Mobility Experiments in Gaseous Mixtures and Aging Experiments in Pure Gases

By NORRIS E. BRADBURY
Physical Laboratory, University of California

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Gases to which a trace of NH_3 has been added have been known to show an abnormally high value for the mobility of the positive ion. In the experiments reported here, the method of Tyndall and Grindley for measuring ionic mobilities under conditions of high gas purity and resolving power has been employed to determine the ion spectra in the case of H_2-NH_3 and N_2-NH_3 mixtures. In the former case when the partial pressure of NH_3 was reduced to 0.15 mm, a positive ion of mobility 9.4, which is substantially equal to that of the negative ion in impure H_2, was observed. In the case of the N_2-NH_3 mixtures, a positive ion of mobility 1.83 was observed in addition to the normal positive ion in the pure gas of mobility equal to 2.09. No negative ions were observable. The aging experiments reported previously (Phys. Rev. **37,** 1311 (1931)) have been continued under conditions of high gas purity using the Tyndall and Grindley method. No aging was observed in pure N_2 at ion ages as great as 0.5 seconds. Air, however, where chemical reaction products could be formed by the x-ray ionization source, showed similar aging effects to those reported previously.

A. Mixture Experiments

SINCE the mobility measurements on pure gases reported in another paper had resulted almost uniformly in only a single class of ion at ages of 4×10^{-2} seconds, it was of interest to investigate the nature of the mobility curves of certain gaseous mixtures which had been observed to indicate specific molecular attachments to ions. The Tyndall and Grindley method, as it has been employed in these and the pure gas experiments with x-ray ionization, and high gas purity and resolving power, gives an admirable method of testing for the simultaneous appearance of several ions. The shape of the curves, normally having straight sides and a sharp apex, permits more than a single class of ions to be readily observable. The same apparatus and methods of measurement as used in the experiments in pure gases have been employed here, and the same discussion applies. The two mixtures studied were hydrogen and ammonia, and nitrogen and ammonia. Previously Loeb[1] observed an abnormally high value for the positive ion when traces of NH_3 were present in air.

The nitrogen and hydrogen were prepared as described in the preceding paper. The ammonia was formed by the interaction of C.P. $(NH_4)_2SO_4$ and a concentrated solution of NaOH. The gas so formed was passed through a trap cooled to $-35°$, through a long tube filled with broken sticks of KOH, and condensed in a trap surrounded by liquid air. The ammonia was distilled off by removing the liquid air, and was then refrozen in another trap. Subsequent fractional distillation yielded NH_3 relatively free from water vapor.

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

The resulting curves for the nitrogen-ammonia mixtures are shown in Fig. 1. Curve *A* shows the sharp peak for pure nitrogen with a maximum corresponding to a mobility of 2.09. Addition of 1 mm partial pressure of NH_3 gave curve *D* with a very broadened peak indicating two or more mobilities.

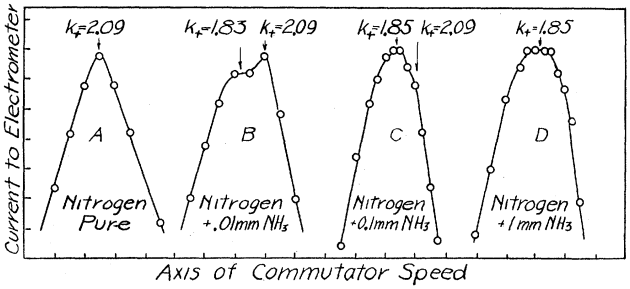

Fig. 1. Curves for mixtures of nitrogen and ammonia showing the deviation from the type of curve obtained with the pure gas.

Reduction of the ammonia to 0.1 mm gave the curve shown in *C* in which the appearance of the 2.09 peak is indicated on the high mobility side of the curve. Further reduction of the ammonia present to 0.01 mm gave the curve shown in *B* which is intermediate between *A* and *C*. Evidently in the case of nitrogen-ammonia mixtures an ion of mobility 1.85 exists in addition to the normal mobility of 2.10. This is in agreement with the results of Loeb who found an anomalous high mobility for the positive ion of 1.8 in the case of ammonia-air mixtures. The action of ammonia was found by him to be specific for the positive ion. Since in these measurements no negative ions could be detected, this effect could not be verified. It was, however, definitely verified in the case of impure hydrogen.

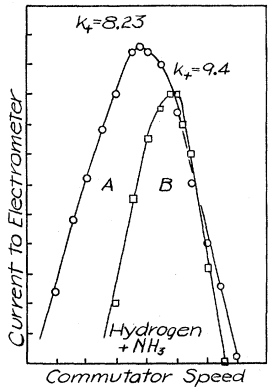

Fig. 2. Hydrogen and ammonia mixtures showing the increase in mobility of the positive ion as the percentage of ammonia is decreased.

The hydrogen-ammonia mixtures gave curves of the type shown in Fig. 2. The curve *A* corresponds to a partial pressure of 1.5 mm NH_3 and a mobility of 8.23. Curve *B* is that obtained for 0.15 mm NH_3 and corresponds to a mobility of 9.4. Its appearance is perhaps predicted by the slight asymmetry

in curve A on the high mobility side. A preliminary series of runs in which the purification of the ammonia was not entirely satisfactory gave the 8.3 value and indications of a hump at the usual 6.7 value.

The results were then repeated in impure hydrogen in which negative ions were present. The hydrogen in this case was dried merely by passing over liquid air. In these experiments a mobility of 9.6 was obtained for the negative ion and curves very similar to those in Fig. 2, for the positive ion with a final high mobility of 9.4. *This is seen to be practically equal to that for the negative ion.* Such a result is not, however, surprising in the light of Erikson's[2] and Mahoney's[3] experiments, who found a mobility of the positive ion in air-ammonia mixtures equal to that of the negative. No change in the mobility of the negative ion could be detected which confirms Loeb's results on the specificity of the effect of the ammonia on the positive ion. He found 7.88 for the positive ion where traces of ammonia were present and 9.36 for the negative ion.

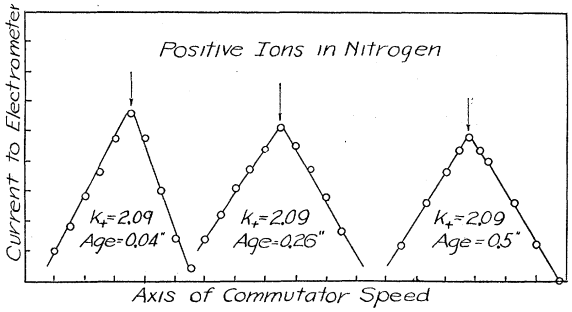

Fig. 3. Aging experiments in nitrogen. No noticeable change in the shape of the curves or a shift of the position of the maximum is present.

It can thus be said from these experiments that the mobility of the positive ion in pure hydrogen has a value of 8.2; that the addition of traces of ammonia raises this value to 9.4; and that this value is substantially equal to that for the negative ion in the case of impure hydrogen.

Aging Experiments

Aging experiments have previously been reported on air in a metal chamber.[4] In these experiments it was found that with ion ages greater than a tenth of a second the average mobility appeared to decrease and become spread out over a wide range as if the ions had attached a wide variety of impurities or reaction products of the x-rays. The existence of the glass chamber used in the above measurements made it possible to test these effects under conditions of greater gas purity. Two series of runs were carried out—one on positive ions in pure nitrogen and the other on positive and negative ions in air. The results in the case of nitrogen are shown in Fig. 3. In this case, with a gas

[2] H. A. Erikson, Phys. Rev. **30,** 339 (1927).
[3] J. J. Mahoney, Phys. Rev. **33,** 317 (1929).
[4] N. E. Bradbury, Phys. Rev. **37,** 1311 (1931).

of high purity, and no chance of reaction products such as nitric oxides, ozone, and the like formed by the x-rays, we obtain *no decrease in mobility*, and *no noticeable broadening* of the maximum of the peak. But one class of ion is formed and remains so throughout the aging time up to 0.5″. The measurements were not carried beyond this as the air experiments had shown very apparent aging effects at these times.

The results for the positive ion in air are shown in Fig. 4. The results are much the same in magnitude and appearance as those previously reported. The broadening and shift of the maximum of the peak in the case of the positive ions shown is very noticeable. The breadth of the spectrum is not quite

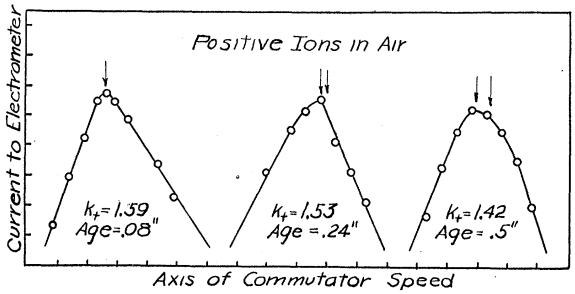

Fig. 4. Aging experiments on positive ions in air. The right hand arrow indicates the position of the peak for *new* ions. The shift and flattening of the curves is evident.

as great as in the earlier experiments, owing, doubtless, to the increased purity of the gas. The aging of the negative ions was not quite as great as that for the positive which is to be expected in view of the greater electrochemical affinity of the positive ion for the type of impurity liable to be present.

The comparison of the two results, for air and nitrogen, rather definitely confirms the scheme of ionic behavior under such circumstances which has been advanced by Loeb and the author.[5] The results in air are in agreement with those of Zeleny[6] who, however, was forced to work under conditions permitting no great control of gas purity.

Conclusion

The results in the mixture experiments may be summarized in Table I.

Table I. *Summary of results.*

Gas	Purity	k	k
Nitrogen+NH_3 (trace)	p	1.83 2.09	e
Hydrogen+NH_3 (trace)	p	9.4	e
Hydrogen+NH_3 (trace)	i	9.4	9.6

The chemically stable NH_4^+ ion in many compounds presents, perhaps, an explanation of the specific effect of NH_3 on the positive ion alone. The re-

[5] Loeb and Bradbury, Phys. Rev. **38**, 1716 (1931).
[6] J. Zeleny, Phys. Rev. **38**, 969 (1931).

sultant effect is evidently the protection of the positive ion from attachment by some bulkier molecule with a consequent increase in the observed mobility of the final ion. The extent of this protective effect has been discussed by Loeb.

In conclusion, it is desired to thank Mr. Daniel Posin, who assisted in taking some of the measurements, and Professor L. B. Loeb for his suggestions and assistance in the interpretation of the experimental data.