THE EFFECT OF VARIABLE MOISTURE CONTENT
ON THE ELECTRICAL RESISTANCE
OF THIN FILMS OF LITHIUM HALIDES

by

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INTRODUCTION

The electrical resistance of a thin film of a hygroscopic salt supported between two electrodes will change when the moisture content of the surrounding atmosphere changes. Change in resistance of such films has been used extensively for the measurement of relative humidity. Such electrodes and their associated equipment are called electric hygrometers. Recent work on the electric hygrometer has been done principally to improve the efficiency and accuracy with which measurements can be made.

The electrodes of electric hygrometers are bifilar helices. The film of salt is bound to the electrodes with a plastic in order that very moist conditions will not cause the salt film to be lost or displaced. Humidity measurements by this means are a more rapid and more positive means of humidity control. Also, these hygrometers are very adaptable to recording of humidity changes by automatic instruments.

Dunmore (2) reported on the construction and use of electric hygrometers in meteorology. For this work the units were constructed and employed in a radio circuit to send a signal from a sonde balloon. The signal varied as the temperature and humidity varied. Dunmore (2) reported that these units were very well adapted to upper atmosphere meteorological surveys.

The American Instrument Company lists humidity detection and control instruments composed of "humidity sensing elements". These instruments employ the principle of conductivity of thin
films of lithium chloride. The advantages of this instrument as stressed by this company, are its small size, and the reliability, accuracy and rapidity of response of the sensing elements.

Evans and Davenport (3) reported on an attempt to adapt the electric hygrometer to measurements of water in oil. They concluded that this method was not adapted to the measurement of water in oil. However, their report furnished information of a more fundamental nature than the Dunmore (2) report. In the Evans and Davenport report attempts were made to show the properties of and the mechanism by which the hygrometer functions. In their paper they reported the amount of water bound to a hygrometer unit under equilibrium conditions and gave interpretations to their graphs of electrical resistance of hygrometer units versus vapor pressure. These interpretations will be discussed later in this thesis.

The objective of this research was not clearly defined initially. It was considered that the problem would be of an exploratory nature. It was hoped that data could be obtained which would permit correlation of a hygroscopic salt's known characteristics and its behavior when used as an electric hygrometer. It was originally considered necessary to duplicate, to a certain degree, the work of Dunmore (2). The Dunmore (2) report does not contain methods of calibration of the hygrometer units suitable for this work. It was thought that if a simple apparatus and technique for establishing known vapor pressure systems could be devised and if the effect of concentration of
a hygroscopic salt could be shown to be similar to Dunmore's (2) work the problem would be on a firm basis.

It was convenient to substitute materials other than those used by either Dunmore (2) or Evans and Davenport (3) for construction of the hygrometer units. For these reasons the problems of this research were many and of a widely divergent nature. The principal problems involved were:

1. An apparatus and acquiring a technique that would permit control of water vapor pressure.

2. The construction of the hygrometer units.

3. The polarization of the hygrometer units observed among the very first units constructed.

4. Selection of a suitable substitute for palladium wire that was used by Dunmore.

Associated with each of these major problems were many of a smaller magnitude.

Work done earlier by this author indicated the inadvisability of attempting to use nichrome or chromel wire as a substitute for palladium. Also, methods of calibration of the hygrometer units by means of constant vapor pressures maintained by saturated solutions of salts were shown to be impossible. In this earlier work it was noted also that construction of reproducible hygrometer units by hand would be difficult since the length and spacing of the wire was critical where units were expected to have predictable characteristics.
METHODS AND APPARATUS

Construction of the Hygrometer Unit

During the time this work was done the details of construction of the hygrometer unit were changed many times. These changes were brought about by improved methods which became apparent only after some experience had been gained.

In the original construction special attentions were directed to the support for the bifilar windings, the kind and size of wire to be used, the plastic used to bind the hygroscopic salt and the length and spacing of the wires. Methyl methacrylate tubing was chosen as the supporting media for the wire. Silver wire having a B & S gage of 36 was selected. This wire has a diameter of .005 inches. Silver wire was selected since it is readily obtainable. Dunmore (2) used palladium, but since this wire was more expensive it was thought that silver would do as well since the hygrometer units would not be used for long periods.

Earlier work indicated that methyl methacrylate was a suitable plastic. The plastic selected had to be soluble in a solvent capable of dissolving the salt. The methyl methacrylate was soluble in acetone to which small amounts of water and methyl alcohol had been added. The water and alcohol were found to be necessary in order that the salts chosen would go into solution. A tendency for the hygroscopic salts to dehydrate and separate from the acetone was noted unless at least a small amount of methyl alcohol was added. Three drops of methyl alcohol were
found to be a minimum requirement when 125 milliliters of acetone was used to dissolve up to 1 gram of lithium chloride.

The length of wire for each of the bifilar windings was 35 centimeters. This length was found to be the length most suitable for this work. However, added length did change the behavior of a hygrometer unit to some degree so it was necessary that each unit have the same length of wire. The spacing of the bifilar windings was originally made by using various sizes of thread. This gave uniform, though very close, spacing. The hygrometer units made by this method were entirely satisfactory in operation. However, due to mechanical difficulties, it was decided to space the wires at 1/24th of an inch. It was found that the methyl methacrylate could be scored on a machine lathe with the threading gear. The gear used was 12 threads to the inch. In order to obtain grooves for bifilar windings it was necessary to score the tubes twice, starting the second groove just 1/24th inch from the first. In order to insure that the grooves were exactly 1/24th inch, it was found advantageous not to change the scoring tool in the lathe, but to disengage the threading clutch. The clutch was then re-engaged when the threading gears on the lathe had revolved through a half cycle from the time the gears had been disengaged. These precautions were found necessary to give reproducible units.

The groove in the plastic tubing was cut with a 60° thread cutting point. It was found that the depth of the groove affected the behavior of the hygrometer unit so that when reproduc-
ibility was being studied an attempt was made to cut the grooves approximately 0.005 inch deep.

After cutting bifilar grooves in the plastic tubing, the tubing was ready for winding with wire. Placing the wire in the grooves with tension enough to hold them in place was found to be very difficult. For this reason a simple device was constructed whereby winding was greatly facilitated and made more accurate with respect to wire tension and placement. This device consisted of a brass tube threaded on the outside with 12 threads per inch. This tube was equipped with a crank on one end and was tapered on the inside at the other end. The plastic cylinders were inserted into the taper and held tightly by friction (Fig. 1). By mounting the tube through a split block of wood in which corresponding threads had been burned the grooves on the plastic tube could be advanced by turning the crank on the brass tube. This operation permitted accurate winding of the hygrometer unit. After the plastic tubes were inserted in the brass cylinder for winding, the silver wires were attached one at a time by fusing the plastic with a hot, clean soldering iron. The wires were fastened at the other end by the same method. A small lead wire was left extending from the second fastening to the plastic. This lead wire was then attached to a copper lead or to an electrode pin cemented to the plastic tube by cement made of cellulose nitrate dissolved in acetone.
EXPLANATION OF PLATE I

Fig. 1. Top Elevation of Hygrometer Winding Device

Fig. 2. Side Elevation of Hygrometer Unit Showing Bifilar Windings and Electrodes
EXPLANATION OF PLATE II

Fig. 3. Diagram of Instruments for 60 Cycle Resistance Measurements

A - Leeds and Northrop Wheatstone Bridge
B - Leeds and Northrop A. C. Galvanometer
C - Source of 60 Cycle 1.5 Volts Alternating Current
D - Direct Current Galvanometer
E - Switch to Direct Current Galvanometer
F - Hygrometer Unit

Fig. 4. Diagram of Apparatus for Measurement of the Effect of Frequency

A - Leeds and Northrop Wheatstone Bridge
B - Electronic Null Point Detector
C - 1 to 1 Transformer
D - Variable Frequency Audio Oscillator
E - Hygrometer Unit
Construction of an Enclosed System for Controlling Water Vapor Pressure

The nature of this work necessitated the use of a constant temperature bath and a system in which the vapor pressure could be changed readily. Originally the apparatus consisted of a water bath of five gallon capacity equipped with cooling coils, stirring motor and two electric heaters regulated by a thermostat control to ± 0.5°C. Submerged in the water bath was a one liter three necked flask with ground glass fittings. In one neck a thermometer was placed. The electric leads to the hygrometer unit were attached through the center neck. A dry ice trap was connected from the third neck in series with a manometer filled with Cenco High Vac vacuum pump oil whose density was 0.6501. The manometer was equipped with a by-pass that was opened and closed with a stopcock. The manometer was connected to a vacuum pump with a three way stopcock. Drying tubes were connected with rubber tubing to the third connection on the stopcock. There were three drying tubes. Drying tubes providing a source of dry air were incorporated into the apparatus so that operations could take place at atmospheric pressure. The drying tube opening to the atmosphere was filled with anhydrous calcium chloride. The other two tubes contained magnesium perchlorate. Much of the work that was done with this system was very similar to the apparatus finally adopted. It is diagramed on Plate I.

This apparatus was used as follows. Air was saturated with water vapor by heating water in a three liter balloon flask
equipped with a two hole rubber stopper. This flask connected in place of the three necked flask containing the hygrometer was, in turn, connected to a tube which extended to the bottom of a thousand milliliter graduated cylinder filled with water. The dry ice trap was then dipped into a mixture of dry ice and acetone. With the manometer by-pass open, air was slowly pumped from the flask of water saturated air through the dry ice trap where the moisture was frozen. The amount of water vapor needed was calculated from knowledge of the total volume of the system and the calculated amount of saturated air drawn into the system. The amount of saturated air taken into the system was determined by direct reading of water removed from the thousand milliliter graduated cylinder. When water saturated air had been passed through the dry ice trap to be equivalent to the amount of water vapor desired in the system, the flask containing saturated air was disconnected and the flask containing the hygrometer reattached. The entire system was then evacuated to a pressure of about one millimeter of mercury. When evacuated, the manometer by-pass could be closed and the oil in the manometer would be stationary. With the by-pass closed the dry ice trap was removed and a beaker of warm water put in its place. All the dry ice was melted and the water vaporized. The amount of water vapor was then accurately measured with the manometer. After the vapor pressure was measured, air was admitted through the drying tubes to allow operation at atmospheric pressure. The apparatus and technique just described was similar to that reported by Brunauer, Emmett
and teller (1). This apparatus served satisfactorily for several months but since the operation was time consuming a more simple and more accurate scheme was developed. A diagram of this apparatus may be found on Plate III.

In place of the dry ice trap and the flask of air saturated with water an outer joint of a ground glass fitting was sealed off two inches below the ground glass. This was filled with water and fitted over the inner joint which was connected to the apparatus between the manometer and the three necked flask. A stopcock was provided to close off the water when desired.

The following procedure was used to obtain a desired vapor pressure in this apparatus shown in Fig. 3. The entire system was evacuated to less than one millimeter of pressure by closing stopcock D and with the manometer by-pass C open and stopcock A turned to the pump. Stopcock B could be opened or closed depending on whether the mercury column was used or not used. With the pump still removing air and water vapor, stopcock D was opened and closed alternately and the water at E allowed to vaporize. This vaporization was made rapid by heating the water at E with a hot water bath. After about a minute or when the vapor from E had permeated the entire system, stopcock D was closed and immediately thereafter stopcock C was closed. When stopcock C was in a closed position the oil in the manometer would be displaced by an amount equal to the water vapor pressure corrected for oil density. The correction which was made gave the pressure translated to millimeters of mercury.

If the vapor pressure obtained was not the pressure desired,
EXPLANATION OF PLATE III

Diagram of System for Establishing Known Vapor Pressure

A - Three way stopcock connecting drying tubes and vacuum pump to apparatus

B - Stopcock to allow the exclusion of the mercury column

C - Stopcock to by-pass manometer

D - Stopcock to regulate the amount of water vapor coming into system

E - Water supply

F - Drying tube with CaCl₂

G - Drying tube with Mg(ClO₃)₂

H - Drying tube with Mg(Cl)₃₂

I - Mercury reservoir

J - Mercury column

K - Manometer

L - Point mentioned with reference to error of system

M - Hygrometer container

N - Thermometer
stopcocks C or D could be opened to adjust it to an exact value desired. Stopcock C was opened momentarily to reduce the pressure or stopcock D could be opened to increase the amount of water vapor in the system. For a short period of time after evacuation, stopcock D was alternately turned open and shut with stopcock C open.

The time during which the vacuum pump operated with both stopcocks C and D open was considered necessary to remove a large amount of the air left in the system at the greatest vacuum the pump was able to maintain. This also allowed the hygrometer units to take on a part of the water they would eventually absorb at the desired vapor pressure. This operation was helpful since immediately after closing stopcock C the displacement of the oil in the manometer did not represent an equilibrium condition between the water vapor and the hygrometer unit. As the hygrometer units took up moisture the vapor pressure in the system would be reduced. For this reason water vapor was usually added to obtain a constant vapor pressure as read on the manometer. This usually required from thirty to ninety seconds.

When the manometer oil showed a constant displacement, thereby indicating equilibrium between the hygrometer and the water vapor, the stopcock at A was turned ninety degrees. This sealed off the system while stopcock C was opened. Stopcock A was then slowly turned to a position so that air entered through the drying tubes F, G and H. The air was admitted slowly and regulated by observing the falling mercury in the mercury column J.
A small error was introduced by this procedure when stopcock C was opened after closing stopcock A because of the increased volume occupied by the water vapor. This increased volume was contained in the tubing from stopcock C to A and from the junction with the line A to C and the top of J. When A was opened the water vapor occupying all the tubing from point L just above the hygrometer unit to stopcock A was forced into the flask containing the hygrometers. This allowed the water vapor occupying tubing A to J to be trapped. However, it is considered probable that any error would be due to the moisture in the volume from point L to stopcock C.

In either case this theoretical error would need be very small since all tubing was seven millimeter in diameter and lengths outside the hygrometer flask were minimized. The ratio of the volume of all tubing filled with water vapor to the volume of the hygrometer flask was 0.01. This justified calculation and report of vapor pressures as accurate to a tenth of a millimeter of mercury.

The accuracy of this method of obtaining water vapor pressures was checked by two experiments. In the first experiment a hygrometer unit was calibrated by both the apparatus described by Brunauer, Emmett and Teller (1) and by the modified version which is diagramed on Plate III. Within experimental error, one method checks the other.

The second experiment will be described in connection with another phase of this work.
Methods and Apparatus Used to Measure Resistance of Hygrometer Units

The apparatus used to make resistance measurements was a Leeds and Northrop Wheatstone bridge. The null point was indicated by various means. Since most of the measurements were made with alternating current of 60 cycles, an alternating current galvanometer was used for the null point indication. All measurements at 60 cycles were made at 1.5 volts.

During the time that the polarization effect was being studied, a direct current galvanometer was arranged in the circuit of the hygrometer unit by opening the battery switch and galvanometer switch on the B and C Wheatstone bridge and closing switch A outside the bridge circuit (Fig. 3). In this manner the current and voltage developed by the hygrometer unit was measured immediately after polarization by the 60 cycle alternating current or by a direct current applied through the battery terminals of the Wheatstone bridge.

The effect of frequency change was measured by incorporating an audio frequency oscillator, variable between the limits of twenty to twenty thousand cycles per second, into the circuit. The null point with this circuit was determined with head phones or by an electronic null point indicator (Fig. 4).

The advantage of the electronic null point indicator was its convenience of visual indication. The transformer was placed in the circuit between the audio oscillator and the Wheatstone bridge to eliminate any possibility of a direct current component tending to increase the polarization of the hygrometer unit.
Much of the early experimentation was done with only one to three hygrometer units in the enclosed system. However, for the purpose of this thesis, twenty hygrometer units were wound and placed in the enclosed system at once. This was done so the experimental conditions would be identical for all units and any difference noted could be ascribed to the controlled variations of the hygrometer units.

RESULTS

The Effect of Constant Temperature and Variable Vapor Pressure

The hygrometer units held at a constant temperature were calibrated at different vapor pressures. This was done by establishing various vapor pressures in the enclosed system and measuring the resistance after equilibrium had been established between the unit and its atmosphere.

The resistance readings were then plotted, ohms versus vapor pressure. Figures 5, 6 and 7 were produced from such data. Efforts were made to find a relationship which would give a straight line curve. Such a relationship was not found. Neither the log or resistance gave a curve reducible to a straight line. The data for Fig. 5, 6 and 7 were obtained at the same time with eleven hygrometer units in the same container held at 25°C. for all readings. The voltage was 1.5 volts of alternating current alternating at 60 cycles per second. The hygrometer units were coated with a 1.5 percent stock solution of the plastic which was prepared in a large container and
portions of it were removed to make up individual solutions of salts.

The salts used for these data were lithium fluoride, lithium chloride, lithium bromide and lithium iodide. One hundredth, 0.05 and 0.1 molar solutions of each salt were used. It was found that the 0.05 molar lithium chloride unit gave resistances in a more moderate range of vapor pressures and three such units were made to demonstrate the reproducibility of the construction process.

Lithium fluoride is not hygroscopic and the resistance of the hygrometer unit of this salt had a very high resistance. The 0.1 molar lithium fluoride unit had the following resistances at the indicated vapor pressures.

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<tr>
<th>Vapor pressure in millimeters of mercury</th>
<th>Resistance</th>
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<tr>
<td>11.1</td>
<td>10,000,000 ohms</td>
</tr>
<tr>
<td>19.5</td>
<td>10,000,000 ohms</td>
</tr>
<tr>
<td>22.7</td>
<td>9,000,000 ohms</td>
</tr>
</tbody>
</table>

The maximum measurable resistance with the instruments available was 10,000,000 ohms.

The Effect of Concentration of Salt in the Hygrometer Film

The concentration of hygroscopic salt in the plastic film was affected by two factors. The concentration of the salt in the solutions used to coat the hygrometer units was adjusted to the desired values of 0.01, 0.05 and 0.1 molar. Different concentrations showed changes in vapor pressure range in which the
Fig. 5

A - 1M LiCl
B - 0.05 M LiCl
(3 units)
C - 0.01 M LiCl

Vapor Pressure mm Hg

Ohms Resistance X 10^-3
Fig. 6
Vapor Pressure (mm Hg)

Fig. 7

Key:
A = 0.1 M LiI
B = 0.05 M LiI
C = 0.01 M LiI
hygrometer unit was affected and to a slight degree the behavior of the hygrometer unit.

The solutions used to coat the hygrometer units had to be very accurately adjusted with respect to the concentration of methyl methacrylate. It was found that very minor differences in concentration caused great changes in viscosity of the solutions. The change in viscosity had a very great effect on the amount of the salt in the dry film on the hygrometer. The differences produced by differences in concentration of the plastic were greater than those produced by differences in salt concentration.

Viscosities of coating solutions were eliminated as a factor in hygrometer salt concentration by dissolving enough plastic to make up all the desired solutions of various salt concentrations.

The hygrometer units used to study the effects of salt concentration were coated to show the effect of varying the hygroscopic salt for the lithium halides, the chloride, bromide and iodide. In addition three hygrometer units were coated with 0.05 molar lithium chloride solutions in order to indicate the reproducibility of the units. The reproducibility of the points on a curve was indicated by the various resistances obtained at approximately the same vapor pressure. The graphs in Figs. 5, 6 and 7 were made from data in Table 1. It was noted that with each salt used for these data the change in concentration toward higher concentrations shifted the upper part of the curve toward the lower vapor pressures. This shift, where lithium chloride
<table>
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<th>Vapor pressure mm of Hg</th>
<th>LiCl : 0.01 M</th>
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### Table 1 (cont),

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was used, was greater than when lithium bromide or iodide was used. It was also observed that higher concentrations produced graphs with shorter arcs. These curves shifted upward from the nearly straight portion at high vapor pressures.

A graph of the effect of changes in concentration of hygrometer films was made by plotting resistance versus concentration at a constant vapor pressure and temperature (Fig. 8).

This graph is typical of those for any vapor pressure. The curve is similar to the graph of resistance versus vapor pressure for a single hygrometer unit. These curves are not only similar in shape, they could not be manipulated into a straight line by plotting logs or square roots of resistance or concentration values.

Effect of the Use of Various Lithium Halides as the Hygroscopic Salt for the Hygrometer

The behavior of the lithium halides varies from one salt to another. The resistance of the hygrometer units coated with lithium chloride, bromide and iodide was of a progressively higher value for the same vapor pressure and in the same order that these halides appear in the periodic table. This was true at least with the units having the higher concentrations of the salts. The units with lower concentrations of hygroscopic salt show a significant deviation from the order of these elements in the periodic chart.

The graphs of resistance versus vapor pressure were arranged so that units having different salts at the same concentration
Fig. 8

Key:
A = LiCl
B = LiBr
C = LiI

Molar Concentration of Salts
were on the same graph. This arrangement indicated that with the higher concentrations of salts, the hygrometer units responded in a vapor pressure range which depended upon the salt (Figs. 9, 10 and 11). The lithium chloride hygrometer units for the 0.1 molar and 0.05 molar concentrations always responded in the lowest vapor pressure range. It was observed that for these concentrations the effect of the different salts was in the same order that these halides appear in the periodic table. However, when the hygrometer units were coated with 0.01 molar concentrations or less the hygrometer units no longer responded in this order. Under these conditions the lithium bromide unit responded at a lower vapor pressure than the lithium chloride unit.

This reversal of order of the lithium chloride and lithium bromide also appears when the resistance was graphed versus salt concentration (Fig. 8).

The Effect of Constant Vapor Pressure and Variable Temperature

Considerable temperature effect was found with these hygrometers. As the temperature was raised the resistance increased in a rather irregular manner. Once again the concentration of salt in the hygrometer seemed to have considerable influence.

When the resistance was plotted versus the temperature at a constant vapor pressure a graph was produced which contained many deviations from a smooth curve. The concentration of the
Fig. 9

Key:
A - .1 M LiCl
B - .1 M LiBr
C - .1 M LiI

Vapor Pressure mm Hg
Vapor Pressure mm Hg

Key:
A = .05 LiCl
B = .05 LiBr
C = .05 LiI

Fig. 10
Vapor Pressure (mm Hg)

Key:

A - 0.01 M LiCl
B - 0.01 M LiBr
C - 0.01 M LiI

Fig. 11
hygroscopic salt did not change the position with respect to temperature of these breaks but for each vapor pressure the salt concentration seemed to effect the amplitude of the breaks in the curves. The lower concentrations produced graphs in which deviations from a smooth curve were larger than the higher concentrations.

The variation of resistance with changes in temperature was investigated more thoroughly than any other effect since it seemed to lend itself more readily to correlation with other known chemistry of the salts used. It was found that some of the breaks in the curves of LiCl and LiBr coated units corresponded approximately with decomposition temperatures of known hydrates of the LiCl and LiBr (Figs. 12 and 13). It was not practicable with the present apparatus to investigate the melting points of more than a few of the hydrates of these salts. However, each time a hygrometer unit was heated through the range of decomposition of a known hydrate of that particular salt, a break in the temperature effect curve appeared at the decomposition temperature of that salt. The melting points of hydrates, within the range of temperatures investigated, are LiCl·2H₂O, 21.5°C and LiBr·2H₂O, 14°C. These temperatures are represented approximately by breaks in the curves (Fig. 13 and 14). The vapor pressure, during the raise in temperature, was 18.0 millimeters of mercury. This vapor pressure accounts for the trend toward lower resistances at the lower temperatures. The vapor pressure was established with the enclosed system at 25°C after which the system was cooled to 12°C. For this
reason the temperature range from 13° C. to 20° C. represents an increase in vapor pressure and the curve would be expected to have a minimum at that point.

The method of establishing exact vapor pressures was checked by this means. The system was evacuated, then moisture was admitted to a certain vapor pressure. The system was then cooled to a temperature below that which represented a saturated condition with reference to that vapor pressure. The system was then allowed to raise in temperature slowly. The resistances of the hygrometer units were graphed versus the temperature and the lowest point in the curve represented the highest vapor pressure attained. This temperature could then be referred to saturated vapor pressure tables and the vapor pressure of the system obtained. This check, performed many times, gave excellent agreement with vapor pressure readings made with the manometer.

Effect of Constant Relative Humidity and Variable Temperature

It was desirable to determine if the resistance of hygrometer units would increase with rising temperatures when the air was saturated.

Hygrometer units were placed in an enclosed system which contained an excess of water. The temperature of the system was raised slowly over a period of several hours to allow equilibrium to be established in the system. Once again the resistance of the hygrometer units was plotted versus the temperature.
Key:  
A = LiCl  
B = LiBr  
C = LiI  

Temperature - degree centigrade  
Constant vapor pressure  

Fig. 12
Key:
A - .05 Li Cl
B - .05 Li Cl
Figure 14 was plotted from these data.

The fact that this curve retains the breaks shown by the curves where the vapor pressure was constant and the temperature varied was regarded as a significant indication that they were characteristic of this type of hygrometer. These curves also indicate that the effect of temperature on the hygrometer units was related to the hygroscopic film as well as to the equilibrium between the film and an unsaturated surrounding atmosphere. Under these conditions the only way the films used could increase their resistances was to have the vapor pressure of the film increase to a value above that of water. This was indicated by the curves at the higher temperatures (14).

The Effect of Direct Current Polarization

In the early work on this problem, measurements of resistance were attempted by using a direct current. It was found that the direct current caused a very rapid polarization and was not a practicable means of resistance measurement. Later the effect of direct current was studied briefly in a rather qualitative manner.

It was found that very low voltages and low currents were sufficient to polarize the hygrometer units. In fact there seemed to be no lower limit to these voltage and current values which could be measured with present equipment. The current supplied by measurements with an electronic ohmmeter which supplied an exceeding low current was sufficient to cause a very rapid increase in resistance of these hygrometer units.
Resistance in Ohms

Temperature °C

Key:
A = .05 Li Cl
B = .05 Li Br

Vapor Pressure saturated at all temperatures

Fig. 14
For these reasons further investigations were not conducted since the problem was intended to be of an exploratory nature.

However, it was found that a unit once polarized, if immediately connected to a galvanometer, would generate an appreciable current. Rough measurements were made and it was found that a hygrometer unit remained polarized for approximately the same length of time that a direct current polarized it. A unit subjected to a direct current for one minute would depolarize in about one minute. It was also found that the amount of current generated by the hygrometer was a function of the time the unit was polarized.

The salt in the plastic film was also a factor in polarization. Lithium iodide was the most susceptible to polarization of the hygrometer units. Lithium chloride was least susceptible.

The vapor pressure of the hygrometer unit's atmosphere also greatly affected the polarization of these units. The greater the vapor pressure the more rapid and the greater the polarization.

The voltages developed by polarized hygrometer units were measured and it was found possible to obtain 1.5 volts from a lithium iodide unit in an atmosphere saturated with water vapor at 25° C. Lithium bromide and lithium chloride would furnish 1 volt and .7 volts respectively, under the same conditions.
The Effect of Alternating Current Polarization

It was found that alternating current of 60 cycles would also polarize the hygrometer units. The effect of such an alternating current was not as great as direct current. However, change in resistance was great enough at higher vapor pressure to give erroneous readings if the current was allowed to flow for long periods during resistance measurements.

The Effect of Resistance Measurement at Reduced Pressure

Most of the work on this problem was done at atmospheric pressure. However, it was considered desirable to determine the effect of air on the behavior of the hygroscopic film toward water vapor.

The procedure to establish certain vapor pressures followed those of other measurements except no air was admitted. The resistance measurement was made at a total pressure equal to the vapor pressure in the enclosed system. No difference in resistance values could be detected. This was true even though immediately after the resistance measurement at reduced pressure dry air was admitted and the resistance again noted.

The Effect of Variable Frequency on Resistance of Hygrometer Units

For these measurements a variable frequency oscillator was used as an electrical source for the Wheatstone bridge. The null point was indicated with an electronic null indicator. The
frequency was varied from 60 to 20,000 cycles per second. This effect was investigated only briefly due to insufficient time. However, the general effect typical of all units was plotted as resistance versus frequency at a constant vapor pressure and constant temperature (Fig. 15). The effect of higher frequency was a lowered resistance. The effect was greater with hygrometer units in which resistance was higher than those units which had a low resistance.

Result of Aging of Hygroscopic Film

Dunmore (2) reported that after initial drying of the hygroscopic film the resistance of the film was not constant. He reported that the film gave a constant resistance if allowed to age for a period of several weeks at room temperature or in twenty-four hours at a temperature of 100° C.

During this work it was found that after the hygrometer units had been air dried they had a very high resistance. It was thought that aging to a constant resistance for any vapor pressure could be accomplished by alternate evacuation and saturation of the atmosphere around the hygrometer unit. Six to ten alternate evacuation and saturations were required to give a constant resistance at a given vapor-pressure.

Result of X-ray Photographs of Hygroscopic Films

X-ray photographs made of the hygroscopic films failed to show any evidence of any crystalline material in the hygroscopic
Key:
A = .01 Li Cl
B = .05 Li Cl
C = .1 M Li Cl

Frequency - Cycles per second
Constant vapor pressure at 25° C

Fig. 15
X-ray Photographs of Hygroscopic Films Used

Fig. 16
film. In films containing lithium chloride, bromide and iodide which were subjected to x-rays none showed evidence of an orderly arrangement in the film (Fig. 16).

DISCUSSION

The change of resistance with variable vapor pressure (Fig. 5) for lithium chloride shows good agreement with previous work reported by Evans and Davenport (3) and by Dunmore (2). Evans and Davenport (3) interpret the curve in the following manner. The lower portion at the higher vapor pressures were considered to be the resistance due to unsaturated solutions of lithium chloride. The sharp break toward higher resistance represented a state of saturation while the upper portion was caused by a mixture of solid hydrate and solution of lithium chloride. Thus the change in resistance was due to the change in the number of ions available to carry current.

The results of this work substantiate this interpretation. That is, the resistance of the hygroscopic film depends upon the number of ions in the film available to carry current (Fig. 8). The presence of irregular resistance values at temperatures near the melting points of LiCl · 2H₂O and LiBr · 2H₂O indicates the presence of small amounts of molecules of these hydrates. However, x-ray photographs do not show the presence of a crystalline structure in the plastic film (Fig. 16). Further indication that there is only a very small amount of these hydrates at vapor pressure below the range in which the salt goes into a water solution is furnished by the fact that unaged
films show much larger breaks at the melting points of known hydrates. This is reasonable if it is considered that the aging process must consist of removal and replacement by water of unevaporated acetone and methyl alcohol. Therefore due to the lower solubility of the various salts in acetone and methyl alcohol there would be, probably, considerable hydrate, stable at the prevailing temperature, in an unaged hygrometer unit.

Further, if, in an aged hygrometer unit, a considerable quantity of solid hydrate existed, a greater break (Fig. 13 and 14) in the curves would occur at the melting points of the hydrates. This is probable since these hydrates melt without immediate loss of water from the liquid hydrate. Mellor (6) reports that an additional 5° C. to 10° C. rise above the melting point of these fused salts for them to throw off the water furnished during the decomposition

\[
\text{LiCl} \cdot 2\text{H}_2\text{O} \xrightarrow{21.5\degree\text{C}} \text{LiCl} \cdot \text{H}_2\text{O} + \text{H}_2\text{O} \text{ and } \\
\text{LiBr} \cdot 2\text{H}_2\text{O} \xrightarrow{141\degree\text{C}} \text{LiBr} \cdot \text{H}_2\text{O} + \text{H}_2\text{O}.
\]

The International Critical Tables (5) indicate also, that the various lithium halide hydrated salts show a maximum vapor pressure. In the case of LiCl \cdot 2\text{H}_2\text{O} the temperature is as much as 30° C. above the decomposition temperature of the hydrate.

This refutes the probability that solid material is present in large quantities at any time in the plastic-salt film after the aging of the film. The indication is, that after aging, and where a plastic is used to bind the hygroscopic salt to the electrodes, the principal condition existing is one of solution of the salt. At the lower vapor pressure the salt is dissolved.
in the plastic with a minimum of water. Then since the plastic is porous to water vapor the change in resistance was probably due to a change in mobility of the ions as the water content of the film changes.

The result of using different hygroscopic lithium halides shows certain regularities (Figs. 9, 10 and 11). The vapor pressure range in which hygrometer units with the same salt concentration responded, is affected by the salt used. In the case of the higher concentrations of the three salts the vapor pressure in which each salt responded was in the same order as chlorine, bromine and iodine appear in the periodic table.

However, Figure 8 shows that the effect of salt concentration is least in the case of lithium bromide and the effect is greatest in the case of lithium chloride. The reason for this effect can not be directly correlated with any known properties of the salts.

The effect of temperature on the resistance of these hygrometer units presents evidence that the plastic film which was used to bind the hygroscopic salt has an effect on the vapor pressure of the solutions of these salts. In the experiment where an excess of liquid water was added to the enclosed system and the temperature raised, the change in resistance can only be attributed to a loss of water by the film. Therefore the equilibrium was between the vapor pressure of water and the vapor pressure of the film. The resistance shows a downward trend in the temperature range from 13° C. to about 35° C. At this temperature the resistance shows a very rapid increase to
about 50° C. where several breaks in the curves appear. Therefore it appears that at a temperature of approximately 35° C. to 40° C. the vapor pressure of the film exceeds that of the water and throws off moisture. In this connection a certain lag was noted in behavior of the resistance when the hygrometer unit was heated rapidly. When the unit was heated rapidly it was noted that the minimum in the curve did not occur at 35° C. to 40° C. but at 45° C. to 50° C. The rate of heating very materially affected the temperature at which the resistance started to increase. It was also noted that after rapid heating, if the temperature was held at the highest temperature attained, the resistance of the unit continued to increase. This indicated a certain retardation of equilibrium by the film.

The curves representing the effect of changing temperature show several very definite breaks. With only a few exceptions these breaks appear at the same temperature for each of the three salts used on the hygrometers. The very definite breaks which occur at known hydrates are attributed to the presence of small quantities of those hydrates. Mellor's, Comprehensive Treatise of Inorganic Chemistry (5) lists three definite hydrates of all three lithium halides used in this work. They are Li·H₂O, Li·2H₂O and Li·3H₂O. In addition to these hydrates there is evidence of other unknown hydrates but their unstability has prevented their separation and characterization. There has been (5) some evidence of the hydrates LiCl·5H₂O and (LiCl)₂·3H₂O. These hydrates have been suspected where the salts were crystalized from solutions of water and alcohol.
This evidence of uncharacterized hydrates of the lithium halides lends credulence to the possibility that these breaks represent the release of water bound in the film in such a manner that it does not permit added freedom of the ions present.

The results give a cooling curve (Fig. 12) of those hygrometers which were raised in temperature. This cooling curve does not retrace the heating curve. However, the breaks which occur on the heating curve are shown on the cooling curve at approximately the same temperatures. However, the breaks are reversed. This reversal of the breaks on the cooling curve is not unreasonable upon the assumption that the breaks are due to unknown hydrates. The unbound water content of the film just prior to the formation of hydrates would be higher than just after hydrate formation. For this reason the resistance just before hydrate formation would be less than just after hydrate formation. Many of these breaks in the curves are shown at about the same temperature for each of the lithium halides. This indicates that some of these hydrates may involve only the lithium ion.

The failure of the cooling curve to retrace the heating curve is similar to that reported by Evans and Davenport (3). They reported that there was a hysteresis effect in their vapor pressure curves. They attributed this hysteresis to a difference in the rate of adsorption and desorption. The hysteresis effect was also experienced in this research but under slightly different experimental conditions than those of Evans and Davenport (3). When the atmosphere about a hygrometer unit
at a given vapor pressure was evacuated it was noted that the resistance did not retrace the resistance versus vapor pressure curve for that unit. Instead the resistance remained very low until virtually all the atmosphere had been pumped off. At this time the pressure in the enclosed system would remain at a constant value. It sometimes required twenty to thirty minutes before the resistance returned to more than ten million ohms at which time the pressure in the system would reach a minimum value.

The current provided by the polarization effect was regarded as being similar to the current of a concentration cell. The effect of the direct current was to change the concentration of ions around the electrodes by migration of the ions. The regeneration of the current by the polarized hygrometer unit showed a reversal of polarity to that during polarization. It seems certain then, that the current furnished by a polarized hygrometer was due to the diffusion of the ions through the plastic film away from higher concentrations about the electrodes. The ease with which hygrometers in high vapor pressure systems became polarized and depolarized indicates a high degree of ion mobility.

The fact that units in atmospheres of low vapor pressures and even unaged units were capable of polarization is further evidence of a state of solution of ions in the hygrometer film. This is further substantiated by the fact that longer applications of direct current were necessary for polarization of hygrometer units in atmospheres of low vapor pressure. Also, the depolarization effect lasted longer with hygrometers in a dry atmosphere.
CONCLUSIONS

The concentration of the salt in the plastic film of the hygrometer affects the resistance of the hygrometer. This dependance on salt concentration is produced by the number of ions in the plastic and the variable moisture content of the film which is a function of the amount of hygroscopic salt present.

The effect of salt concentration is greatest with lithium chloride and least with lithium bromide. The hygrometers in which salt concentrations are above 0.02 molar show the effects of various lithium halides to be regular and in the order in which the halide appears in the periodic table.

It was not possible in this work to show what characteristics of the halide ions caused the differences observed in the hygrometer units coated with different lithium halides.

The effect of temperature is to change the resistance by changing the vapor pressure of the hygroscopic film and by hydrate decomposition or formation. Certain breaks in resistance versus temperature graphs were attributed to known hydrates. Other breaks not corresponding to temperatures of known hydrate decomposition were attributed to possible unknown hydrates and to lithium ion hydrates.

The hygrometer units may be polarized by either a direct current or by alternating current of low frequency. The effect of polarization is to increase the resistance of the hygrometer unit for a variable time depending upon the duration of the
polarizing current. Once polarized a hygrometer unit is able to furnish a current during the time of depolarization. The amount of polarization of a unit depends also upon the salt used and the vapor pressure of the atmosphere of the unit.

The resistance of a hygrometer unit changes with various frequencies. The resistance decreases rapidly with increasing frequency from 60 cycles per second to 1000 cycles per second. From 1000 to 20,000 cycles per second the resistance decreases more slowly.
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THE EFFECT OF VARIABLE MOISTURE CONTENT ON THE ELECTRICAL RESISTANCE OF THIN FILMS OF LITHIUM HALIDES

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AN ABSTRACT

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The purpose of this research was to investigate the principles which permit thin films of hygroscopic salts to be used as electric hygrometers. The problem was intended to be of an exploratory nature.

A technique for construction of hygrometer units was devised and tested. In this respect materials not previously used were found to be adaptable to this problem. The principal substitutions were silver wire instead of palladium and methyl methacrylate for a plastic binder instead of vinyl chloride.

The control of the variables, vapor pressure and temperature, constituted a very specific problem for this work. A technique and apparatus for controlling these variables was developed. The accuracy of the method was checked by three unrelated methods.

Resistance measurements of the hygroscopic films were made by several adaptations of a Wheatstone bridge. The larger portions of the data were obtained with a 60 cycle alternating current and an alternating current galvanometer. However, the effect of frequency was measured with an audio frequency oscillator with an electronic null point indicator.

Polarisation of the hygrometer units was observed and an effort was made to briefly study this effect.

The effects of constant temperature and variable vapor pressure and of different salt concentrations were studied. It was concluded from the results of these studies that one factor which governed the resistance of hygrometers of this type was the number of ions available in the film to carry current. The availability was
increased by the moisture content of the film which was controlled by the amount of hygroscopic salt present.

The effect of the use of various lithium halides was studied. It was concluded that the results were approximately as expected by consideration of the order in which these salts appear in the periodic table.

The effect of variable temperature and constant vapor pressure was studied and it was concluded that graphs of resistance versus temperature showed breaks which corresponded to temperatures of decomposition of known hydrates of the salts used. Other breaks on these curves were attributed to unknown hydrates and to lithium ion hydrates.

A summation of conclusions from all results lead to a consideration of the state which existed in the film of the hygrometers. It was concluded that the hygroscopic salts were dissolved in the plastic of the film at all times after the film had been subjected to an aging process. The changes in resistance, the polarizability, and general behavior of the hygrometers were considered to result from the relative mobility of the ions of the salts.