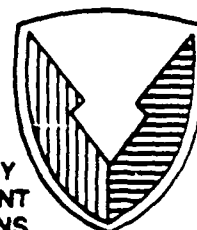④

# CHEMICAL RESEARCH, DEVELOPMENT & ENGINEERING CENTER

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## ELECTRICAL PROPERTIES OF ATMOSPHERIC MOIST AIR: A SYSTEMATIC, EXPERIMENTAL STUDY

Hugh R. Carlon
U.S. Army Fellow

RESEARCH DIRECTORATE

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Systematic new measurements of the electrical properties of atmospheric moist
air in a closed container near sea level are presented. Data were taken
using a vapor electrical conductivity cell of new design. The cell consisted
of 40 parallel square plates, each 26.5 $cm^2$, and separated by 0.66 cm. The
cell insulators were isolated from the cell plates by use of a technique that
completely eliminated insulator leakage as a source of experimental error.
Thus, very sensitive measurements could be made in still or moving air even
at near-saturation humidity. Measurements were made over a wide range of
humidities and electric field strengths ranging from near zero to 3 kV/cm.

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   Atmosphere
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19. ABSTRACT (Continued)

   Many new insights into the behavior of moist air in electric fields were
   gained, including: (1) a very steep equilibrium dependence of conduc-
   tivity (ion or charge carrier content) upon humidity; (2) "hysteresis"
   effects; (3) increasing complexity of behavior at field strengths
   greater than a few hundred volts per centimeter; and (4) regions where
   the conductivity of near-saturated air was constant over a range of
   field strengths. All results were consistent with the view that ions
   are produced in moist air from thin water films on conductive surfaces
   between which an electric field exists. This effect could contribute
   significantly to the earth's global current.

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PREFACE

The work described in this report was authorized under a U.S. Army Science and Engineering Fellowship. This work was started in May 1986 and completed in May 1987.

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# ELECTRICAL PROPERTIES OF ATMOSPHERIC MOIST AIR: A SYSTEMATIC, EXPERIMENTAL STUDY

## 1.    INTRODUCTION

This report presents results of a detailed, systematic study of the ion content and electrical properties of moist air at atmospheric pressure. Electrification of moist air by evaporating liquid water, particularly if the evaporation is energetic so that a finely divided fresh surface is produced, has attracted the interest of theoreticians and experimentalists for over two centuries. In 1782, Volta may have been the first to suggest that electrical charges are liberated by evaporating water,[1] and Faraday wrote in 1844 that jets of escaping wet steam can produce strong electrification.[2] Lenard (1892) found that the splashing of water produces charging,[3] while Simpson (1909)[4] and Nolan and Enright (1922)[5] observed charging from the violent breaking of droplets, which depended to some extent upon dissolved substances, but they could not measure electrification due to the gradual production of a new water surface. Blanchard (1961)[6] showed that ions can be generated by bursting water bubbles.

Carlon (1980) first reported the very large ion or charge carrier populations that can be generated in closed containers by boiling water.[7] Data were taken using large electrical conductivity cells of a new kind, which used compensation for insulator leakage currents. The basic design of these cells is being used in the present work but with further, important refinements. Measurements were extended to conditions of simple evaporation of stagnant water by Carlon,[8] and it was shown that boiling water is not necessary to produce very large ion populations in moist air, although boiling did produce larger populations than did simple evaporation. This work showed that the ions as measured between the cell plates were present in equilibrium populations that depended strongly upon relative humidity (RH) and, to some extent, upon the way in which evaporation (humidification) was carried out. For conductivity cells smaller than those described below and elsewhere by Carlon, the conductivity of the water ions in moist air between the cell plates and that due to leakage through thin films of water that condense on insulator surfaces can become comparable.[7-9] Both instances of conductivity show a very steep dependence upon humidity that is nearly identical for the insulators and for the moist air itself.

Moore discussed the insulator effects,[10] but the conductivity of moist air was not understood at that time. Investigations with better insulators and improved mechanical cell designs[9] confirmed that a new design that effectively eliminated the insulators as a source of experimental error was required if

unequivocal data were to be obtained, giving true ion populations in the vapor, particularly in conditions approaching saturation at high temperatures. This design, which has been proven in the present work, will be discussed in detail in this report.

Measurements were made at electric field strengths $E(V/cm)$ ranging from near-zero to 3 kV/cm, thus including regions where the electrical conductivity of moist air is linear with $E$ (i.e., where Ohm's law is obeyed), and those where the conductivity is decidedly nonlinear. Measurements were carried out in still and moving air over a wide range of RH and a limited, near-ambient range of temperatures. The new cell is shown schematically in Figure 1, and the series electrical measurement circuit is shown schematically in Figure 2. The supply or "bias" voltage, $E_b$, provided by one of two regulated power supplies, was thus divided between the cell voltage $E_c$ and the voltage $E_v$ read by a Schlumberger Model SM-5228 vacuum-tube voltmeter (VTVM) that had a constant electrical resistance of $R_v$ = 11 M $\Omega(1.1 \times 10^7 \ \Omega)$ regardless of the voltage range selected. Thus:

$$E_b = E_v + E_c \tag{1a}$$

or

$$E_c = E_b - E_v . \tag{1b}$$

Since the electric current i in a series direct current (dc) circuit is everywhere the same, the cell current $i_c$ in amperes can always be given by:

$$i_c = E_v/R_v = E_v/1.1 \times 10^7 = 9.1 \times 10^{-8} E_v . \tag{2}$$

Equation (2) can be used to calculate the cell current, but in this report the proportional voltage $E_v$ will always be used in the equations and figures because:

a.   It is much more convenient to express $E_v$ as read directly from the VTVM than to convert it to cell current [see Equation (2)].

b.   The ratio $E_v/E_b$ describes some very interesting properties of moist air, as will be shown.

Because both cell current $i_c$ and cell voltage $E_c$ were measured, the electrical power dissipated per cubic centimeter of vapor in the cell could be calculated accurately for given operating conditions. The vapor electrical conductivity cell described in the next section of this paper was operated at $E_b$ = 0 to 2 kV, thus producing electric field strengths of $E = E_b/0.66$ = 0 to 3 kV/cm.
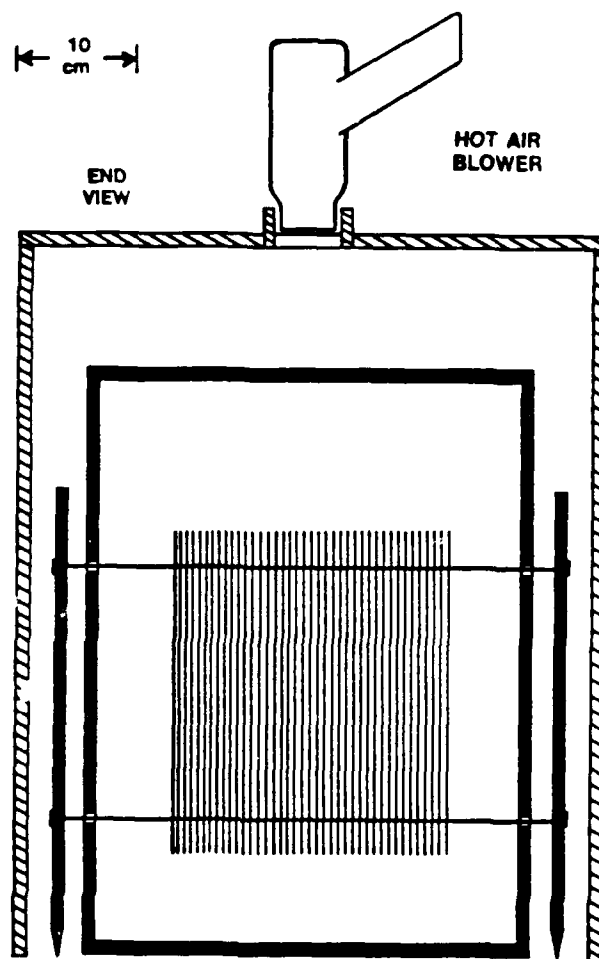
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Figure 1.   Diagram Showing How Cell Insulators Are Kept
Warm and Perfectly Dry by Hair Dryer in Duct
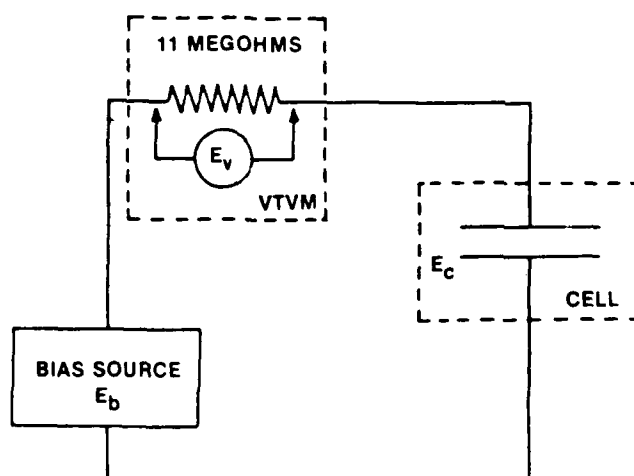or "Saddle" Outside Box



Figure 2.   Schematic Diagram of Electrical
Measurement Circuit for Cell

2.      APPARATUS AND METHOD

A Lucite box 105 cm long by 35 cm wide by 46 cm high contained the following apparatus:

a.      A large vapor conductivity test cell or capacitor (Figure 1)

b.      Probes to measure dry bulb temperature and dew point

c.      A 10-cm-diameter muffin fan that provided air circulation at about 1 m/s when desired

d.      A 600-cc Pyrex beaker containing a 500-W immersion heater and three plastic tubes that could be used to deliver cool fog into the box from an external ultrasonic nebulizer, liquid water into the beaker for boiling, or liquid water onto the floor of the box for evaporation, respectively.

A Yellow Springs Instrument Co. (YSI) Model 91 HF-calibrated precision electronic dew point hygrometer was connected to the probes and provided a direct meter readout of dew point and air temperature in the box.  It gave precision readings with the fan on or off, after stabilizing to one or the other condition for 3-5 min.  The muffin fan was a Dayton Model 100.  The external ultrasonic nebulizer, a medical instrument, was a Bennett Model US-1, which provided energy control settings on a scale from 0 to 10 to determine the fog output rate.  Lucite was chosen for the apparatus wall material because it had been used for many years in earlier work with no detectable difficulties,[7-9] and it allowed visual examination of water vapor condensation on the walls that were often wet during experiments except beneath the heated saddle as discussed below.  A 10-cm hole in the end of the box opposite the cell allowed access for tubes and wires.  The hole was sealed during experiments that were carried out at atmospheric pressure.  The box itself was sealed with rubber gaskets and wing nuts on threaded studs around two access panels that were used to remove or service the large cell or to clean the box.

The cell consisted of 40 square aluminum plates, each 26.5 cm square with an average separation of 0.66 cm between the plates.  Alternate plates were electrically connected to pairs of threaded stainless steel rods that carried the weight of the plates and to which leads were connected for conductivity readings.  The steel rods passed through small (1.3-cm diameter) clearance holes in the walls of the box to the insulators outside the box.  The insulators were vertical strips of polytetrafluoroethylene (PTFE) 1.2 cm thick by 2.5 cm wide by 39 cm long, machined to sharp points at their bottom ends (Figure 1).  The points rested on PTFE shims that were used to center the steel rods in the clearance holes.  There were two sets of 20 plates

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each, carried on their own steel rods and insulators, that were intertwined but otherwise not in direct physical contact. Thus, the two sets of plates could be adjusted horizontally by moving the insulators and vertically by using the shims to avoid contact between the rods and clearance holes and between the two sets of nested plates.

The insulators were enclosed in a removable duct or "saddle" (shown by cross-hatching in Figure 1) that was used to control their environment and, thus, to keep them dry during experiments. This was the novel feature of this apparatus design compared to earlier designs,[7-9] and it yielded unequivocal experimental results. Since the same water surface films condense on the cell plates and on unprotected insulators, any insulator leakage could confuse experimental results because it has the same functional dependency on temperature and water vapor partial pressure as the electrical conductivity of the moist air between the cell plates. By eliminating the insulator effects altogether, as in the present work, the true vapor conductivity can be measured.

The saddle containing the insulators was 32 cm wide and 5 cm thick along the side walls of the box, where the insulators were housed and the steel rod clearance holes were located. At its top, the saddle had a plenum with a height of 10 cm above the top of the box, and a hole was provided at its top center to mount a two-heat (600/1200 W) domestic hair dryer. The 600-W dryer setting proved adequate for all experiments. In the plenum were a Cole-Parmer Instrument Co. (CP) Model 3310-40 certified temperature and RH indicator and a precision CP Model 3310-20 RH indicator. In operation, typical conditions monitored in the plenum with the dryer operating at 600 W were 60 °C and <15% RH (the lower limit of the RH indicator). The dryer produced a slight overpressure in the saddle, thus preventing the escape of moist air from the rod clearance holes, further insuring that moist air in the box during experiments did not reach the saddle-housed insulators to confuse the vapor conductivity data. The bottom of the saddle on both sides of the box was left open, allowing hot air from the dryer to flow down over the insulators, across the insulator points and the PTFE shims, and back into the atmosphere. An electronic thermometer (Electromedics Incorporated, Model M-99) monitored the air temperature at the insulator points and shims. Readings of 50 °C were typical here. In most experiments, the standard practice was to maintain a differential of at least 6 °C between the temperature at the insulator points and shims in the saddle and the dew point in the box although differences of 20 °C or more were common. But even if the saddle dry air and box dew point temperatures were permitted to approach one another, insulator leakage currents were not measurable because of the extremely conservative design of the apparatus. This could be demonstrated during the experiments, since the current through the cell was not changed by starting or stopping the hair dryer.

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The water ion or charge carrier populations in moist air between charged plates (electrodes) are very strongly dependent on RH, as will be shown in the discussion of experimental results. The new cell design provided the experimental conditions needed to study the electrical properties of moist air with minimal error. The cell was used over a wide range of humidities and bias voltages down to zero. These were conditions yielding relatively low cell current densities, thus requiring excellent insulators.

The cell was wired in series (Figure 2) with either of two dc-regulated power supplies [0-400 V dc Shlumberger Model SP-2719 or 0-2000 V dc (2 kV) Brandenburg Model 475R] and the VTVM. Under most experimental conditions, results revealed that when the supply or bias voltage was kept at 400 V dc or less, plots of data for $E_v$ versus $E_b$ were perfectly linear, i.e., Ohm's law was obeyed. Thus, many humidification experiments were conducted using the 400-V dc power supply, which gave linear behavior for singly charged water ions except under extremes of humidity, as will be discussed below. A variety of experiments could be performed with a large cell and its apparatus; humidification could be carried out by using the ultrasonic nebulizer, by boiling, or by evaporation of standing water in the box. Drying could be effected either by heating (i.e., by continuing to run the dryer after humidification had ceased) or simply by allowing drying to occur over many hours under ambient conditions. The voltage $E_b$ could be kept constant or varied over the range of 0-2000 V dc (0-2 kV), producing in the latter case very interesting data plots of $E_v$ versus $E_b$. Measurements could be made in either still or moving air. Operation of the fan produced negligible ion populations in the moist air.

3.      RESULTS AND DISCUSSION

The current density in $A/cm^2$ (j) for water ions in moist air between the plates of a cell similar to those used in these experiments is given by

$$j = I_{cc} \ e \ N \ u \ E \tag{3}$$

where

$I_{cc}$ =   the number of ions per $cm^3$ of vapor at any instant

e =   the value of the electronic charge (1.6 x $10^{-19}$ C)

N =   the number of charges per ion

u =   the ion mobility

E =   the electric field strength (V/cm)

Except where noted here, N is taken as unity and u as 1 $cm^2/V$ s, which are typical parameters for singly charged small cluster ions of perhaps 10-12 or more water molecules such as are almost certainly being measured in this work.[11] For these measurements of electrical conductivity in moist air the dc resistance or reciprocal conductance of the cell in ohms, $R_c$, is related to $I_{cc}$ by the equation

$$I_{cc} = \frac{L}{A} \frac{1}{R_c e\ N\ u} \tag{4}$$

where L is the plate spacing in centimeters and A is the total plate area of the cells in square centimeters. The large cell consisted of 40 square metal plates, each 26.5 cm square, separated by an average spacing of 0.66 cm. Thus, A = $(26.5)^2$ x 39 = 27,388 $cm^2$.

For the series circuit in Figure 2,

$$R_c = R_v\left(\frac{E_b}{E_v} - 1\right) \tag{5}$$

where the constant resistance of the VTVM was $R_v$ = 11 M$\Omega$ = 1.1 x $10^7\Omega$. Combining equations and evaluations gives the following equation for the cell:

$$I_{cc} = \frac{L}{A} \times \frac{1}{R_v\left(\dfrac{E_b}{E_v} - 1\right)e\ N\ u} = \frac{1.37 \times 10^7}{\left(\dfrac{E_b}{E_v} - 1\right)N\ u} \tag{6}$$

For example, if the cell were used to measure singly charged ions (N = 1) having an average mobility u = 1 $cm^2/V/s$, and if the VTVM reading (Figure 2) were $E_v$ = 2 V dc at a bias or supply voltage $E_b$ = 400 V dc, Equation (6) indicates that the average ion or charge carrier population per cubic centimeter of moist air would be $I_{cc}$ = 6.9 x $10^4$.

The most precise data taken with the new cell were those for which the ultrasonic nebulizer was used to humidify the large box. In a typical experiment starting with a dry box, the humidity was gradually increased by nebulizing a cool water mist or fog through a plastic tube and into the box. As the humidity increased, voltage readings ($E_v$, Figure 2) were taken using the VTVM at intervals of 1 min or less. As humidification proceeded in such experiments, it was found that $E_v$ and the equivalent

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ion or charge carrier population between the cell plates [Equation (6)] in the vapor increased very rapidly. At higher humidities the functional dependence of this increase at a given temperature was approximately the 13th power of relative humidity, i.e.,

$$I_{cc} = \tilde{K}_t \left(\frac{\%RH}{100}\right)^{13} \tag{7}$$

where $K_t$ is the value of $I_{cc}$ at saturation (100% RH) and tended to increase with temperature, but $K_t$ was by no means constant between experiments, particularly at higher bias voltages as will be discussed. The continuity of the bias voltage $E_b$ also affected $K_t$. When bias was applied continuously, $K_t$ was reduced by a third or more compared with when bias was applied only to read $E_v$. Typical values (bias to read) were $K_t = 2.5 \times 10^5$ at 25 °C, and $5.7 \times 10^5$ at 35 °C; but regardless of how $K_t$ varied for different experimental conditions, the 13th-power dependence of $I_{cc}$ or $E_v$ on RH was remarkably consistent for $E_b = 400$ V dc and humidities above 70% RH.

Similar steep humidity dependencies had been observed by the author for insulator leakage due to surface water films in earlier experiments carried out to evaluate these leakage effects. But until the present work, in which the large cell insulators in the saddle could be dried to very low humidities at higher temperatures while the cell plates measured moist air conductivity under much wetter conditions inside the box, it was not known unequivocally that the ion population between cell plates in moist air varies as $\sim f(s)^{13}$, where s = %RH/100, under typical, humid atmospheric conditions. These results suggest that the ion or charge carrier species that are present in moist air and that account for its electrical conductivity with steep humidity dependence are also present in thin, condensed films on conductors from which they are released into the moist air in the presence of an electric field.

Figure 3 shows data for the humidification of the large box using the ultrasonic nebulizer in an initially dry box, fan on, $E_b = 400$ V dc. The data points are closely placed along the line approximating $f(s)^{13}$.
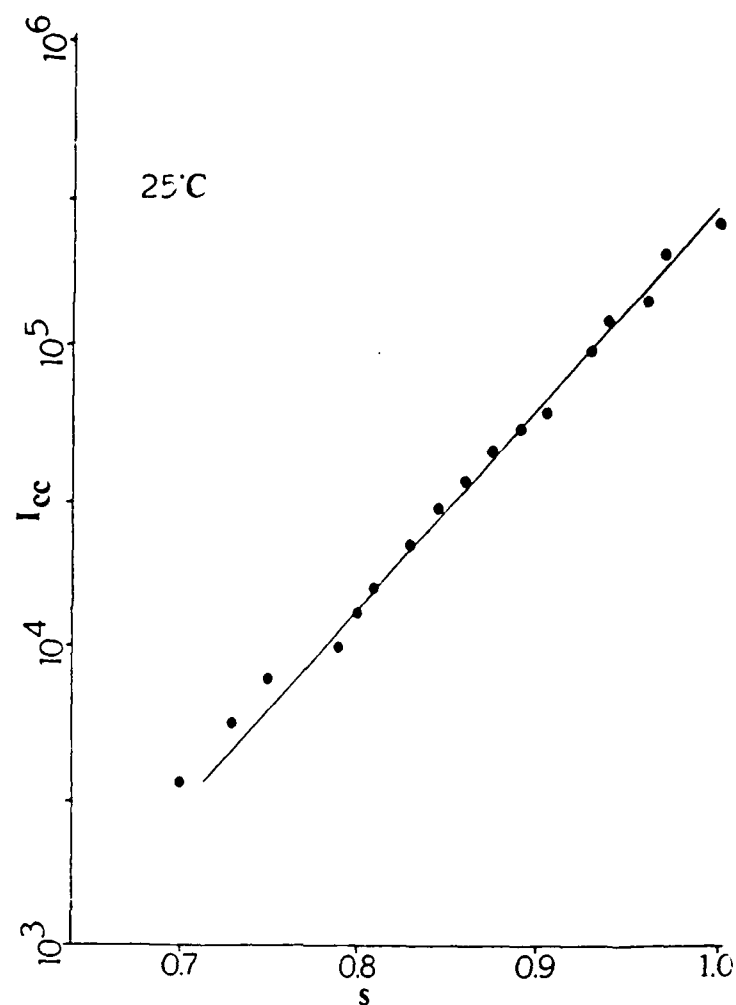
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Figure 3. Ion or Charge Carrier Population per Cubic
Centimeter of Vapor, $I_{cc}$, vs. Saturation Ratio
(s = %RH/100)


When $E_b$ was raised above 400 V dc in many experiments
(electric field E = $E_b$/L = 400/0.66 = 600 V/cm), the electrical
properties of moist air became more complex than in smaller
fields where Ohm's law was obeyed. This is illustrated in
Figures 4-6 for bias voltages of 0.4, 1.0, and 1.5 kV, respec-
tively. Note that Figure 4 has a different ordinate scale than
Figures 5 and 6. Temperatures were 24-26 °C. The solid points
show data for humidification of the large box using the ultra-
sonic nebulizer, followed by drying (hollow points) by mixing
with the drier room air without heating. Although the data
points cluster about the dashed lines, approximating an f(s)[13]

dependency, the values represented are not always as close to the
equilibrium values as they were, for example, in Figure 3.
Rather, "jumps" or "zigzags" of $E_v$ with s were observed. In

effect, the moist air was electrically "noisy." Such behavior

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10⁻⁶  10

10⁻⁷  1

AMPERES

Eᵥ

10⁻⁸  10⁻¹

10⁻⁹  10⁻²

$E_b = 0.4$ kv

0.7          0.8          0.9          1.0

S

Figure 4.   Data Plots of Voltmeter Reading, $E_v$ (Figure 2),
and Cell Current from Which Average Moist Air
Ion or Charge Carrier Populations per Cubic
Centimeter between Cell Plates Can Be Calculated
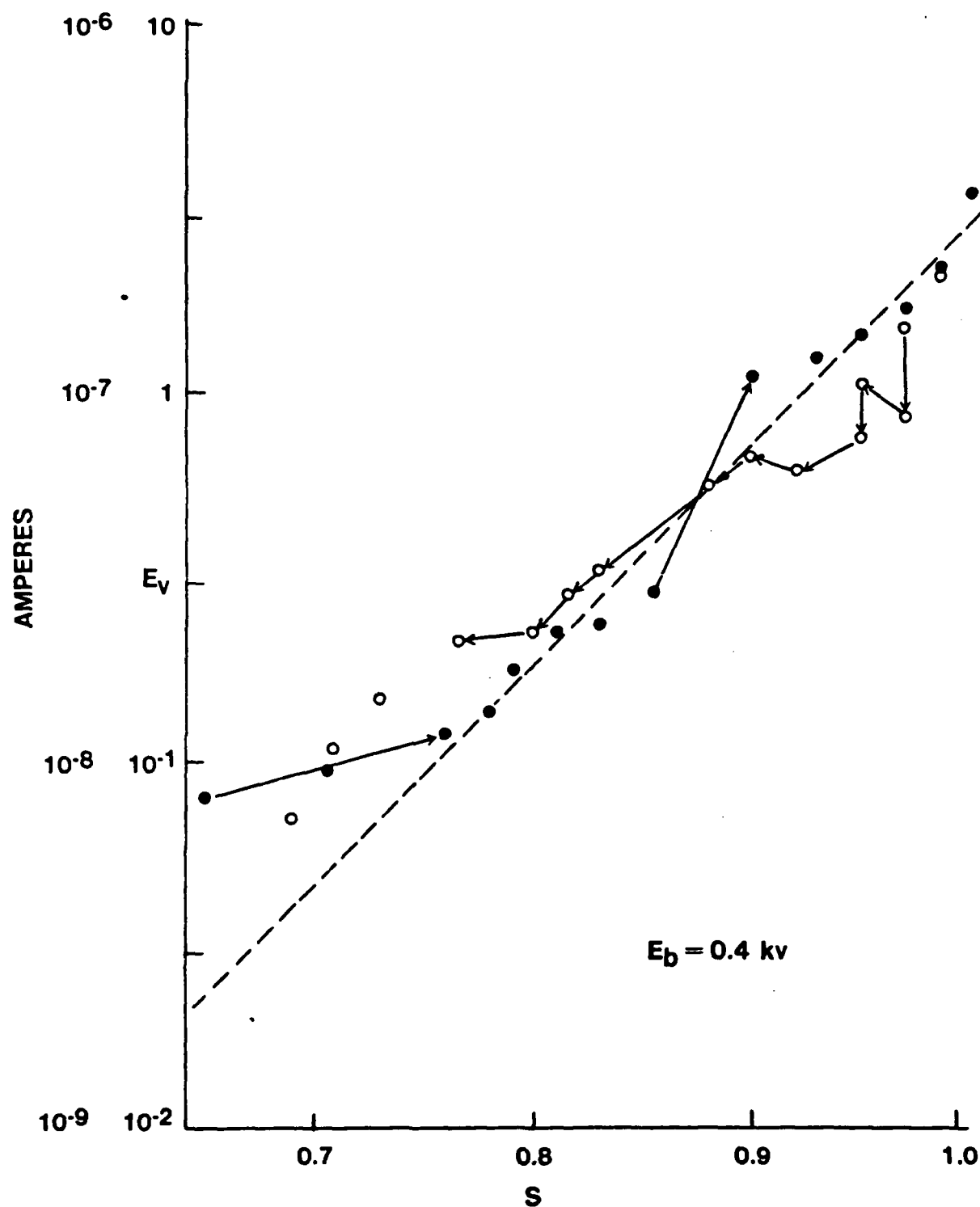($E_b$ = 0.4 kV)

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Figure 5.  Data Plots of Voltmeter Reading, $E_v$ (Figure 2),
and Cell Current from Which Average Moist Air
Ion or Charge Carrier Populations per Cubic
Centimeter between Cell Plates Can Be Calculated
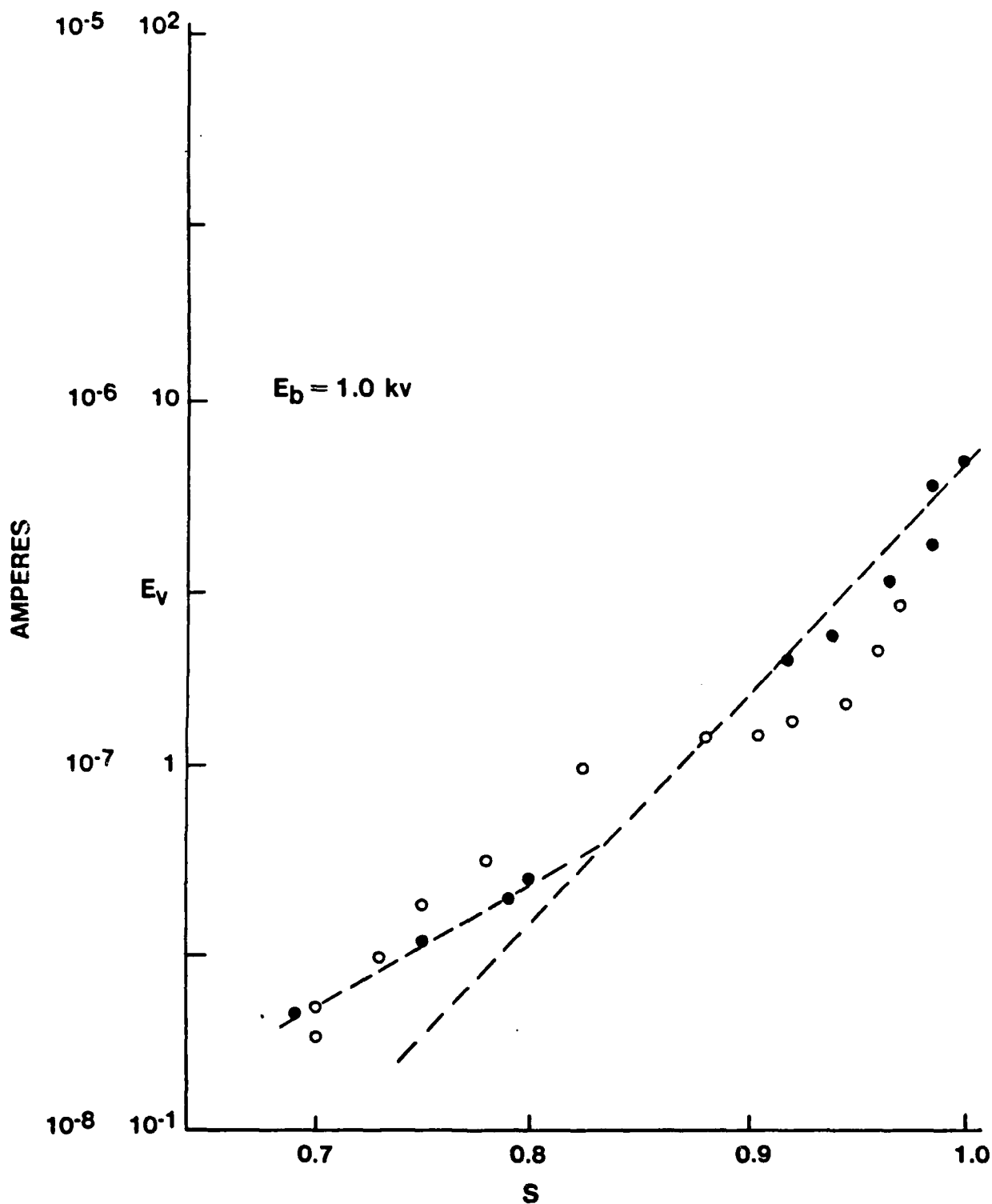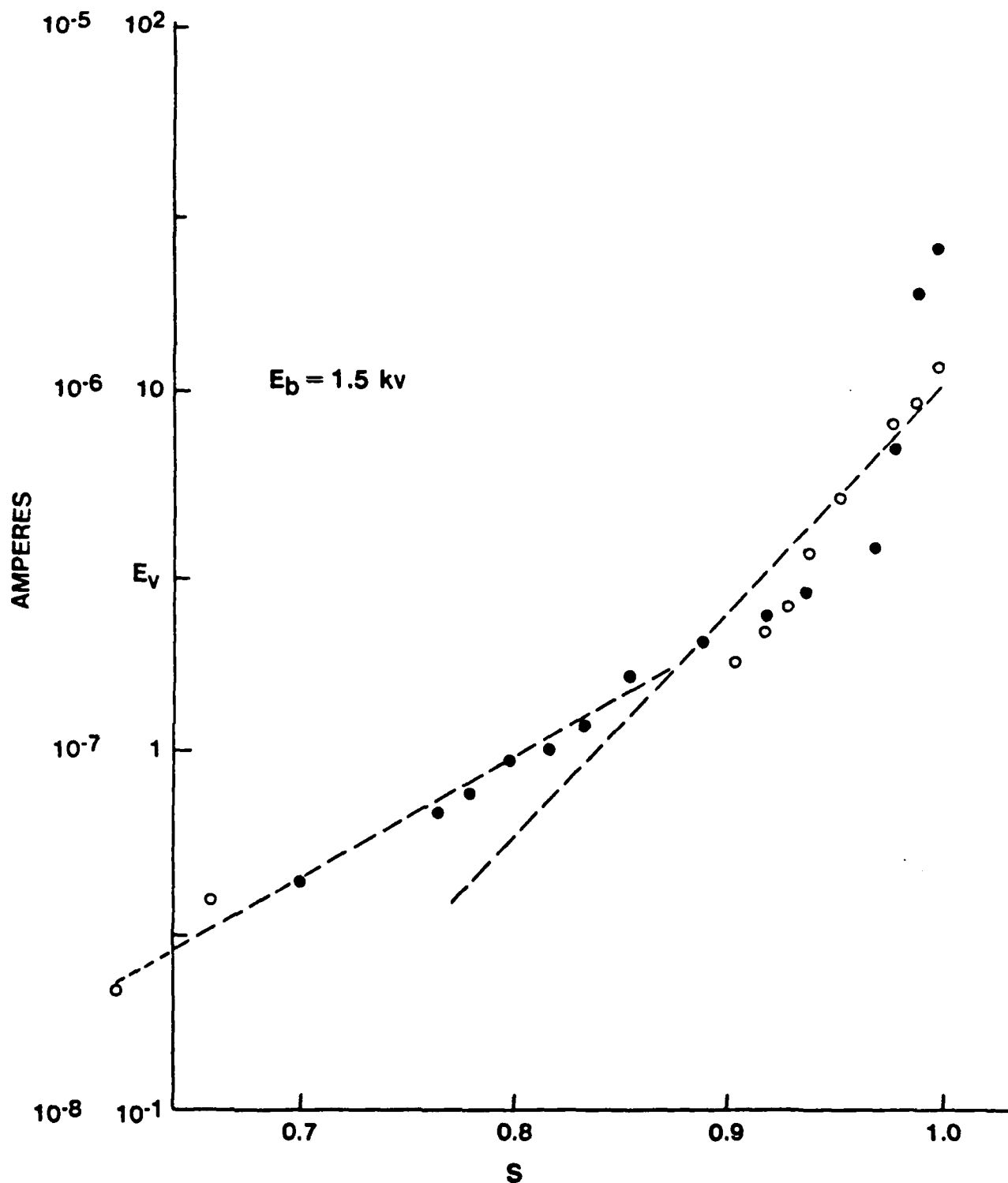($E_b$ = 1.0 kV)

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Figure 6. Data Plots of Voltmeter Reading, $E_v$ (Figure 2), and Cell Current from Which Average Moist Air Ion or Charge Carrier Populations per Cubic Centimeter between Cell Plates Can Be Calculated ($E_b$ = 1.5 kV)

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was observed repeatedly in many experiments; it did not originate from instrumental artifacts or experimental problems, but was real. This behavior could be due to changes in the rate at which ions leave water films on the cell plates and enter the vapor in response to changing experimental conditions or to sudden changes in average mobility of the ions corresponding to changes in the average numbers of water molecules they contained [Equation (6)]. The "jumps" were instantaneous, and the frequently observed values of $E_v$ had simple integer relationships, e.g., $E_v$ might jump (or drop) by a factor of 2:1, 4:3, 5:2, etc. Examples are seen in Figure 4. Behavior that could be called "hysteresis-like" also was observed. An example is shown in Figure 5, where the (hollow) data points for drying first fell below the dashed equilibrium line $[f(s)^{13}]$ to the right of this line and then, as dehumidification continued, crossed over the equilibrium line and rose above it, where they remained at lower humidities. Such hysteresis effects were often seen during humidification as well. Occasionally, a true "hysteresis loop" was formed by data points about the equilibrium line during cyclical (humidification and drying) experiments. This behavior first suggested that water films condensed on the cell plates could be contributing to vapor conduction in some previously unknown way.

Yet another interesting property of electrified moist air seen in Figures 4-6 is that a "knee" or discontinuity occurs where the slope of the curve changes from $\sim f(s)^{13}$ at higher humidities to $\sim f(s)^7$ or $\sim f(s)^8$ at lower humidities. The location of this knee is seen to depend on the bias voltage or electric field strength. In Figure 4, for $E_b = 0.4$ kV ($E = E_b/L = 600$ V/cm), the knee is near $s = 0.75$ (75% RH); in Figure 5, for $E_b = 1.0$ kV ($E = 1500$ V/cm), the knee is near $s = 0.83$; in Figure 6, for $E_b = 1.5$ kV ($E = 2250$ V/cm), the knee is near $s = 0.90$. From such data plots, it is possible to construct average or near-equilibrium curves like those shown in Figure 7, for a variety of bias voltages. Because of hysteresis effects similar to those seen in Figures 4-6 it was seldom possible to reproduce precisely the curves of Figure 7 in experiments; but these curves are very useful in analyzing the expected electrical behavior of moist air between the cell plates under given conditions. For example, Figure 7 suggests that above some values of $E_b$, perhaps in the range 2 to 3 kV, the $\sim f(s)^{13}$ dependency of $E_v$ seen to the right of the dashed line (which is the locus of the knees seen in Figures 4-6) will no longer be observed regardless of the saturation ratio, $s = $%RH/100. If so, this could indicate that above some bias voltage or electric field strength the ions being measured are multiply charged ($N > 1$) at all humidities, or are supplemented by other kinds of atmospheric ions, and that the smaller slope of the solid curves to the left of the dashed line in Figure 7 corresponds to these conditions.
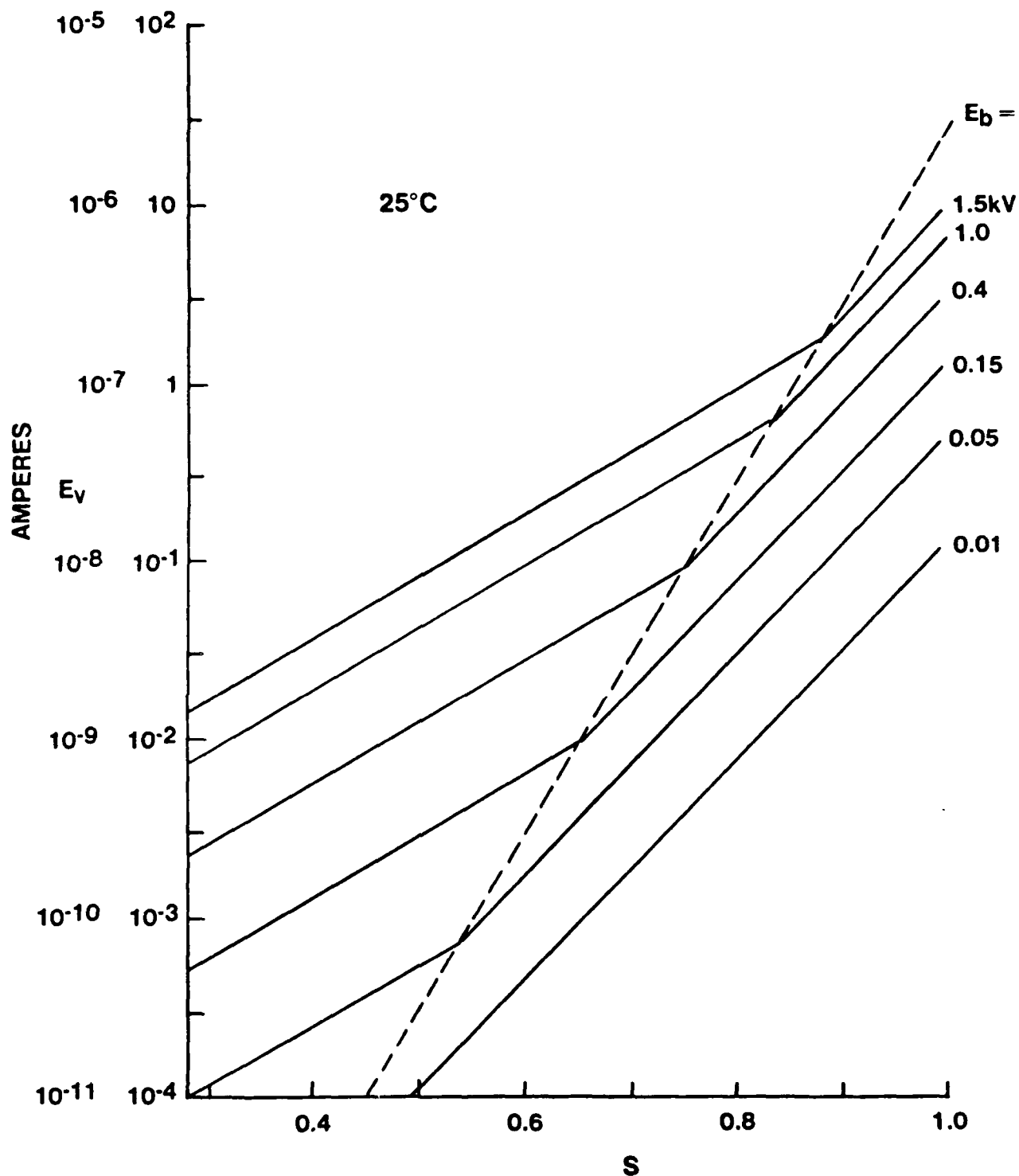
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Figure 7. Using Data Like Those in Figures 4-6, These Curves Were Constructed for Near-Equilibrium Conditions with Bias Voltage Applied Continuously to the Large Cell

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From curves like those in Figure 7, one can construct the average or near-equilibrium curves in Figure 8, which give important insights into the expected interrelationships between $E_v$ and $E_b$. These interrelationships can be investigated experimentally. Figure 8 indicates that for low bias voltages or field strengths where Ohm's law is obeyed and the ions are singly charged (to the left of the dashed line), $E_v$ will increase linearly with $E_b$ at a given humidity (solid curves) up to some value of $E_b$, where $E_v$ will begin to increase more rapidly than $E_b$. Experimentally, this was the result found. Figure 9 shows typical data and indicates that even relatively minor experimental parameters affect the data obtained, such as whether the bias voltage $E_b$ was increased or decreased as the corresponding values of $E_v$ were recorded. In experiments where $E_v$ was measured over a range of values of $E_b$, it was preferable to apply the bias voltage continuously as it was varied, so as to read all values quickly at a given humidity. This resulted in somewhat lower values of $E_v$ being read than if the bias voltage $E_b$ as applied only to read $E_v$, but the observed functional dependencies were not otherwise affected.

Very useful experiments were performed in which the large box was humidified to near-saturation and then dried or dehumidified while values of $E_v$ versus $E_b$ were recorded at various humidities. Typical data are shown in Figures 10 and 11. Figure 10, which depicts humidification of the cell in its box at 23 °C using the ultrasonic nebulizer, shows upturning of the right-hand ends of the curves for various increasing humidities, as in Figures 8 and 9. However, as saturation is approached, the curves begin to flatten. In Figure 11, which is a continuation of data from Figure 10, the upper curves actually invert and exhibit flattened tops over the range of bias voltages at the maximum humidity reached in these trials (98% RH). This behavior seems to indicate that when moist air between moist electrodes approaches saturation, some sort of limit or upper value is reached, at least over a range of bias voltages or field strengths, where the total population of ions available to carry all of the electric charges cannot exceed some maximum number. Figure 12 also shows this curve-flattening, which is seen in virtually all experiments when "hard" saturation (100% RH) is achieved by using steam from boiling water to humidify the box. Here, over the range of $E_b$ shown, the curve-flattening is more pronounced than in Figure 11 and actually shows negative resistance characteristics not unlike those exhibited by some semiconductors; i.e., for the top curves in Figure 12, the cell
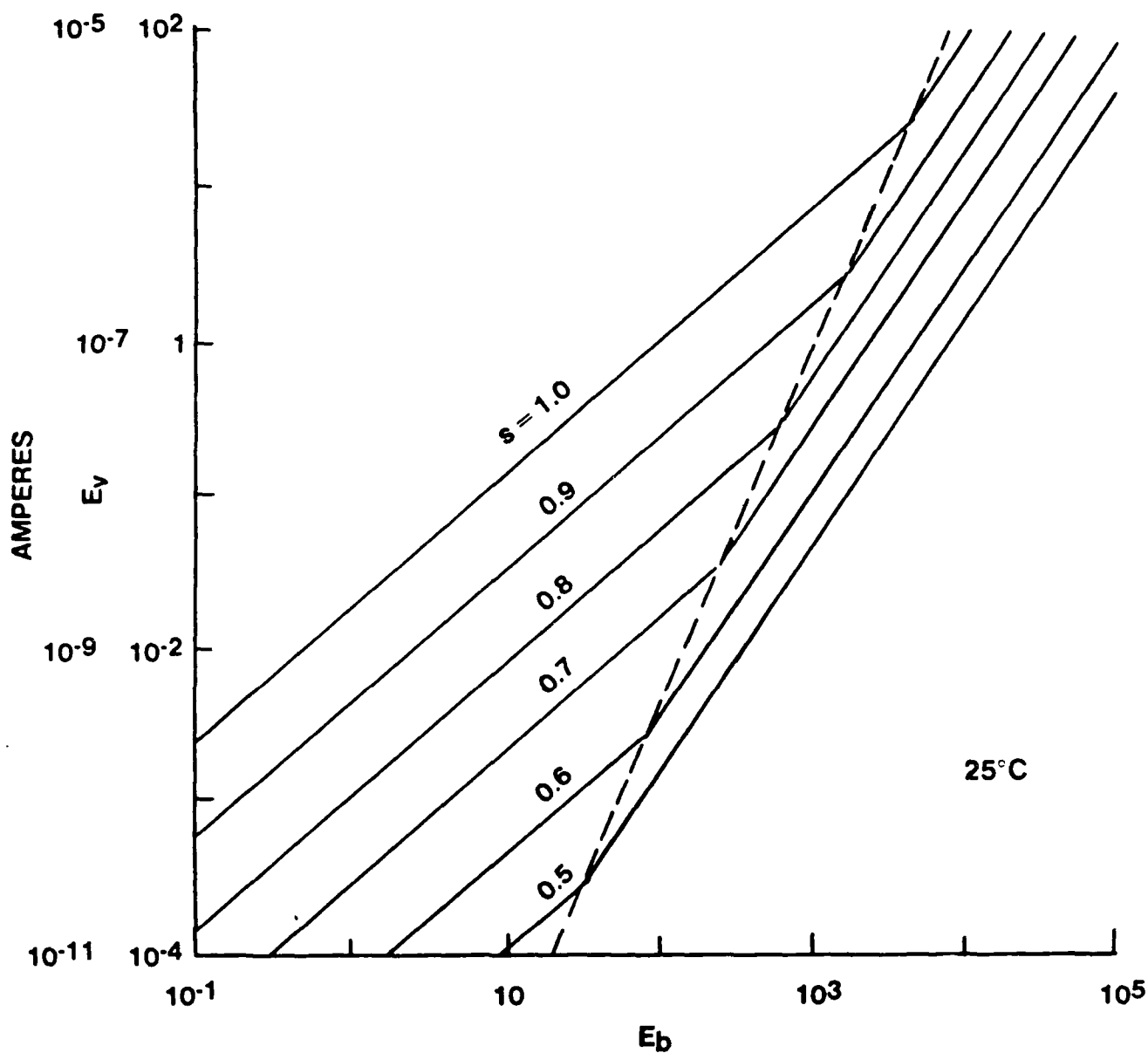
Figure 8. From Figure 7, These Curves Were Constructed for Near-Equilibrium Conditions with Bias Voltage Applied Continuously to the Cell
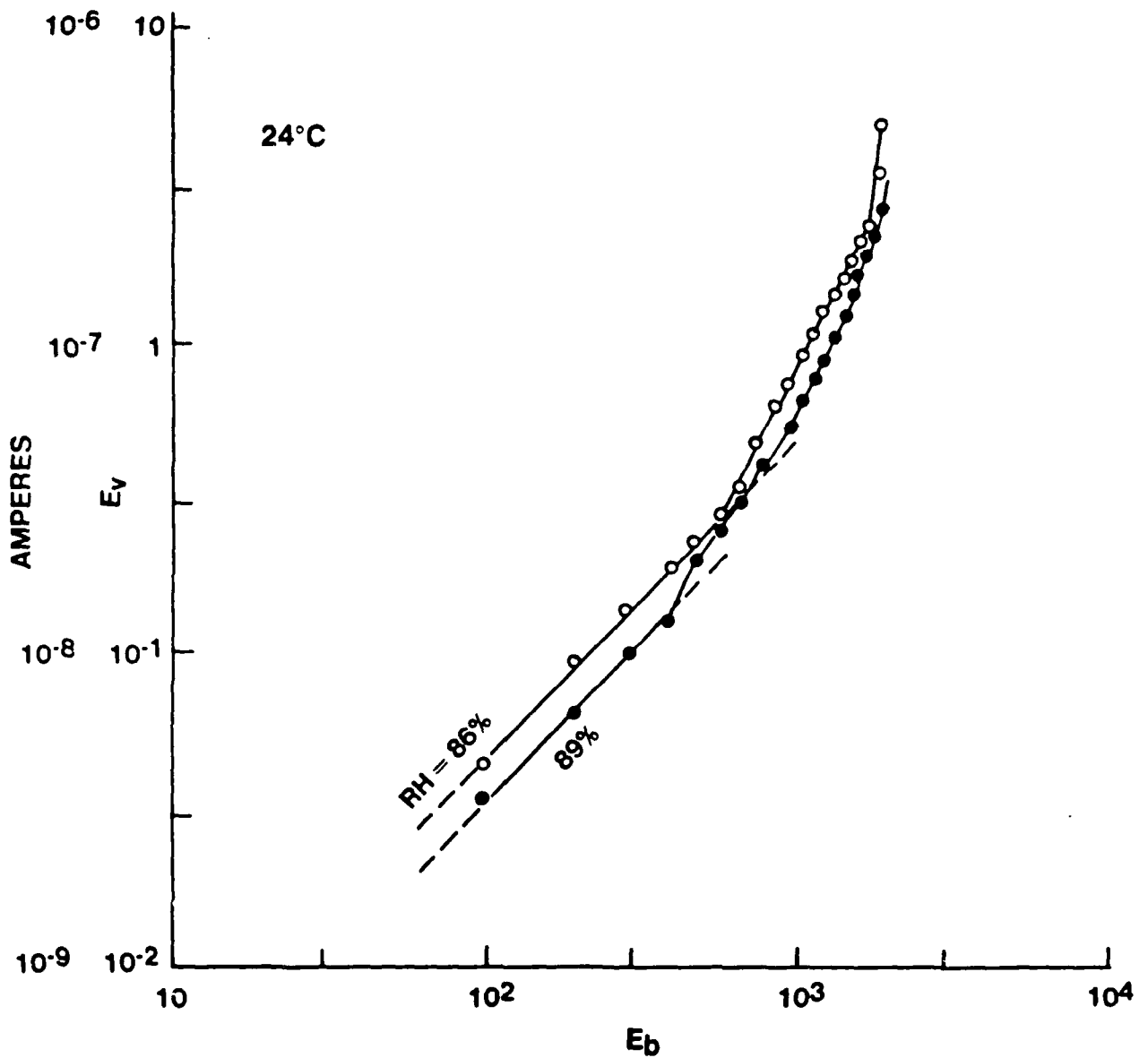
22

Figure 9.    Data Taken for Moist Air at 24 °C, Fan On, Continuous
Bias Voltage, Showing Departure from Linear
(Ohm's law) Behavior at Higher Bias Voltages

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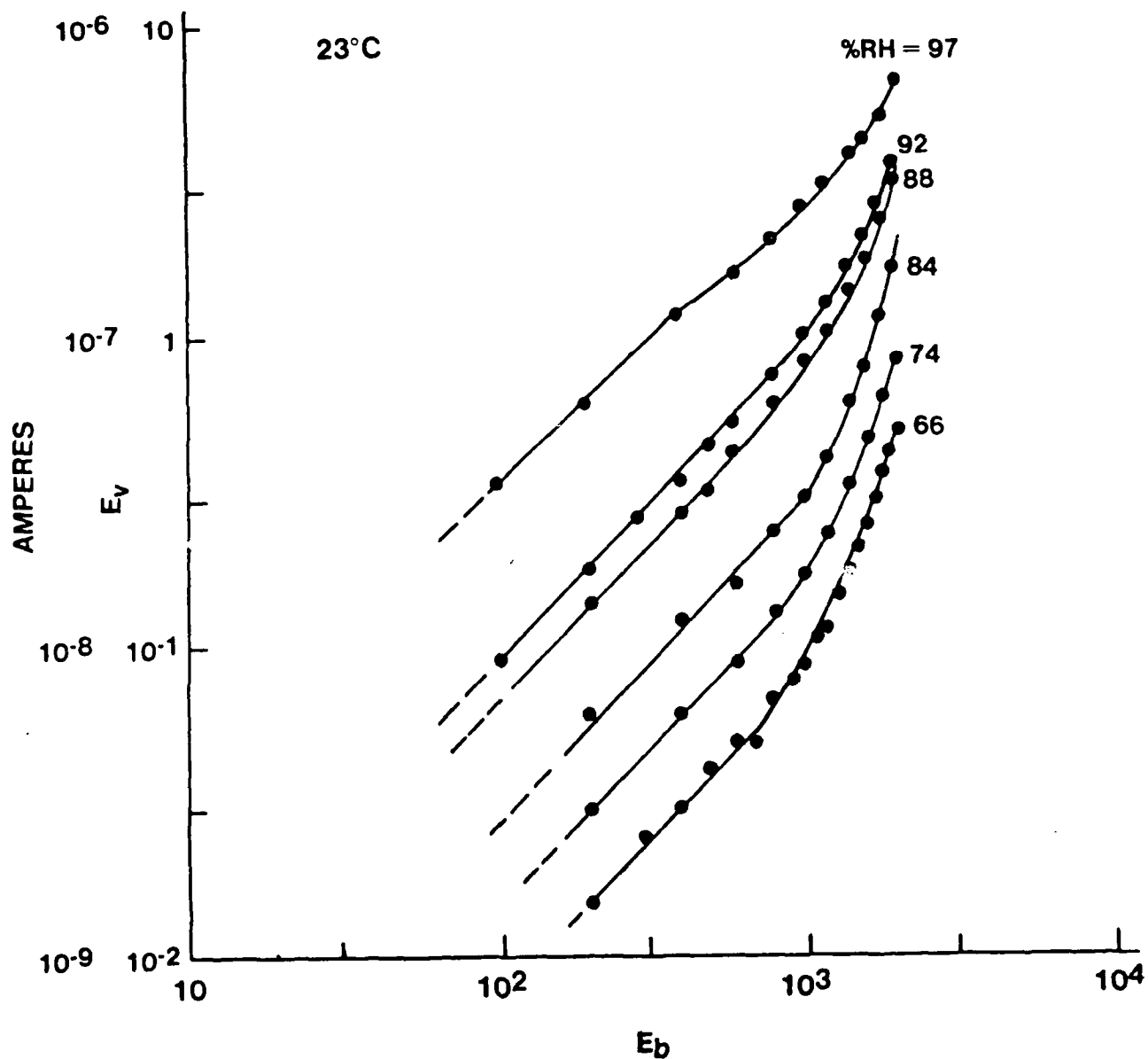
Figure 10. Data Taken for Air at 23 °C Being Humidified Using Ultrasonic Nebulizer, Fan Off, Continuous Bias Voltage Decreasing for Readings
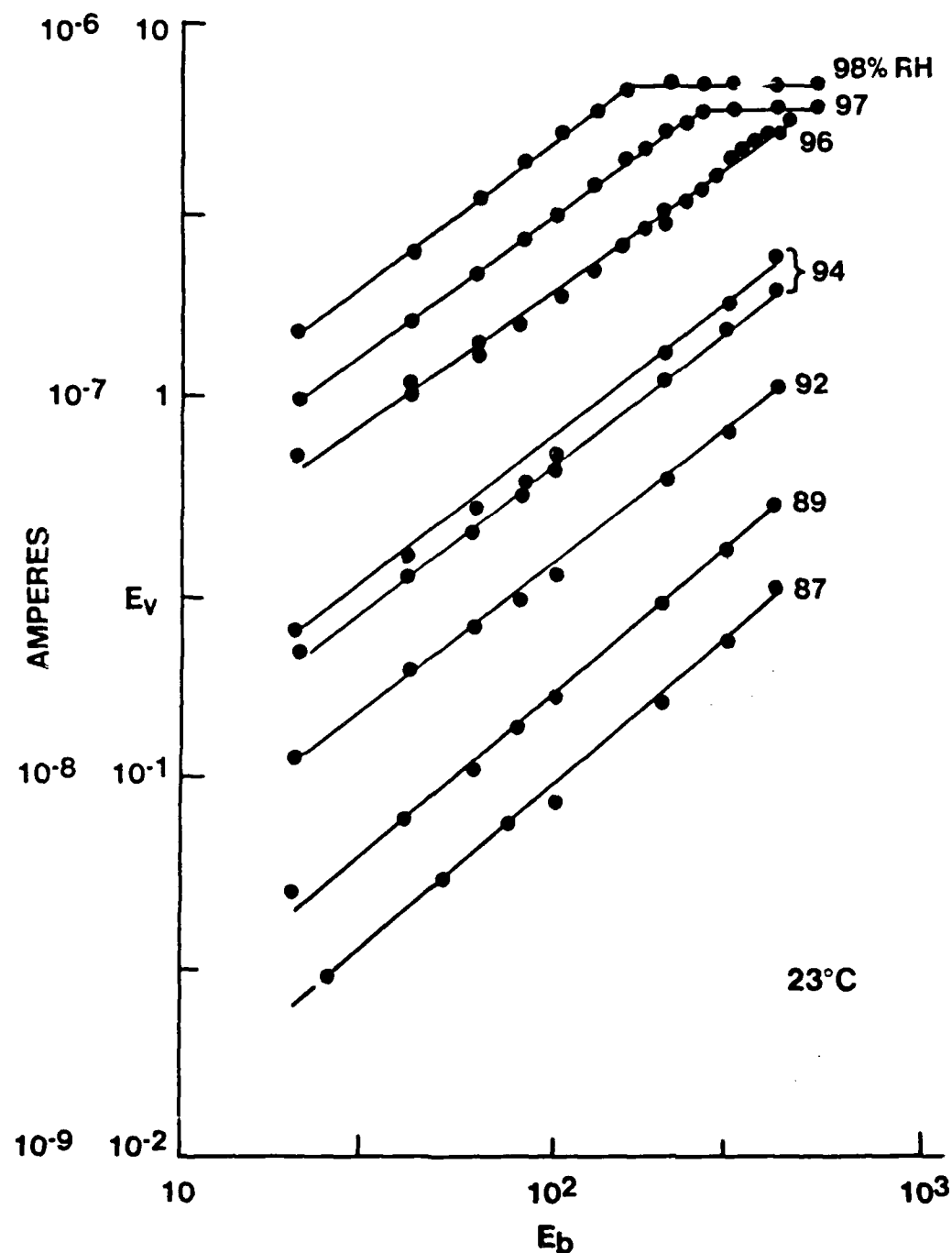
24

Figure 11. Continuation of Data in Figure 10 for Air Near
Saturation, "Drying Down" Without Heating, Fan Off,
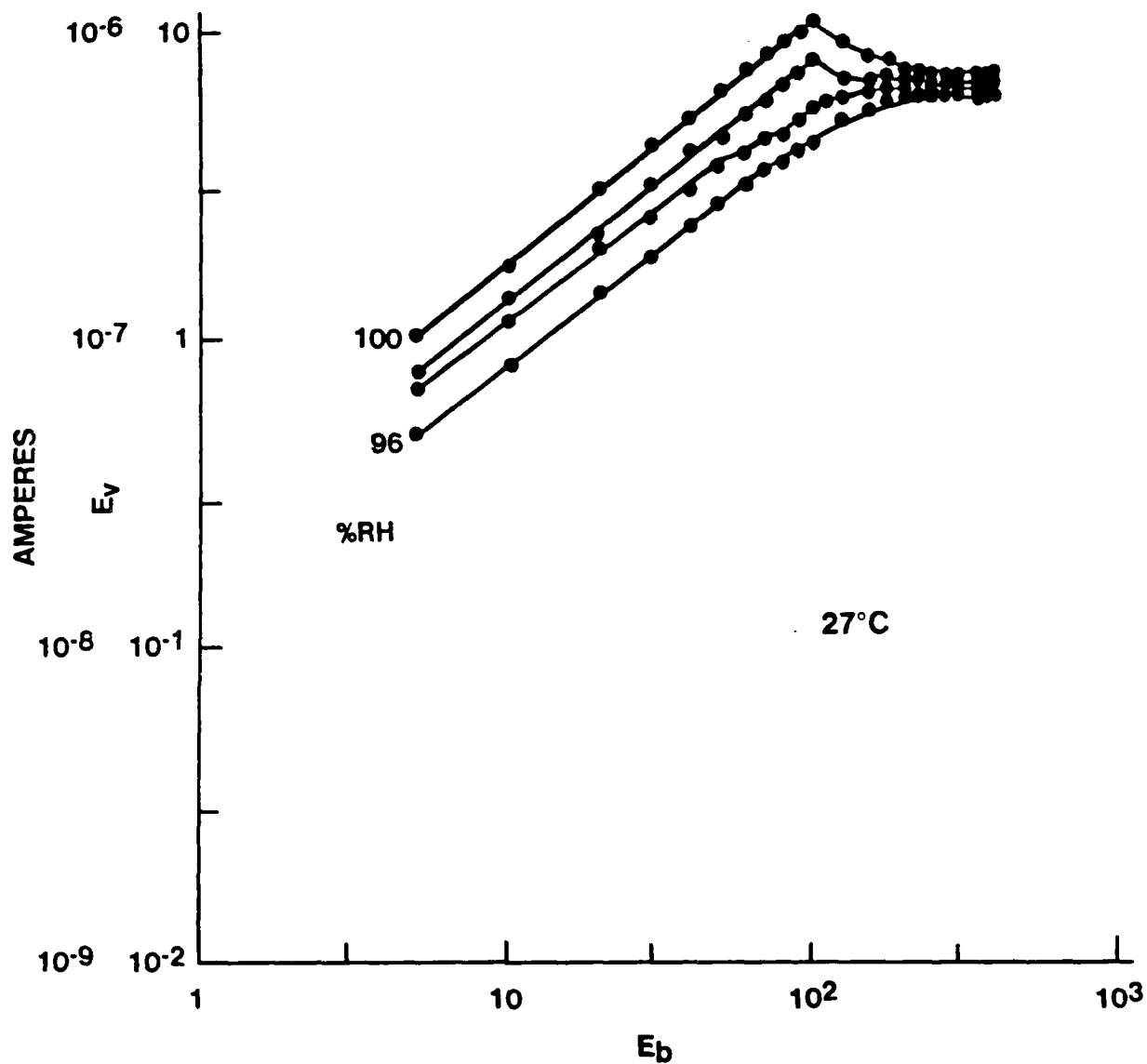Continuous Bias Voltage Decreasing for Readings

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Figure 12.   Data Taken for Air at 27 °C Being Humidified to
"Hard" Saturation by Steam from Boiling Water,
Fan Off, Continuous Bias Voltage

current as measured by $E_v$ [Equation (2)] actually decreases with increasing $E_b$. This condition is relieved as RH falls toward 96%.

Returning to Figure 11, it can be seen here too that as RH falls, there is an orderly progression of quite linear curves for $E_v$ versus $E_b$ towards lower values. However, if the "drying down" curves of Figure 11 are compared with those for initial humidification in the same experiment (Figure 10), it will be noted that curves for comparable relative humidities in the two figures do not show comparable values of $E_v$ for given values of $E_b$.

Thus, in humidification versus dehumidification, the "hysteresis" effects about equilibrium values, as discussed earlier, are again manifest. This behavior could be explained by the formation of thin water films on the cell plates during humidification and delayed evaporation of the films upon drying, provided that the water films themselves were sources of water ions or charge carriers.

The following description of moist air conductivity is suggested by the compilation of all data from the past year's research.

In the atmospheric electric fields ranging from fair-weather values ($\sim 0.5$-$100$ V/cm or more), moist air conductivity obeys Ohm's law. At a given RH and temperature, the current between two electrically conductive bodies is exactly proportional to the field between them.

In this Ohm's law region, increasing RH in a given field strongly increases the current between the two bodies; the equilibrium current increase as $\sim(RH/100)^{13}$. The current increase is due to surface water films on the bodies, whose thickness increases with RH, and it arises from charge carriers that leave the water films and cross the gap between the bodies:

$$\left( H_2O \right)_n^{\pm} \: e \: \rightleftharpoons \: \left( H_2O \right)_n^{\pm} \tag{8}$$

The number n is of the order 10-12 (Chalmers, 1967).[11] The current resembles that due to any surface leakage of insulators supporting the conductive bodies and can be easily mistaken for such.

As long as the RH is 50-60% or less, the number of charge carriers is not large compared with other atmospheric ions. If the bodies are electrodes in a vapor conductivity cell, their size and separation will determine the observed cell current, as would be expected for an air-dielectric capacitor. But as RH increases, the charge carriers [Equation (8)] soon outnumber other ions. If the surface water films are

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"perfect"*, this behavior continues to saturation vapor pressure where currents up to $10^5$ times larger than those in dry air can be measured. However, if the surface films on the electrodes are disturbed under these conditions, e.g., if they coalesce into bulk liquid water, the cell current can fall precipitously by orders of magnitude. Measurements show that bulk liquid water does not produce ions from its surface even in large electric fields.

For larger atmospheric electric fields of several hundred volts per centimeter or more, including those leading to thunderstorm activity, moist air conductivity no longer obeys Ohm's law but instead becomes nonlinear with field strength. Although RH still contributes to the current between two conductive bodies in a given field, the current in the nonlinear region increases as $\sim(RH/100)^{7-8}$, rather than $\sim(RH/100)^{13}$ as in the Ohm's law region. The total current increases rapidly as ions, including water ions, are formed in these larger fields by molecular dissociation:

$$\left(H_2O\right)_{m+n+1} \rightleftharpoons H^+\left(H_2O\right)_m + OH^-\left(H_2O\right)_n \tag{9}$$
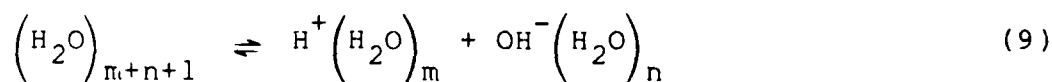
As in the Ohm's law region, perfect water films on electrodes in the larger fields of the *nonlinear* region are found to increase the conduction current markedly, but bulk liquid water on an electrode gives no current increase; instead, droplets are produced that are attracted away from the electrode to the nearest surface of opposite polarity.

To summarize, in fair-weather atmospheric fields at higher RHs, surface water films produce large conduction currents between conductive bodies that are due to charge carriers that leave the surface water films on the bodies and cannot be measured by conventional means. In larger fields, including foul-weather ones, ions are produced by molecular fragmentation of water and other substances, but surface water films also contribute to conduction. These effects are fundamental to an understanding of atmospheric electricity because they could have a significant effect on the earth's global current.

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*In practice, a "perfect" water film can be achieved by fresh condensation on a smooth surface, suggesting that it is finely structured. Evaporation of standing water in a closed container can produce such a film on a surface although its thickness and thus its activity will not be as great as that for fresh condensation at saturation humidity on the surface when an active evaporation source (nebulizer, boiler, etc.) is employed.

## 4. CONCLUSIONS

Some of the experimental results presented in this report indicate electrical behavior that has not been previously observed in atmospheric moist air. Careful technique and replication of experiments have shown unequivocally that the data presented here are real and do not arise from insulator leakage effects. New findings in this work can be summarized as follows:

a. In uniform electric fields of a few hundred volts per centimeter or less, moist atmospheric air between the cell electrodes (plates) is comparatively well-behaved. Ohm's law is obeyed, and conductivities measured can be explained by the presence of singly charged ions or charge carriers comprising an average of 10-12 water molecules that carry a single charge from the thin water film on a given plate to the opposite plate [Equation (8)]. The total current is found to be steeply dependent upon RH, varying approximately as the 13th power of the "saturation ratio", $s = \%RH/100$. In other words, the charge carrier density between the plates varies as $\sim f(s)^{13}$, which must indicate an average or "equilibrium" condition for thin water films on plates in humid air. Thus, greater film thicknesses and unusually high charge carrier densities will occur at high humidities [Equation (7)].

b. These equilibria involving cell plates and water films, whose thicknesses increase with RH in moist air, are tenuous or "fragile." The methods used to humidify, dry, or heat an air sample, or to apply the field, can cause variations in equilibrium that will appear as "hysteresis" effects, i.e., data points will sometimes cross over the equilibrium curve or follow different paths near it for humidification versus dehumidification, as the nature of the surface water film on the cell plates varies with ambient conditions.

c. In uniform electric fields larger than a few hundred volts per centimeter, the behavior of moist air between the cell plates becomes more complex. Deviations from Ohm's law occur, suggesting that molecular fragmentation is producing additional ions [Equation (9)]. The $\sim f(s)^{13}$ dependency of conductivity on RH is seen to occur only at higher RHs with increasing field strengths, becoming $\sim f(s)^7$ or $\sim f(s)^8$ at lower RHs.

d. In uniform electric fields larger than a few hundred volts per centimeter, as saturation humidity is approached, the behavior of moist air between the cell plates suggests that their surface water films can only produce a finite or equilibrium population of molecular water clusters that are available as charge carriers [Equation (8)]. When this "limit" is reached, the total current through the vapor can remain constant over a range of field strengths (Figure 11) or, at a given RH, even exhibit negative resistance characteristics (Figure 12).

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e.    When the electric field strength reaches 1 to
2 kV/cm or more, the conductivity of moist air can no longer be
explained by equilibrium populations of water cluster charge
carriers leaving the cell plates [Equation (8)].   The formation
of additional water ions must occur by molecular fragmentation
[Equation (9)], due to the energy then available across the gap
between the cell plates.   Ionization increases rapidly and
proportionately with further increases in field strength.

f.    If ions (charge carriers) can be produced directly
from thin water films on conductive bodies (including fine water
droplets) in an electric field, and the observed total current
between such bodies is directly proportional to the field
strength, this effect could contribute significantly to the
earth's global current; yet the charge carriers would not be
detectable using standard measurement techniques.

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