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ION MOBILITIES USING THE ERIKSON METHOD ON GASES OF CONTROLLED PURITY

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Abstract

Measurements of mobilities of ions in air and air mixed with known quantities of other gases, were made with the Erikson air-blast method under conditions in which the nature of the purity of the gas could be reasonably controlled. The results show that there is no ageing effect as observed by Erikson in air dried over P_2O_5 and liquid air, or even in air passed slowly over $CaCl_2$. In these two cases the normal positive and negative ionic mobilities are observed. If air from the room of 60 percent or 90 percent relative humidity at 20°C, is used the well-known ageing effects of Erikson are observed. With mixtures of 5 percent and 25 percent HCl no ageing effects are observed and the mobilities show the same general behavior observed by Loeb with the A. C. method. With 5 percent NH_3 the positive ion has the same mobility as the negative ion, but at ages over about 0.01 seconds both negative and positive ions show an apparent ageing, the positive ion going over to the usual value observed while the negative ion forms an ion having a mobility between the old and new positive ions. In pure C_2H_2 positive and negative mobilities were observed in agreement with those found by Loeb and Du Sault and Wahlin while in dry air with 5 percent C_2H_2 normal air mobilities were observed with no ageing effect. It is concluded that the ageing of positive ions in dry air in general proceeds very much more rapidly than Erikson assumes and possibly consists in the attachment of the initial positive ion to a bulky molecule of some impurity present. Water vapor and NH_3 inhibit this action either by forming groups which delay attachment to molecules of impurities present, or by removing the latter. Thus Erikson's ageing effects do not appear to be the true ageing but rather retarded ageing effects due to the action of water vapor or other substances.

Introduction

THE gas ion mobility determinations of Todd,[1] Wahlin,[2] Tyndall and Grindley[3] and Erikson[4,5] have shown the importance of considering the influence of the age of an ion on its mobility. Of the various methods proposed for investigating the change of mobility with age that of Erikson seems to be the simplest and enables one to operate without changing the pressure of the gas. The greatest draw-back in Erikson's method was the fact that in general he was constrained to work with either air taken directly from the room in a continuous stream or else with a continuous flow of gases from a generator or tank. The recent work of Loeb and others on mixtures has shown that the control of the purity of the gas is of great importance in the study of mobilities. In an attempt better to control the purity of the gas and to extend the mobility measurements of Erikson to mixtures of known constitution the apparatus of Erikson was modified as shown below.

[1] G. W. Todd, Phil. Mag. **25**, 163 (1913).

[2] H. B. Wahlin, Phys. Rev. **20**, 257 (1922).

[3] Tyndall and Grindley, Proc. Roy. Soc. **110A**, 341 (1926).

[4] H. A. Erikson, Phys. Rev. **28**, 372 (1926).

[5] H. A. Erikson, Phys. Rev. **30**, 339 (1927).

Description of Apparatus and Method

The arrangement of the apparatus was as shown in Fig. 1. The galvanized iron pipe containing the fan F and the condenser plates A and B could be evacuated by sealing at S and around the shaft of the motor M during exhaustion. Pure gas was then introduced, bringing the pressure in the blast pipe up to atmospheric pressure in all the gases investigated. On starting the synchronous motor M a uniform blast of gas of velocity about $1{,}270 \pm 60$ cm/sec. was forced between the condenser plates A-B. The space between the top and bottom plates of the condenser was divided into five exactly similar channels by vanes 8 mm apart as shown. On the bottom of the uppermost channel and 2 mm below the plate A was placed a very thin moveable copper plate which had been electroplated with polonium. The vanes were each 40 cm long, thus producing a nearly uniform gas velocity at all points of the gas stream above the collector plate at D. The cross sectional dimensions of the gas blast between A and B were 5 cm wide by 3.2 cm high. On passing over the polonium some of the gas was ionized by alpha-particle bombardment. A thin layer, not exceeding 2 mm vertical dimension, of these ions was thus subjected to the force of the electric field A-B, on emergence from the ionization chamber *Po*. The uppermost channel containing the polonium, and the plate A were kept at the same potential. The polonium could be placed at some chosen point relative to the down-stream end of the vanes, and this point determined the age of the ion whose mobility was being measured. By moving the entire group of vanes horizontally the down-stream distance D traversed by the ions, before being caught by the electrometer collector plate, was noted. Thus, when the distances D as abscissa are plotted against the current to the electrometer, the ordinate maximum (or maxima) of the curve is at a distance D which is inversely proportional to the mobility, according to the equation derived by Erikson.[6] In a large number of his investigations Erikson used the same

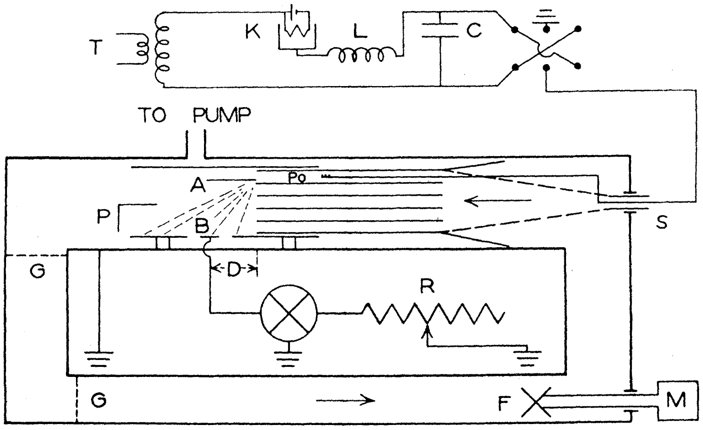

Fig. 1. Arrangement of apparatus.

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[6] H. A. Erikson, Phys. Rev. **20**, 117 (1922).

method of obtaining his curves. The earthed gauzes G prevented most uncollected ions from getting back to the measuring chamber, although it is very unlikely that ions were able to pass through the 40 cm long vanes between which there was a potential gradient, due to leakage over the hard rubber sides of the condenser, without being caught.

The exact linearity of the field across these plates is questionable. If the leakage across the ebonite insulators was large compared to the irregular ionization leakage, the field should have been nearly linear. It had been intended to maintain these plates at uniform potentials relative to each other but difficulties introduced by bringing in the leads in the confined space made this inadvisable. The effect of non-linearity of the field between the plates would be most serious when the plates approached the electrometer collector plate for small values of D. In all measurements D exceeded one centimeter, and it was only within this range that evidence of irregularity was obtained as indicated by the electrometer. In most of Erikson's measurements no precautions were taken to maintain linearity of the field.

The gas velocity was found by the method of averaging, using a Pitot tube and differential inclined manometer as developed by Weeks.[7] It was found that Pitot tube readings were the same for all the gases tested except for 25 percent HCl-75 percent air (discussed in connection with Fig. 9.) This constancy of gas velocity is not surprising on considering the fact that air was the main constituent in all cases except the case of pure acetylene, and the densities of the gases employed were nearly equal. The impact pressure formula $p = 1/2\ mv^2$, where p is the impact pressure of the gas, v the velocity, and m the density, gave as a velocity for all the gases (with the one exception mentioned above) 1270 cm/sec. The condenser potential (usually 3350 volts) was obtained by using a transformer T and kenetron K, and reading the potential on a Kelvin Electrostatic voltmeter. A large capacity C was in parallel with the condenser A-B. A high inductance L was in series with one side of the condenser C. These precautions were taken to obtain the constant high potential. The plate B, excepting the electrometer collector plate of dimensions 4.6 cm × 1.5 mm, was earthed at all times. The Cambridge type of Dolezalek electrometer, of sensitivity 320 mm per volt at one meter scale distance, was arranged to give steady readings proportional to the ionic current. This was accomplished by earthing one pair of quadrants and connecting the collecting pair of quadrants through a high resistance xylene-ethyl alcohol resistance R to earth.

The absolute value of the mobility was computed from the equation[6]

$$k = hHv/VD$$

where H is the distance between the plates A, B; V the potential difference between plates A, B; v the mass velocity of gas; k the mobility of ion; h the average distance the ions travel at right angles to the stream of air; D the downstream distance corresponding to peak of mobility curve. The mobility therefore varies inversely as the downstream distance D. Therefore

$$k_1/k_2 = D_2/D_1$$

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[7] W. S. Weeks, Ventilation of Mines.

The polonium was set consecutively at distances of 0, 10, 20, 30 and 40 cm from the downstream end of the ionization chamber. The ages of the ions on emergence into the field were thus approximately 0.0, 0.0075, 0.0150, 0.0225, 0.0300 seconds. The time taken for the ion to travel from A to B, assuming the negative air ion to have a mobility 2.2, and the mobility to be independent of field strength,[8,9] is about 0.0014 sec. The positive and negative ion mobilities were determined for each of the five positions of the polonium. In the graphs (except Fig. 3), the two curves at extreme left are for the ions of the least age, the age increasing in the succeeding curves.

INSTRUMENTAL CONTAMINATION

By the method above outlined the gas to be studied could be introduced into the tube at the beginning of a run and the measurement could be made on the same sample of the gas for all the curves. There may have been contamination of the gas from the walls of the container and from the lubricating oil of the fan. As regards the latter, the motor was outside of the chamber and two drops of distilled Cenco pump oil were applied to the outside edge of the bearing during a week's work. The joint was sufficiently tight under these conditions so that no oil was discovered inside the chamber after a run. While filling the chamber with the given gas, the bearing of the motor shaft was made gas tight with Universal wax, which was removed as soon as the chamber was filled to atmospheric pressure, thus danger of contamination was reduced to a minimum in this respect. As regards vapors given off by the walls the problem was more difficult, particularly after the use of such reactive gases as HCl. The only recourse under these conditions was the neutralization of the gases by repeated washing with some gas which removed it, e.g., NH_3 in the case of HCl, and the evacuation to 0.1 mm or less and refilling with dry air over liquid air until normal mobilities in air had been obtained. In general, three or four repetitions of this treatment sufficed to give satisfactory results. The pumping to 0.1 mm or less on the average was, as a rule, continued for three hours using two Cenco pumps in connection with a Jones single stage mercury vapor pump through liquid air traps. Measurements were carried on in the following gases: Air dried over P_2O_5 and liquid air, air dried over $CaCl_2$ alone, undried but filtered air from room, air saturated with water vapor at about 16° C, HCl-air mixtures containing 5 percent and 25 percent HCl, 5 percent NH_3 mixed with air, and pure C_2H_2 and 5 percent acetylene and air.

EXPERIMENTAL RESULTS

Dry air. The apparatus was exhausted to 0.1 mm or less and filled with dry air, re-exhausted and filled to atmospheric pressure. A series of readings was taken. These are shown in Fig. 2. The air was dried by passing over glass wool, soda lime, calcium chloride, phosphorus pentoxide and two liquid air traps in series. Contrary to the results of Erikson,[5] Tyndall and Grindley,[3] Wahlin,[2] and Nolan and Harris,[10] only one positive ion and one negative ion

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[8] L. B. Loeb, Phys. Rev. **8**, 633 (1916).

[9] L. B. Loeb, Jour. Franklin Inst. **196**, 537 (1923).

[10] Nolan and Harris, Proc. Roy. Irish Acad. **36**, 31 (1922).

were found. The writer places great confidence in the above result as a set of the dry air measurements was made on at least ten samples of air. The mobilities as calculated for each of the ions in Fig. 2, are:

$$k_- = \frac{hHv}{VD} = \frac{3.1 \times 3.2 \times 1{,}270}{3{,}350 \times 1.9} = 1.98 \text{ cm/sec per volt/cm}$$

$$k_+ = \frac{hHv}{VD} = \frac{3.1 \times 3.2 \times 1{,}270}{3{,}350 \times 2.6} = 1.45 \text{ cm/sec. per volt/cm.}$$

These values were obtained from the peaks of the curves of this set and represent an average value of the mobility. The method is entirely unsuited to any accurate determination of the absolute mobility inasmuch as irregularities of the field, turbulence, and uncertainties in the true value of the average wind velocity are of such a magnitude as to make one have little confidence in the absolute numerical values. The error introduced by the effects of varying high fields on the mobility are eliminated by the method used. The *relative* values should be nearly correct for the differently aged ions in the different gases, except for whatever errors were introduced by the irregularities in the field from the plates with changing values of D. The absolute values obtained are slightly higher (10 percent) than those obtained by Erikson in such a way as to be more in accord with the new absolute mobilities in air observed by Loeb,[9] Kovarik,[11] and Tyndall and Phillips. The curves shown in Fig. 2 are those obtained on a single sample of air and coincide with all the others taken within 5 percent. The value of mobilities computed from different samples of dry air are the same within 5 percent. However, the mobility of the negative ion in dry air, with $D = 1.8$ cm, is in all cases a little greater (5 percent) than for greater values of D. This is doubtless due to the irregularities of the field between the plates mentioned before.

It is noted that the positive ion curves are distinctly broader than the negative peaks in Fig. 2, though the areas are about equal. The question arises as to whether this difference is due to an actually greater spread of the mobilities of the positive ions than of the negative ions. However, the spreading of the beam is closely correlated with the downstream distance D. To see whether a positive ion having its D equal to that of the negative ion has approximately the same width, measurements were made on the positive ions using a potential of 4,580 volts. The results may be seen in Fig. 3 in which all the curves are for positive ions, plotted under the negative ions of Fig. 2, to whose downstream distance D, they correspond. The total number of positive ions was closely equal to that of the negative ions, so that the positive curves have been slightly elongated in order to plot them to the same scale of ordinates. On the whole it is seen that the width of the positive ion peaks under these conditions are not greatly different from those of the negative ions for the same down-stream distance D. They are slightly broader at the base, an effect which possibly could be accounted for by the

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[11] A. F. Kovarik, Phys. Rev. **30**, 415 (1910).

irregularities at the higher fields. It is in any case unlikely that these differences are due to any great difference in homogeneity in the nature of the positive ions, relative to the negative ions, though the slight residual differences might be accounted for on some such basis. It appears from these results that there is only one ion of each sign in the air of these measurements, after an interval of 0.0014 seconds.

Moderately dry air. Fig. 4 shows the measurements on air from the room which had slowly been passed through a meter long tube of calcium chloride. The results are analogous to those of the carefully dried air.

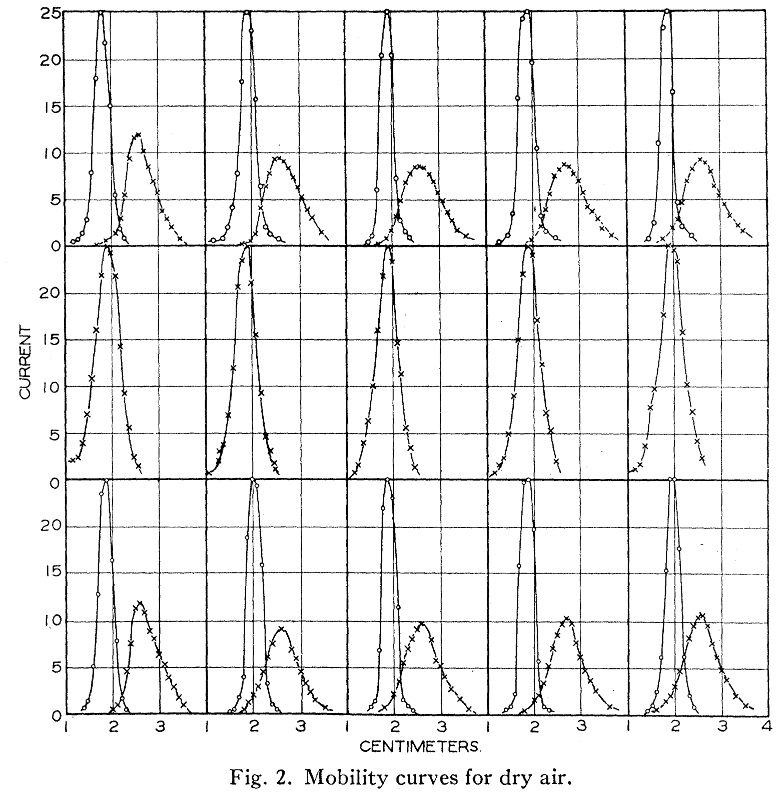


Fig. 2. Mobility curves for dry air.
Fig. 3. Showing effect of increased voltage on positive ion curve.
Fig. 4. Mobility curves for moderately dry air.

Moist air. Air from the room of relative humidity 60 percent at 20°C was introduced into the evacuated chamber. The results are shown in Fig. 5. It is seen that with this air the initial positive ion has the same mobility as the negative, in complete accord with the results of Erikson. As the ions of increased age were measured it is seen that the initial positive ion gradually changes over into a final positive ion, the negative ion remaining unchanged. In this case the mobilities of the initial negative and positive ions were 1.80, and the mobility of the final positive ion was 1.40. Erikson finds the mobility for what he terms dry air from the room to be 1.87 and 1.41, which agree with the values in what is here termed moist air. Wahlin[2] found the time of transformation to be about 0.01 sec., while Erikson found the transformation time to the final positive ion to be 0.02 sec. Fig. 5 shows that there are nearly equal quantities of the two positive ions at an age of 0.03 sec.

Air saturated with water vapor. The air was introduced from the room after passing through a tube of cotton wool soaked in water cooled to 16°C, corresponding to a relative humidity of about 90 percent at the temperature of measurement, 20°C. It was thought advisable not to use 100 percent relative humidity as the latter would result in the deposition of water vapor on the insulation. The results for very wet air are seen in Fig. 6 and do not differ materially from Fig. 5, the mobilities for the initial ions being 1.80 and 1.4 for the aged positive ions.

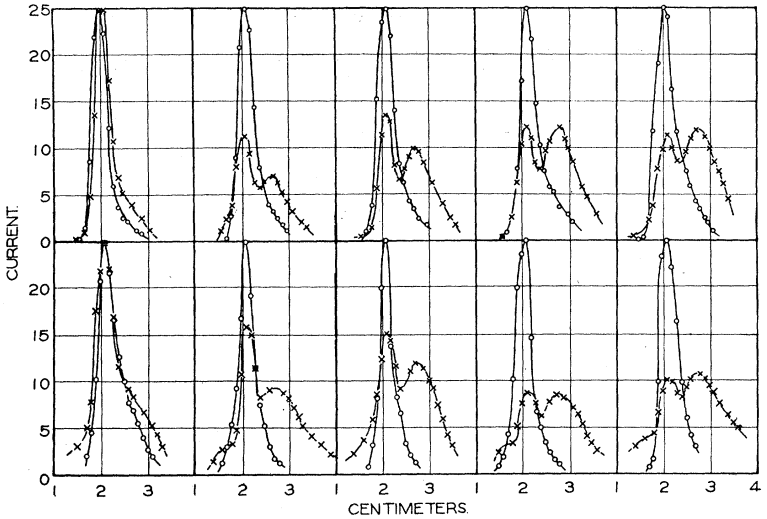
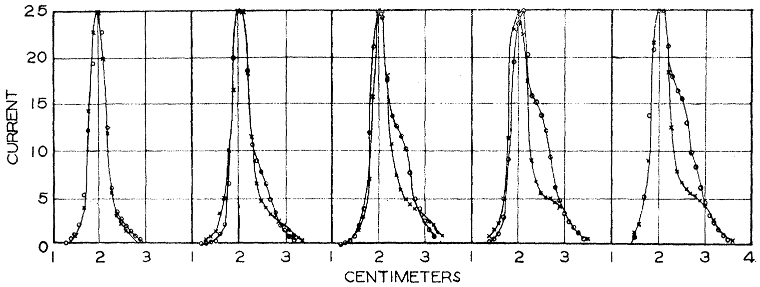


Fig. 5. Mobilities in air of 60 percent humidity.
Fig. 6. Mobilities in air of 90 percent humidity.

On comparing the widths of curves and depths of the depressions in Fig. 5 with those of Erikson[5] one may estimate that the present apparatus has a resolving power about 50 percent higher than that of Erikson's apparatus.

Effect of 5 percent ammonia. The result is shown in Fig. 7. The ammonia was obtained from a commercial cylinder supplied by the Power Specialities Co., San Francisco. It was freed of dust and dried by passing through glass wool and two liquid air traps in series cooled to −30°C, then frozen in a liquid air trap. The frozen ammonia was then allowed to evaporate into the apparatus to the requisite pressure. Air, carefully dried and purified as described for Fig. 2 was introduced, bringing the pressure to atmospheric. An analysis of the ammonia by the chemistry department showed no amines to be present. It is seen that the NH_3 caused the positive ion to acquire an increased mobility equal (within experimental error) to that of the negative.

This effect was first observed by Loeb[12] and was also reported by Erikson using this method, the values of the mobilities being 1.84 for both ions in this case. These mobilities are slightly less than for dry air. Erikson[6] found a very small peak in the positive NH_3-air curve corresponding to a mobility of the slower positive ion in moist air. The writer found an indication of a second positive peak at the same place. This peak is hardly noticeable in Fig. 7 but is very evident in the original large scale graph. Erikson could not give the quantity of ammonia used in his experiment owing to his method, thus making an exact comparison difficult. To the writer's knowledge the gradual broadening of the negative curve on the down-stream side for ions of increasing ages has never been observed before. It may indicate the formation of a negative complex of lower mobility similar to that of the positive ion in moist air, and of mobility about 1.6. Before hazarding an explanation



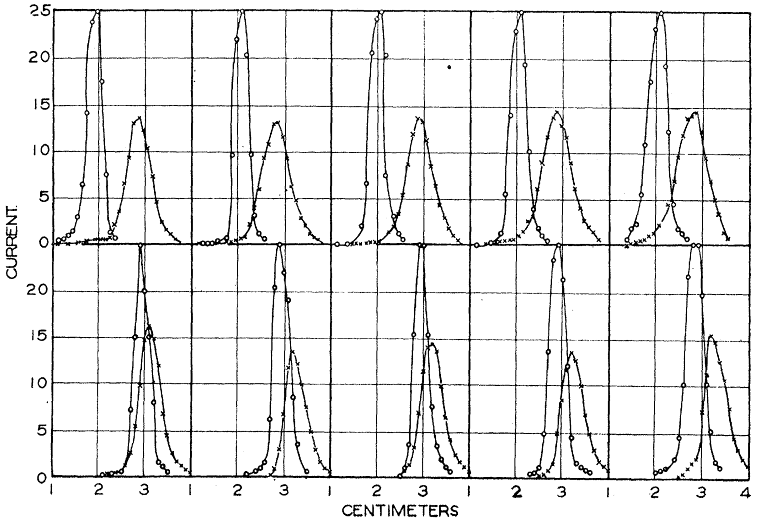


Fig. 7. Showing effect of adding 5 percent ammonia to air.
Fig. 8. Effect of adding 5 percent HCl to air.
Fig. 9. Effect of adding 25 percent HCl to air.

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[12] L. B. Loeb, Proc. Nat. Acad. Sci. **12,** 677 (1926).

it is necessary to make determinations with widely varying percentages of ammonia prepared from C. P. chemicals.

Effect of 5 percent HCl. The HCl was prepared by dropping Baker's C.P. concentrated H_2SO_4 on Baker's C.P. NaCl. It was then passed through P_2O_5, through two liquid air traps in series surrounded by an ethyl alcohol bath cooled to $-75°C$, which removed the water vapor. The HCl then passed on and was frozen in a third liquid air trap from which it was evaporated into the apparatus to the requisite pressure. Fig. 8 shows the results. There was only one kind of ion of each sign. The mobility for both positive and negative ion was distinctly less than in dry air, thus showing the clustering effect of HCl as found by Loeb.[13] The mobilities are 1.8 for negative and 1.35 for positive ions while Loeb, using another method, found the values 1.6 and 1.25 respectively.

Effect of 25 percent HCl. The HCl and air in this case were introduced exactly as in the case of 5 percent HCl. The result is shown in Fig. 9. It is seen that the positive and negative ion mobilities are almost equal, the negative mobility being the higher. The values are $k_- = 1.31$, $k_+ = 1.21$. Using the Rutherford-Franck[14,15] method and with gold plated electrodes Loeb[13] found the positive and negative mobilites to be $k_- = k_+ = 1.0$. The discrepancy between the absolute values of the two results lies within the relative inaccuracy of the two methods, and might be due to contact potentials in this apparatus. Fig. 9 is not immediately comparable to Fig. 8 as the gas velocity was found to be slightly higher for the same fan speed in the case of 25 percent HCl. This was the only appreciable variation from a constant gas velocity throughout this entire series of experiments.

Effect of 5 percent acetylene. The results are shown in Fig. 10. No. C.P. calcium carbide was listed in the chemical supply catalogs. The acetylene was therefore prepared by dropping distilled water on carbide from the National Carbide Company, carbide of the highest purity obtainable. The acetylene was passed through concentrated sulfuric acid, phosphorus pentoxide, two liquid air traps cooled to $-70°C$, and then frozen in three liquid air traps in series to give sufficient gas. The solid acetylene was next allowed to evaporate into the apparatus to the requisite pressure. The additional amount of dry air necessary to bring the experimental gas to atmospheric pressure was then introduced. Only *one* negative and *one* positive ion were found. Erikson had found a positive ion of the same mobility as the negative ion, when the acetylene remained in the air only a short time before ion formation and measurement. In Erikson's[5] latest work the acetylene was allowed to remain in the air a relatively longer time and his results in the latter case were identical with those of Fig. 10. The mobilities are $k_- = 1.87$ and $k_+ = 1.35$.

Acetylene 100 percent. Fig. 10 shows the result of using acetylene prepared exactly as above. It was found that the positive and negative acetylene ions

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[13] L. B. Loeb, Proc. Nat. Acad. Sci. **12**, 35–41 (1926).

[14] J. Franck, Ann. D. Physik **31**, 972 (1906).

[15] Rutherford, Proc. Camb. Phil. Soc. **XI**, (1898).

had nearly the same mobility, which looks strikingly similar to the results found by Erikson for ionized C_2H_2 measured in air, except that the value of the mobility here is much less. As the distance D of Fig. 1 could be varied only from 0 to 4.5 cm, the voltage used was increased to 5600 to make possible the measurement. The absolute mobilities were found to be $k_- = 0.835$, $k_+ = 0.78$. These agree quite well with the results of Loeb and Du Sault[16] and Wahlin[17] using different methods.

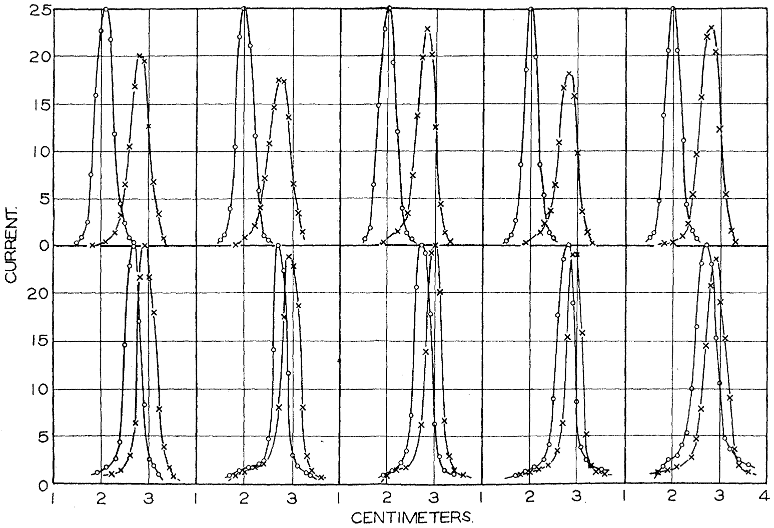

Fig. 10. Curves for 5 percent acetylene in air.
Fig. 11. Showing mobilities in pure acetylene.

Discussion of Results and Conclusions

In a recent article on the nature of gaseous ions Loeb[18] has shown from a study of mobilities in mixtures of gases that three types of behavior of the mobilities seem to occur. The first of these types occurs in mixtures of gases such as, H_2, CO_2, Air, and C_2H_2; and indicates that if the ion is a cluster it is one which does not change its constitution as the composition of the mixture is varied. The second type of behavior is exhibited by mixtures in which, while the nature of the ion is not essentially changed by the presence of one of the constituents of the mixture, the ion shows the influence of both types of gases in a way which indicates a labile or statistical[19] clustering favoring the more strongly attracted gas. This is shown by the case of the negative ion in NH_3-H_2 mixtures, SO_2-H_2 mixtures, and by the positive ions in Cl_2-O_2 mixtures. The third type of behavior can only be ascribed to the preferential clustering, or addition, of one of the gaseous constituents, even when present in small traces, to one or both ions. This occurs for the positive ion in mixtures of NH_3, ether, or SO_2 with H_2 or air; and for HCl and H_2O

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[16] Loeb and Du Sault, Proc. Nat. Acad. Sci. **13**, 510 (1927).

[17] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).

[18] L. B. Loeb, Phys. Rev. **32**, 81 (1928).

[19] L. B. Loeb, Kinetic Theory of Gases, p. 472.

with air for both ions; and for Cl_2 and Br_2 in air and H_2 for negative ions. The clustering of this type depends on the chemical constitution of the gas and the sign of the charge on the ion.

One is therefore confronted with gases showing a specific cluster formation, characteristic of the gas and sign of the charge; with others where the ion is of a more labile type; and with gases where the existence of a specific cluster formation characteristic of each gas is highly doubtful. It is now of interest to see to what conclusion the ageing experiments described in this paper lead one on the basis of these facts. In HCl for both ions and NH_3 for positive ions the formation of ion complexes with traces of these gases is definitely established from the mixture studies of Loeb. In the present experiment in HCl-Air mixtures the observed mobilities indicate that the clustering effects have taken place (lowering of positive and negative mobilities in HCl and increase of positive mobility in NH_3), in a time period of less than 0.0014 seconds which is the shortest period measured in the present work. In dry air again the low mobility positive ion has formed in less than the 0.0014 seconds of the shortest timed mobility measurement. The addition of water vapor in appreciable amounts apparently produces a retarding effect on the formation of the low mobility positive ion, as does the presence of NH_3 in a much greater measure. Thus what Erikson observed and interpreted as an ageing effect was in reality an ageing effect. It was, however, not a normal one as he supposed but a retarded ageing of the positive ion due to the presence of water vapor. This gives at once a plausible reason for the difference in the rates of formation of the slow ion reported here (0.03 seconds), and those of Erikson (0.02 seconds) which may be easily ascribed to the presence of a smaller amount of the inhibiting water vapor in the case of Erikson's work than in the present case. This action of water vapor in retarding the ageing of the positive ion was first reported by Tyndall and Grindley[3] although the method which they employed was of such a nature that it did not permit of great certainty. The conclusion of Tyndall and Grindley has also been borne out by the work of Leila Valasek[20] in Erikson's laboratory using a different method. However, the striking conclusions from the present experiments which go much farther, are that ageing (and possibly cluster formation) occurs in all these gases under the experimental conditions in much shorter time intervals than usually supposed, and that the ageing observed by Erikson is not the real ageing but a retarded effect due to the action of water vapor.

As to how water vapor acts to retard ageing one can at present only conjecture. As it may stimulate further thought on the subject, one might venture to speculate to a slight extent. One may first ask to what ageing could be due. The specific electrochemical effects of certain gases on ions observed in these mixture studies enable one to hazard a reasonable supposition that in gases like CO_2, N_2, O_2 and H_2 where the dipole moments are small and large cluster aggregates are unlikely, it is possible that positive and negative ions have nearly the same mobilities. Again the presence of certain impurities in these gases which go preferentially to the positive ion forming

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[20] L. M. Valasek, Phys. Rev. **29**, 542 (1927).

a stable and large group is not unlikely. When one considers that a "chemically pure" gas (less than 1 part in 10^5 of impurity) still can have 10^{14} molecules of impurity per cm^3 in it, and that an ion in a gas makes some 10^6 or 10^7 impacts in 0.001 second, the chance of picking up an impurity is relatively great. Now experiment has shown that the positive ion is exceedingly sensitive to NH_3 and still more so to ethyl ether, the latter forming a more stable and slower positive ion than NH_3. Thus it is quite justifiable to assume that the initial positive ion in air has the same mobility as the negative ion, but that in dry air* it quickly adds another bulky molecule present as an impurity and drops in mobility.

Addition of water vapor could thus conceivably act in one of two ways, by either forming an H_2O positive ion of a nature that makes picking up the larger impurity less probable, or by reducing the number of molecules of impurity by combining with such molecules to make an inactive group, e.g. with N_2O_4 to make HNO_3. Either means is equally possible. In the case of NH_3 the existence of the faster positive ion and the much decreased formation of the slow positive ions inclines one to the notion that the NH_3 complex with the positive ion acts to decrease the chance of the positive ion picking up a bulkier molecule of impurity even though the latter is more active. The field, however, needs much more quantitative study before such hypotheses can be seriously considered.

It is interesting to note that the mobilities in pure acetylene with this method agree with those of Loeb and Du Sault[16] and Wahlin.[17] It is also interesting to note that the presence of 3 percent of C_2H_2 in air does not produce the appearance of the initial positive ion as observed by Erikson[4] in an earlier paper, but yields only the aged ion with no evidence of an ageing effect. This is similar to the case of pure dry air. This is in agreement with Erikson's later work, and it is thus possible that the earlier anomalous result is a spurious one which is not a characteristic of C_2H_2.

The fact that the Erikson ageing effect is confined to moist air explains why Loeb and Cravath[18] were unable to detect this in dry air using the A.C. method. It also strengthens the suggestion made by Loeb, as Wahlin[21] in his work used dry air, that the change in mobility at low pressures for positive ions as observed by Wahlin was not in reality an ageing effect but was due to the changes produced by variation of the auxiliary fields.

In conclusion, I wish to thank Professor L. B. Loeb, at whose suggestion this problem was undertaken, for his advice and interest during the progress of the experiments.

Physical Laboratory,
University of California,
Berkeley, California,
August 15, 1928.

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* It is possible that impurities present in the closed chamber account for the more rapid ageing than previously observed. However the presumption would be that such air is purer than that drawn from the atmosphere of a physical laboratory without drying or liquid air. Inasmuch as all previously studied gases have never been completely dried the measurements above are very significant.