FACTORS AFFECTING THE NATURE OF IONS IN AIR.

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Abstract

This paper embodies the results of an attempt to determine some of the conditions which affect the nature of ions in air. It is shown that drying agents like $CaCl_2$ and P_2O_5 are not sufficient for drying purposes and that cooling by means of liquid air is essential for the more complete results. In air dried in this manner the initial positive ion transforms into the final ion very slowly, if at all. Results are also given confirming Tyndall, Grindley and Sheppard, that the ionizing process itself gives rise to impurities affecting the ions. It is shown that the effect of water is modified by the presence of the impurities due to ionization. The requirements essential in any method for the study of ions are given at the close of the paper.

IN GATHERING evidence as to the nature of gaseous ions, it is very necessary to keep in mind the purity of the medium involved. Each ion experiences 10^{10} collisions per second. As an ion can attach itself to a neutral body and in certain cases can transfer its charge to other neutral bodies forming an ion often of different mobility, it is clear that impurities may lead to results which are quite misleading. The object of this paper is to publish some results which throw additional light on this situation. It is necessary that the various effects along this line be clarified before we can hope for success in formulating a theory.
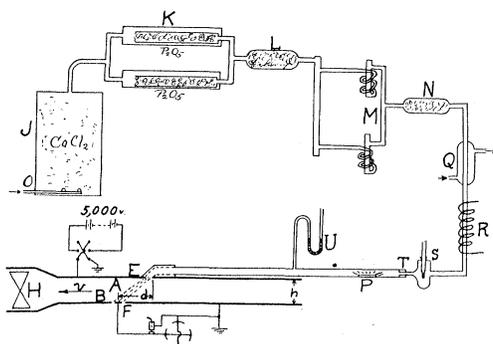

Fig. 1. Diagram of apparatus.

The Effect of Drying the Air

The apparatus used was essentially the same as described in an earlier paper.[1] The arrangement of driers was as shown in Fig. 1.

Air from the compressed air system in the building was passed into the tank J at O. The steel tank J was 40 cm in diameter and 92 cm high and

[1] Erikson, Phys. Rev. **33**, p. 403 (1929).

was nearly filled with granules of $CaCl_2$. The air then passed through two iron tubes K in parallel. In each of these was contained a glass tube 5 cm in diameter and 110 cm long. These glass tubes contained glass-wool and P_2O_5. The air then passed through a glass-wool strainer L, then through two copper coils M in parallel. The copper tubing of each of the coils was 0.6 ¢m in side diameter and 375 cm long wound in 25 turns. These coils could be immersed in liquid air. The air then passed through glass tubing to the glass-wool strainer N. The strainer N quickly became covered with frost so that the air was strained while cold. The air then passed through a glass Liebig condenser Q, than through a glass tube R wound with a nicrome heating ribbon. The current in the heater R was regulated so that the thermometer S registered room temperature. The air dried in this manner then passed into the auxiliary tube TE. The flow of air was regulated so that the pressure of the air in TE was the same as the room pressure as registered by the gauge U containing sulphuric acid. The tube TE was of brass and was 2 cm in diameter and 100 cm long.

A polonium plate was placed at P in the auxiliary tube TE. The polonium P could be placed at different distances from E, where the ions entered the main stream of room air passing through the apparatus due to the fan H. The age of the ions could then be altered by altering the position of P. The speed of the air in the auxiliary tube TE was 160 cm/sec. The speed of the main air stream in the tube ABH was 3300 cm/sec. The difference of potential between the plates AB was of the order of 5000 volts. The time, therefore, required for the ions to pass from E to F was of the order of 0.0003 sec. This short time required for the ionic measurement is very essential on account of the rapid transformation which the ions often undergo. In many cases the above time is amply short, in other cases it is evidently too long. This is true when a small percent of acetylene is present or for example, when the positive ion formed in the impurity due to ionization comes into the presence of water vapor.

Effects Due to Drying the Air

In Fig. 2 are given results showing the effect of the different driers. The polonium was 18 cm back from E and therefore corresponds to an ion-age of about 0.11 sec.

Curve A was obtained when air passed through the auxiliary tube TE directly from the room. The maximum n is due to the initial ions and represents a mobility of 1.87 cm/sec per volt/cm. The maximum m is for the final ion and represents a mobility of 1.36 cm/sec per volt/cm. The relative proportion of these two ions depends upon the age. With the polonium at E, only the initial ion n is obtained, but with the polonium at T, only the final ion m is obtained.

Curve B, Fig. 2, was obtained when the air passing through the auxiliary tube TE had passed through the $CaCl_2$ tank J, only, and then through the coils M without having the coils immersed in liquid air. The other conditions were the same as for A. It is here seen that the initial ions have disappeared, thus giving only the final 1.36 ion m.

Curve C, was for the same conditions as for B but with the P_2O_5 driers K added. It is here seen that there has been no appreciable change from B. A similar test with the P_2O_5 driers alone showed no change from B. Comparing curves B and C with curve A, shows that something favorable to the formation of the final ion had been added. On account of the long closed system this effect can not safely be attributed entirely to the P_2O_5 and $CaCl_2$.
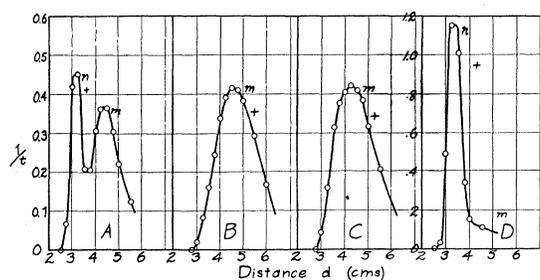
Fig. 2. Showing effect of drying agents.

Curve D, Fig. 2, was obtained when the air passed through the $CaCl_2$ tank J only and then through the coils M immersed in liquid air, the polonium being at 18 cm from E as before. It is here seen that initial ions n, are present and that there is only a trace of the final ions m. A condition now prevails which makes it difficult for the final ions m to form. We are no doubt here dealing with the real initial air ion. The negative ion during the above procedure remained unchanged. Its maximum agrees with that of the initial ion n.
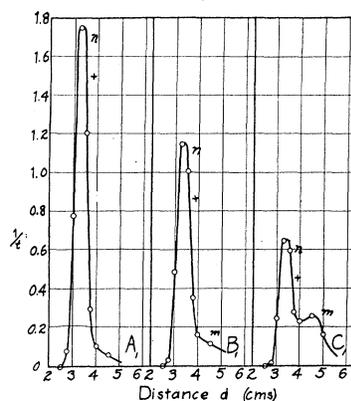
Fig. 3. Showing ageing of initial ion in dry air.

In Fig. 3 are shown results obtained when the air passing through the auxiliary tube TE was dried by passing through the $CaCl_2$ tank J and through the coils M immersed in liquid air. Curve A_1 was obtained when the polonium was at E, giving an ion-age of about 0.02 sec. It is seen that only the initial ion n is present.

Curve B_1 was obtained with the polonium 18 cm from E, giving an ion-age of 0.1 sec. Only a trace of the final ion m is here present.

Curve C_1 was obtained with the polonium 80 cm from E. This corresponds to an ion age of about 0.5 sec. It is here seen that there are less of the ions n and that final ions m have formed. The negative ion during the above remained unchanged. This indicates that in air dried in this manner the positive ion changes into the final ion with age. The transition is, however, much slower than in the case of room air, or in the presence of the impurities added by the $CaCl_2$ or P_2O_5 drying chambers. There is a question if the small change observed is due to a small amount of impurity still remaining in the air, as for example, the impurities due to the ionization.

Effects Due to Drying Nitrogen

A commercial cylinder containing nitrogen of 99 percent purity was connected through a reducing valve to the system immediately before the glass-wool strainer L, Fig. 1. The driers J and K were disconnected. The nitrogen thus passed successively through M, N, Q, R, and S into the auxiliary tube at T.

The results are shown in Fig. 4. Curves A_2 and B_2 are for the negative and positive ions when the polonium was 70 cm from E thus giving ions about 0.4 sec. old. The nitrogen passed through the coils M without liquid-air
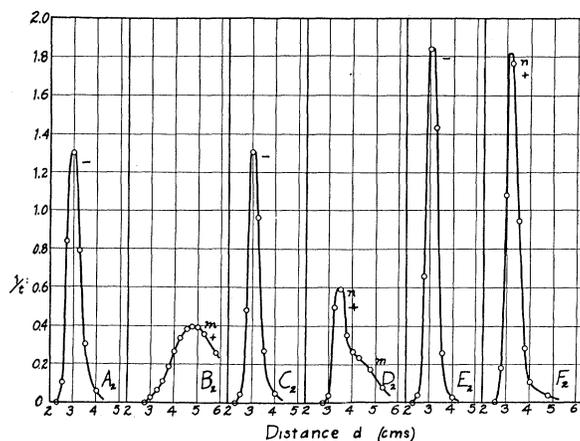

Fig. 4. Showing effect of drying nitrogen.

cooling. It is seen that the normal negative ion, mobility 1.87, is present and that only the final 1.36 positive ion m is present.

Curves C_2 and D_2 are for the negative and positive ions when the nitrogen passed through the coils immersed in liquid air, the polonium being 70 cm from E as before. It is here seen that the negative is unchanged. The positive, however, has changed and now consists primarily of initial 1.87 ions n. There are, however, also a few final 1.36 ions m, comparable to Curve C_1, Fig. 3, which was for the polonium at 80 cm.

Curves E_2 and F_2 were obtained with the polonium close up to E thus giving ions about 0.02 sec. in age. The coils were immersed in liquid air. Here there is present only the normal negative ion and the initial positive ion n, both having the same mobility. The fact that the negative ion is normal in nitrogen at this short age must mean that the free electrons known to exist in nitrogen become attached when entering the main room-air stream at E.

It is thus seen that the results with nitrogen are smilar to the results for air, and that the final ion forms more quickly in nitrogen taken directly from the cylinder without liquid-air drying. With the liquid-air drying, however, it is seen that the initial ion attaches itself with difficulty.

IMPURITIES DUE TO IONIZATION

Tyndall, Grindley and Sheppard[2] suggested that impurities may be formed which are due to the ionizing action of the rays and obtained results indicating this. In order to test this point, a rectangular brass chamber 7.4 cm square and 23 long was inserted between S and T, Fig. 1. No special care was taken to clean the surfaces of the chamber. A metal rod connected to earth extended through this chamber and into the tube TE. This gave a potential
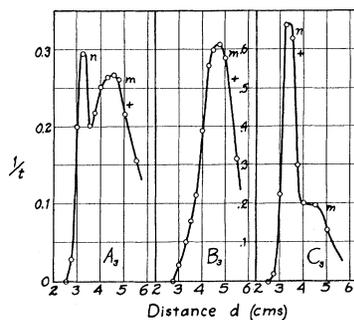

Fig. 5. Showing effect of ionizing air in a metal chamber.

of 5000 volts between the rod and the chamber and tube. A powerful source of beta-rays was introduced into the chamber. The air in the chamber was thus ionized very heavily but the ions were removed by the time the air passed the downstream end of the rod. The polonium was placed a short distance downstream from the end of the rod thus reionizing the air, and giving ions of an age of about 0.3 sec. The air was dried by passing through the $CaCl_2$ tank J and the coils M immersed in liquid air.

The results are shown in Fig. 5. Curves A_3 and B_3 were obtained simultaneously, that is, after a reading for A_3 without the beta-rays had been obtained, the rays were introduced into the chamber and a reading for curve B_3 obtained. This procedure more fully insures identical conditions. It is thus seen that curve A_3, which is for air which had not been ionized, shows the presence of initial ions n, whereas curve B_3, which is for air which

[2] Tyndall, Grindley and Sheppard, Proc. Roy. Soc., **A121,** 185 (1928).

had been ionized, shows that the initial ions have been transformed. It is thus clear that the ionizing process gives rise to something which greatly enhances the transition into the final ion. Presumably this is due to the formation of oxides of nitrogen and ozone.

DIRECT EFFECT OF THE CHAMBER

In Fig. 5, Curve C_3 was obtained under conditions similar to those for curve A_3, but without the chamber. It is here seen that without the chamber, mostly initial positive ions are obtained whereas with the chamber the final ions predominate as shown by curve A_3. The chamber itself had a contaminating effect.

In order to test further the effect of ionization, a glass bulb W, 12 cm in diameter was inserted between S and T, Fig. 1. The upper side had been caved in so as to form a recepticle into which the decayed emanation tubes giving beta-rays could be placed. A rod X connected to earth passed centrally in the auxiliary tube ET, as shown in Fig. 6. The auxiliary tube was at 5000 volts, thus giving a field which removed the ions due to the beta-rays in W from the air before it reached the polonium P, where it was reionized.
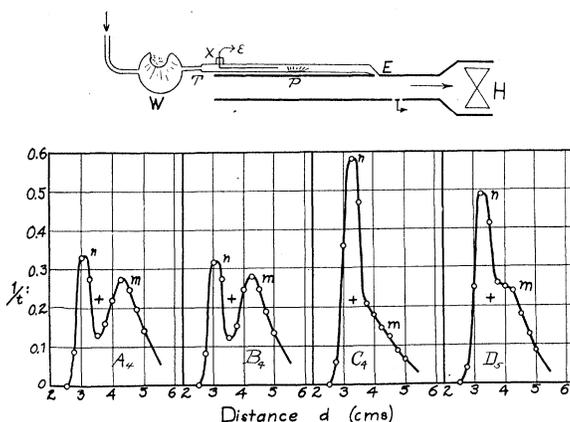

Fig. 6. Showing effect of impurities due to ionization.

The results are shown in Fig. 6. Curve A_4 was obtained when room air entered directly into the vessel W. This shows the presence of initial ions n and final ions m. Curve B_4 was obtained when the room air entering W was heavily ionized by the beta-rays. No appreciable change from A_4 was obtained. n had been slightly lowered and m slightly raised. This unchanged result is apparently due to the water present in the room air which, as will be seen later, has an opposite effect to that of the impurity due to ionization in dry air.

Curve C_4 Fig. 6, was obtained with no rays in W and the air dried by passing through tank J and the coils M immersed in liquid air. It is seen as before that practically all the ions are initial ions n. Curve D_4 was obtained under identical conditions as for C_4 but with the beta-ray tubes in the re-

cepticle in W. It is seen that final ions m have been formed. The day was cold and dry so that the room air passing through the main tube AB, Fig. 1, had a low humidity.

The curves in Fig. 7 were obtained when a glass bulb W, 12 cm in diameter was inserted between S and T, Fig. 1. Through an opening at the top a thin aluminum capsule 2.6 cm in diameter and 5 cm long was inserted. This capsule could be filled with the beta-ray tubes thus ionizing the air in W more heavily than in the case of Fig. 6.

Curves A_5 and B_5 are for room air without beta-rays and with beta-rays in the aluminum capsule. As in A_4 and B_4 in Fig. 6, no appreciable differ-
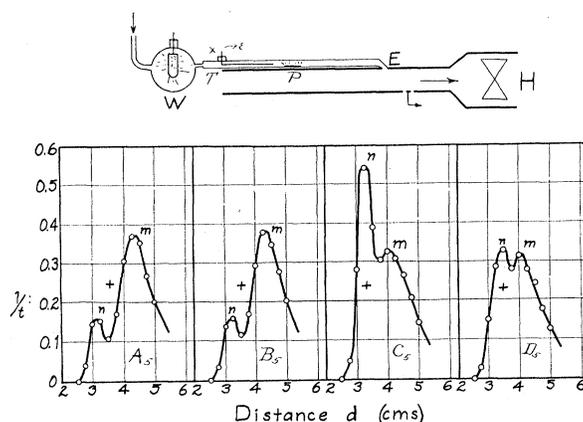

Fig. 7. Showing effect of impurities due to ionization

ence was obtained. Only a slight lowering of n and raising of m was obtained. Curve C_5 was obtained when the air entering W passed through the tank J and the coils M immersed in liquid air. No rays were present in the aluminum capsule in W. It is seen that more final ions m were present there than in the case of C_4, Fig. 6, presumably due to greater contamination by the vessel W. Curve D_5 was obtained with the rays in W, conditions otherwise being the same. It is seen that there is a marked diminution in the number of initital ions similar to D_5 Fig. 6.

It is therefore apparent that impurities are formed in the ionization process which increases the rate of transition of the initial into the final ion.

THE EFFECT OF WATER

In order to test the effect of humidity, distilled water was added to bulb W. The air passing over this evaporated the water.

The results are shown in Fig. 8. Curve A_6 was obtained when the bulb W was dry and the entering air had passed through the tank J and coils M immersed in liquid air. No rays were present in W. Practically only initial ions n are present. Curve B_6 was obtained when distilled water was placed in the bulb W; no rays were present in W. It is seen that final ions m have formed. These are due to the ageing of the initial water ions as was shown in an earlier paper.

Curve C_6 was obtained with the conditions the same as for B_6 except that that the beta-ray bulbs were placed in the receptacle in W. It is seen that fewer final ions m and more of the initial ions n were present than in the case of air containing moisture alone. The final ion m in B_6 is, on the writer's view, a two-molecule water ion. This ion apparently is simplified back to a
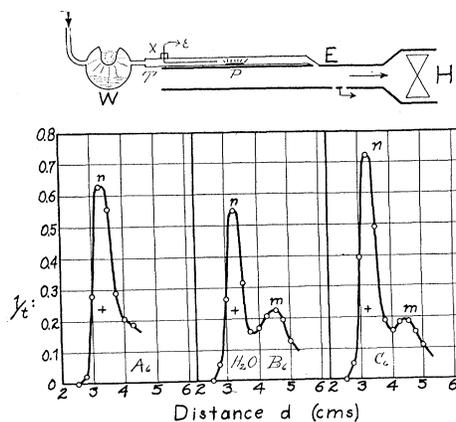

Fig. 8. Showing effect of water and the ionization impurity.

one molecule ion n. The behavior is as if the impurity due to ionization deprives the ion m of a water molecule or that the impurity is molecular and gives up an electron to the ion m and itself becoming a one molecule positive ion n. By means of a modified method it will be possible to clarify this point.

DISCUSSION OF RESULTS

From the above it is apparent that in a study of the air ions it is necessary to work under very definite conditions. In the first place the air must be thoroughly dried. Drying by passing through concentrated H_2SO_4 adds an impurity which alters the ions. From the above, drying agents like $CaCl_2$ and P_2O_5 apparently do the same. Even a closed vessel, especially if of metal, alters the ions. Any drying process must include cooling by means of liquid air and careful straining while the air is cold to remove water dust, etc. When the air has been thoroughly dried, the transition of the initial positive ion into the final positive ion is very slow, being of the order of one second for half-value. This transition even, may be due to traces of impurity still remaining. On the writer's view the initial positive ion is one molecule large. It has the same mobility, namely of the order of 1.87 cm/sec per volt/cm, as the negative air ion which is also one molecule large. The negative ion does not change with time. The initial positive ion, however, does change with time into a definite ion of a lower mobility, of the order of 1.36 cm/sec per volt/cm. This ion is, on the writer's view two molecules large. The rate of transition into the slower ion depends upon the character of the impurity present. If water is added to the dry air the initial air

ion becomes a one molecule water ion (H_2O^+). This is undoubtedly due to the fact that the ionizing potential of H_2O is of the order of 13, where as that of N_2 or O_2 is of the order of 16. This permits an electron to pass from H_2O to N_2^+ or O_2^+. The H_2O^+ ion thus formed and being one molecule large has the same mobility as the N_2^+ or O_2^+ ions and also the same as the N_2^- or O_2^- ions.

The H_2O^+ ion, it was found in an earlier investigation, unites with another molecule forming the slower 1.36 ion. This transition is quite rapid having a half-value period of the order of one-tenth second.

It is apparent from the work of Tyndall, Grindley and Sheppard and from the above results that in air the ionizing process itself gives rise to molecules which will alter the ions. This impurity, which presumably is an oxide of nitrogen, is very rapid in its attack on the initial one-molecule positive air ion, resulting in a positive two-molecule ion of mobility 1.36. This transition is so rapid that even to minimize it introduces a serious experimental difficulty. In fact, it practically bars the use of a closed vessel method. The ions will have to be drawn out of the ionized region in a time which is shorter than the time necessary for the impurity to act. Care will then also have to be exercised that the air which was ionized does not itself enter the measuring vessel.

As seen above if water is also present the situation is further complicated. The ionizing impurity and the water both attack the initial air ion and the ions so formed, have themselves an interaction.

It thus seems that any method in order to give clarifying results must accomplish the following: 1. It must remove the ions from the ionized regions in an interval not to exceed 0.001 sec after formation; 2. It must not admit any of the air from the ionized region into the measuring part; 3. It must have a region through which the ions pass and to which definite impurities may be added for varying intervals of time; 4. It must permit the ions to be removed from this region into a region of definite character such as pure dry air; 5. It must permit the measurement to be made in a definite interval preferably not in excess of 0.001 sec. The writer has begun the use of a method embodying these features.