VARIATION WITH PRESSURE OF THE RESIDUAL IONIZATION OF GASES

BY HAL F. FRUTH

ABSTRACT

Residual ionization in air, nitrogen, oxygen and CO_2 under high pressures.—The measurements made by K. M. Downey for air using a steel sphere of one foot inside diameter, have been extended to pressures of 75 atmospheres. (1) *Purified gases.* Air and oxygen gave curves for ionization vs. pressure, first slightly concave upwards (1-15 atm.) then concave downwards (15-35 atm.), then concave upwards (35-53 atm.), then horizontal, the values increasing from 8-10 ions/cc/sec. at 1 atm. to 62-68 for 60 atm. For CO_2 the horizontal part was reached at 61 atm., the limiting value being 97 ions/cc/sec. (2) *Gases containing dust and water-vapor* gave similar curves except that the ionization did not reach a limiting value but continued to increase. (3) *Anomalous behavior of nitrogen.* When prepared from air by the liquifaction process, or by absorption of the oxygen by alkaline pyrogallate, nitrogen showed no upper limit with increasing pressure, either alone or when mixed with oxygen, although air showed this limit. Evidently the process of preparation used, either introduced some long period radioactive impurity or gave the nitrogen some peculiarity such as a tendency to ionize spontaneously. (4) *Penetrating radiation* can apparently be responsible for only a small part of this ionization, not more than 1 ion per cc per atm. per min. as otherwise it would not reach a limit and would not depend so much on the purity of the gas.

INTRODUCTION

IT IS a well known fact that there is a seemingly spontaneous ionization in gases in closed vessels. It is generally conceded that this ionization is too great to be wholly accounted for by the known radioactive substances in the soil, air and surrounding materials. The surplus ionization is generally termed "residual ionization" and is often attributed to an ionizing source from without the vessel, called the "penetrating radiation." A large number of observers have studied this radiation, especially McLennan,[1] Wigand,[2] Wilson,[3] Gockel,[4] Swann,[5] and Downey.[6] The last named observer made a special study of the residual ionization and its variation with pressure, and obtained a linear relation up to 20, and

---

[1] McLennan, Phil. Mag. **26**, pp. 740-752, 1913; Phys. Rev. **26**, pp. 526-631, 1908.

[2] Wigand, Phys. Zeit. **18**, pp. 1-6, 1917.

[3] Wilson, Proc. Cam. Phil. Soc., **11**, pp. 32, 1900; **11**, pp. 428-430, 1902.

[4] Gockel, Phys. Zeit. **16**, pp. 345-352, 1915.

[5] Swann, Bull. Nat. Res. Coun., **17**, pp. 65-73, 1922.

[6] Downey, Phys. Rev. **16**, pp. 420-437, 1920; **20**, pp. 186-193, 1922.

a slowly decreasing slope up to 40 atmospheres pressure. In a later work, however, she obtained a saturation value at 46 atmospheres. The object in the present investigation was to carry out some of the above mentioned experiments at higher pressures with greater sensitivity and to study the natural ionization with respect to pressure and other conditions, such as age, dust and moisture, in air and in other gases in order to try to throw light upon the nature of the agency causing this ionization.

DESCRIPTION OF APPARATUS

The form of the apparatus was suggested by Prof. W. F. G. Swann. The general arrangement is shown in the diagram Fig. 1 and the ionization chamber, one of the cast-steel spheres used by Dr. Downey, was 1 ft in internal diameter and had a capacity of 14.8 liters. The walls were 1 inch thick. The two hemispheres of which it was composed were held together by twenty-four ¾ inch bolts and screws. Red rubber gaskets were used between the hemispheres and great force was applied to the screws until a pressure of 85 atm. could be sustained. A hard rubber ring and cone, coated with resin and bees-wax, and separated by a brass guard ring, were used at the point where the central electrode entered the sphere. The central electrode consisted of an iron rod 10 in. long. Its outer part was connected to the inside of a subsidiary condenser *C*, the outside of which was fastened to, but insulated from, the steel sphere. This central system was connected to one pair of quadrants of a quadrant electrometer. The sphere and the outside of the condenser *C* were connected to the opposite ends of a high resistance, immersed in oil, which in turn were connected to a high tension battery of storage cells. A point between the terminals of the high resistance was joined to the electrometer case as were also all shields and guard rings.

This arrangement is adapted to measurements of high accuracy as it readily compensates for any effects due to fluctuations of the battery.[7] The potential of the needle of the quadrant electrometer was kept at 100 volts by a battery of high constancy. The system was kept balanced by moving the point of contact between the terminals of the high resistance and by altering the capacity of the variable condenser *C*, until a point was reached where $Q=CV=C'V'$, i.e. where voltage times capacity on one side equals voltage times capacity on the other. If this condition holds, the voltage across the high resistance may be thrown off and on without causing a deflection of the needle when the central system is freed from earth. In the present work such refinement

---

[7] W. F. G. Swann, Phys. Rev. **17**, pp. 240-242, 1921.

was obtained that 1,000 volts could be thrown off and on the resistance without causing a deflection of more than 1 mm of a spot of light reflected from the mirror on the needle, upon a scale 1 meter away. Since a fiber sensitive to 1,000 mm per volt was used, the effect is roughly the same as if the battery were constant to one part in one million.

To facilitate the use of a null method, a potentiometer system D with a voltmeter W was used to keep the deflection at zero while the central system was being charged by the ionization current.

All parts of the system were supported on plugs of sulphur, the material also used to insulate every part of the central system, except as described above. The parts of the insulated system not otherwise shielded were surrounded by shields connected to the electrometer case. Guard rings were used to protect the central system against any leakage from points of high potential; these were, of course, connected to the electromteter case.

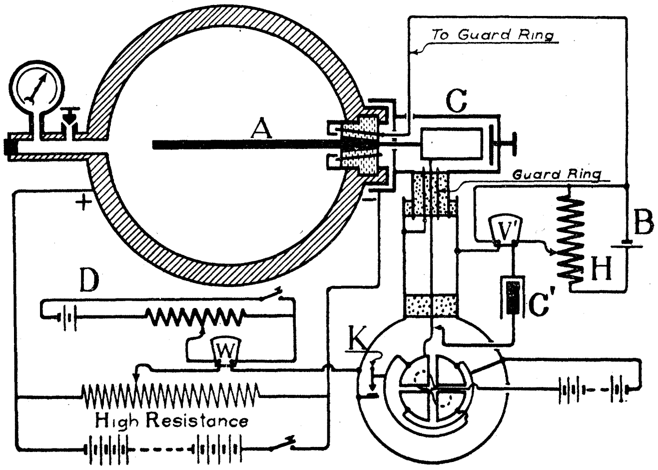

Fig. 1

METHOD AND CALCULATIONS

If V is the alteration in potential recorded by the voltmeter W during the time t, while the electrometer needle is kept at zero deflection, the rate at which charge leaves the central system is kV/t, where k is a constant, and the rate of production of ions per cc in the vessel is $Q = kV/etv$ where v is the volume of the sphere (14.8 liters), and e the elecronic charge (4.8×10^{-10} e.s.u.).

The constant k was determined by means of the device H (Fig. 1). A known voltage V' was put on the outer member of the condenser C'

whose inner member was joined to the central system. The central system was released from the electrometer case, and the capacity of C' was changed by a known amount ΔC, the resulting deflection being brought back to zero by means of the potentiometer system D. The change of reading R of the voltmeter W was noted and the constant k was obtained from the relation $V'\Delta C = kR$.

In obtaining the relation between $V'\Delta C$ and R as described above, a considerable difference was found according as the plus or the minus terminal of the cell B was connected to the outside of the condenser C'. Experiment showed that this was due to a contact potential between the inner and outer cylinders of the standard condenser C'. This was eliminated by taking the mean reading for V' corresponding to equal positive and negative potential applied to C'.

Voltages necessary for practical saturation. It was necessary to ascertain the minimum voltage required to produce any assigned approximation to saturation. The attempt was made to find a point on the voltage-ionization curve where the voltage might be doubled without increasing the ionization current by more than 3 per cent. Thus with 70 atm. air pressure in the sphere, 200 volts produced 61 ions per cc per sec., whereas 500 volts produced 61.5. The change of ionization during the experiment was often greater than this, nevertheless to insure practical saturation a potential of at least 200 volts above this point was used in all the main readings.

General procedure. Pressure in the sphere was obtained from compression tanks and read from a calibrated Bourdon gauge. With the high tension batteries connected across the terminals of the high resistance, the central system was disconnected from the case. After any slight initial kick had subsided, the electrometer spot was brought to its zero mark by means of the system D, and the reading of W was taken. The spot was then kept at zero for four minutes longer and the change in the reading of W was noted. The rate of production of ions per cc was then calculated as indicated above. In view of the fact that the volume of A was about 200 times that of C no correction was necessary on account of the current resulting from ionization in the latter.

All insulation was carefully tested. No leak was detected for periods of 30 minutes under a wide range of temperature and moisture conditions. All the main readings were taken between 7 p.m. and 2 a.m., the interval giving the smallest range of diurnal variation. In any given set of readings the ionization current for the highest pressure was always measured first; the pressure was then released in steps of 2 to 5 atm.

at a time, and the readings taken for each step. All the readings were taken over periods of 4 minutes. No definite relation could be found between the amount of ionization and the time that had elapsed after the pressure was released and before the 4-minute period was begun. The currents over the four-minute periods were very constant; the various values of Q obtained for successive 4 minute periods never differed from each other by more than 2 per cent. It was found necessary to obtain a new balance of the system after every 5 atm. decrease of pressure, as the dielectric constant of the gas in the sphere and, therefore, the capacity of A varied with pressure.[8] Several calibrations of the system were made using various voltages, and various parts of the condenser C'. A mean value of k was used in all calculations since a value of k obtained when the sphere contained 75 atmospheres of air did not differ appreciably from the mean k.

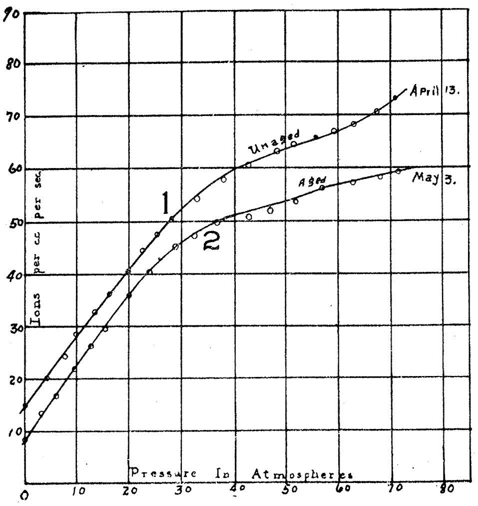

Fig. 2. Results for air, aged and unaged.

RESULTS

Unpurified gases. A number of readings on air at one atmosphere were taken and values ranging between 8.15 and 15 pairs of ions per cc per sec. were obtained. Measurements on ordinary air were made over a range of 70 atmospheres. The results are given by curve 1, Fig. 2.

---

[8] It may be of interest to remark that it is possible to deduce *the relation between dielectric constant and pressure* by observing the change of balance necessary as a result of altering the pressure. The author has measured the dielectric constant of air at various pressures by this method and obtained values agreeing well with those given in Smithsonian Tables.

The air used had been compressed into tanks by the liquid air machine on the previous day and transferred into the sphere three hours before the readings were begun. Curve 2, Fig. 2, obtained 3 weeks later, represents readings on air from the same cylinders. The two curves are parallel up to 27 atm., but the slope of curve 2 at higher pressures is less than that of curve 1. The curves of Fig. 3 give a comparison between the pressure-ionization relations of various gases. All the gases were aged more than 3 weeks to allow most of the radium emanation to decay, but no special effort was made to render them dry and dust free. The slope of the oxygen curve 3 is less than that of air at lower pressures but greater at higher pressures. The nitrogen curve 4 is lower than air and oxygen at 1 atm. but higher and much steeper at higher pressures. The CO_2 curve has a horizontal portion from 61 to 65 atm.

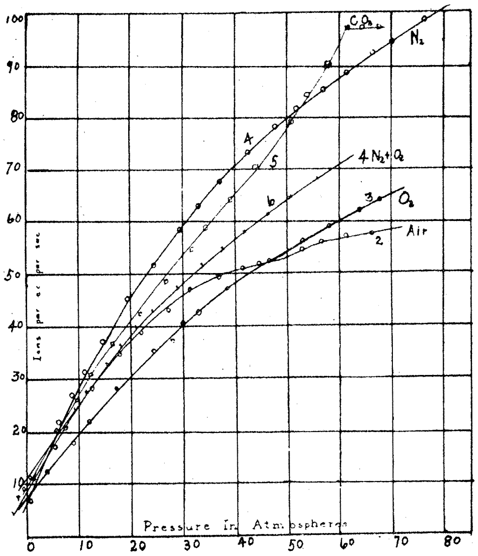

Fig. 3. Results for air, oxygen, nitrogen, CO_2 and $4N_2+O_2$, all at 26°C.

The oxygen curve being lower, and the nitrogen curve being higher than the air curve, one might expect to reproduce the air curve up to 30 atm. by taking readings on a mixture of 4 parts of nitrogen to 1 part of oxygen. A comparison of this artificial air curve 6, with that of ordinary air, curve 2, Fig. 3, shows that the two curves are almost identical up to 27 atmospheres, but the artificial air curve is much steeper at higher pressures. In order to determine whether this deviation of the artificial air curve is due to some radio-active material in the nitrogen, another reading was taken on the same sample of nitrogen 8 days later.

It is known that by far the most important radio-active contamination in a gas is radium emanation, having a half period of 3.8 days. If a gas containing radium emanation is allowed to age, it should show a marked decrease in ionization. A curve obtained from the same sample of gas 8 days later showed no tendency towards a decrease either in initial value or in slope; in fact it was a very close reproduction of curve 4, Fig. 3.

In most curves obtained, it was noticed that, if the curve showed any departure from linearity at pressures below 20 atmospheres and above 1 atmosphere, they would tend to become concave upwards. This tendency was more closely examined, and the results are given in Fig. 4. All curves show a slight tendency towards being concave upwards.

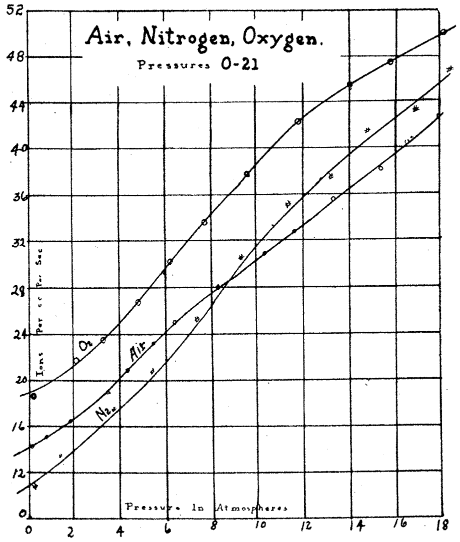

Fig. 4

It might be mentioned at this point that the nitrogen used in this work was purchased from the Cleveland Wire Division of the General Electric Company; it was manufactured by the partial distillation of liquid air, and contained two-thirds of the original amount of argon and all of the neon and helium.

Gases, aged, dried, and dust-free. It was suspected that impurities in gases, especially moisture and dust, would have a large influence upon the pressure-ionization relation. This was definitely investigated by taking readings on gases that had been especially rendered dry and dust-free. The purifying process consisted in passing the gases through a two inch pipe, 3 feet long, filled with glass wool and cotton to collect the dust, and thence through a similar pipe containing P_2O_5 placed in three trays provided with slanting vanes to cause complete circulation of the gases over this drying agent. The curves obtained from gases thus treated are given in Fig. 5. The oxygen and the two air curves show a decided departure from those of the untreated gases in becoming parallel to the pressure axis at about 53 atmospheres, showing that there is no further increase of ionization with pressure. The nitrogen curve is not only much steeper than the others but it also fails to reach a limiting value. The artificial air curve is nearly parallel to the natural air curve up to 52 atmospheres, but it, like the nitrogen curve, does not become horizontal. In order to ascertain whether this exceptional property of the nitrogen curve was due to some peculiar property that this "commercial nitrogen" had acquired during the process of manufacture, the sphere was filled with nitrogen made in the laboratory by absorbing the oxygen from air by means of potassium-pyrogallate. Since the absorption of oxygen had to be carried out at high pressure and on a large scale, a strong iron cylinder of about 7 liters capacity

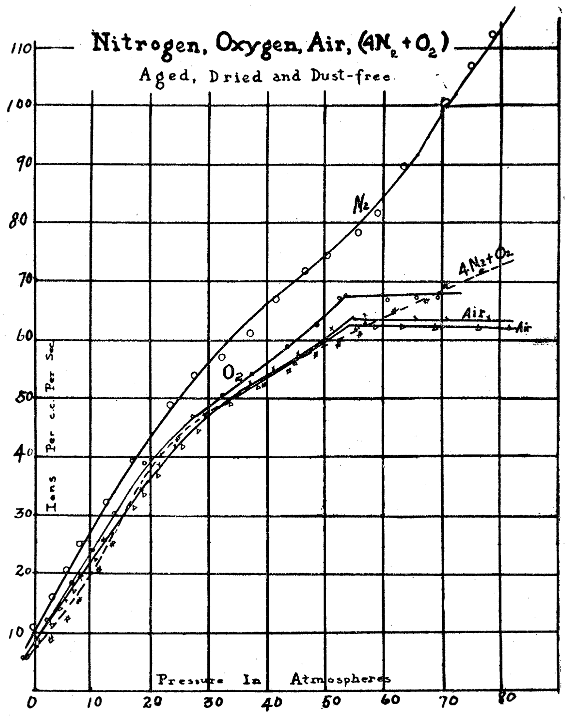

Fig. 5

was nearly filled with potassium pyrogallate, and air was slowly passed through it. Owing to the large amount of heat evolved it was, of course, necessary to cool the cylinder efficiently during the process.

An analysis showed that the nitrogen prepared in the above manner still contained 4 per cent of oxygen. It also contained the original amounts of the inert gases. Readings taken on this gas are shown in Fig. 6. They show the same characteristic features as those obtained from the commercial nitrogen, and fail to show the horizontal portion at the higher pressures. That the existence of this horizontal part in the case of ordinary air is not due, however, to some peculiar property of the oxygen in annihilating the ionization of the nitrogen is borne out by the fact that when nitrogen and oxygen were mixed in the proportions to form air, the air so produced was found to give an ionization curve which is approximately the additive resultant of the ionization curves corresponding to the partial pressures of the two constituents out of which it was composed. Fig. 4 shows this clearly in the case of the untreated gases.

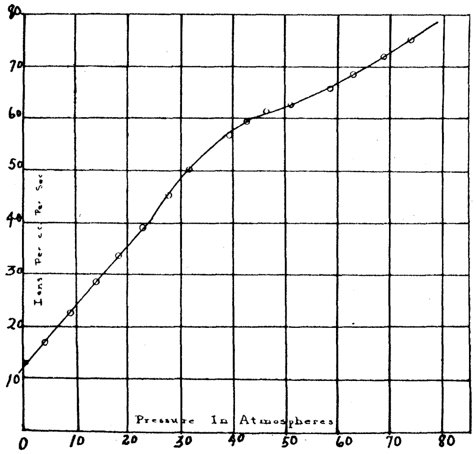

Fig. 6. Results for nitrogen (pyrogallic acid method), aged, dried and dust-free.

It would thus seem that the failure of nitrogen to show the horizontal portion of the curve is due to some peculiarity which it acquires when prepared by either the pyrogallic acid process or by the liquefaction process, and which it retains even when it is again mixed with oxygen. This peculiarity may consist either in the presence of an impurity which is introduced by both methods of preparation, or it may lie in some tendency of the gas to ionize spontaneously for some time after its preparation.

DISCUSSION OF IONIZATION PRESSURE RELATIONS

Information as to the nature of the agency responsible for the residual ionization should be given by the effects of pressure upon the ionization. If the ionization is caused by the easily absorbable alpha and beta types of radiation from the walls of the vessel it would reach a saturation value at one or two atmospheres pressure in a vessel whose linear dimensions are comparable with the range of alpha and soft beta particles at one atmosphere pressure. An increase of pressure would merely shorten the paths of the radiation, already within the vessel, but it would not increase the number of molecules affected by it, hence the ionization would remain constant. This would be the case if the ionization in these experiments were due to the impurities in the walls of the vessel, for the steel would very probably partake of the ionization character of the soil which, according to Eve[9] is mostly of the alpha type.

If one admits the existence of a radiation which is so penetrating that it is not appreciably absorbed in passing through the air in the vessel even at the higher pressures, its ionization in the vessel may be classified under the following heads:

1) Direct ionization of the gas by the primary penetrating radiation.

2) Secondary ionization by the slowly moving electrons emitted from the gas by the primary radiation.

3) Secondary ionization by the rapidly moving electrons which are emitted from the gas, and whose penetration at atmospheric pressure is greater than the linear dimensions of the vessel.

4) Ionization due to emission of electrons from the walls of the vessel by the action of the primary radiation. This case is indistinguishable from that of ionization by electrons emitted from the walls as a result of radioactive impurities.

Ionization under (1) and (2) should vary linearly with pressure until the pressure becomes so high that the primary radiation itself is absorbed in passing through the vessel. Effects resulting from (3) should vary approximately as the square of the pressure if we assume that the ionization along the path of the electrons is uniform and that these paths are not completed within the vessel, for they would vary with the number of molecules per cc and with the number of ions produced by each electron that is shot out by these molecules when affected by the penetrating radiation. This would cause the curve to become concave upwards. The ionization under (4) should obey a linear law until the pressure becomes so high that all the electrons would complete their

---

[9] A. S. Eve, Phil. Mag. **21**, pp. 26-40, 1911.

paths within the vessel. At such pressure there would be no further increase of ionization with pressure. But since the ionizing power of the electron is greatest towards the end of its path, the pressure-ionization curve would become steeper shortly before it would become parallel to the pressure axis. If, therefore, complete parallelism should be reached one would be forced to attribute the ionization mainly to (4) i.e., to the emissions of electrons from the walls of the vessel either directly by radioactive contamination in the materials of the walls or by the primary penetrating radiation, and (2) and (3), i.e., the ionization by the direct and indirect action of the radiation *on* the gas, would have to be ruled out as immeasurably small. From a detailed consideration of these factors, Swann[10] has given reasons for believing that in so far as ionization is due to a radiation of a penetrating type, or to secondary rays emitted by such radiation, the rate of production of ions per cc in the open air at one atmosphere is less than, or at most equal to, the rate of production of ions per cc per atmosphere increase of pressure for that portion of the ionization pressure curve where the slope is least, that is about 1 ion per cc per minute.

Discussion of Experimental Results

From a survey of the pressure ionization curves obtained, one can form the following generalizations:

1) In so far as the curves depart at all from linearity at low pressures they show a tendency toward being concave upwards from 1 up to about 15 atm.[11]

2) From 15 to 27 atm. the variation of the natural ionization with pressure obeys a linear law.

3) From 27 atm. upwards there is a large decrease in slope, in most cases, up to about 35 atm. and then another increase.

4) In the cases of the purified gases examined, with the exception of nitrogen, a saturation value is reached at about 52 atm. Shortly before this point there is a rather rapid increase in ionization with pressure.

The results for air are in very good agreement with those of Dr. Downey.[12] Thus, Dr. Downey finds for the range from one atmosphere

---

[10] W. F. G. Swann, Bull. Nat. Res. Coun., **17**, pp. 65-73, 1922.

[11] This remark does not apply to the region between zero pressure and one atmosphere, for the very considerable magnitude of the ionization at the latter pressure shows that over this range the curve must show a strong concavity downwards. The concavity is very easily accounted for by α particles which are shot out from the walls of the vessel, and which for the most part complete their range within the vessel before the pressure of one atmosphere is attained.

[12] Downey, Phys. Rev., **20**, pp. 186-193, 1922.

pressure to 27 atm. an increase of 1.23 ion and for the range from 27 atm. to about 45 atms an increase of 0.58 ion per cc per second per atmosphere, while the corresponding results obtained by the writer are 1.23 and 0.60. Also Dr. Downey's curve attained a sharp parallelism with the pressure axis at 46 atm. while the writer's curve attains parallelism at 52 atm.

The upward concavity of the curves in the regions of low pressure as exemplified more in detail in Fig. 4 presents interesting fields for speculation. It could be accounted for by the emission of long range electrons by an external gamma radiation, but if such were its origin we might expect the upward concavity to persist to higher pressures, since the air would not even at the highest pressures, cause an appreciable absorption of the gamma rays. A view which has some advantages is the following. Suppose that as a result of radioactive impurity, or through the medium of an external radiation, electrons are emitted from the walls of the vessel with sufficient range to pass across the vessel. As the pressure is raised each of these electrons will complete more and more of its range within the vessel. The portions of the electronic path near the end of the range are however more active than those near the beginning, so that as the ends of the paths become drawn within the vessel the ionization will increase at an increasing rate with the pressure instead of linearly as it would do if the ionization were constant along the path of the electron. The pressure ionization curve will thus show an upward concavity which will persist until the effect of increased ionizing activity near the end of the path of the electron is counterbalanced by the loss of further increase with pressure on the part of those electrons whose range has been completed within the vessel. When this condition is reached the curve will straighten out and will tend to bend over towards the pressure axis.

While it is possible to account along the above lines for some of the properties of the curves for purified gases, the most striking feature of the curves for purified gases, the suddenness of the attainment of parallelism with the pressure axis, is difficult to reconcile with ionization by any external agency.[13] The sharp breaks resemble those in vapor pressure curves and suggest that the effect may be associated with a gas which begins to condense out at a critical pressure. Then there is the marked change in the characteristics of the curves as a result of the presence of moisture or dust, changes which seem inconsistent with the

---

[13] An interesting feature is presented by the fact that the maximum ionization in CO_2 is about 1.4 times that in oxygen. If the ionization were produced by the complete absorption of a radiation from the walls of the vessel, we might expect the ionization of different gases to be inversely proportional to the energies necessary to produce an ion. It may be of significance to note that the ionizations *per unit volume* produced by β or γ rays in CO_2 and oxygen are in the ratio 1.4 to unity.

additive nature of the ionization by external agency. Finally there is the anomalous behaviour of nitrogen which has been extracted from the air, as compared with that of the nitrogen in the air. Many of these features receive a more ready explanation on the assumption of a spontaneous ionization in the gas. However, until further data under varied conditions are available, it is hardly worth while elaborating upon this question.

In conclusion the writer acknowledges with pleasure his gratitude to Professor W. F. G. Swann at whose suggestion and under whose guidance the investigation was made, at the University of Minnesota. Thanks are also due to Professor H. A. Erikson for his interest in the work and to Mr. C. H. Dane for help in the mechanical difficulties of the problem.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
March 12, 1923.[14]

---

[14] The experimental work was completed at the University of Minnesota before June 1922.