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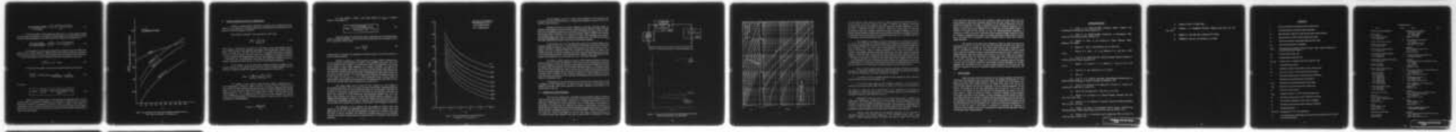

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ELECTRICAL CONDUCTIVITY OF MOIST AIR

I. CELL DESIGN AND FABRICATION FROM THE WATER ION CLUSTER THEORY

LEVEL II

by

Hugh R. Carlon

Research Division

May 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
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(U) Beginning with the infrared water ion cluster theory, this report outlines the development of equations leading to the design of an air conductivity cell, which has been fabricated. In earlier work, we showed that anomalous "continuum" absorption by the atmosphere of infrared radiation could be attributed to intermolecular, hydrogen bonds in polymolecular ion clusters of → next page

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20. ABSTRACT (Continued)

water which are always present in equilibrium concentrations in samples of water vapor. For example, these clusters can have the form $H_3O(+)(H_2O)_n$, where n = 10 or 11 in moist air, paired with more mobile ions such as OH^-. Therefore, electrical conductivity measurements of moist air should show direct correlations with water cluster concentrations and hence with infrared transmission of the atmosphere. Agreement of preliminary experimental data from the cell with theory is good, suggesting new avenues of investigation in electrostatics such as space charge dissipation.

PREFACE

The work described in this report was authorized under the In-house Laboratory Independent Research Program. The work was started in August and completed in November 1977. The experimental data are recorded in notebooks 9613 and 9615.

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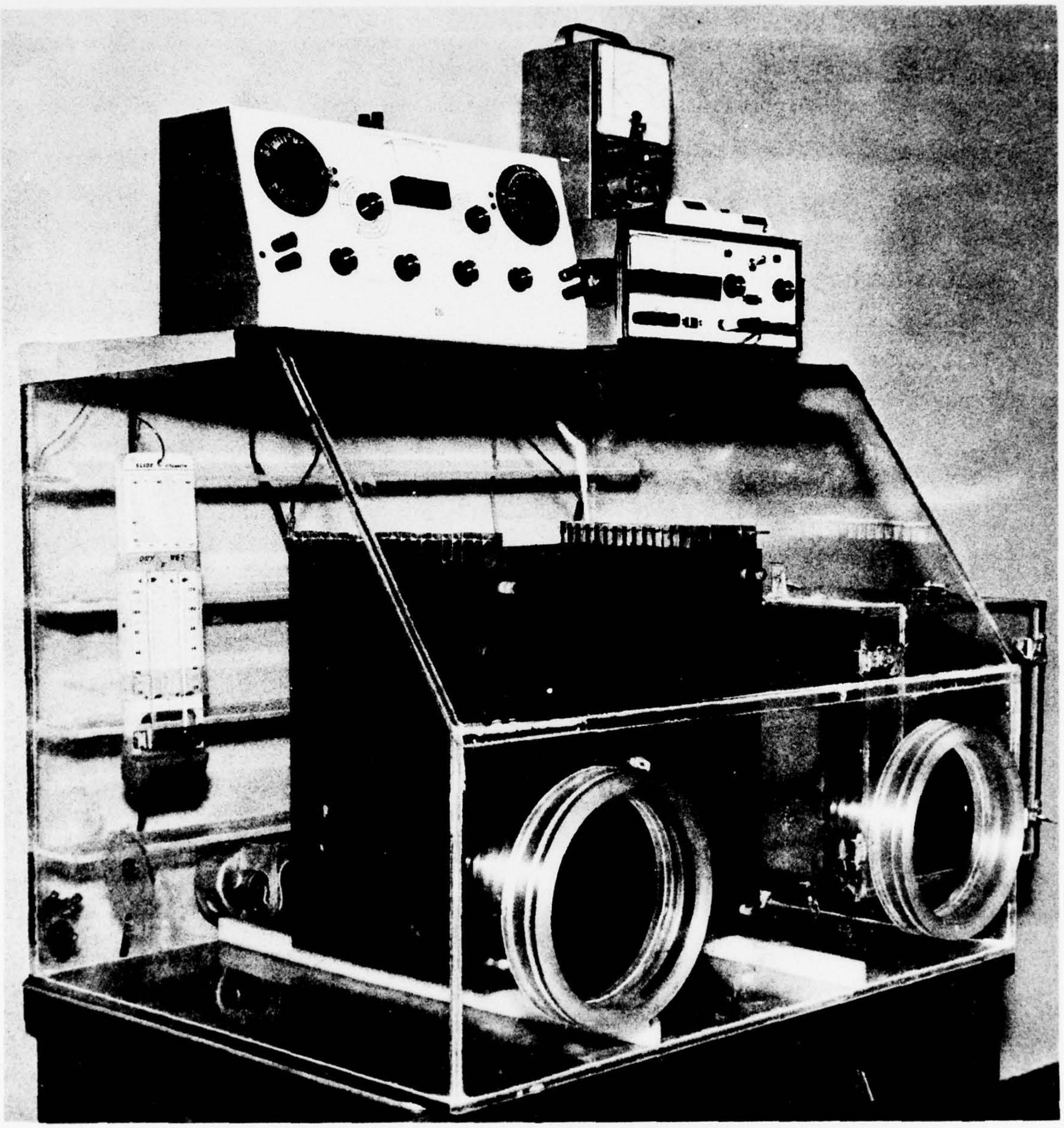

Frontispiece: Air Conductivity Cell

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ELECTRICAL CONDUCTIVITY OF MOIST AIR

I. CELL DESIGN AND FABRICATION FROM THE WATER ION CLUSTER THEORY

I. INTRODUCTION.

This is the first of two reports dealing with the electrical conductivity of moist air and its measurement. This report discusses cell design and fabrication; the second report will describe actual conductivity measurements and results. The purpose of this work was to give some physical basis to the measurement of polymolecular water ion clusters (ion hydrates) found in water vapor and in moist air, other than their infrared absorption. The hydrogen bonding of polymolecular water ion clusters accounts for strong absorption of infrared radiation by the atmosphere[1,2] at wavelengths from about 3 μm to at least 20 μm. This absorption increases steadily with increasing wavelength.

Infrared measurements of atmospheric absorption alone cannot establish unequivocally that this absorption arises from water ion clusters and not from some other atmospheric constituent including water vapor (monomer) itself. Conversely, simple ion mobility measurements of moist air cannot establish the ionic species present, and the identity of such species has been the subject of long conjecture in the literature. The objective of the work reported here was to investigate specific connections between infrared absorption attributed to water ion clusters in the atmosphere and the electrical conductivity of moist atmospheric air producing that infrared absorption.

II. INFRARED OBSERVATIONS LEADING TO THE CELL DESIGN.

For about 40 years, an infrared "continuum" absorption of the atmosphere has been known to exist and to be associated in some complex way with water vapor concentration. Varanasi, *et al.*,[3] found such "anomalous" absorption and suggested that it might be due to hydrogen bonding between water molecules. Bignell[4] made confirmatory measurements, called this "e-type" absorption after his term "e" for partial water vapor pressure, and discussed the water dimer (i.e., the homogeneous cluster of size two) as the possible cause. Roberts, *et al.*,[5] recently summarized measurements of this absorption by many workers in the infrared. Our own measurements and observations[1,2] taken radiometrically (i.e., by thermal emission) have characterized the magnitude and spectra of anomalous absorption and emission. In addition, we have found clearly aerosol-like characteristics of the "anomalous species" which, with wavelength shifts of observed spectra[6] and other evidence, point almost conclusively to distributions of ion clusters of water having mean sizes of 11 to 13 molecules per cluster as the species responsible for anomalous infrared "continuum" absorption.

The spectral properties of liquid water have been extensively characterized in the infrared.[7] Liquid water is nearly completely hydrogen-bonded or clustered,[8-10] and its anomalous infrared absorption between interatomic bands is attributed to intermolecular or lattice-vibrational ("librational") bonding which should be analogous to this bonding found in smaller clusters in the vapor phase. Thus it was seen possible to approximate the peak absorption intensity due to hydrogen bonds in clusters in the vapor phase from those already carefully measured for liquid water. These developments were carried out over a considerable period of time, but they can be summarized as follows:

Water clusters in moist air or in water vapor can be considered as tiny aerosol particles and can be treated by the approximations of aerosol spectroscopy[11] which apply when the mean particle diameter is much smaller than the wavelength of observation; i.e., the Rayleigh approximation case. Thus, if the anomalous absorption due to clusters in water vapor is considered alone (at wavelengths where there is only negligible absorption due to the water monomer and other atmospheric constituents), the Beer-Lambert law can be written:

$$\ell n(1/T_\lambda) = (\alpha_c)_\lambda C_c L, \qquad (1)$$

where $(\alpha_c)_\lambda$ is the mass absorption coefficient of water clusters, m^2/gm, and C_c is the cluster concentration, gm/m^3. These and subsequent terms are defined in the glossary.

Atmospheric spectroscopists measuring anomalous infrared absorption specify the absorption coefficient in another way, referring to it as the "self-broadened" absorption coefficient of water "vapor" having the symbol $(C_s^o)_\lambda$ and the units cm^2/molecule-atmosphere (of vapor). This refers the anomalous absorption, which we are here attributing to hydrogen bonding, to a useful, averaged molecular basis.

When conversion factors are included, it is straightforward to show that $(C_s^o)_\lambda$ can be expressed in terms of the cluster mass absorption coefficient $(\alpha_c)_\lambda$, cluster concentration, C_c, and other parameters as:

$$(C_s^o)_\lambda = \frac{0.77 \times 10^{-18} (\alpha_c)_\lambda C_c \theta_k}{(s)^2 (p_o)^2} \qquad (2)$$

From absorption measurements of liquid water[12] near the 15-μm wavelength where an absorption maximum attributed to intermolecular hydrogen bonding occurs, it is found that $(\alpha_c)_{\lambda_{max}} = 3370/(n_c)_\ell$ cm^2/gm, where $(n_c)_\ell$ is the mass fraction of clustered molecules in liquid water, stated[9] to be near 1.0. Substituting this expression into equation 2 and expressing cluster concentration in the vapor phase as a mass fraction, $(n_c)_v$, of total water vapor yields

$$(C_s^o)_{\lambda_{max}} = \frac{7.6 \times 10^{-17} (n_c)_v}{(s)(p_o)(n_c)_\ell} \qquad (3)$$

If the assumptions to this point are reasonably valid, equation 3 becomes a very important link between atmospheric infrared absorption measurements (already carefully made by many spectroscopists[5] under a wide variety of meteorological conditions) and the physical nature of the water clusters themselves; i.e., their sizes and concentrations accounting for infrared absorption in the vapor phase over a wide range of temperatures and saturation ratios. It then becomes a simple matter to substitute experimental data for $(C_s^o)_\lambda$ into equation 3 and to learn directly the relationship between the fraction of water vapor which is clustered, $(n_c)_v$, and the saturation ratio (fractional relative humidity), (s). For example, at 20°C, this relationship for the cluster species absorbing near 10.4 μm in the infrared is found to be:

$$(n_c)_v = 6 \times 10^{-5}(s) \qquad (\theta_c = 20°C) \tag{4}$$

Furthermore, since $(C_s^o)_\lambda$ has been measured at many temperatures, it is found that, over a range of temperatures above 10°C, an empirical relationship exists so that for the cluster species in the vapor absorbing near $\lambda = 10.4$ μm:

$$(n_c)_v \approx 6.6 \times 10^{-7}(s)(\theta_c)^{1.5} \tag{5}$$

where equation 4 is a special case of equation 5 for $\theta_c = 20°C$. Note that θ_c is the Celsius temperature, *not* absolute temperature. It then follows that an empirical equation for the concentration of this species derived from infrared measurements of the atmospheric spectroscopists can be written

$$C_c \approx \frac{1.9 \times 10^{-4}(s)^2(p_o)(\theta_c)^{1.5}}{\theta_k} \tag{6}$$

Equation 6 is plotted in figure 1.

An important observation by spectroscopists concerning $(C_s^o)_\lambda$ is that the values obtained are quite consistent regardless of where or when the measurements were made. It is found that, to within a factor of two to three, measurements of $(C_s^o)_\lambda$ taken under conditions ranging from the purest of water vapor samples to the most contaminated of atmospheres show this order of agreement. Further, there is no correlation between the cleanliness of an experiment and the magnitude of anomalous absorption, assuming, of course, that care has been taken to avoid optical extinction by large aerosols formed on foreign nuclei in the sample path. From a water cluster standpoint, this indicates a rather constant cluster mixing ratio or equilibrium concentration for stable temperature and humidity conditions. One possible source of ions for the formation of ion clusters in the vapor would thus be the dissociation of water itself according to

$$H_2O \rightleftharpoons H^+ + OH^- \tag{7}$$

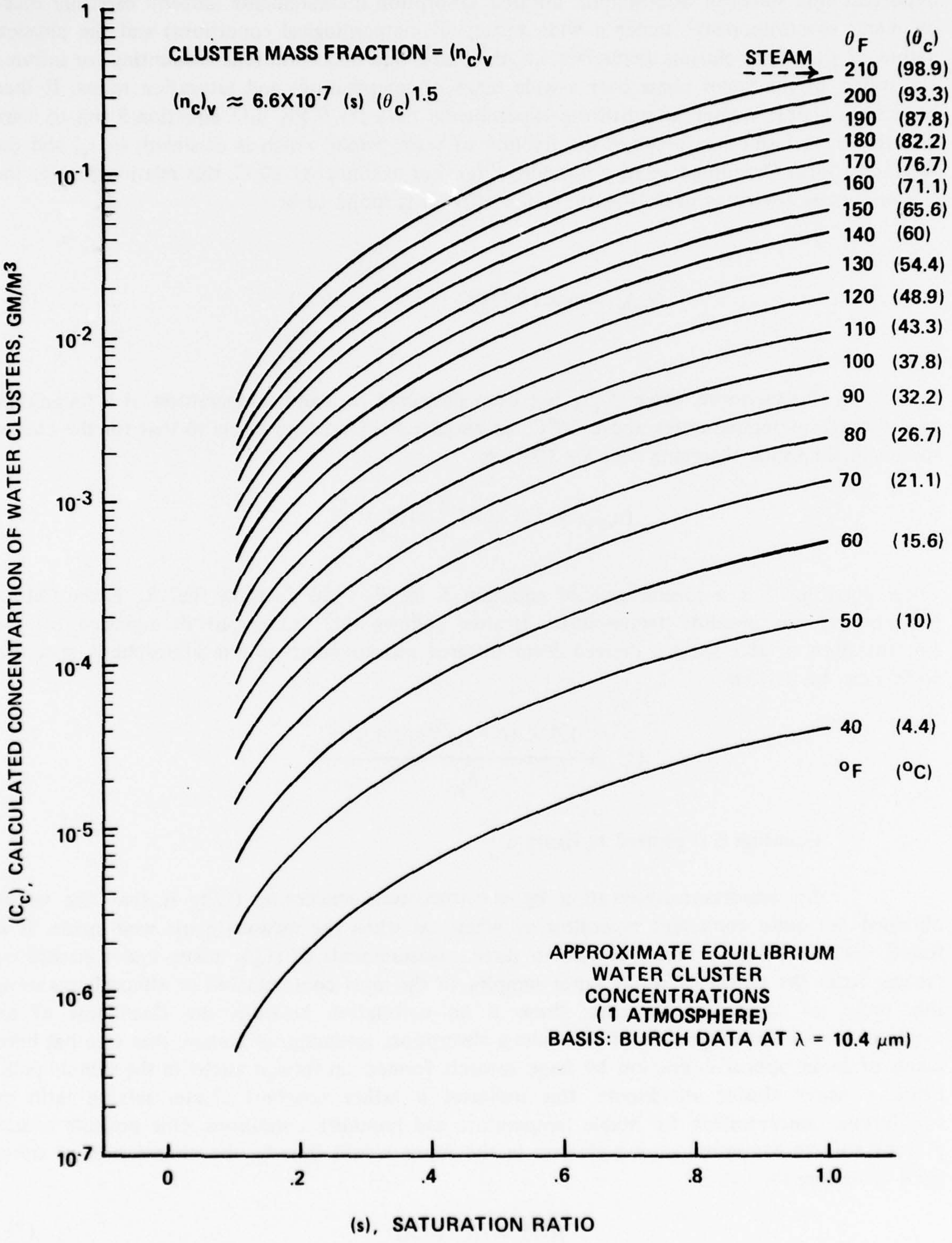

Figure 1. Approximate Equilibrium Water Cluster Concentrations (1 Atm), from Equation 6 (Burch data: reference 5)

followed, for example, by

$$H^+ + H_2O \rightleftharpoons H_3O^+ \tag{8}$$

where the hydronium and hydroxyl ions become "nuclei" necessary to begin the formation of polymolecular water clusters of some size distribution, and the mean size or cluster number will be determined primarily by the saturation ratio, (s). In this way, even triply-distilled water vapor in a closed optical cell free of foreign nuclei and ions could spontaneously produce its own clusters and $(C_s^0)_\lambda$ values comparable to those found in much more contaminated environments.

Another clue to the ionic dissociation of water vapor as a source of cluster "nuclei" is the curious term $(\theta_c)^{1.5}$ found empirically and shown in equation 5 and equation 6. It is well known that vapor pressure has a steep nonlinear temperature dependency; for example, water vapor, in going from 10°C to 60°C, exhibits a 16-fold increase in its equilibrium vapor pressure. This is nearly the same value as the 15-fold increase over this temperature range required by the empirical term $(\theta_c)^{1.5}$. The indication is that *cluster concentration is directly proportional to water vapor pressure.* But there is another property of water which has an even larger temperature dependency; namely, its dissociative ion product. For example, liquid water shows a 33-fold increase in its ion product[13] over the temperature range from 10°C to 60°C. The ion product is derived from equation 7 as follows:

For the ionization of water, the equilibrium constant is defined as

$$K = \frac{a_{H^+} \, a_{OH^-}}{a_{H_2O}} \tag{9}$$

where a is the molar concentration of the subscripted species. Since, for water, ionization is at best slight, the concentration of un-ionized water is unaffected and the ion product is written simply as

$$K_w = a_{H^+} \, a_{OH^-} \tag{10}$$

We shall use this same expression for the vapor phase. Thus it becomes possible on the basis of the foregoing assumptions to derive an expression for K_w in the vapor phase in terms of water cluster and vapor parameters.

Beginning with equation 6 in liter units and Avogadro's number (N_{avo}), from which the number of clustered molecules per gram of liquid water is found to be $0.33 \times 10^{23} (n_c)_\ell$, the product of these expressions becomes

$$\frac{\text{No. of clustered molecules}}{\text{liter of sample}} = \frac{0.64 \times 10^{16} (s)^2 (p_o) (\theta_c)^{1.5} (n_c)_\ell}{\theta_k} \tag{11}$$

If N is the number of ions required per cluster and (c - 1) is the number of bonds per cluster, then from equation 11 the number of ions required in the total of water molecules present is directly proportional to the cluster mass fraction (equation 5) and has the form

$$\frac{\text{No. of ions required}}{\text{No. of water molecules}} = \frac{(n_c)_v (N)}{(c-1)} = \frac{6.6 \times 10^{-7} (s)(N)(\theta_c)^{1.5}}{(c-1)} \tag{12}$$

The ionization of a water molecule (equation 7) produces an ion pair. Rather than assign the role of cluster "nucleus" or charge carrier to either the H^+ or OH^- ion, it is useful to work with the concentration of either since presumably their concentrations will be the same in a given water vapor sample. Thus from equation 10 and for the vapor phase, we can write

$$\left(\sqrt{K_w}\right)_v = a_{H^+} = a_{OH^-} \tag{13}$$

It follows that the number of ions per water molecule (equation 12) is equal to

$$\frac{(n_c)_v (N)}{(c-1)} = \left(\sqrt{K_w}\right)_v (N_{avo}) \frac{\theta_k}{(0.289)(s)(p_o)} \cdot \frac{18}{(N_{avo})(n_c)_\ell} \tag{14}$$

from which

$$\boxed{\left(\sqrt{K_w}\right)_v = \frac{k(C_c)(N)}{(c-1)} = \frac{0.106 \times 10^{-7} (s)^2 (p_o)(\theta_c)^{1.5} (N)}{(\theta_k)(c-1)}} \tag{15}$$

Equation 15 is plotted in figure 2, which also shows for comparison the ion product of liquid water as a function of temperature. It is important to realize that the ion product reflects only the degree of ionization of molecules present in a phase of water. Hence, the comparability of the ion products of liquid water and, for example, saturated vapor in figure 2 should not be cause for concern. The $(n_c)_v$ term will correct for actual cluster concentrations in a given water vapor sample.

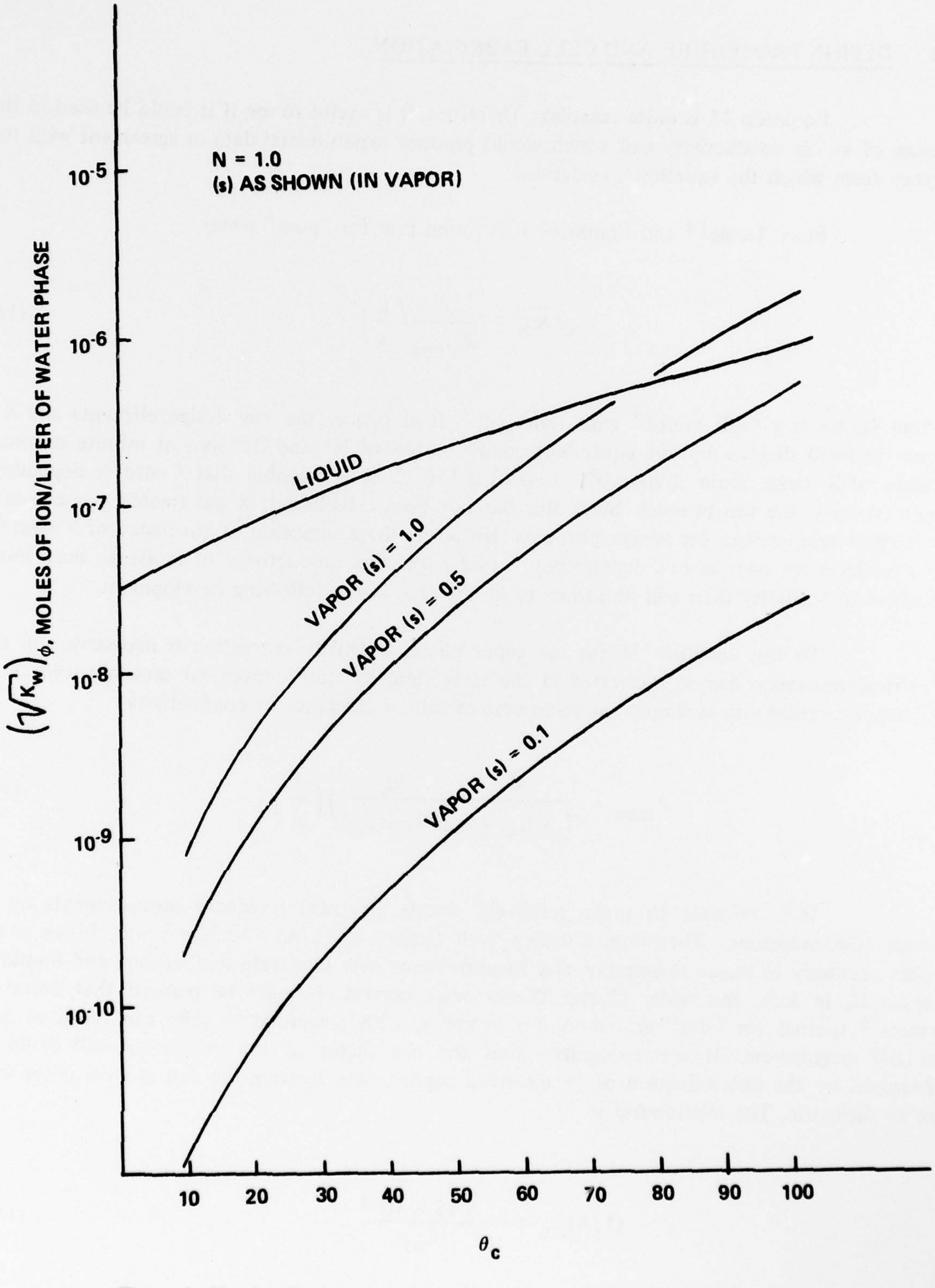

Figure 2. The Ion Product for Liquid Water Compared to Calculated Values for Water Vapor from Equation 15, Assuming N = 1

III. DESIGN PROCEDURE AND CELL FABRICATION.

Equation 15 is quite complex. Therefore, it is useful to see if it could be used in the design of an air conductivity cell which would produce experimental data in agreement with the theory from which the equation was derived.

From Lange[14] and Franks,[15] it is found that for "pure" water

$$\sqrt{K_w} = \frac{X}{R_{ohms}}\left(\frac{L}{A}\right) \tag{16}$$

where (L/A) is a "cell factor" with units cm^{-1} (and hence, the key design element) and X is equal to 1000 divided by the equivalent conductivities of H^+ and OH^- ions at infinite dilution. Values of X range from 2.90 at 0°C to 0.73 at 156°C. It is possible that X also is dependent upon (s), as is the ion product. Since this has not been established, X was treated as a constant at a given temperature for design purposes. However, the assumption of constancy of X with (s) is a conservative one, as this dependency would make the conductivity of moist air even more sensitive to humidity than will be shown to be the case in the following development.

To use equation 16 for the vapor phase, a density correction is necessary and the electrical resistance can be converted at the same time to more convenient megohm units (cell resistance or resistivity is simply the reciprocal of cell conductance or conductivity)

$$R_{meg} = \frac{X}{\left(\sqrt{K_w}\right)_v}\left(\frac{\theta_k}{289\,(s)\,(p_o)}\right)\left(\frac{L}{A}\right) \tag{17}$$

It is possible to make relatively simple electrical resistance measurements up to about 1000 megohms. Therefore, a design "cell factor" of $(L/A) = 10^{-5}\,cm^{-1}$ was chosen as the value necessary to insure reasonably easy measurements over moderate temperature and humidity ranges if, in fact, the water cluster theory were correct. It must be realized that literature values[16] quoted for "dry" air taken, for example, with a Gerdien[17] tube can reach as high as 10^{26} megohm-cm. It was recognized that the cell factor of the completed cell could be measured by the determination of its electrical capacitance, treating the cell as a capacitor with an air dielectric. The relationship is

$$(L/A)_{cm^{-1}} = \frac{8.85 \times 10^{-8}}{C_{\mu f}}\ . \tag{18}$$

It is also possible to obtain a very useful equation for R_{meg} by combining equation 15 and equation 17

$$\boxed{R_{meg} \approx \frac{3.3 \times 10^5 (X)(\theta)_k^2 (c-1)}{(s)^3 (p_o)^2 (\theta_c)^{1.5} (N)} \left(\frac{L}{A}\right)_{cm^{-1}}} \tag{19}$$

Note that equation 19 indicates that a given conductivity cell at a fixed temperature will have a resistance dependent only upon (s) and mean cluster size (c). For example, at 25°C if $N = 1$ and $(L/A) = 10^{-5} cm^{-1}$, then

$$R_{meg} \approx \frac{8(c-1)}{(s)^3} \tag{20}$$

assuming that X is constant with changing (s) as discussed earlier. If not, then (s) will have a power even larger than three.

Equation 20 predicts, at a fixed temperature, that R_{meg} is directly dependent only upon the mean size of polymolecular ion clusters of water present and the inverse cube of (s); i.e., the fractional relative humidity. If experimentally verified, this information could reshape present theories of space charge dissipation as a function of humidity. For example, the uncomfortable static shocks experienced in the dry air of heated homes in wintertime could be more reasonably correlated with an inverse cubic dependency upon (s) than with a simple, linear one. The $(c - 1)$ term in equation 20 is important in determining the cluster species present. For example, if the water dimer $(c - 1 = 1)$ were responsible for observed cell resistances rather than an ion cluster of, say, size 13 $(c - 1 = 12)$, then experimental values of R_{meg} should be approximately 12 times smaller for the dimer than for the suspected species, given that the dimer were an ion in the first place which, if homogeneous, it would not be.

The chosen design value of $(L/A) = 10^{-5} cm^{-1}$ resulted in a cell consisting of 40 1-mm-thick steel plates, each 41 cm square and spaced 0.66 cm apart. Alternating plates were connected to either of two bus wires running the length of the cell, somewhat in the fashion of the plates in an automotive storage battery but with moist air as the electrolyte in this case. The plates were supported by five 8-mm-diameter resin-impregnated fiberglass rods with nylon spacers. These materials were selected for their high electrical resistance, computed to have negligible shunting resistance compared to expected cell resistances for moist air from the water cluster theory. Nevertheless, care was taken to minimize contact area between the rods, spacers, and steel plates. The completed cell is shown in its test cabinet in the frontispiece of this report.

The capacitance of the completed cell was measured as 0.010 μf. Thus, from equation 18, the cell factor was determined as $(L/A) = 8.85 \times 10^{-6} cm^{-1}$, which is close to the design value of $10^{-5} cm^{-1}$. This value was substituted into equation 19 to produce a very useful plot shown in figure 3. This figure was reproduced in multiple copies for use as a laboratory worksheet upon which cell data points can be plotted directly for comparison with theoretical predictions.

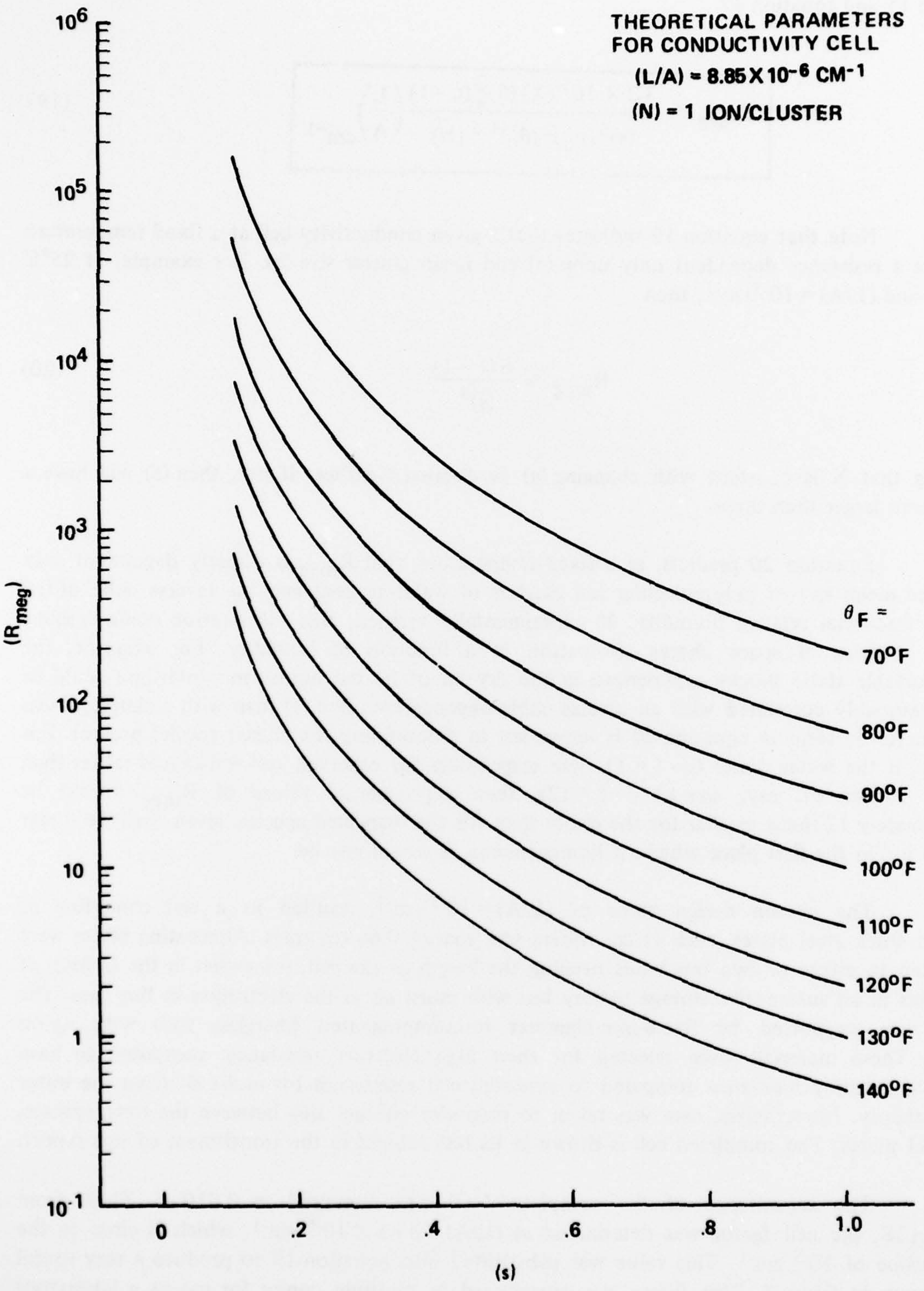

Figure 3. Theoretical Parameters for the Conductivity Cell
Assuming N = 1, from Equation 19

The cell resistance is read by a simple series arrangement of the bias source, the vacuum-tube voltmeter (VTVM) having an 11-megohm input impedance, and the cell itself. The schematic is shown in figure 4.

Obviously, the level of the supply voltage E_b is of concern, since high voltages can themselves cause ionization of moist air and any contaminants present. Therefore, a series of voltage trials was run at different temperatures and humidities to determine how R_{meg} of the cell varied with the bias voltage, E_b. Results of a few trials are summarized in figure 5 where it can be observed that, although R_{meg} varied about as predicted by theory with temperature and humidity (parameters affecting water ion cluster concentration), the effects of E_b up to 100 volts upon R_{meg} were small, falling within the range of theoretical and experimental inaccuracy.

A bias voltage of $E_b = 20$ v was selected for general use. A worksheet (figure 6) was prepared including E_b values of 1, 5, 50, and 200 volts as well, which can be used as needed for graphical solutions to determine R_{meg} directly from E_{VTVM} and E_b and then can be used to compare the results to theoretical values from equation 19 for the actual cell constant used. Extensive tests were run with the completed cell to insure that insulator leakage was not a factor in the measurements, especially under higher-humidity conditions. These tests established that leakage was not significant even at (s) values near 0.7 (i.e., 70% relative humidity).

The 0.66-cm cell-plate spacing was chosen to allow adequate circulation of moist air between plates and to reduce the likelihood of short circuits due to contamination which might have been troublesome with closer spacing. A larger spacing would have increased the cell factor or required larger cell dimensions, both undesirable alternatives. Even so, it is found in practice that the cell is short-circuited from time to time by lint or "whisker"-like contamination which finds its way between adjacent plates. We have found that the cell can be "cleaned" and restored to normal "quiet" operation by the momentary application of 400 volts directly across the plates. Therefore, this procedure will be used before all experiments are run and the data will be reported in a subsequent report.

Interestingly, the cell itself develops an electromotive force of about 0.02 volt. This is negligible in most measurements, and when taken into account it is found that the cell resistance is the same under normal operating bias voltages, regardless of the polarity of the voltage applied to the cell.

IV. RESULTS OF OTHER WORKERS.

From its first operation, the conductivity cell has produced resistance readings of moist air close to the values predicted by the water ion cluster theory and having the correct trends with temperature and humidity. Although it is a relatively simple device, we have not been able to find references to the construction or use of a similar device in the literature of electrostatics or cloud physics. But correlations do appear to exist between our work on ion clusters and that of other workers who have investigated ionic phenomena such as ion mobilities in their studies of atmospheric electricity.[18] For example, Wright[19] believed that the masses of the "small ions" which he investigated in moist air were equal to those of clusters of *10 or 12 water molecules*, and Chalmers[18] states that the general result of investigations of Wright

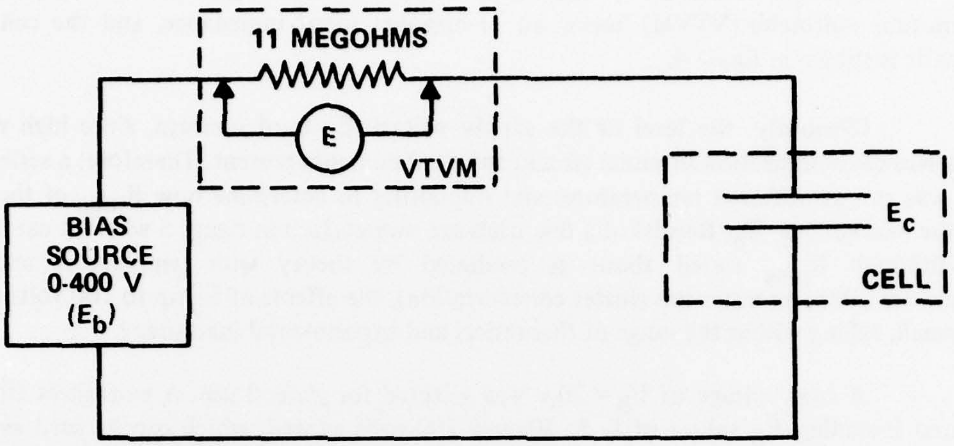

Figure 4. Electrical Connections to the Conductivity Cell

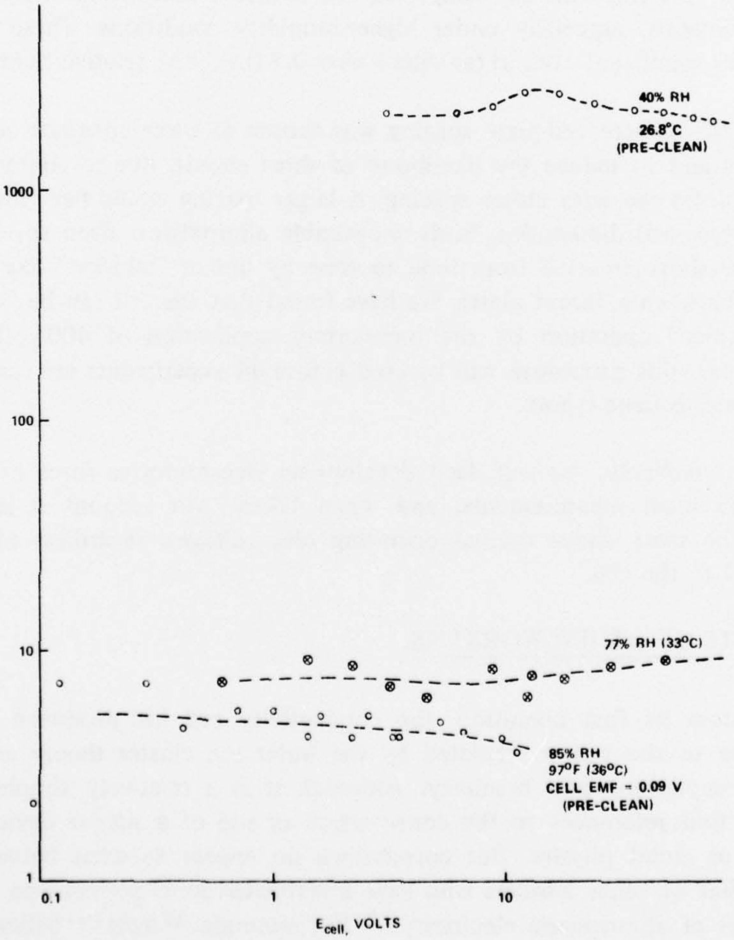

Figure 5. Effect of Bias Voltage Upon Cell Resistance for Three Different Temperatures and Humidities

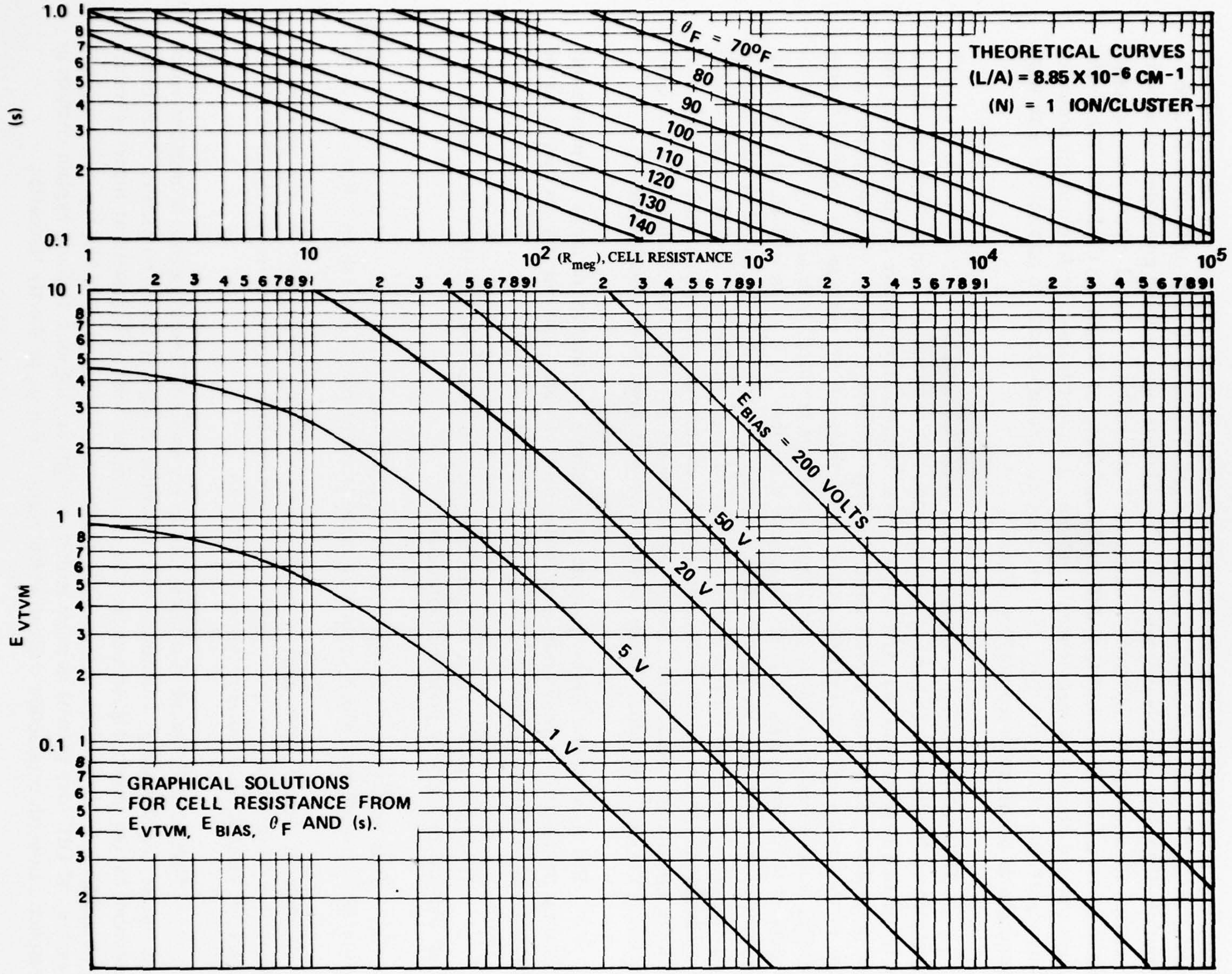

Figure 6. Graphical Solutions for Cell Resistance from E_b, E_{VTVM}, θ, and (s) for Five Values of E_b

and other workers is that a small *"ion consists of a single ionized molecule with other molecules clustered around it, and kept together by the charge"*. It would be very difficult to find better descriptions than these of polymolecular water ion clusters such as those postulated by us to be the cause of atmospheric infrared "continuum" absorption,[1,2] based upon our (spectral) measurements which are completely different from those of Wright or Chalmers. Yet it was through infrared absorption measurements and the subsequent theoretical development presented in this report that our conductivity cell was designed, leading directly to correlations with work in atmospheric electricity as reported by others.

The mobility of ion clusters of water is on the order of 1 to 2 cm/sec for 1 v/cm[19]. It is known to be dependent upon (s), total pressure, and temperature. Under similar conditions, it is found that negative ions (e.g., OH^- ion of a pair from equation 7) have greater mobility than those of positive "ions" [e.g., a water cluster of $H_3O^+ \cdot (H_2O)_n$]. Clearly, these mobilities are a factor in the design of a device to measure conductivity of air, such as the Gerdien[17] tube. Typically, small sampling cylinders containing conductors are used, with air drawn through the cylinders at sufficiently high velocities to insure that Ohm's law holds. Indeed, for the static conditions of our own cell, we performed bias voltage measurements described in this report to satisfy ourselves that Ohm's law holds over the stated range of bias voltages. If the air velocity and other parameters are known, it becomes possible to compute air conductivities or mean ionic mobilities directly. In a crude sense, slower ions are blown out of the tube before they can travel from one electrode to the other. Hence, conductivity goes down as air velocity goes up.

But it is for the specific purpose of measuring conductivity of moist air, presumably due mainly to dissociative equilibrium ion cluster pairs of water, that our cell has been designed and fabricated. In this sense, our cell may be unique in two respects:

1. It is large in size (L/A is small) compared to usual conductivity tubes, which have modest dimensions and very poor cell factors, and

2. It is used to measure static air under equilibrium conditions as a direct measure of water-related ions present, which might otherwise be swept out of the cell in a flowing system.

For example, it would seem that a measurement of "air" conductivity in the absence of water-related ions would be quite useless to a meteorologist trying to relate conductivity to atmospheric electricity, weather patterns, and so forth.

Mühleisen[20] found that moist air in an enclosed space acquires a negative space charge under high-humidity conditions and a positive charge at lower humidities. This could correspond to the much higher concentration of water ions and clusters at higher (s) values (equation 15), with the positive ions partially neutralized in water clusters like $H_3O^+ \cdot (H_2O)_n$ and an excess of OH^- ions present as more mobile, charge-carrying ions. It could explain changes in atmospheric air-earth conduction current which occur at sunrise or shortly thereafter.

Moore[16] states that usually the ions primarily responsible for the conduction of atmospheric electricity "are clusters comprised of a few molecules carrying either a single positive or negative elementary charge." This agrees well with our results. Yet in noting how certain electrostatic phenomena, such as the charging of a person who walks across a rug, very nearly disappear at high relative humidities, Moore states that some workers "have *erroneously* attributed this sensitivity to humidity of electrostatics to the electrical conductivity of the air." Rather, he attributes this to increased electrical conductivity of dielectric substances, due to adsorbed moisture layers above 50% RH ($s = 0.5$), which drain off accumulated charges in a fraction of a second. We have pointed out that our theoretically-derived dependence of conductivity of moist air upon (s) is much greater than previously thought (equation 20). Thus, the "erroneous" explanation above ought to be carefully reexamined in light of this new finding, since it has much more to recommend it than an insulator theory to which many exceptions suggest themselves.

The numbers of ions which must necessarily be present in moist air to account for conductivities found in our trials to date with the conductivity cell seem much larger than previously thought. For example, the water cluster theory predicts that, for saturated air at 20°C, a mass fraction $(n_c)_v = 6 \times 10^{-5}$ of clusters should exist (equation 5). Since an average cluster under these conditions contains 13 water molecules but only one ion ($N = 1$ assumed), the original fraction of water vapor ionized must have been $(6 \times 10^{-5})/13 = 0.46 \times 10^{-5}$ ion pairs of all water molecules. Since the concentration of saturated water vapor at 20°C is 0.0173 gm/liter or 5.8×10^{20} molecules per liter, the ion concentration is $5.8 \times 10^{20} \times 0.46 \times 10^{-5} = 2.65 \times 10^{15}$ ion pairs per liter or roughly 10^{15} ions per liter in unsaturated moist air. This figure is several orders of magnitude larger than values usually quoted for atmospheric ion densities, suggesting that water-related ions have not been properly accounted for previously. But their existence is essential to account for atmospheric infrared attributed to them, as discussed in this report.

V. CONCLUSIONS.

Initial data taken with the conductivity cell are in good agreement with theoretical predictions of the polymolecular water ion cluster theory. The measured conductivities are much greater than those obtained using traditional, flowing air sensors such as the Gerdien tube, indicating that under some conditions moist air can contain on the order of 10^{15} ions per liter, some of which originate from the ionic dissociation of water molecules themselves. The ions formed, for example, are of the form $H_3O^+ \cdot (H_2O)_n$, where in moist air "n" is on the order of 10 or 11. The positive ions are those referred to as polymolecular ion clusters in the water cluster theory, to which we attribute the infrared "continuum" absorption of the atmosphere. The numbers and kinds of ions necessary to explain atmospheric infrared absorption therefore are consistent with the ions necessary to explain electrical conductivities of moist air measured in initial operations with our cell. We conclude that the initial results suggest that the same species are responsible for infrared absorption attributed to water ion clusters in the atmosphere and the electrical conductivity of moist atmospheric air. A future report will discuss measurements to be made of moist air under a wide variety of conditions. In particular, the dependence of conductivity upon saturation ratio will be investigated for implications affecting present theories of electrostatic space charge dissipation.

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GLOSSARY

a	Molar concentration of subscripted species, moles per liter
A	Cross-sectional area of cell plates, square centimeters
α_c	Mass absorption coefficient of water clusters, square meters per gram
(c)	Mean cluster size, number of water molecules per cluster
C_c	Cluster concentration in vapor phase, grams per cubic meter
$C_{\mu f}$	Cell electrical capacitance, microfarads
$(C_s^o)_\lambda$	"Self-broadened" absorption coefficient of water "vapor", square centimeters per molecule-atmosphere (of vapor)
E_b	Cell bias supply voltage, volts
E_c	Voltage dropped across cell, volts
E_{VTVM}	Voltage read by 11 megohm vacuum-tube voltmeter, volts
k	A proportionality constant
K	Equilibrium constant for ionization of water, moles per liter
K_w	Ion product of water, moles squared per liter squared
L	Optical path length, meter, or cell plate spacing, centimeters
λ	Wavelength of spectral observation, micrometers
$(n_c)_v$	Mass fraction of clustered molecules in water vapor
$(n_c)_\ell$	Mass fraction of clustered molecules in liquid water
N	Number of ions per cluster
N_{avo}	Avogadro's number, 6×10^{23} molecules per gram-mole
p_o	Saturation vapor pressure of water, millimeters of mercury
R	Cell resistance, subscripted in units ohms or megohms
(s)	Saturation ratio (fractional relative humidity), % RH/100
T	Optical transmittance
$\theta_F, \theta_c, \theta_k$	Temperature, °F, °C, or °K, respectively
X	A constant, equal to 1000 divided by the equivalent conductivities of H^+ and OH^- ions at infinite dilution

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