

Fig. 8.

The pressure of the gas gradually diminished during the course of a set of observations owing to a decrease in the amount of gas in the supply bulb. The pressures at the beginning and at the end of a set of observations are indicated for each gas. To save space, the ionization curves and the corresponding velocity distribution curves are shown for four gases only. They are chosen so as to illustrate the greatest variation in the shapes of the curves. These will be taken as types and the curves for the other gases will be indicated by reference to one or other of these four types.

An uncoated platinum filament was used to supply the electron current in the experiments on the first gases worked with, viz., ethylene, methane, ethane and carbon dioxide. A lime-coated filament was used in all the succeeding experiments. The electron currents were unusually small in the gases carbon dioxide, oxygen, hydrochloric acid, chlorine and bromine, and the filament had to be heated almost to its melting point. On account of their chemical activity, the experiments on bromine and chlorine were troublesome to carry out and consequently only one set of observations was made for each of these gases.

The Results.

Mercury Vapor.—The ionizing potential of mercury vapor was found by running the condensation pump until the pressure was below .00001 mm. (the limit of the gauge). As the traps were not cooled by liquid air, the only gas present in appreciable quantity was mercury vapor. The ionization curve for mercury vapor is shown in Fig. 5. The curve starts from the axis at 9.5 volts; we shall refer to this point as the "break point." The velocity distribution curve obtained in mercury vapor is shown in Fig. 6. The actual accelerating potential for the electrons was 9.66 volts, the velocity distribution curve shows that the fastest of them had a velocity corresponding to 10.35 volts. We therefore correct the applied potentials in the ionization curves by adding 10.35 − 9.66 volts to the value 9.5 volts which gives 10.19 volts as the ionizing potential for mercury vapor. No evidence of ionization in mercury vapor by electrons with velocities corresponding to 4.9 volts, or to any potential between this and 10.2 volts, was obtained. The pressure of the mercury vapor was not specially adjusted so as to give the maximum amount of ionization. If ionization is produced by electrons with velocities below 10.2 volts, it is clear that it is of a different order from that produced by electrons with velocities greater than this value. We believe, however, that the explanation given by Bohr[1] and by Van der Bijl,[2] that the ioniz-

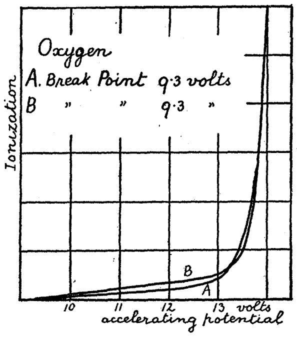

Fig. 9.

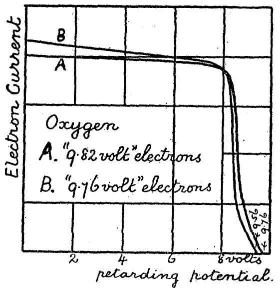

Fig. 10.

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[1] Bohr, Phil. Mag., XXX., p. 410, Sept., 1915.

[2] Van der Bijl, Phys. Rev., IX., p. 173, Feb., 1917.

ation produced by electrons whose velocities are below 10.2 volts is a secondary effect, and does not represent real ionization by impact, is probably correct.

Hydrogen.—Hydrogen was prepared by the action of pure caustic potash on pure aluminum. It was passed through a tube of red hot copper gauze to remove traces of oxygen and then through a spiral immersed in liquid air. The supply bulb was filled several times with hydrogen so prepared and pumped out completely between each filling.

It will be noticed that the ionization curve in hydrogen differs somewhat from that in mercury vapor. The velocity distribution curve *A* was obtained immediately after the ionization curve *A* and the former was used to deduce the correction to the ionizing potential as obtained from the latter. The pressures given are those obtained at the beginning and at the end of the set of observations.

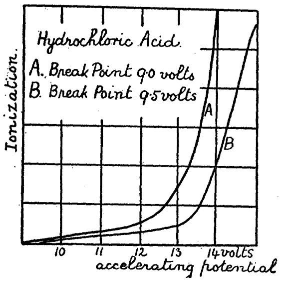

Fig. 11.

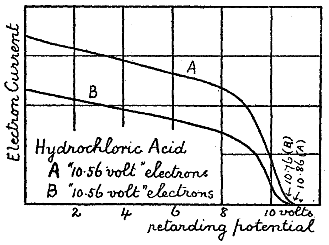

Fig. 12.

A. Pressure .0303 – .0176 mm.
Break point 9.5 volts.
Correction from the velocity distribution curve, 11.56 – 10.86 volts.
Ionizing potential 9.5 + .7 = 10.2 volts.

B. Pressure .0152 – .0137 mm.
Break point 9.5 volts.
Correction from the velocity distribution curve, 11.56 – 10.86 volts.
Ionizing potential 9.5 + .7 = 10.2 volts.

To test whether the ionization curve was really due to hydrogen, the flow of gas was stopped, and in a short while the pressure was down to .00001 mm. At the same time, the ionization current for 14.46 volts accelerating potential was reduced from 101 to 5, showing that the ionization curves were almost entirely due to hydrogen.

Oxygen.—Oxygen was prepared by the action of water on "Oxone" cartridges. The oxygen was said to be 99.4 per cent. pure. It was passed through a soda lime tube to dry it. Several liters were prepared and condensed in a tube surrounded by liquid air. About one third of this was allowed to boil away, the next third was used to wash out the supply bulb and finally to fill it, and the last third was rejected. There is reason to believe that the oxygen actually used in the experiment was very pure. The ionization curve for oxygen rises slowly from the axis for several volts and then very quickly, as though the gas is much more easily ionized by electrons whose velocity is a few volts above the ionizing potential. Owing to the small electron currents and the correspondingly small ionization currents, it was difficult to decide exactly where to place the break point.

A. Pressure .0176 – .0160 mm.
Break point 9.3 volts.
Correction from the velocity distribution curve 9.76 – 9.82 volts.
Ionizing potential 9.3 – .06 = 9.24 volts.
B. Pressure .0116 – .0102 mm.
Break point 9.3 volts.
Correction from the velocity distribution curve 9.56 – 9.76 volts.
Ionizing potential 9.3 – .20 = 9.10 volts.

Hydrochloric Acid.—Hydrochloric acid gas was prepared by dropping sulphuric acid on pure sodium chloride. The gas was condensed by liquid air, and allowed to evaporate, the middle portion being taken to wash out the supply bulb and to fill it with the gas to be tested. The electron current from the filament was much smaller than usual. The shape of the velocity distribution curve indicated that electrons of all velocities were present or else that some electrical distribution around the edge of the hole caused the electrons to deviate from their straight line paths to a considerable extent. Such a state of affairs might possibly be brought about by a small polarization layer on the surface of the electrode *D*. The ionization curve is similar to that of oxygen.

A. Pressure .0116 – .0116 mm.
Break points 9.0 volts.
Correction from the velocity distribution curve 10.86 – 10.56 volts.
Ionizing potential 9.0 + .30 = 9.30 volts.
B. Pressure .0221 – .0212 mm.
Break point 9.50 volts.
Correction from the velocity distribution curve 10.76 – 10.56 volts.
Ionizing potential 9.50 + .20 = 9.70 volts.

Carbon Monoxide.—Carbon monoxide was prepared from formic acid and concentrated sulphuric acid. The gas passed through caustic potash solution and then through a spiral immersed in liquid air. The supply bulb was filled and pumped out several times before the final filling.

Ionization curve: hydrogen type.

Velocity distribution curve: hydrochloric acid type.

A. Pressure .0212 – .0185 mm.
Break point 7.45 volts.
Correction from the velocity distribution curve, 7.10 – 7.52 volts.
Ionizing potential 7.45 – .42 = 7.03 volts.

B. Pressure .0144 – .0130 mm.
Break point 7.45 volts.
Correction from the velocity distribution curve, 7.10 – 7.46 volts.
Ionizing potential 7.45 – .36 = 7.09 volts.

C. Pressure .0116 – .0109 mm.
Break point 7.50 volts.
Correction from the velocity distribution curve, 7.32 – 7.42 volts.
Ionizing potential 7.50 – .10 = 7.40 volts.

Carbon Dioxide.—Carbon dioxide was prepared by heating sodium bicarbonate. The gas was passed through concentrated sulphuric acid and then solidified in a tube surrounded by liquid air. This was then allowed to evaporate, the middle portion being used to wash out the apparatus and to fill the supply bulb. Fractionating a gas from the solid state instead of from the liquid state is probably less satisfactory as a means of purification. The vapor traps in these experiments were cooled by a mixture at – 90° C. instead of by liquid air.

Ionization curve: hydrogen type.

Velocity distribution curve: oxygen type.

A. Pressure .0137 – .0123 mm.
Break point 9.85 volts.
Correction from the velocity distribution curve, 10.2 – 10.0 volts.
Ionizing potential 9.85 + .20 = 10.05 volts.

B. Pressure .0168 – .0168 mm.
Break point 9.70 volts.
Correction from the velocity distribution curve, 10.20 – 10.00 volts.
Ionizing potential 9.7 + .2 = 9.9 volts.

Nitrogen.—Nitrogen was prepared by heating sodium nitrite and ammonium chloride with a little distilled water. The gas was passed through concentrated sulphuric acid and through a tube containing red hot copper gauze. Several liters of gas were generated and used to wash out the apparatus before the final filling of the supply bulb was made.

Ionization curve: mercury vapor type.

Velocity distribution curve: oxygen type.

A. Pressure .0123 – .0116 mm.
Break point 7.45 volts.
Correction from the velocity distribution curve 7.72 – 7.52 volts.
Ionizing potential 7.45 + .20 = 7.65 volts.

B. Pressure .0102 – .0096 mm.
Break point 7.8 volts.
Correction from the velocity distribution curve 7.52 – 7.52 volts.
Ionizing potential 7.8 + 0 = 7.80 volts.

C. Pressure .0250 – .0221 mm.
Break point 7.9 volts.
Correction from the velocity distribution curve 7.32 – 7.52 volts.
Ionizing potential 7.9 – .2 = 7.70 volts.

Hydrogen Sulphide.—Hydrogen sulphide was prepared by the action of dilute sulphuric acid on ferrous sulphate. The gas was washed through dilute sulphuric acid and then frozen by liquid air. This was allowed to liquefy and then to evaporate, the middle portion being used to wash out the apparatus and to fill the supply bulb with the gas for the experiment. As this gas liquefies easily, the traps were surrounded by a mixture at about –70° C.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrochloric acid type.

A. Pressure .0160 – .0152 mm.
Break point 9.2 volts.
Correction from the velocity distribution curve 10.40 – 10.16 volts.
Ionizing potential 9.20 + .24 = 9.44 volts.

B. Pressure .0123 – .0116 mm.
C. Pressure .0109 – .0102 mm.
D. Pressure ? – .0032 mm.

Break point for *B*, *C*, and *D* 8.5 volts.
Correction from the velocity distribution curves, 10.76 – 10.16 volts.
Ionizing potential 8.5 + .6 = 9.1 volts.

Nitric Oxide.—Nitric oxide was prepared by the action of nitric acid on pure copper. The gas was passed through distilled water and caustic soda. It was then liquefied and as usual the middle fraction of the evaporating liquid was passed into the supply bulb.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrogen type.

A. Pressure .0176 – .0152 mm.
Break point 8.9 volts.
Correction from the velocity distribution curve, 10.10 – 9.62 volts.
Ionizing potential 8.9 + .48 = 9.38 volts.

B. Pressure .0130 – .0123 mm.
Break point 8.8 volts.
Correction from the velocity distribution curve, 10.10 – 9.56 volts.
Ionizing potential 8.8 + .54 = 9.34 volts.

C. Pressure .0109 – .0103 mm.
Break point 8.5 volts.
Correction from the velocity distribution curve, 10.30 – 9.56 volts.
Ionizing potential 8.50 + .74 = 9.24 volts.

Ethane.—Ethane was prepared by the action of ethyl iodide on alcohol in the presence of a zinc copper couple. The gas was passed through alcohol and then through concentrated sulphuric acid and was finally liquefied by liquid air. About five c.c. of the liquid were obtained. About a third of the gas was allowed to evaporate and the middle third was used to wash out the apparatus and to provide the sample for the experiment, the remainder being rejected.

Ionization curve: mercury vapor type.
Velocity distribution curve: oxygen type.

A. Pressure .0203 – .0176 mm.
Break point 8.60 volts.
Correction from the velocity distribution curve 9.92 – 8.52 volts.
Ionizing potential 8.60 + 1.40 = 10.0 volts.

B. Pressure .0109 – .0096 mm.
Break point 8.55 volts.
Correction from the velocity distribution curve, 9.92 – 8.52 volts.
Ionizing potential 8.55 + 1.40 = 9.95 volts.

Methane.—Methane was prepared by heating a mixture of sodium acetate and soda lime. The gas was passed through caustic soda solution and through concentrated sulphuric acid and was then liquefied. This was distilled, the middle portion being used to wash out the apparatus and to fill the supply bulb.

Ionization curve: hydrogen type.
Velocity distribution curve: hydrochloric acid type.

A. Pressure .0260 – .0221 mm.
Break point 8.22 volts.
Correction from the velocity distribution curve, 11.30 – 9.92 volts.
Ionizing potential 8.22 + 1.38 = 9.60 volts.

B. Pressure .0109 – .0096 mm.
Break point 7.8 volts.
Correction from the velocity distribution curve, 10.10 – 8.52 volts.
Ionizing potential 7.8 + 1.58 = 9.38 volts.

C. Pressure .0185 – .0168 mm.
Break point 7.9 volts.
Correction from the velocity distribution curve, 10.10 – 8.52 volts.
Ionizing potential 7.9 + 1.58 = 9.48 volts.

Acetylene.—Acetylene was prepared from calcium carbide and water. The gas was washed through caustic potash solution, a silver nitrate solution, and concentrated sulphuric acid. It was then solidified by liquid air. As in the case of carbon dioxide, fractional distillation from a solid is not likely to result in so pure a product as from a liquid.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrochloric acid type.

A. Pressure .0230 – .0212 mm.
Break point 8.80 volts.
Correction from the velocity distribution curve, 12.20 – 10.72 volts.
Ionizing potential 8.80 + 1.48 = 10.28 volts.
B. Pressure .0137 – .0130 mm.
Break point 8.4 volts.
Correction from the velocity distribution curve, 10.90 – 9.46 volts.
Ionizing potential 8.4 + 1.44 = 9.84 volts.
C. Pressure .0090 – ? mm.
Break point 8.30 volts.
Correction from the velocity distribution curve 10.90 – 9.46 volts.
Ionizing potential 8.30 + 1.44 = 9.74 volts.

Ethylene.—Ethylene was prepared from sulphuric acid and alcohol. The gas was passed through a condenser immersed in ice, caustic potash solution, and concentrated sulphuric acid. The gas was liquefied and distilled. The first third was allowed to boil away, the next was used to wash out the apparatus and fill the supply bulb, and the remainder was rejected. The gas used was probably very pure.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrochloric acid type.

A. Pressure .0336 – .0271 mm.
Break point 8.40 volts.
Correction from the velocity distribution curve 9.65 – 8.22 volts.
Ionizing potential 8.40 + 1.43 = 9.83 volts.
B. Pressure .0144 – .0130 mm.
Break point 8.40 volts.
Correction from the velocity distribution curve 9.70 – 8.22 volts.
Ionizing potential 8.40 + 1.48 = 9.88 volts.

Chlorine.—Chlorine was prepared by the action of sulphuric acid on potassium permanganate. It was liquefied by liquid air and distilled as usual. The electron current was unusually small, making it difficult to determine the exact position of the break point.

Ionization curve: oxygen type.
Velocity distribution curve: hydrochloric acid type.
Pressure
Break point 9.10 volts.
Correction from the velocity distribution curve 7.9 − 8.8 volts.
Ionizing potential 9.1 − .9 = 8.2 volts.

Bromine.—Bromine was introduced into a small tube in place of the supply bulb. Its own vapor pressure was sufficient to drive enough vapor through the capillary tube into the apparatus. As there was no stopcock between the bromine tube and the experimental part of the apparatus, it was unnecessary to cool the trap *T*. The bromine was condensed in the trap *S*, causing a constant flow of bromine vapor through the apparatus. The electron current was small in this experiment.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrochloric acid type.
Break point 10.5 volts.
Correction from the velocity distribution curve 8.1 − 8.6 volts.
Ionizing potential 10.5 − .5 = 10.0 volt.

Sulphur.—The ionizing potential of sulphur was not looked for directly, but in the course of the experiments, results were obtained which might be used with some justification to calculate the ionizing potential of sulphur vapor. In the experiment following that on hydrogen sulphide, some anomalous results were obtained, for on reducing the pressure to below .00001 mm. by the pump and preventing mercury vapor from entering the experimental tube by liquid air, a large electron current was still obtained. This result was quite contrary to what we had been led to expect from our other experiments. From one ionization curve, when corrected as usual, a value of 8.44 volts was obtained for the ionizing potential, and from another ionization curve a value of 8.24 volts was obtained. That this is probably due to sulphur may be inferred from the fact that there was no appreciable amount of gas or mercury vapor in the experimental tube, and also that on heating the experimental tube at the end of the observations some sulphur was driven out. This had probably been the result of a partial decomposition of the hydrogen sulphide by the hot filament. On cutting down the experimental tube and cleaning out the sulphur by heating in a current of air, and repeating the experiments again, it was found that the source of the ionization curve was removed and normal results were obtained. These values, attributed to sulphur, hardly deserve as much credit as the other results.

SUMMARY OF RESULTS.

The results are summarized in the following table, in which the values of the ionizing potentials are given to the nearest tenth of a volt. One can hardly claim an average accuracy of more than about .2 or .3 volt, as it is difficult to say exactly where the ionization curve begins and where the velocity distribution curve cuts the axis. (Theoretically, of course, it never actually cuts the axis.) However, for purposes of comparison between the different gases, one can probably claim an average accuracy of about .2 volt.

Ionizing Potentials.

Gas.	This Investigation.	Franck and Hertz.	Goucher.	Bazzoni.	Compton's Theory.	Atomic Volumes.	Atomic Radii.
He	—	20.5	—	20.0	22.8	23.5	1.11×10^{-8}
Ne	—	16	—		16.8	19.2	—
A	—	12	—		8.2	28.0	1.81
H_2	10.2	11	10.25?		11.8	9.2	1.34
O_2	9.2	9	—		8.4	11.2	1.81
N_2	7.7	7.5	7.4		8.05	13.7	1.90
S	8.3?		—		4.25	15.5	—
Cl_2	8.2		—		4.94	21.4	2.68
Br_2	10.0		—		—	25.6	—
Hg	10.2		10.0		4.65	14.8	—
HCl	9.5				6.50		—
CO	7.2				—		1.88
CO_2	10.0				6.47		2.28
NO	9.3				—		1.86
CH_4	9.5				6.54		—
C_2H_6	10.0				—		—
C_2H_4	9.9				—		2.75
C_2H_2	9.9				—		—

The experimental results obtained by Franck and Hertz, by Goucher, and by Bazzoni, are shown in the table. Where comparison is possible, there is good agreement. The values predicted from Compton's theory[1] are also given in the table. In the last two columns will be found the atomic values taken from a paper by Harkins and Hall,[2] and the atomic radii taken from Jeans's Dynamical Theory of Gases (2d edition, p. 341).

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[1] Compton, PHYS. REV., VIII., p. 412, Oct., 1916.

[2] Harkins and Hall, Am. Chem. Soc. Jour., XXXVIII., p. 169, Feb., 1916.

DISCUSSION OF THE RESULTS.

Shape of the Ionization Curves.—The variations in the shape of the ionization curves are greater than can be accounted for by differences in the velocity distribution curves. This implies that the way in which the ionization by collision depends upon the velocity of the electron (above the ionizing potential) differs for different cases. If we assume that the ionization per collision is constant for velocities above the ionizing potentials then it can be shown that the straight part of the curve, when produced, intersects the axis at a point which gives approximately the ionizing potential, provided we refer this point to the voltage corresponding to the most probable energy of the electron, and not as we have done hitherto, to the energy of the fastest electrons. Such is the case for ethylene, and approximately so for mercury vapor, but not at all the case for oxygen. (Some of the curves have no straight portions.) As these experiments were not designed primarily to investigate this relation, the matter will be left without further comment.

Ionizing Potentials of the Elements.—A knowledge of the ionizing potentials of the elements should furnish material for testing theories of atomic structure. The only theory which is sufficiently well developed to enable us to make a quantitative comparison is that due to Bohr,[1] and even Bohr's theory is only worked out in sufficient detail to allow us to test the results for hydrogen and helium.

Bohr pictures a hydrogen atom as one electron rotating about a positive nucleus possessing one unit positive charge. The only orbits which are possible are those in which the electron has angular momentum equal to some integral multiple of $h/2\pi$. The negative energy of the atom is

$$W = \frac{2\pi m e^4}{h^3}\frac{1}{\tau} = K\frac{1}{\tau},$$

where τ is the number of the orbit, being 1 for the innermost orbit, 2 for the next, and so on, and K is Rydberg's constant, 3.29×10^{15}. This will give the energy required to remove the electron from the orbit to infinity. The work required to remove the electron from the mth orbit to the nth is

$$K\left(\frac{1}{m^2} - \frac{1}{n^2}\right).$$

For purposes of comparison with experiments, it is convenient to express the work in terms of equivalent volts. On this basis, K corresponds to 13.5 volts, and this measures the energy required to remove the electron

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[1] Bohr, Phil. Mag., XXVI., p. 857, Nov., 1913.

from the innermost ring. We should expect this to represent the energy necessary to ionize the normal atom. The work required to move the electron from the first to the second ring would be

$$K\left(\frac{1}{1^2}-\frac{1}{2^2}\right), \quad \text{or} \quad 10.1 \text{ volts}.$$

This is very close to the ionizing potential of hydrogen as found by experiment, but does not, on the other hand, represent the work required to remove an electron completely, which we should naturally consider to be the work of ionization.

It might be argued that we are working with the hydrogen molecule and not with the hydrogen atom. According to Bohr, the molecule may be pictured as two positive nuclei with two electrons rotating about the line joining them. Each electron has angular momentum equal to some multiple of the constant of angular momentum. The molecule in its normal state has unit angular momentum for its electrons. The negative energy of such a molecule is $2.20K$ and the negative energy of such a molecule with one electron completely removed is $.88K$. The work required to remove the electron is therefore

$$2.20K - .88K = 1.32K, \quad \text{or} \quad 17.7 \text{ volts}.$$

Bohr however shows that the positively charged molecule is unstable, and prefers to regard the ionization of the hydrogen molecule as the disintegration of the molecule into a single nucleus and a hydrogen atom. This requires energy of the amount

$$2.20K - K = 1.20K, \quad \text{or} \quad 16.2 \text{ volts}.$$

Bohr pictures the normal helium atom as two electrons rotating round a doubly charged positive nucleus, each electron having angular momentum equal to some multiple of the unit angular momentum. The negative energy of the normal helium atom, the electrons being in the innermost ring, is $6.13K$, and the negative energy of the positively charged helium atom, with one electron in its innermost orbit, is $4K$. The work to remove one electron is therefore

$$6.13K - 4K = 2.13K, \quad \text{or} \quad 28.6 \text{ volts}.$$

The work to remove one electron, not to infinity, but to the next orbit, will be some fraction of this. Its value will depend upon the assumptions as to the rearrangements of the orbits; we may probably assume that it will not be very different from 3/4, the value previously obtained for the hydrogen atom. This gives 21 volts. It is significant that the ionizing potentials of hydrogen and helium do not agree with the values calculated for the complete removal of an electron from the respective atoms, but do seem to agree with the values of the energy required to move an electron from the innermost ring to the next. Moreover, the experiments of Bazzoni show no traces of any extra ionization setting in at 28.6 volts, nor do our experiments show any discontinuity in the curves for hydrogen at 13.5 volts or at 16.2 volts. It may be inferred that the ionization does not consist of the direct expulsion of an electron from an atom by the impact of another electron, but, as Bohr has suggested in the case of helium, is the result of a transition from the normal state of the atom to the next stationary state. This may come about in several ways. To test whether ionization consists in the transfer of an electron from the innermost orbit to the next, followed by a complete removal from that orbit by a second collision with an electron, we measured the ratio of the ionization currents to the electron currents. If we assume that atoms with electrons displaced to the second orbit tend to go back to the normal state, then, if the electron current is small, almost all the atoms will go back to their normal state before they are hit a second time, while if the electron current be large, there would be a much greater chance for an atom to be struck a second time before it had got back to its normal state. Our experiments showed that the ionization current was doubled when the electron current was doubled, and therefore this linear relation gives no support to this particular view of the mechanism of ionization.

For gases other than hydrogen and helium, we must do without so definite a theory and content ourselves with searching for general relations. There is no clear connection between the ionizing potential of an element and its electronegative or electropositive character. On Bohr's theory we have seen that the closer the electron is to the nucleus, the more is the energy required to take it away. We might therefore try the effect of comparing the ionizing potential with the radius of the atom. Provided we keep to elements which are not too widely separated in character, an increase in atomic volume and atomic radius is accompanied by a decrease in the ionizing potential. This is the case for the inert gases, if we disregard neon, as its atomic volume is not so well established as that of the other gases. It is also the case for hydrogen, oxygen, and nitrogen. It is not the case however for bromine and chlorine. It is well to remember that the experimental difficulties were greater in the case of these gases than in the case of other gases. This relation is similar to one noticed by one of the authors,[1] viz., that there is

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[1] Hughes, Phil. Trans., CCXII., p. 205, 1912.

a regular decrease in the energy required to detach a photo-electron from a metal as the atomic volume increases. This relation holds only for elements within the same column of the periodic table; there is a discontinuity (always in the same direction, however) as we pass from one column to the next. A close relation between the atomic radius and the ionizing potential for all the elements could hardly be expected, as the arrangement of the electrons in the atom must be a factor in determining the energy required to detach an outermost electron in addition to the radii of their orbits. According to Ludlam[1] chlorine is not ionized by the ultra-violet light which is capable of ionizing air. This is in agreement with these experiments if the ionization of air by ultra-violet light is due to the ionization of nitrogen alone, but not so if the oxygen is ionized as well.

Compton[2] recently proposed a theory from which he deduced a relation between the ionizing potential V and the specific inductive capacity K of a gas.

$$V = \frac{.194}{\sqrt{K - 1}}.$$

This formula agrees fairly well for most of the elements; the agreement is poor however for mercury, chlorine, and sulphur, if our value be correct.

Ionizing Potentials for Compounds.—The results do not point to any definite relations for compounds. The ionizing potential for hydrochloric acid is intermediate between that of hydrogen and that of chlorine. The same relation holds for hydrogen disulphide, hydrogen, and sulphur, but does not for oxygen, nitrogen, and nitric oxide. In working on the photo-electric effect of solid compounds[3] it was noticed that, in general, the more stable the compound (measured by its heat of formation) the less was its photo-electric effect and presumably the more difficult it was to detach an electron. It might be reasonably expected therefore that the ionizing potentials would be greater for the more stable compound gases. On testing this out no sort of agreement could be found. Indeed, the ionizing potential is almost constant for the four hydrocarbons, two of which are exothermic and two endothermic.

The values of the ionizing potentials calculated from Compton's theory, are little more than half the experimental values. Compton does not expect a good agreement on account of the uncertainty in the values of the specific inductive capacity K for the compound gases.

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[1] Ludlam, Phil. Mag., XXIII., p. 757, 1912.

[2] Compton, Phys. Rev., VIII., p. 412, Oct., 1916.

[3] Hughes, Phil. Mag., XXIV., p. 380, 1912.

SUMMARY.

The ionizing potentials of fifteen gases have been measured by a method similar in principle to that of Franck and Hertz. A second method of measuring the ionizing potential was worked out, but gave satisfactory results only in the case of mercury vapor.

The ionization of mercury vapor by electrons whose energy is somewhat greater than that corresponding to the ionizing potential is much more intense than is the case for the other gases.

Several relations which might be expected to account for the values of the ionizing potentials have been suggested. The experimental values, however, do not agree well with any of them.