

MOBILITIES OF INJECTED IONS IN LIQUID WATER

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## ABSTRACT

Mobilities of Injected Ions in Liquid Water  
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The original objectives of this project were to develop methods for measuring the mobility of ions in water by means of ion injection techniques with the ultimate goal of using these data to investigate the feasibility of using the Hall effect to measure impurity ion mobilities at dilute ionic concentrations. A number of preliminary studies proved to be necessary in order to accomplish the primary goals. These experiments which have been completed include ion mobility studies in water vapor, studies of corona discharges from fine points in water vapor, injection of ions into water using corona methods, and ejection of ions from water into water vapor. These measurements were performed for both positive and negative ions. Results indicate that injection techniques using coronas are not suitable for ion mobility measurements in water because injected charge densities are insufficient to overcome the natural conductivity of water even in its purest state. On the other hand, these studies have yielded new information which appear to be relevant to nucleation studies.

Keywords - ions, mobility, vapor

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## Introduction and Objectives

Theory predicts that a swarm of a single species of ions in a liquid medium will drift with a well defined and sharp drift velocity in a given electric field. The mobility is the ratio of the drift velocity to the electric field. The mobility is found to be a constant with electric field but varies with such parameters as the temperature, pressure, density, etc. However, different species of ions are known to have different but distinct mobilities in a given medium.<sup>1</sup> Ion mobility investigations using ion injection methods have proved to be powerful techniques for studying dielectric liquids such as the liquefied gases.

Ion mobilities in water are important because of their bearing on conductivity, ion-clustering or hydration, ion-solvent interaction and microscopic viscosities.

The original objectives of this project were to develop methods for measuring the mobility of ions in water by means of ion injection techniques with the ultimate goal of using these data to investigate the feasibility of using the Hall effect to determine impurity ion mobilities at dilute ionic concentrations in water. A number of preliminary studies proved to be necessary in order to accomplish the primary goals. These experiments which have been completed include ion mobility studies in water vapor, studies of corona discharges from fine points in water vapor, injection of ions into water using corona methods, and ejection of ions from water into water vapor. These measurements were performed for both positive and negative ions.

### Methods of Investigation

Figure 1 is a diagram of the ion injection and time-of-flight apparatus used in the direct measurement of the ion mobilities.

The basic method is to measure the time-of-flight of a swarm of ions in an electric field between two electrodes such as C-D in Figure 1. From this drift time one can compute the ion drift velocity.

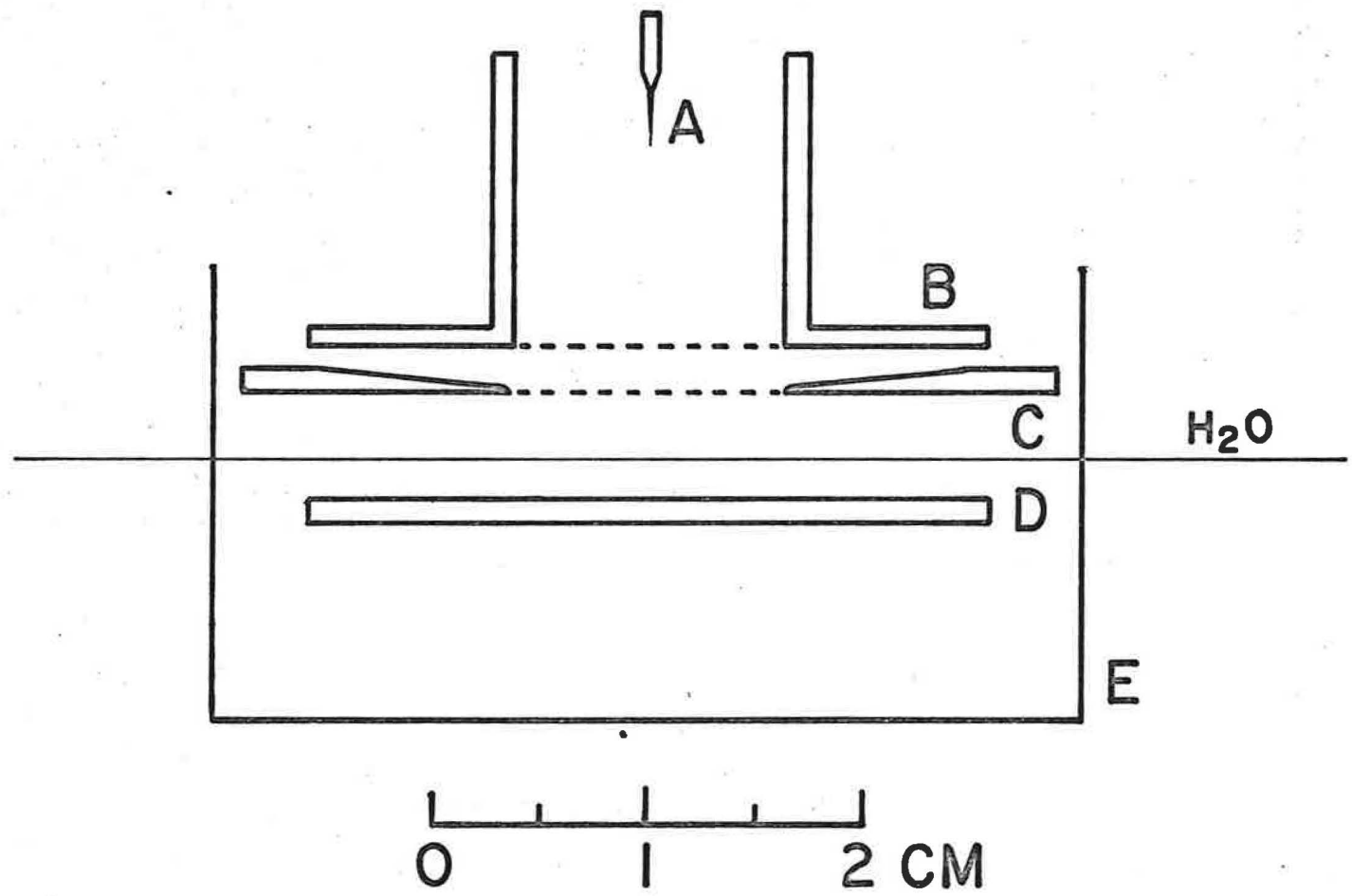
In the technique used here ions are produced in the vapor above the water near A in Fig. 1. The region B-C acts as an electronic gate which with suitable grid potentials either allows ions to enter region C-D or prevents them from doing so.

To obtain the time-of-flight of a swarm of ions between C-D the electronic gate is opened until the current collected on electrode D is constant and then the gate is closed. The time-of-flight across the drift space is determined from the decay of the current from electrode D.

The water surface shown in Fig. 1 was lowered so that ion mobilities were measured above the liquid surface in the vapor using electrode D as the ion collector. The water level was then raised to a known position in the drift space region C-D and the mobility measurements were repeated. In principle, if the charge densities in the injected ion swarm were high enough to overcome the residual charge density in the liquid it would be possible to obtain ion mobility information in the liquid from these two sets of data.

FIGURE 1

Diagram of the ion source and  
time-of-flight spectrometer used  
for ion mobility measurements.



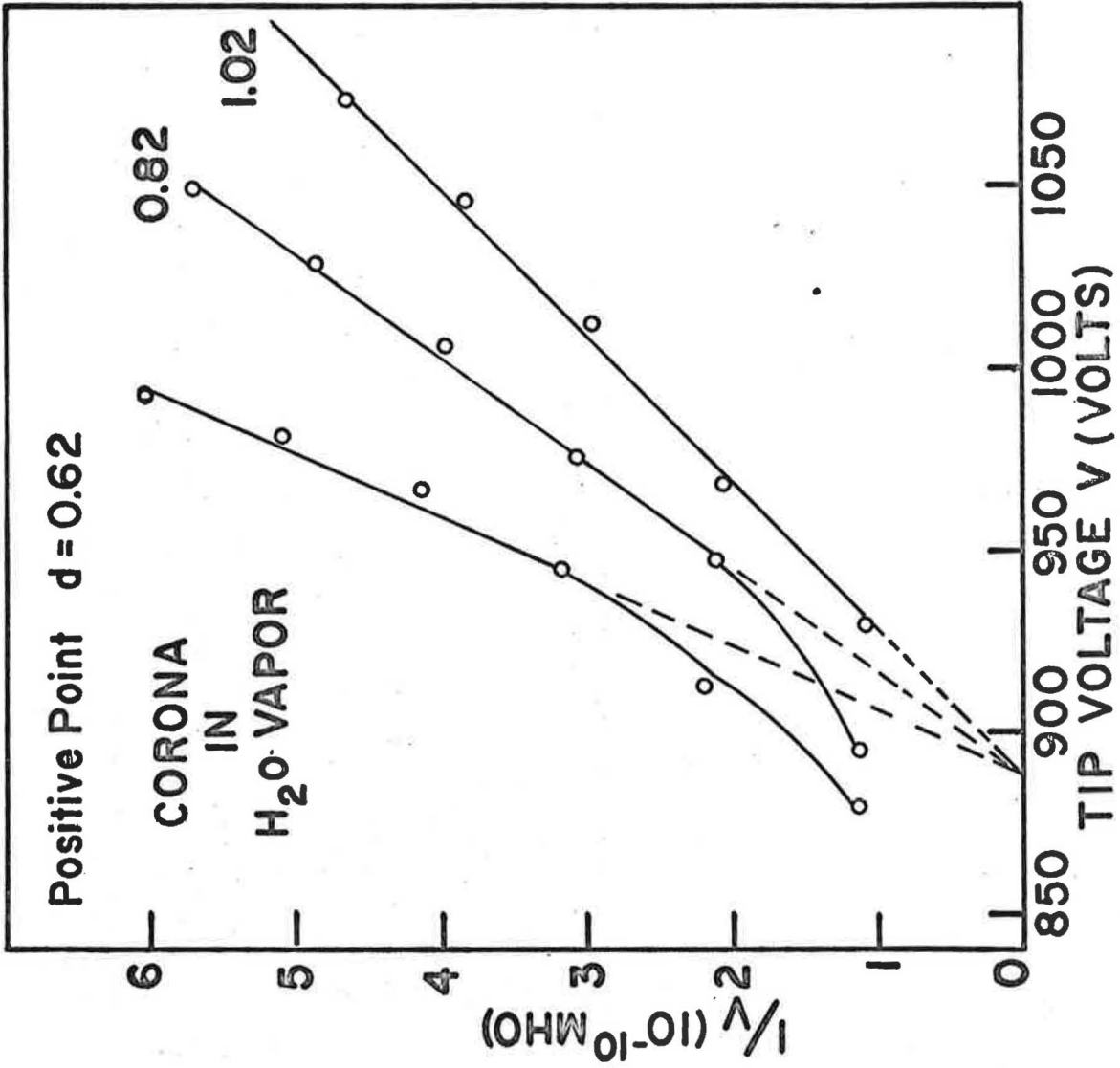


A sharp tungsten point A is used for the ion source. It is etched to a radius of about 200-2000 Å. Ions or electrons are produced in the vicinity of this point by field ionization, field emission and corona discharge<sup>2</sup> when high voltages are applied. This source produces either positive or negative ions depending upon the applied voltage polarity. The types of ions produced will depend upon the atmosphere above the water surface which can be varied. If only water vapor is present one would expect only  $H^+$ ,  $H_3O^+$ , electrons,  $H^-$ ,  $OH^-$  or hydration of these basic ions.<sup>3,4</sup>

This type of ion source and time-of-flight spectrometer have been used effectively for ion mobility studies in such liquefied gases as helium,<sup>5</sup> argon and nitrogen.<sup>6</sup> Figure 2 shows data for a typical point in water vapor at 25°C presented as the ratio of tip current to tip potential vs. tip potential. The linear portion of the curves represent the steady corona region of the corona discharge which is consistent with knowledge of coronas in gases.

FIGURE 2

Characteristic curves for positive point to plane electrode corona discharge in saturated water vapor at 25°C presented as the ratio of current to tip potential vs. tip potential, where  $d$  represents the distance from point to plane electrode in centimeters.



### Results and Conclusions

The ion mobility studies in pure water vapor at its saturated vapor pressure were made using time-of-flight spectrometry in the temperature interval of 20°C to 70°C. These measurements were made for both positive and negative ions directly over a water surface using the liquid water surface as the charge collecting electrode. Similar mobility measurements were also made in water vapor far removed from the effects of the water vapor-liquid interface using a metal collecting electrode. Results indicate that both positive and negative ions have the same mobility which would seem to indicate that the ions are heavily hydrated to form ion clusters of approximately the same size for both ionic species. The temperature dependence of the ion mobilities in both cases can be explained in terms of the classical kinetic theory mobility of ions in gases which yields the equation<sup>7</sup>

$$\mu = \frac{q}{8/3 N \sigma^2 \left( \frac{2\pi m_i m_a}{m_i + m_a} kT \right)^{1/2}}$$

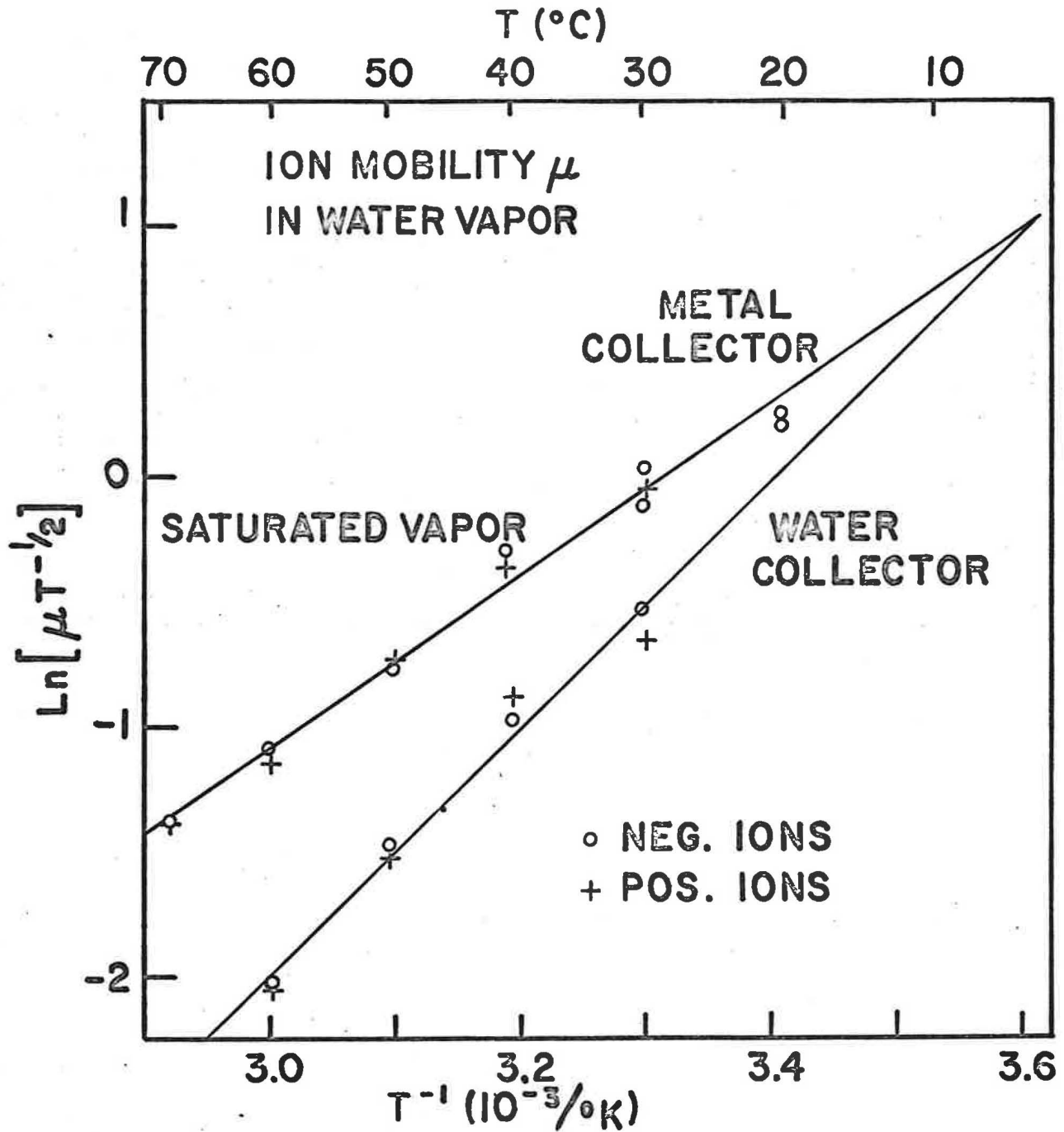
where  $\mu$  is the ion mobility,  $T$  is the absolute temperature,  $q$  is the ionic charge,  $N$  is the number density of the gas,  $\pi\sigma^2$  is the cross-section for momentum transfer between an ion and a gas molecule,  $m_i$  is the ionic mass and  $m_a$  is the mass of a molecule of the gas.

The number density  $N$  varies directly as the pressure and inversely as the temperature  $T$ . It is known that

saturated vapor pressure of water varies as  $\exp[-B/T]$  where B is a constant. Thus one would expect the mobility  $\mu$  to vary as  $AT^{1/2}\exp[+B/T]$  where A is a constant. Figure 3 depicts empirical data for ion mobility presented as  $\ln[\mu T^{-1/2}]$  vs  $1/T$ . The data points lay on straight lines as is suggested by the theory but the slopes are not as predicted above. An experimental value for B is  $5176/^{\circ}\text{K}$  as determined from vapor pressure data<sup>8</sup> taken at the U.S. Bureau of Standards. On the other hand, the slopes of the solid lines which represent the linear least squares fit to the data points are  $3425/^{\circ}\text{K}$  and  $4896/^{\circ}\text{K}$ . Those mobility data measured at the water surface fall on the line with the largest slope (curve II) but have lower mobility values than those on curve I. Thus while the correct functional form for the temperature dependence of the ion mobility appears to be  $KT^{1/2} e^{\epsilon/T}$ , the constants are not as predicted. This leads one to suspect that there is another exponential term missing. This could come from the cross-section for momentum transfer  $\pi\sigma^2$ . The fact that both positive and negative ions were determined to have approximately the same mobility indicates considerable ion clustering or inhomogeneous nucleation about the ions. This clustering would not only have a strong temperature dependence, but would also directly affect the cross-section term  $\sigma^2$ . Homogeneous nucleation in the background vapor<sup>9</sup> would also affect  $\sigma^2$  but this would have a much weaker temperature dependence.

FIGURE 3

Positive and negative ion mobility data in pure water vapor at saturation presented as  $\ln(\mu T^{-1/2})$  vs.  $T^{-1}$  where  $\mu$  is the mobility in  $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$  and  $T$  is the absolute temperature in  $^{\circ}\text{K}$ . The empirical equations of the curves as determined by a linear correlation are  $\ln(\mu T^{-1/2}) = 3425/T - 11.36$  and  $\ln(\mu T^{-1/2}) = 4896/T - 16.68$ .



Clustering of molecules about an ion moving through a background gas was studied theoretically by Bloom and Margenau.<sup>10</sup> Their theory predicted an almost exponential increase in the cluster size with decrease in temperature. In fact, over a small interval of temperature, it is not unreasonable that the cluster size vary as  $\sim e^{b/kT}$ . This term is all that is needed to explain those data for curve I since if  $m_i \gg m_a$  then  $M^{1/2} \sim m_a$  and  $\sigma^2 = (\sigma_i + \sigma_a)^2 \sim \sigma_i^2$ . Any factor of temperature of the form  $T^n$  which might come from  $\sigma^2$  would appear as  $n \ln T$  in the graph and would only slowly vary compared with terms from the exponentials. Thus, one would expect curve I to have a slope  $-B - b$  which indicates why the slope is lower than originally expected.

To explain curve II some other term is needed. For example, curve II has a smaller ordinate intercept and a larger slope than curve I. However, curve II has a smaller slope than would be predicted by vapor pressure variation alone. The possibility of a temperature gradient in the experimental tube can be ruled out because this would cause the curves to cross at room temperature  $\sim 25^\circ\text{C}$ . The curves cross at a temperature  $\sim 3.5^\circ\text{C}$ . The probable explanation is associated with the cloud of microscopic droplets which are known to exist near a water surface.<sup>11</sup> Thus near the surface there would be a mixture of vapor and microscopic droplets thus yielding two values for  $\sigma^2$ . Such mixtures are known to give an average mobility  $\mu$  for an ion given



by  $\mu^{-1} = \mu_1^{-1} + \mu_2^{-1}$ , when  $\mu_1$  is the mobility of the ion through the vapor only and  $\mu_2$  is the mobility through the droplets only. A more complete discussion of mobility of ions through mixtures of gases can be found elsewhere.<sup>12</sup> This equation commonly known as Blanc's law yields a resultant ion mobility that is lower than either the ion mobility through the droplets alone or the mobility through the vapor alone. This would explain why the ion mobility is lower in the vicinity of the water surface. The increase in slope of curve II could come from the expression for the concentration of droplets which one would expect to be  $\sim e^{-g/kT}$  where  $g$  is related to the Gibbs free energy for formation of a droplet.<sup>13</sup> This model is obviously much too simplified but does explain in a qualitative way the difference between curve II and curve I.

It should be noted that Lowke and Rees<sup>14</sup> give a measured value for the negative ion mobility  $\mu_0 = 0.67 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  normalized to a vapor particle density of  $2.69 \times 10^{19} \text{ cm}^{-3}$  at  $20^\circ\text{C}$ . Their measurements were made at pressures less than the saturated vapor pressure. The value for the normalized mobility at  $20^\circ\text{C}$  obtained in this study is  $0.46 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ . This is reasonable since more clustering and hence a lower mobility should occur at saturation.

Ejection of charges from the surface of liquid water was studied using parallel plane geometry. One plane electrode was placed below the surface of water and a parallel plane electrode used as the collector was placed

in the vapor above and parallel to the water surface. Using this technique it was possible to study the ejection of both positive and negative ions from the water surface. Typical data for ejected current vs. electrode potential characteristics for such a diode are shown in the Appendix. It is probable that the current is a result of charged microscopic droplets<sup>15</sup> being ejected into the vapor. It is known that droplets ejected from a water surface will be charged with the same sign as the charge induced on the surface of the water. These data add credence to the hypothesis presented as an explanation for the ion mobility near the water surface.

Publications and Papers Presented

1. One talk on these data was presented at the Sixth Annual Conference of the Missouri Water Resources Research Center - Columbia, Missouri, May 17, 1972.
2. None of these data have been published to date but a manuscript will be submitted for publication in the near future.

References

1. For a more complete discussion, see L. B. Loeb, Basic Processes of Gaseous Electronics (University of California Press, Berkeley, California, 1955) Chapters I and II.
2. B. L. Henson, Phys. Lett. 33A, 91 (1970).
3. M. Eigen and L. de Maeyer, Proc. Roy. Soc. A247, 505 (1958).
4. A. R. Anway, J. Chem. Phys. 50, 2012 (1969).
5. B. L. Henson, Phys. Rev. Lett. 24, 1327 (1970).
6. B. L. Henson, Phys. Rev. 135, A1002 (1964).
7. H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena (Oxford University Press, New York, 1952), p. 367.
8. H. F. Stimson, J. of Res. NBS 37A, 493 (1969).
9. K. C. Russell, J. Chem. Phys. 50, 1809 (1969).
10. S. Bloom and H. Margenau, Phys. Rev. 85, 670 (1952).
11. D. Blanchard, From Raindrops to Volcanoes (Doubleday and Co., Inc., New York, 1967), Chapters 5 and 6.
12. L. B. Loeb, Basic Processes of Gaseous Electronics (University of California Press, Berkeley, California, 1955), p. 130.
13. See Reference 9.
14. J. J. Lowke and J. A. Rees, Australian J. Phys. 16, 447 (1963).
15. See Reference 11, Chapters 7 and 8.

APPENDICES

A. MEASURED MOBILITY OF IONS IN PURE SATURATED WATER VAPOR\*

<u>Temperature T (°K)</u>	<u>Mobility <math>\mu</math> (cm<sup>2</sup>V<sup>-1</sup>sec<sup>-1</sup>) (Metal Collector)</u>	<u>Mobility <math>\mu</math> (cm<sup>2</sup>V<sup>-1</sup>sec<sup>-1</sup>) (Water Collector)</u>
<u>Negative Ions</u>		
293	21.9	--
303	16.2	10.2
313	12.9	6.6
323	8.2	4.1
333	6.1	2.4
343	4.6	--
<u>Positive Ions</u>		
303	16.3	9.0
313	12.2	7.3
323	8.5	3.9
333	5.8	2.4
343	4.5	--

\*These values for ion mobility represent mean values of many measurements taken with electric field from 5 V/cm to 100 V/cm.