

TECHNIQUES FOR EVALUATING CERTAIN PHYSICAL
PROPERTIES OF SOIL MOISTURE

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
LITERATURE REVIEW	4
Vapor Pressure	4
Freezing-Point Depression	7
SPECIFIC OBJECTIVES	11
Vapor Pressure Control	11
Freezing-Point Depression Measurement	12
VAPOR PRESSURE CONTROL	14
Design and Construction of Apparatus	14
Conversion of Measured Data	25
Some Results and Discussion	27
FREEZING-POINT DEPRESSION MEASUREMENT	33
Apparatus	33
Calibration of Thermistors	39
Conversion of Freezing-Point Data to Stress	42
Procedure for Measuring Freezing-Point Depression	43
TIME-TEMPERATURE CURVE CONSIDERATIONS	46
Theoretical Aspects	47
Evaluation of K for Saturated Samples	50
Studies Involving Unsaturated Soils	53
SUMMARY AND CONCLUSIONS	60
Vapor Pressure Control	60
Freezing Characteristics of Soils	61
BIBLIOGRAPHY	65

LIST OF FIGURES

	Page
1. Graph for converting pressure drop to relative humidity and stress	16
2. Diagram of apparatus for controlling the relative humidity of air circulated past a soil sample	17
3. Diagram of apparatus for controlling the water level of the bath depicted in figure 2.	21
4. Circuit diagram for the thermistor-activated phase-sensitive electronic controller which was used to control the bath temperature.	23
5. Changes in moisture percentage with time of soil samples as the result of relative humidity control.	28
6. Block diagram of the freezing-point depression apparatus.	34
7. Diagram of circuit used for measuring the temperature of a soil sample in the freezing-point-depression apparatus.	36
8. Triple-point apparatus with thermistor probe inserted.	38
9. Representative time-temperature curves for soil samples during freezing. These soil samples were initially at one-tenth atmosphere tension.	45
10. Moisture-tension curves for four soils.	55
11. Plot of the calculated amount of ice formed versus time after the soil sample reached 0°C for samples initially at one atmosphere tension (bath temp. -2.2°C).	56
12. Same as Figure 11 except that the soil samples were initially at one-tenth atmosphere tension.	57

TECHNIQUES FOR EVALUATING CERTAIN PHYSICAL PROPERTIES OF SOIL MOISTURE

INTRODUCTION

Moisture is a prime requirement of all plants. For plants growing in a soil medium a method of assessing the availability of the soil moisture to the plants is in demand. Present methods are based mainly on soil moisture tension measurements. Soil moisture tension is defined by Richards (30, p. 95) as the pressure difference across a porous membrane or plate upon which the soil sample has been placed and its moisture content allowed to come to equilibrium under a constant applied pressure. This concept has many useful purposes but tension is not directly related to the free energy of the soil moisture because it does not take into account the osmotic effects due to salts.

The vapor pressure associated with the soil moisture can be related to the free energy of the soil moisture and is therefore a function of both the osmotic pressure of the soil solution due to dissolved salts and the tension due to the soil itself. A measurement of the vapor pressure would seem to be the best evaluation of the availability of soil moisture to plants.

In working with vapor pressure it was found easier to think of it in terms of relative humidity. This eliminates the need for defining the temperature, as relative humidity

is directly related to stress¹ at any temperature, whereas the vapor pressure associated with a given stress will vary with the temperature. The range of moisture available to plants is covered by about one per cent relative humidity, that is, at 100 per cent the soil is saturated and in the vicinity of 98.9 per cent plants growing in the soil would wilt. A procedure which would allow a soil sample to come to equilibrium with water vapor in this range would possibly be quite slow. A relatively rapid method of determining the soil moisture-stress relationship would find a ready place in laboratory procedure.

Another property, the freezing-point depression of the soil solution, is a function of the free energy but the measurement is not made at normal temperatures. However, this technique offers the possibility of obtaining a complete moisture-stress curve from one sample of soil. If a relationship can be discovered between the rate of cooling, which is dependent on the moisture content, and the freezing-point depression which may be converted to stress, a complete moisture-stress curve may be constructed over the range of moisture available to plants.

This work represents two attempts--firstly, to develop

¹ Stress is here used as the sum of the forces acting to lower the free energy of water and includes both the osmotic pressure due to salts and the tension due to the attraction of soil particles for the water.

an apparatus and procedure for controlling and measuring the vapor pressure of a sample of soil under dynamic conditions, and secondly, to develop a relationship between a moisture-stress curve for a soil and a temperature versus time curve obtained as a sample of moist soil freezes.

LITERATURE REVIEW

Vapor Pressure

Various workers through the years have attempted to control and evaluate the water vapor pressure in the atmosphere surrounding soil samples in the laboratory (25, pp. 441-450) 26, pp. 68-88) 37, pp. 409-434) 38, pp. 1-18) 39, pp. 409-418). Thomas (37, pp. 411-412) discussed both the static² and the dynamic³ methods and gave a good review of the literature up to that time. He questioned the value of the static method for moist soils and developed a dynamic method of passing nearly saturated air through his samples. This air was then completely saturated, after which the moisture was completely removed. Knowing the volume of air used, the amount of water necessary to completely saturate it, and the amount of water picked up between the soil chamber and the saturator, he could calculate the relative humidity associated with the soil sample. From his published data it appears that he had only a few samples in the available moisture range.

² The static method of controlling vapor pressure consists of placing soil samples in a closed chamber with a source of water--usually pure water, or an acid or salt solution. The chamber may then be evacuated, which hastens the attainment of equilibrium, and should be kept in total darkness.

³ The dynamic method consists essentially of bubbling air through water, or passing air over an acid solution and then passing it over or through the soil sample.

More recently, Richards made this comment (2, p. 367), "Some effort is being made at this laboratory to develop a vapor-pressure method, but it is too early to predict whether our work will meet with success." To date nothing further has been noted in the literature.

Linford (23, pp. 233-252) developed an apparatus for a static method and discovered the importance of controlling radiant energy. Energy in the form of light raised the temperature of his soil samples considerably above the temperature of the solution in the desiccator. The temperature gradient disrupted the attainment of isothermal equilibrium. Also, he found that long periods of time were necessary for equilibrium to be approached at low moisture tensions. He cautioned (24, p. 235), "At the so-called hygroscopic coefficient, even though the water vapor movement is extremely slow, when measured by moisture content, the soil is far from equilibrium. Serious theoretical mistakes can be made and experimental difficulties caused by assuming equilibrium when the moisture transfer is too slow to be detected by ordinary methods."

Linford (24, pp. 231-233) calculated the need of temperature control of the magnitude of 0.0001°C and a time of as much as 100 years for a soil sample to absorb one gram of water where the stress was approximately 0.01 atmosphere. This is without any air movement, the water being transferred totally by means of diffusion of the vapor. If such

is the case, this form of the static method would appear to be inadequate for characterizing soil moisture in the range of availability to plants.

Edlefsen (14, pp. 29-35), however, developed a system that appears to have been satisfactory for measuring the vapor pressure of soil moisture in this range. He used an evacuated system and controlled the moisture in his sample by introducing or removing water vapor. The soil sample was suspended on a Jolly balance spring in order to weigh the amount of moisture taken up or lost. The spring also served to indicate when equilibrium was being approached. The system was first evacuated to a pressure of 10^{-5} mm. of mercury, then water vapor was allowed to enter from a water chamber. The conductivity of a calibrated glass wool cell was used to indicate the vapor pressure. After equilibrium was reached at this point, some water vapor was pumped out and time was again allowed for equilibrium to be reached. This process was repeated until a sufficient number of points had been observed. The procedure was carried out at 30°C in a constant temperature bath. His results indicate that he was able to attain moisture tensions appreciably below 15 atmospheres. In the light of the promising appearance of these results, it seems strange that this method has not been investigated more thoroughly in the intervening time.

Various methods (8, p. 304) 16, pp. 2439-2449) 17, pp. 102-110) 18, pp. 1162-1171) 22, pp. 54-57) 35, pp. 1291-1296) have been used for measuring the vapor pressure of solutions and comparing their vapor pressures with those of the pure solvents. It is difficult to envision the application of most of these methods to the study of soil moisture at the present time. There is some possibility, however, of measuring the vapor pressure of a static system directly, rather than depending on the movement of water in the vapor phase. It appears that this method, used by Frazer and Lovelace (16, pp. 2439-2449) and referred to by Thomas (37, p. 411), in which the difference between the vapor pressure of a solution and that of the pure solvent in the absence of other gases was measured, might be applied to soils.

Freezing-Point Depression

According to Washburn (40, p. 655) "The colligative properties of a solution are connected by a set of rigorous differential equations which involve no assumptions except the two laws of thermodynamics." He then develops the relationships by means of equations, one of which relates vapor pressure to freezing point. Hosler and Hosler (19, pp. 126-132) have discussed the relationship between freezing point and capillary radius. It

appears that these principles apply to soil-water systems as well as to solutions, and various workers have used the freezing-point depression to characterize soil moisture stress (1, pp. 221-232) 2, pp. 356-371) 3, pp. 201-206) 7, pp. 65-71) 9, pp. 221-229) 10, pp. 1-55) 27, pp. 289-292) 31, pp. 70-74) 32, pp. 429-436) 33, pp. 47-50) 34, pp. 644-653).

The freezing-point depression of soils has been approached in two ways. In the dilatometer method (1, pp. 221-232) 27, pp. 289-292), the sample is placed in a special type of pycnometer. A liquid is introduced above the sample and rises in the calibrated stem. The temperature of the sample is recorded as it is cooled in a freezing bath. As the sample cools, the changing volume is indicated by the changing level of the liquid in the calibrated stem. The appearance of ice in the sample is marked by a change in slope of the volume versus time curve. This method will give a complete moisture-stress curve from one sample, as the temperature can be converted to stress and the water frozen out can be calculated from the volume changes.

In the other method, and the one with which we will be concerned here, the temperature at which a sample freezes is determined. The sample is supercooled in a freezing bath, freezing is initiated and the subsequent

maximum temperature which the sample reaches is considered the freezing point of that sample. Richards and Campbell (32, pp. 429-436) have developed and described equipment for, and have worked out some of the problems of freezing-point depression measurement.

Day (12, pp. 397-399) compared the results from a static vapor pressure method to those from the freezing-point depression method and found slightly higher moisture content for the latter method. The moisture content of his samples were somewhat below wilting, however. Recently, Cannell (10, pp. 18-27) compared freezing-point depression results with pressure membrane data for various soils and soil materials by means of the Schofield equation⁴. For a synthetic soil (the only one for which he reports correction factors) he found a correction to the equation necessary, which was, $FPD_{corr.} = 0.38 FPD + 0.02$. He was unable to explain the significance of these correction factors.

⁴ The Schofield equation is as follows:

$$T = \frac{L}{10330g} FPD$$

where L = heat of fusion of water (-3.33×10^9 ergs/gram), θ = absolute temperature ($273.18^\circ K$), g = acceleration of gravity (980 cm/sec^2) and T = soil moisture stress in atmospheres.

It must be remembered, when different methods are being compared, that the osmotic pressure due to salts is taken into consideration when vapor pressure and freezing-point depression methods are used but not by the imposed pressure methods (28, pp. 451-454) 29, pp. 105-110). Comparison is usually made between the freezing-point depression and pressure plate methods in the range of moisture available to plants, however, because of the difficulty of controlling and measuring vapor pressures in this range. The wilting point is associated with approximately 98.9 per cent relative humidity, which gives only slightly over one per cent relative humidity for the whole range of soil moisture available to plants.

Much remains to be learned concerning the properties of soil moisture and it is hoped that this study will contribute materially to the present fund of information.

SPECIFIC OBJECTIVES

Vapor Pressure Control

The first objective of this study was to design and construct equipment that would allow the maintenance of a constant relative humidity in an atmosphere surrounding a soil sample. The range of relative humidity of interest was that associated with soil moisture between saturation and the wilting point, or from 100 per cent to about 98.9 per cent. The sensitivity of this equipment must be such that the relative humidity might be controlled to ± 0.05 per cent. To attain this, precise temperature control would be essential. Also, the equipment must be designed so as to allow the measurement of the moisture content of a soil sample as it came to equilibrium with the surrounding atmosphere at a constant relative humidity.

Such equipment would be used primarily for obtaining vapor pressure versus moisture content curves for different soils. However, other uses, such as calibration of moisture measuring devices are evident.

It would not be expected to make rapid routine measurements with this equipment, but it would be used primarily to obtain standards to which tension and freezing-point depression measurements could be referred.

Freezing-Point Depression Measurement

To assess the stress of the moisture in the soil at any time, the freezing-point depression approach has many merits, providing techniques can be improved. This approach has promise also of providing a rapid method for obtaining a moisture-stress curve for any soil. Such a method would require calibration against some standard, as relative humidity, before stress at normal temperatures could be ascertained.

The second objective of this study was to improve the design of equipment and the procedure previously used to obtain freezing-point depression measurements. This would require construction of equipment of improved design and testing of new procedures. The equipment to be constructed and tested was essentially that described by Cannell (10, pp. 3-5). Apparent heating of the thermistor indicated a need for altering the measuring circuit. In order to hasten thermistor response, a new probe design appeared desirable. Equipment changes also would include using a recording potentiometer to draw temperature versus time curves.

It was proposed to investigate the various factors which influence the time it takes a soil sample to freeze. It seemed that it should be possible to relate the time

involved to the water content of the sample. As freezing-point depression is directly related to stress, it should then be possible to develop a complete moisture-stress curve from one soil sample.

VAPOR PRESSURE CONTROL

Design and Construction of Apparatus

The dynamic method of controlling relative humidity was chosen here because of the much shorter periods of time required for a soil sample to approach equilibrium as compared to the static method.

There is apparently no way of measuring relative humidity in the range of interest, at least to any degree of accuracy. It was thus necessary to know what the relative humidity was from the means of control. This suggested making use of a fundamental principle described by gas laws. If air is saturated with water vapor at a certain pressure, removed from contact with the liquid phase and then the pressure is reduced, the pressure of the water vapor will also be reduced in the same ratio. Represented symbolically, at constant temperature

$$P_f/P_i = R.H.$$

where P_f = the final total pressure, P_i = the pressure under which the air was humidified in contact with free water and $R.H.$ = the relative humidity. This holds true where $P_i \geq P_f$. This method is supposedly most satisfactory between 90 and 99 per cent relative humidity (4, p. 159) but we have applied it to our range of interest,

98.9 to 100 per cent.

The difference between the pressure at which the air was saturated and that where the soil sample was placed would be a little over eleven centimeters of water for a relative humidity in the soil chamber of 98.9 per cent. The relationships between relative humidity, stress and pressure difference are shown in figure 1.

There were two alternatives for saturating the air with water vapor. One method would make use, essentially, of bubbling air through water, then letting it expand into another chamber, using new air continuously. In the other method the same air would be recirculated. The latter was chosen on the assumption that saturation would eventually be reached, if not the first time through.

The constructed apparatus (figure 2) consisted of two chambers, a free water chamber and a soil chamber, connected by two lengths of tubing so as to form a cycle. A pump was placed in the top of the water chamber at the end of the return tubing from the soil chamber. This allowed for pumping the air from the first chamber into the second chamber and back to the first, in a continuous cycle. After considerable search for a pump of suitable design, an aspirator with water circulated through it was chosen for two reasons. The air flow is continuous, in contrast to a pulsating flow developed by

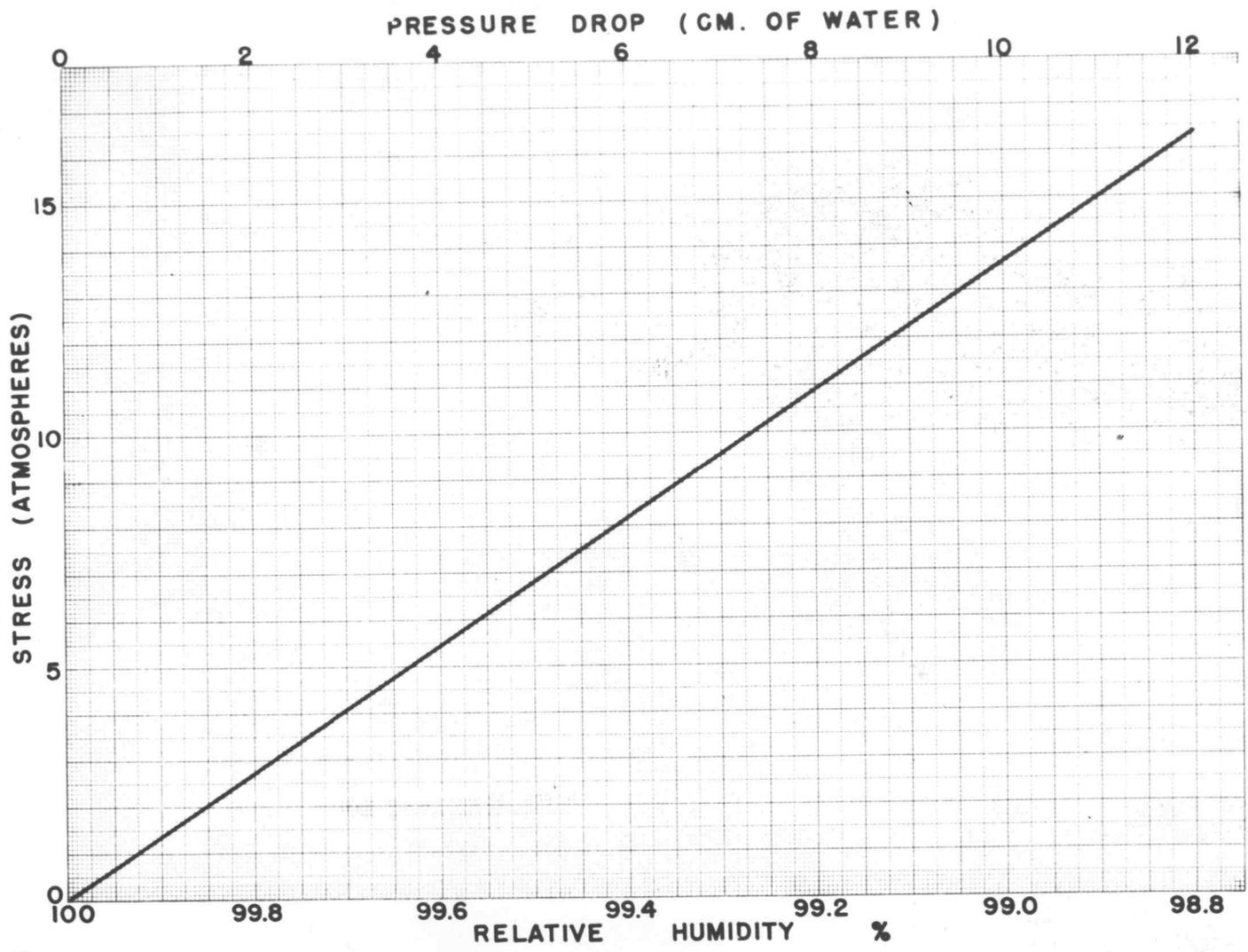


Figure 1. Graph for converting pressure drop to relative humidity and stress.

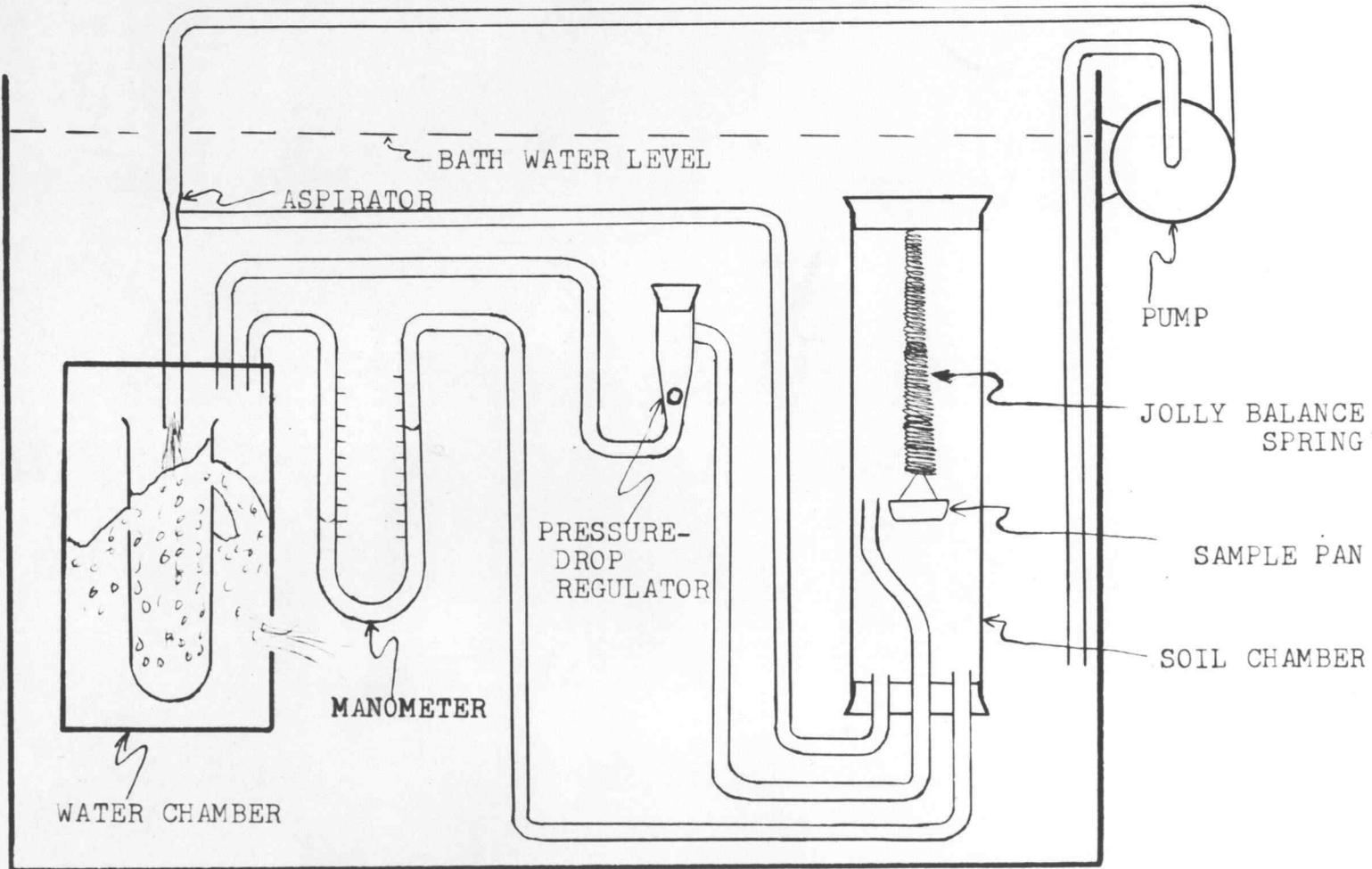


Figure 2. Diagram of apparatus for controlling the relative humidity of air circulated past a soil sample.

all other pumps investigated, and the air is under the greatest pressure in the aspirator when it is in contact with water. The increase in pressure resulting in other pumps during compression would give the maximum pressure in the pump or the line adjacent to the pump, which would tend to cause the water to condense out where the highest pressure is developed. This would be disastrous to this system, which was based on using saturated air that was allowed to expand, to lower the relative humidity. To allow the air to expand after it leaves the saturation chamber, some means of creating a pressure drop was necessary. When a restriction was placed in the line, the pressure drop was not constant. Eventually the principle of a common flowmeter (rotameter) was used. A piece of tapered glass tubing was placed in the line through which gas passed from the water chamber to the soil chamber. A steel ball rode in this tapered tube, suspended by the current of gas. As the flow increased, or decreased, the ball would rise or fall, but always constituted a constant pressure drop dependent on its mass.

Discarded ball bearings from an electric motor repair shop were used as source material. The steel balls were inserted and removed from the constructed apparatus by means of a small magnet. It was necessary to lower the water of the bath or to have the connecting tubing flexible

so that the tapered glass tube could be raised above the bath level for removing the ball. With the water chamber opening directly into the bath, as was eventually done, it was necessary to close off the line on both sides of this apparatus so that air was not forced out by water entering from below when the ball was changed. The pressure difference was measured by a dibutyl phthalate manometer.

This whole system except for the manometer and the water pump was located in a constant temperature water bath. The bath container was made of 20 gauge galvanized steel and had the dimensions of 18 inches by 24 inches by 24 inches deep with an open top and a window of plexiglass about 6 inches by 18 inches in one side (figure 2).

The water pump for circulating water through the aspirator was mounted outside and was a 3/4-inch-outlet centrifugal pump. In the final arrangement water was pumped out of the bath and through the aspirator into the water chamber. The water then returned to the bath through an opening in the bottom of the water chamber. This arrangement diminished the heating by the pump of the water which passed through the aspirator. However, some air was lost from the air system, either through leaks or more likely by being carried out with the water. This was easily replenished periodically by blowing through a T in the manometer line. The air above the water in the water

chamber was cycled through the soil chamber and back through the aspirator, where it came into intimate contact with the water and was carried into the liquid phase of the water chamber. A system of baffles allowed the air bubbles to rise to the surface of the water before they were carried out the opening in the bottom.

The water chamber was a glass jar with a capacity of approximately one gallon. The soil chamber was a piece of glass tubing about 20 inches long and 2 inches inside diameter sealed at both ends by rubber stoppers. Plastic tubing was used initially but it eventually checked and rendered observation of the sample difficult.

The soil was placed on an aluminum pan about an inch in diameter which was suspended from the top rubber stopper by means of a Jolly balance spring. The spring served to weigh the soil sample, as well as to indicate the approach of equilibrium. The readings were made with a cathetometer.

A simple automatic water level control device (figure 3) was set up to take care of the lowering of the water level in the bath due to evaporation from the surface. A distillation flask was mounted so that it could be adjusted vertically, with a continuous source of water and an overflow, and a capillary syphon to the bath. This proved quite satisfactory as long as it was checked

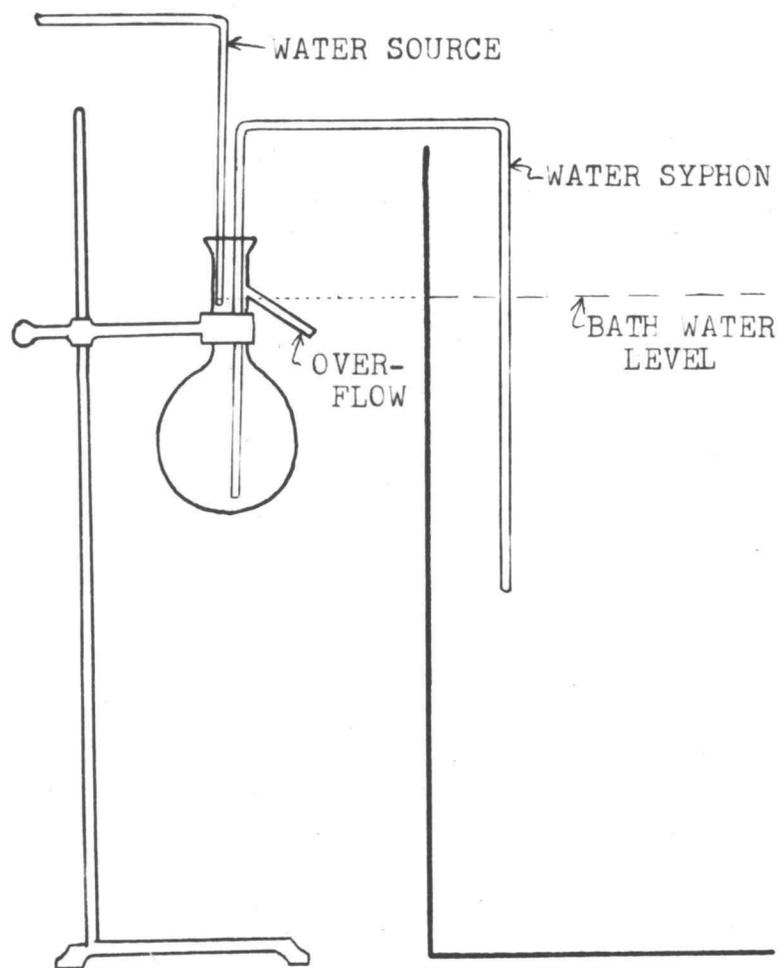


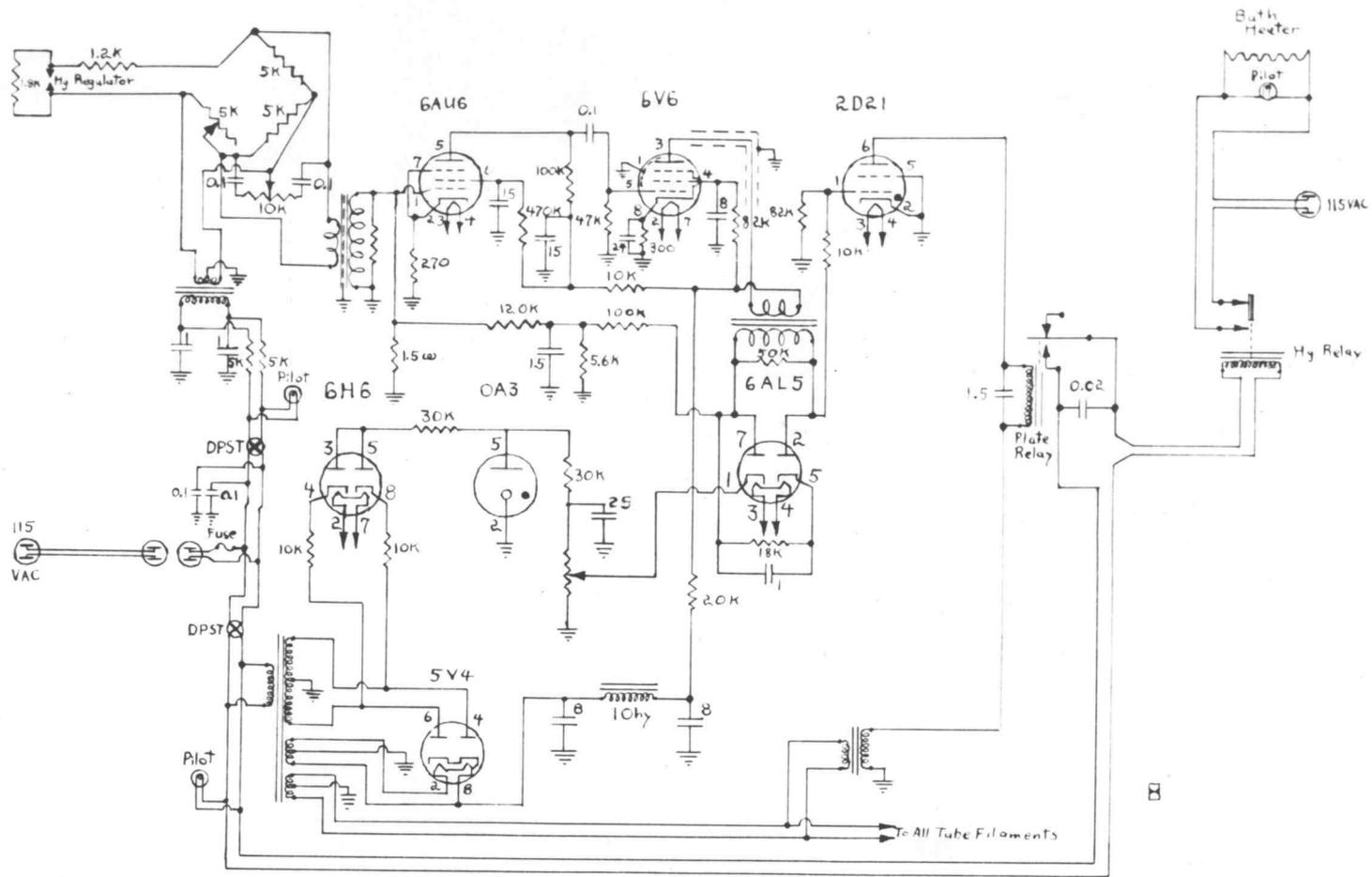
Figure 3. Diagram of apparatus for controlling the water level of the bath depicted in figure 2.

occasionally for air bubbles in the capillary syphon.

When the centrifugal pump was turned on and primed, the aspirator drew air from over the water in the first chamber through the soil chamber. It was assumed that the air would eventually become saturated as it passed through the aspirator. Even with the pressure drop created between the two chambers by the steel ball, the air should come back to the original pressure some where in the aspirator system, and should also pick up what moisture was lost at the soil sample.

For such a system to work, however, it would be necessary to control the temperature within rather narrow limits. A difference of one hundredth of one degree centigrade between the water chamber and the soil chamber, if the latter were at the higher temperature, would reduce the relative humidity by about 0.05 per cent at 30°C. As may be seen from figure 1, this is equivalent to approximately 0.8 atmospheres of tension. If it were in the opposite direction the air might become supersaturated.

To achieve this type of control a thermistor-activated phase-sensitive electronic controller (see figure 4 for circuit diagram) was built. This instrument is an amplifier built around a wheatstone bridge, one arm of which is a thermistor. As the temperature changes, the resistance of the thermistor changes and causes an unbalance



all resistors in Ω all capacitors in μfd $K = 10^3$ $\omega = 10^6$

Figure 4. Circuit for the thermistor-activated phase-sensitive electronic controller which was used to control the bath temperature.

of the bridge. The direction of change of resistance determines the direction of unbalance and thus the direction of current flow. The amplifier picks up the small signal (fraction of a milliampere) and operates a mercury relay, turning on or off, depending upon the direction of current flow, a 125 watt heater in the bath. Such an instrument should respond to small temperature changes of the magnitude of thousandths of a degree centigrade.

The controller requires a constant line voltage, however, and as the voltage in the laboratory varied over a rather wide range--as much as 10 or 15 volts in a day--the thermistor did not prove satisfactory. The temperature would vary with the line voltage, although for short periods of time the temperature could be controlled to better than 0.01 degree. A voltage regulator was tried but it did not give satisfactory control. The wave shape was also poor, either with or without the voltage regulator. Because of the temperature fluctuation with time it was necessary to substitute a mercury thermoregulator for the thermistor⁵.

⁵ The controller should lend itself to other applications, with minor adjustments being necessary in some cases. The detection of small differential temperatures by means of two thermistors in the bridge, use as a flow meter or as a vacuum manometer by taking advantage of the voltage-current characteristics of thermistors, and proportionate control are only a few of the possibilities (13, pp. 89-91).

Although the bath was uninsulated, the temperature could be held within $\pm 0.01^{\circ}\text{C}$ for some time. The variation in temperature throughout the bath appeared to be of about the same magnitude. In order to attain this degree of control, rather vigorous stirring with a one-thirtieth horsepower electric stirrer was necessary. Insulating the bath would probably have improved the temperature control somewhat.

The apparatus was set up in a constant temperature room with a temperature of $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$. The bath temperature was held at $30^{\circ}\text{C} \pm 0.01^{\circ}\text{C}$.

Conversion of Measured Data

Assuming a constant temperature throughout the air system and also that the air was completely saturated in the water chamber, the relative humidity in the soil chamber could be calculated from the difference in pressures between the two chambers. As stated earlier, the pressure drop was measured with a dibutyl phthalate manometer. Water could not be used as it would have contributed vapor and thus tended to unbalance the control in the system. One centimeter of difference in the pressure between the two chambers at 20°C and one atmosphere pressure in the saturation chamber would give 99.9 per cent relative humidity in the soil chamber. The calculations were made

from the following equation:

$$100 \times \frac{(1 - \Delta p \times d)}{P} = \text{Relative humidity}$$

where Δp is in centimeters of dibutyl phthalate, d is the density of dibutyl phthalate at 20°C and P is the centimeters of water equal to one atmosphere. The conversion can be made graphically using figure 1. Thus one centimeter on the manometer is equal to approximately one-tenth of one per cent relative humidity.

From figure 1 it is also possible to convert the difference in pressure directly to soil moisture stress. The conversion is based on equation 1, presented by Edlefsen and Anderson (15, pp. 134-142) which relates change in vapor pressure of water to stress and absolute temperature.

$$\Delta p = \frac{1.002 (P - 2 \times 10^{-5} P^2)}{\frac{4.548T}{p_0} + \left[1 - 26.3 \left(\frac{373}{T} \right)^{10/3} \right]} \quad 1$$

where Δp is the change in vapor pressure, P is the stress in atmospheres, p_0 is the vapor pressure of free water at temperature T and T is 303°K.

The Jolly balance spring was calibrated by using a five gram weight. It was found that a change of five centimeters in the length of the spring was very nearly equal to one gram. The readings were made to one-hundredth of a centimeter by means of a cathetometer supplied with a vernier. One-hundredth of a centimeter was equal

to 0.002 gram, and if a one-gram soil sample were used, which was a convenient size, this would correspond to two-tenths of one per cent moisture. This was within the range of precision desired.

Some Results and Discussion

Some results have been obtained on soil using the previously described equipment essentially in its final form. Considerable less reliable data were collected during the time the details of the equipment were being perfected. These data are not presented, however.

One to two days appeared to be necessary for equilibrium to be approached when a soil sample was placed in the system. Figure 5 indicates some typical curves. Air dry samples of Chehalis silty clay loam were placed on the pan and moisture percentage on an oven-dry weight basis was measured as a function of time. It can be noted that the moisture content increased rather rapidly at first, then gradually leveled off. The higher the stress, as obtained from figure 1, the lower the apparent moisture content as equilibrium was approached, as would be expected. For two of the cases presented, the relative humidity was changed when the samples appeared to be approaching equilibrium. In one case the relative humidity was increased and the moisture content also increased. In the other case the relative humidity was decreased,

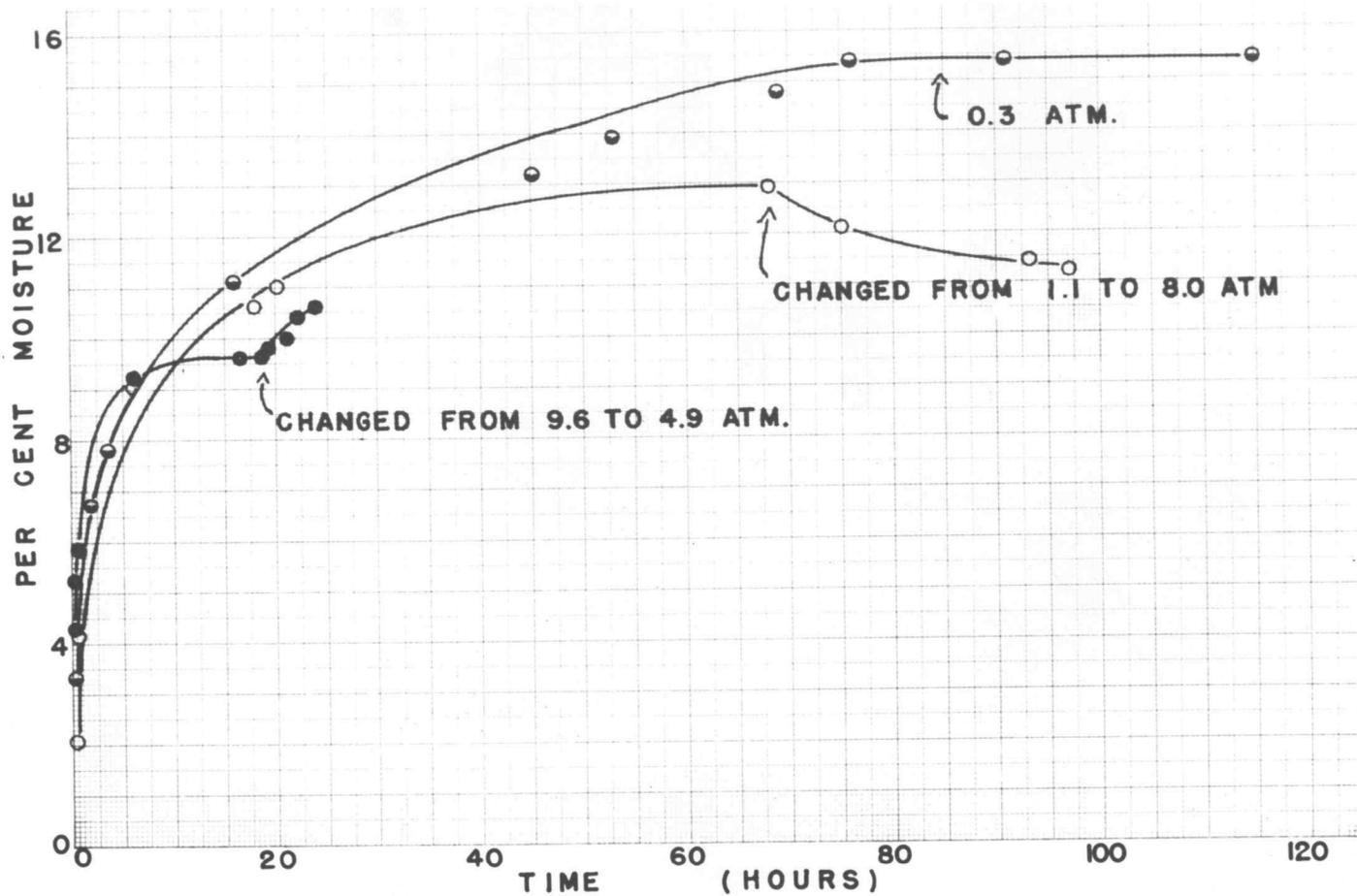


Figure 5. Changes in moisture percentage with time of soil samples as the result of relative humidity control.

and the moisture content also decreased. This behavior indicated that a true equilibrium was being approached. However, the moisture content of the soil was always much lower than expected for the calculated value of stress. This is shown in Table 1 in which the stress from figure 1 is tabulated with the apparent equilibrium moisture content. Along with these data are the moisture contents determined by the pressure membrane method for the same soil at tensions corresponding to the tabulated stress. The divergence of the two moisture contents is quite obvious.

Table 1

The moisture percentage in the soil samples from the vapor pressure apparatus compared with the moisture percentage from the pressure membrane for Chehalis soil at the same calculated stress

Calculated stress in atmospheres	Percentage moisture in soil sample	Percentage moisture from pressure membrane
9.6	9.5	15
8	10.5	16
4.9	11	24
1.1	13	28
0.3	14	31

Similar results were obtained using sulfuric acid and sodium chloride solutions in place of soil samples. These were used in an attempt to evaluate the relative humidity of the air stream more accurately, as the vapor

pressure of these solutions has been tabulated (4, p. 158) 21, pp. 293-297). There is actually no method available for measuring the relative humidity directly in the soil chamber, although it may be arrived at by calculations from the pressure drop. Common methods of measuring relative humidity have not been calibrated in the range of interest and probably do not have the requisite accuracy.

In spite of our attempts to saturate air with water vapor and to control the moisture level in the soil by passing the air containing water vapor over the soil, much remains to be desired. The failure of the samples to reach the expected moisture contents may be attributed to a variety of things, which will now be discussed.

The first assumption was that the air was saturated when it left the water chamber. It would appear that eventually that would be the case, but this may not be true. Perhaps the air in going through the aspirator and bubbling up through the water failed to become saturated with water vapor. Of course complete saturation in the soil chamber could never quite be reached because a flow of air requires a pressure drop. However, with proper design an appreciable flow could be acquired with a very small pressure drop.

In the choice of method used here for controlling relative humidity, the Joule-Thompson effect was taken

into consideration. When a gas is allowed to go from a higher to a lower pressure, it expands and cools. A calculation of this effect showed that for a pressure drop corresponding to a relative humidity of 99 per cent, the attendant temperature lowering would be of the order of two or three thousandths of a degree centigrade. This was within the limits of the bath temperature control, and the Joule-Thompson effect was considered unimportant in this investigation.

There was also a possibility of other temperature effects in the system. If the water at the point of saturation were lower in temperature than the air in the soil chamber, saturation might not be reached; and if the air were saturated at that lower temperature, the control would be lost when the temperature of the air was raised farther along in the system. Also, if the temperature anywhere along the line were lower, water would condense out. This was observed on numerous occasions. The bath temperature did not seem to vary, however, more than $0.01 - 0.02^{\circ}\text{C}$ at the most. The effect of a difference of 0.01°C would change the stress from 0 to approximately 0.75 atmospheres, for example. This is far short of the differences calculated from the observations.

Another temperature effect may have been the rise in temperature of the soil sample due to interception of

energy--probably mostly in a form associated with light. It has been shown before (23, pp. 233-252) and corroborated here that light will raise the temperature an appreciable amount. If energy absorbed by the mercury of the Beckman thermometer were sufficient to raise its temperature 0.01°C , as was observed, it might affect a dark-colored body such as a soil sample to a greater degree. Even with pasteboard over the top and windows, some energy was quite likely to enter as long as the lights were on. What effect the cylindrical chamber had in enhancing the energy absorbed by the sample because of focusing is only a matter of conjecture at this point.

FREEZING-POINT DEPRESSION MEASUREMENT

The various colligative properties of a solution--vapor pressure, osmotic pressure, freezing-point depression, et cetera--are directly related to the amount of solute present in a solvent. These properties are useful in characterizing the solution. As a soil-water system appears to have the characteristics of a solution these properties should also serve to define the stress of such a system, which is a function of its free energy.

Apparatus

The apparatus designed and constructed for studying the freezing characteristics of moist soil is shown diagrammatically in figure 6. The construction of the apparatus was similar to that of Cannell's (10, pp. 1-55). It consisted in part of a rectangular freezing bath with a capacity of about forty gallons. A water-antifreeze solution in a ratio of about 5 to 1 was used as the coolant. The bath was stirred with a one-thirtieth horsepower electric motor supplied with a five-inch aluminum model airplane blade turning at about 1500 r.p.m. The bath was cooled by a one-fourth horsepower Freon refrigeration unit. The temperature was controlled by an American Instrument Company bimetallic thermoregulator (cat. no. 4-235A) and electronic relay (cat. no. 4-5301)

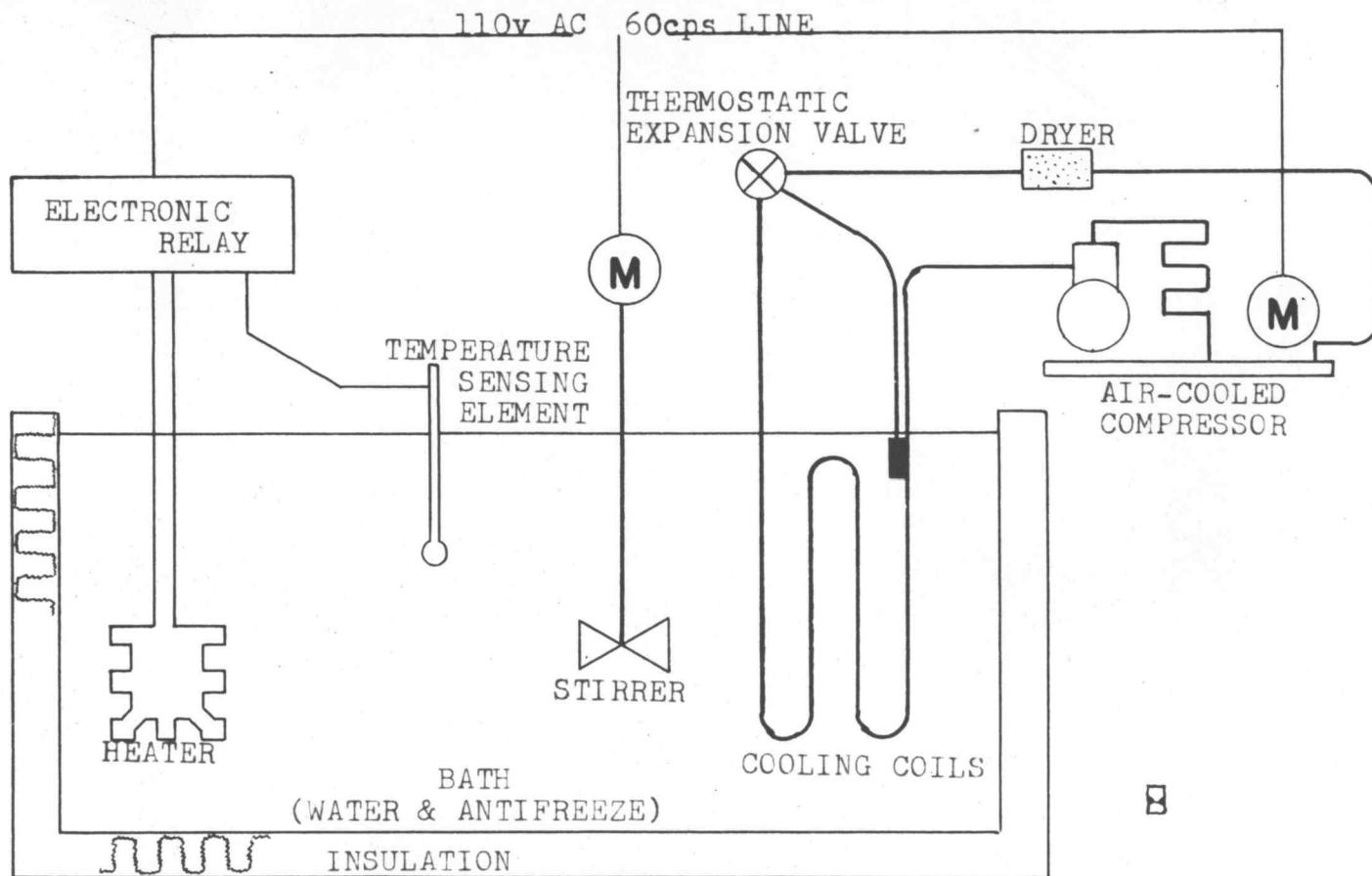


Figure 6. Block diagram of the freezing-point depression apparatus.

which operated a 125 watt heater.

A quarter-inch sheet of plastic, drilled to accept 29-mm.-diameter test tubes, was mounted over the surface of the coolant. The heater was mounted at one end of this sheet. The test tubes served as jackets for the sample containers, which were similar to those used by Cannell. The sample container was a 58 by 16-mm. vial, the first jacket was a 180 by 21-mm. test tube and the second jacket was a 200 by 29-mm. test tube. The two jackets were separated at top and bottom by cork spacers. The outer jacket was weighted in the bottom with a lead ball about an inch in diameter. The sample container slipped inside of the inner jacket. The thermistor probe rested on the top of the sample container and fitted loosely in the inner jacket, with the thermistor protruding into the soil sample.

A Western Electric Co., Type 14B thermistor (6, pp. 711-725) 13, pp. 84-91) 20, pp. 94-98), in a wheatstone bridge (L&N n. 17125) was used to indicate the temperature of the soil sample (figure 7). Either a Leeds and Northrup Type E (no. 2430d) galvanometer was used for detecting the null point of the bridge or a Brown recording potentiometer (Model no. Y153X12(VA)-X-9N4G with a chart speed of 1/3 inch per minute and adjustable span and zero) was used to obtain temperature versus time

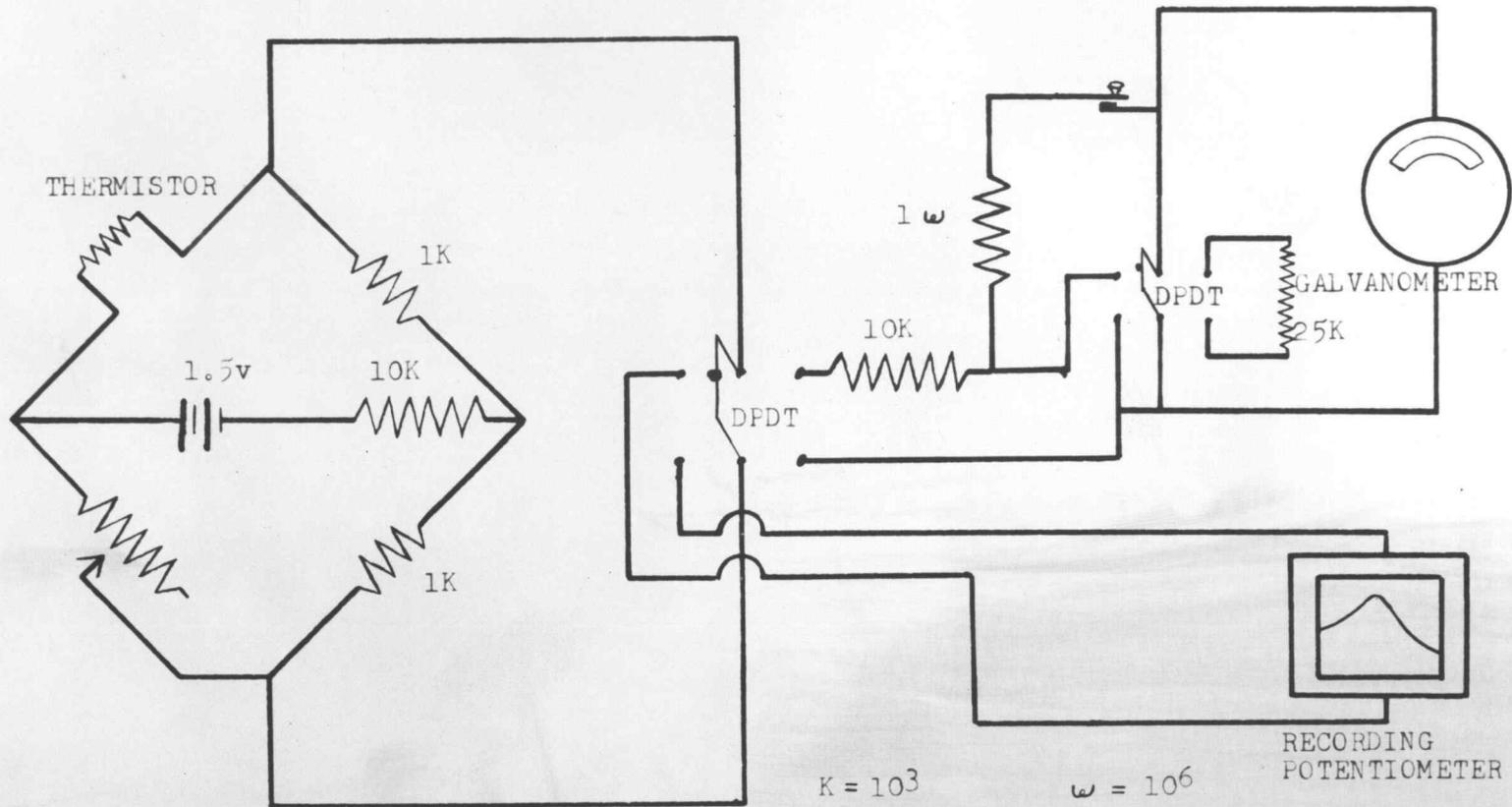


Figure 7. Diagram of circuit used for measuring the temperature of a soil sample in the freezing-point-depression apparatus.

curves. The recorded curves could be read to about 0.005°C . Somewhat greater sensitivity could be attained, but it was desired to get a complete freezing curve over the range of interest (0 to -1.5°C) on the chart. Approximately one-third of a volt was used on the bridge to minimize the self-heating of the thermistor, which will be discussed in the next section.

For the probe, a thermistor was mounted in a length of small glass tubing, with the bead protruding for intimate contact with the sample. The thermistor probe is shown inserted in a triple point apparatus in figure 8. This apparatus will be discussed in the next section, also. The glass tubing was in turn mounted in a plastic tube and the joints sealed with De Khotinsky or plastic cement. This type of mount was much more fragile than the metal shield construction used by Cannell and others, but was considered more satisfactory because of the reduction in time of response to a change in temperature of the sample as well as the possible reduction of the amount of heat that might be conducted into the sample by the metal shield. It appeared that a metal shield around the thermistor introduced considerable lag into the response of the thermistor to the temperature of the sample. For measurements of freezing-point depression this may not be important, but for following the temperature of a sample

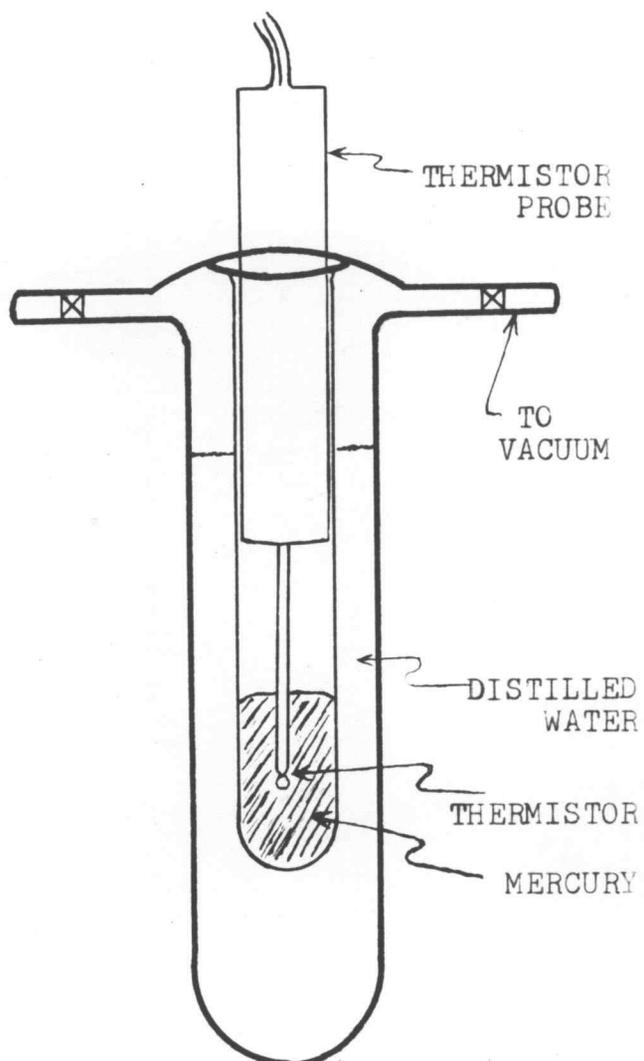


Figure 8. Triple-point apparatus with thermistor probe inserted.

as it freezes, it is important to minimize the lag of the thermistor response as much as possible.

Calibration of Thermistors

Thermistors are commonly calibrated in an ice-salt bath against a Beckman thermometer. However, since the thermal characteristics of the WE 14B type thermistors can be described mathematically (13, pp. 84-91), it seemed preferable to use this latter approach. The appropriate equation is

$$R = R_0 E^{k/T}$$

where R = resistance at any Kelvin temperature T , R_0 = resistance at reference temperature T_0 , $E = 2.7183$ and $k = B (1/T - 1/T_0)$ where B is a constant (approximately) whose value depends upon the thermistor material. To evaluate B two values of resistance at different temperatures must be known. The triple point for water (36, pp. 323-327) and the transition temperature for the change from Na_2SO_4 to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (11, pp. 132-133) were chosen for these two points. The temperature at which the solid, liquid and gas phases of pure water are in equilibrium is called the triple point. The triple point apparatus (see figure 8) was filled about three-fourths with distilled water and evacuated. It was then under-cooled and tapped sharply to initiate freezing. If it

were insulated it would hold the triple-point temperature for an hour or more. The transition temperature is that at which one phase of a substance changes to another phase. This also gives a relatively stable temperature for an hour or so.

The temperature at the triple point of water is 0.0097°C (36, pp. 323-327) and at the transition of Na_2SO_4 to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is 32.383°C (11, p. 132). It was assumed that extrapolation to -1.5° was valid, and also that the function was linear over this short range (0 to -1.5°C). The latter assumption was checked for one thermistor using a Beckman thermometer and an ice-salt bath, and found to be true. The graph of salt-bath temperature versus resistance gave very nearly a straight line over the range of interest.

One of the problems associated with using thermistors for temperature measurement was that of self-heating, which is a function of the power dissipated in the thermistor. The temperature of the WE 14B thermistor will rise 1°C due to self-heating as the result of the dissipation of one milliwatt of power in still air and five milliwatts in liquid, according to its specifications (13, pp. 84-91). If the necessary values of the bridge components are used, it is possible to estimate the rise in temperature due to self-heating by means of the

following equation:

$$\Delta T = \frac{R_t}{K} \left[\frac{(R_3 + R_4) V}{(R_1 + R_2)(R_3 + R_4) + R_5(R_t + R_2 + R_3 + R_4)} \right]^2$$

where ΔT is the rise in temperature of the thermistor due to self-heating; R_t , the resistance of the thermistor; R_2 , the resistance in series with the thermistor; R_4 , the resistance in parallel and opposite the thermistor; R_3 , the resistance in series with R_4 ; R_5 , the resistance in series with the bridge; V , the applied voltage and K , the dissipation constant of the thermistor. For the circuit used (see figure 7) $R_t = R_4 \cong 5000$ ohms, $R_2 = R_3 = 1110$ ohms, $R_5 = 10,000$ ohms, $V = 1.5$ volts and $K = 0.005$ watts per $^{\circ}\text{C}$ in liquid or 0.001 watts per $^{\circ}\text{C}$ in air.

If we assume that a soil sample will dissipate heat at a rate more nearly like that of liquid than of air and use 5 milliwatts per $^{\circ}\text{C}$ for the dissipation constant, a rise in temperature of about 0.003°C may be calculated for the circuit used. If two volts are used directly across the bridge, about one-tenth of a degree rise in temperature may be calculated. This is a factor to be considered in building a thermistor circuit for temperature measurements.

Conversion of Freezing-Point Data to Stress

Edlefsen and Anderson (15, pp. 119-120) presented the relationship between freezing-point depression (ΔT) and tension (ΔP) shown by equation 2, in which L is the heat

$$\Delta P = \frac{L}{Tv} \Delta T \quad 2$$

of fusion, T is the absolute temperature at the freezing-point and v is the specific volume of the solvent.

For the case of water, L is 79.71 calories per gram, T is 273.18° and v is 1.000 cubic centimeter per gram. Using these values, and the factor of 41.311 to convert ΔP to atmospheres, equation 2 reduces to

$$\Delta P = 12.054 \Delta T \quad 3$$

The freezing-point depression can then be easily converted to tension. If there is osmotic pressure present, it is included in ΔP and equation 3 relates the freezing-point depression of a soil sample to the total stress of the moisture in the sample.

The osmotic pressures due to the soluble salts in the soils used in this study are low, but osmotic pressure is present and this should be taken into consideration when results of freezing-point depression are compared with pressure membrane values later in the discussion.

Procedure for Measuring Freezing-Point Depression

One of the uses of the freezing-point depression apparatus was to measure the temperature at which soil moisture started to freeze. The sample of approximately five grams was placed in the sample container, which was inserted into the double jacket. The complete assembly was placed in the bath. When the sample had reached the temperature of the bath, the thermistor was inserted into the supercooled sample, which initiated freezing. The mechanical disturbance or a small crystal of ice left on the thermistor from a previous sample started the freezing process. The temperature rapidly rose as soon as freezing started, reached a maximum and then slowly decreased to the temperature of the bath. The maximum temperature reached after freezing took place was considered the freezing point and the difference from 0°C was the freezing-point depression. The thermistor was then moved to the next sample and the procedure was repeated. After the freezing-points were determined, the samples were removed and the moisture content determined. Moisture percentages were based on an oven-dry weight basis.

To test the freezing-point depression apparatus, soil samples at different tensions obtained by the use of the pressure membrane were frozen. Chehalis silty clay loam, Klamath sandy loam, Condon silt loam and Aiken clay loam

were the four soils used in this study. As has been encountered by others, an amount of supercooling was necessary before freezing could be initiated, which introduced an error into the value arrived at for the freezing-point depression. From figure 9 it may be seen that if the supercooling part of the curve had not been present, a slightly higher maximum or freezing point would have been recorded. The greater the stress of the moisture in the sample the more the supercooling that was apparently needed and the greater the error in freezing-point depression. Difficulty was encountered in freezing the fifteen atmosphere tension samples with the bath temperature at -2.2°C . A steel wire kept in dry ice was tried for initiating freezing by touching it to the soil sample. However, the wire seemed to remove so much heat from the sample that the results were little better than when greater supercooling was allowed and freezing was initiated by jarring.

The error introduced into freezing-point depression measurements due to supercooling as experienced both in the above study and by others lead to the following investigation.

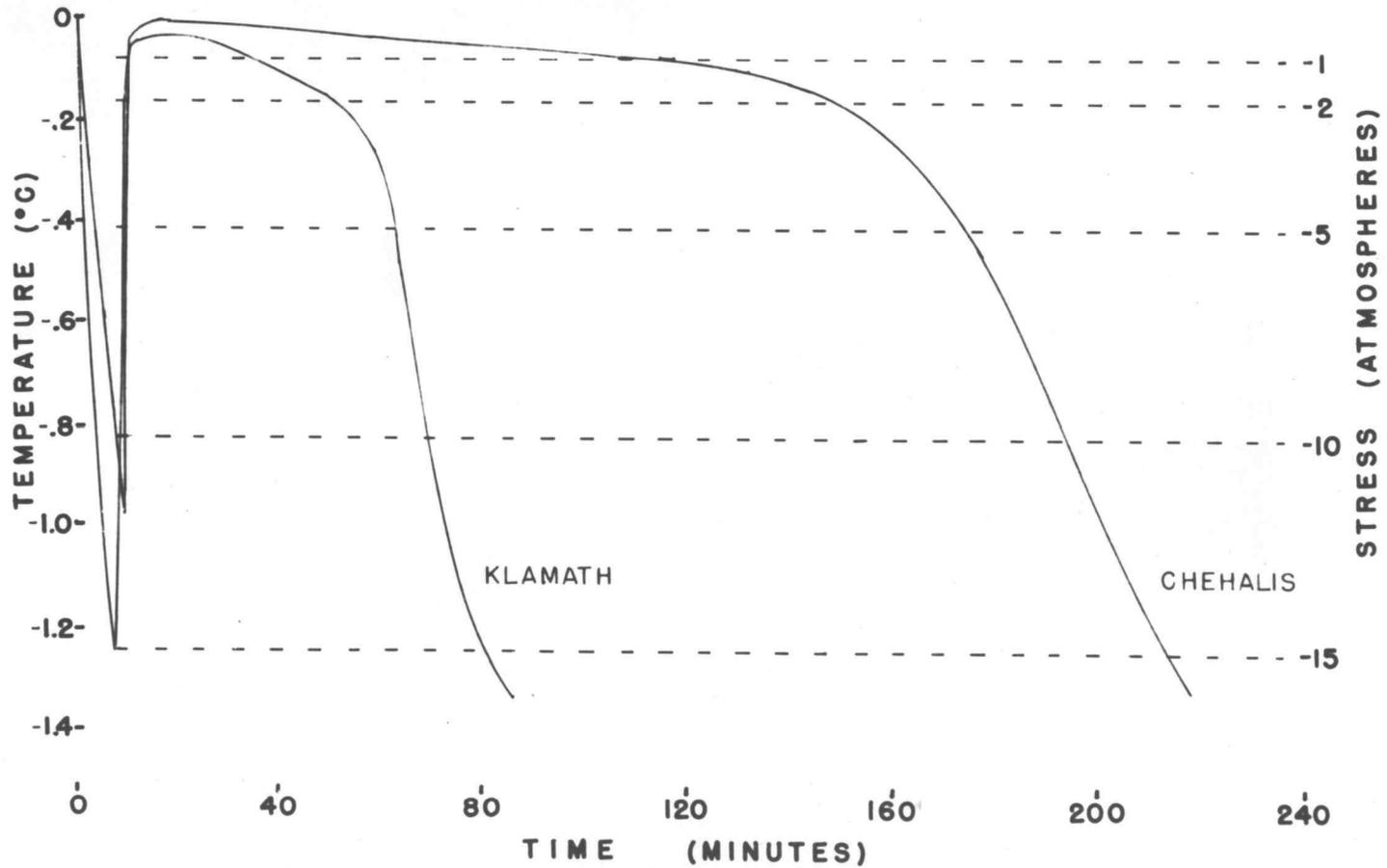


Figure 9. Representative time-temperature curves for soil samples during freezing. These soil samples were initially at one-tenth atmosphere tension.

TIME-TEMPERATURE CURVE CONSIDERATIONS

At the lower moisture stresses, the time required to initiate freezing was somewhat less and didn't appear to introduce as great an error into the value of the freezing-point depression, as the temperature of the sample changed slowly with time at the low moisture stresses. This is illustrated in figure 9 where the slope of the curve at the maximum after freezing is very small. In the light of this observation it was decided to attempt to find a relationship between the temperature of a moist soil sample as it continued to freeze after freezing had begun, and the time from the point where the supercooling curve crossed the temperature axis at the freezing point. If such a relationship could be worked out, the problem of excess undercooling and its concomitant freezing-point error would be obviated.

The procedure was started by placing a soil sample at a low moisture tension, or even saturated, in the bath with the thermistor inserted. The thermistor resistance was noted occasionally until 0°C was approached. The recording potentiometer was then switched on and the sample allowed to cool to about -1°C , when it was given a few sharp taps to initiate freezing. The temperature quickly rose to the freezing point as ice was formed, and then

gradually decreased again as the moisture froze out. Figure 9 illustrates this sequence of events for two different soil types. It may be noted that the soil with the higher moisture holding capacity took longer to freeze as would be expected. The scale of the recording potentiometer was set to read from 0 to -1.5°C .

Theoretical Aspects

If such a temperature versus time curve is to be of any value, a relationship between time and the amount of ice formed must be discovered. The original moisture content of the sample can be found by oven-drying the sample after the curve is traced. The moisture percentage at any subsequent time will then be equal to the initial percentage minus the amount of ice formed. If the temperature is then converted to stress by equation 3, a moisture-stress curve may be drawn for the soil sample. There remains to be determined only the amount of ice frozen out for any given range of temperature of the freezing curve. In an attempt to mathematically relate the time elapsed after freezing had been initiated to the percentage of unfrozen moisture remaining in the sample, the various factors involved in cooling and freezing a soil sample were considered in the following manner. In the absence of ice formation, the time necessary to cool

a sample one degree should depend directly on the mass of the sample and the specific heat of the sample and inversely on the rate of heat loss to the bath; or

$$\text{time/degree} = \frac{(\text{wt}) (\text{spec. heat})}{\text{rate of heat loss}}$$

After the water has started to freeze, the amount of heat loss to the bath will be the sum of both the amount removed in lowering the sample temperature and that lost from the water when ice is formed. The time necessary to cool the sample one degree will now be related directly to the mass and the specific heat of the sample, and inversely to the rate of heat loss minus the heat removed from the water to form ice. The rate of heat loss to the bath now includes that heat removed from the water as ice is formed as well as the heat removed from the sample in lowering the temperature. The heat involved in the formation of ice is the product of the heat of fusion (L) of water (79.71 calories per gram) and the mass of ice formed per unit time. The equation then becomes, after freezing is initiated,

$$\text{time/degree} = \frac{(\text{wt}) (\text{spec. heat})}{\text{rate of heat loss} - L \frac{\text{Amount of ice formed}}{\text{time}}}$$

Stated symbolically, inverted and written in the differential form, we have

$$dT/dt = \frac{K - L \frac{dw}{dt}}{G S}$$

where T is temperature, t is time, K is the rate of heat loss from the sample to the bath, W is the amount of ice formed, G is the weight of the sample and S is the specific heat of the sample. Solving this equation for the amount of ice formed, ΔW , during a definite interval of time, Δt , and temperature, ΔT , yields the following:

$$\Delta W = \frac{K \Delta t - \Delta T(GS)}{L} \quad 4$$

The two factors, K and S, may not be constants, however. The rate of heat loss to the bath (K) will vary with the difference in temperature between the sample and the bath and appears to be a linear relationship. K may then be written as a function of the sample temperature, T and of the bath temperature, T_B as follows:

$$K = k(T - T_B)$$

The specific heat, S, of ice is less than that of water and for that reason, for a constant rate of ice formation, an increasingly smaller rate of heat removal will be required to lower the sample temperature. The specific heat of the sample may be written as a function of the amount of ice present or in terms of ΔW .

Another factor, the heat conductivity of ice, is probably involved. It is greater than that of water, and should also hasten the freezing process. This factor is

more difficult to evaluate and introduce into the equation. An equation was developed, however, in an attempt to take into consideration all of these factors. The magnitude of the correction by this equation to the ΔW from equation 4 did not seem to warrant the use of such an elaborate calculation. Equation 4 was therefore used for subsequent calculations.

Substituting in equation 4 the values for the time and temperature corresponding to any stress range along with the other necessary values, should theoretically give the approximate amount of ice frozen out and thus the approximate amount of moisture held over the range of stress considered. If the amount of moisture held in an interval is calculated for a number of intervals over the stress range of interest, and if the freezing-point depression is converted to stress, then a moisture-stress curve may be developed for the particular soil sample involved.

If a representative value of 0.26 for the specific heat of soil (5, p. 296) is taken, only the evaluation of K remains, for the equation to be useful.

Evaluation of K for Saturated Samples

As mentioned in the previous section, an evaluation of K was necessary before equation 4 could be used to estimate the quantity of water held between any two values of

stress. The initial K may be easily determined from the supercooling curve. It was early discovered, however, that the equation would not yield the correct results if this K were used. Therefore, an evaluation of K was attempted in the following way. Small holes were ground in the bottom of a number of the sample containers and five-gram soil samples were allowed to become saturated in these containers by leaving them in a pan of water for a number of hours. The samples were then removed from the water and set on a paper towel for a few minutes to remove any excess water, weighed and prepared for freezing. A curve was then drawn for each sample (the bath temperature used for this part of the study was approximately -8°C) and the K's were calculated for each interval of stress by the following equation, which results from equation 4 by solving for K,

$$K = \frac{L(\Delta w) + \Delta T(GS)}{\Delta t} \quad 5$$

where ΔT and Δt were taken from the freezing curve and Δw was found from the appropriate soil moisture-tension curve using the difference in tension corresponding to ΔT . The tension values commonly used on the pressure membrane and porous plate were used as interval limits. For instance, ten and fifteen atmospheres are commonly determined on the pressure membrane so these values were used as the

limits for the last interval.

Table II shows how the calculated K appears to have increased with increasing stress, and was not in either case a constant, as might have been expected.

Table II

Values of K for two soils calculated over various stress intervals by equation 5.

	Stress Interval(atm)	K
Chehalis silty clay loam	Initial K before freezing started	.42
	0 - 1	1.25
	1 - 2	1.83
	2 - 5	2.08
	5 - 10	2.19
	10 - 15	1.17
Aiken clay loam	Initial K before freezing started	1.96
	0 - .5	2.50
	.5 - 1	1.15
	1 - 2	2.21
	2 - 5	5.12
	5 - 10	4.06
	10 - 15	5.26

The results shown in Table II are typical. A number of samples were run and numerous calculations made in an attempt to find a relationship between K and some more easily determined factor such as amount of ice frozen out or time period of the various intervals. Also, the equation was corrected for the lowered heat loss from the sample due to its temperature approaching that of the bath, and for the change in conductivity and heat content

of the sample as the water changed to ice. Neither of these corrections effected much change in the calculations of K , however.

Another factor that may have been contributing to the variation of K was the possible existence of temperature gradients in the sample as it was being cooled. These would be difficult to correct for mathematically.

The effects of structure upon the moisture-stress relationship of soil at low tensions have been recognized. As the amounts of water held in the different tension ranges were calculated from the moisture tension curve, the structural influence on stress, where applicable, would cause the calculations of K to be in error. The great quantity of water held at a very low stress in a saturated soil would tend to enhance any errors present. It became obvious, therefore, that some changes should be made in the subsequent procedure.

Studies Involving Unsaturated Soils

In order to minimize the effects of temperature gradients in the sample, the bath temperature was changed to -2.2°C . At the same time it was decided to use soil samples from the pressure membrane at one atmosphere in an attempt to minimize these structural effects.

Instead of solving for K , Δw was plotted against Δt .

This is, in effect, neglecting the contribution made to K by the lowering of the sample temperature.

Time versus temperature curves, of which the two in figure 9 are typical, were drawn by the recording potentiometer as the samples froze. The procedure was similar to that used with the saturated samples described at the beginning of this major section. Time was reckoned from when the temperature of the sample passed 0°C on the cooling curve.

The initial moisture percentage of the sample was taken as zero per cent moisture frozen, and was found by oven drying the sample after the curve was completed. The amounts of ice frozen out between different temperatures as the sample continued to cool after freezing had been initiated were calculated from the moisture-tension curves (figure 10), and were plotted against time in figures 11 and 12. For this purpose the different temperatures were converted to tension by means of equation 3. Figure 10 shows the relationship between moisture percentage and tension from the pressure membrane apparatus for the four soils used in this study. In figure 11, the relationship between moisture percentage, as ice frozen out, and time is shown to be quite linear for the samples initially at one atmosphere. This is perhaps fortuitous and probably indicates a balance between the effect of the changing

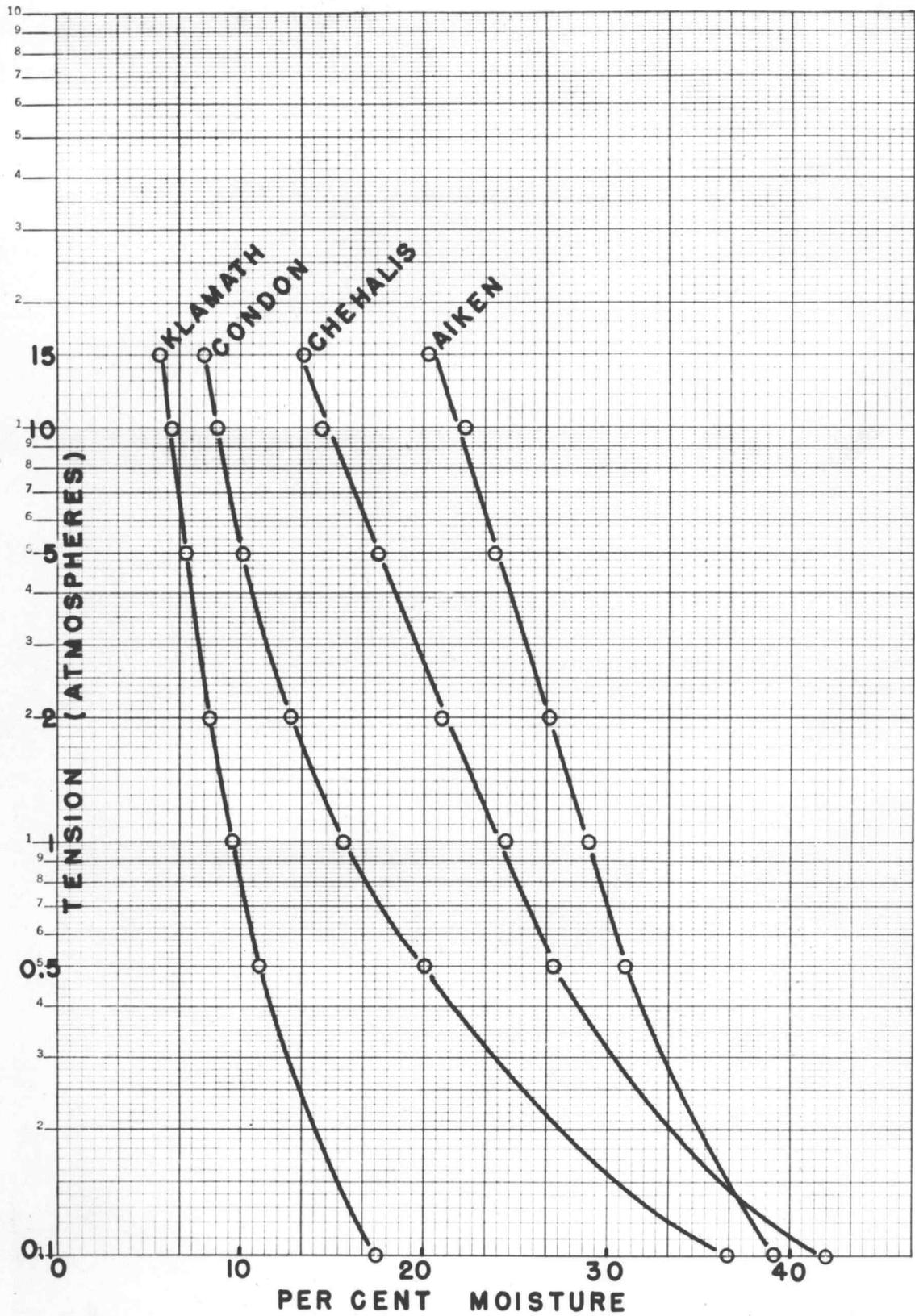


Figure 10. Moisture-tension curves for four soils.

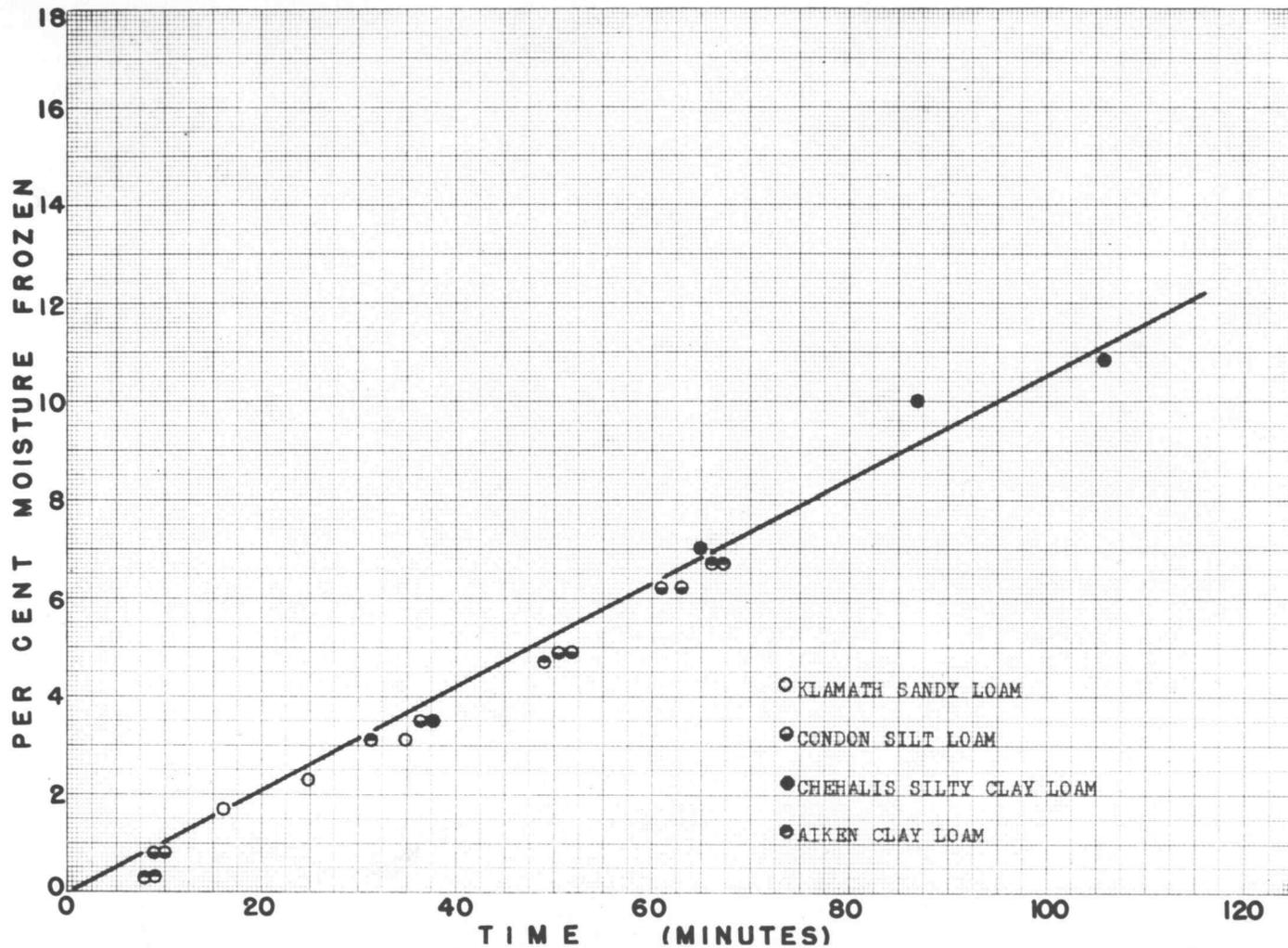


Figure 11. Plot of the calculated amount of ice formed versus time after the soil sample reached 0°C for samples initially at one atmosphere tension (bath temp. -2.2°C).

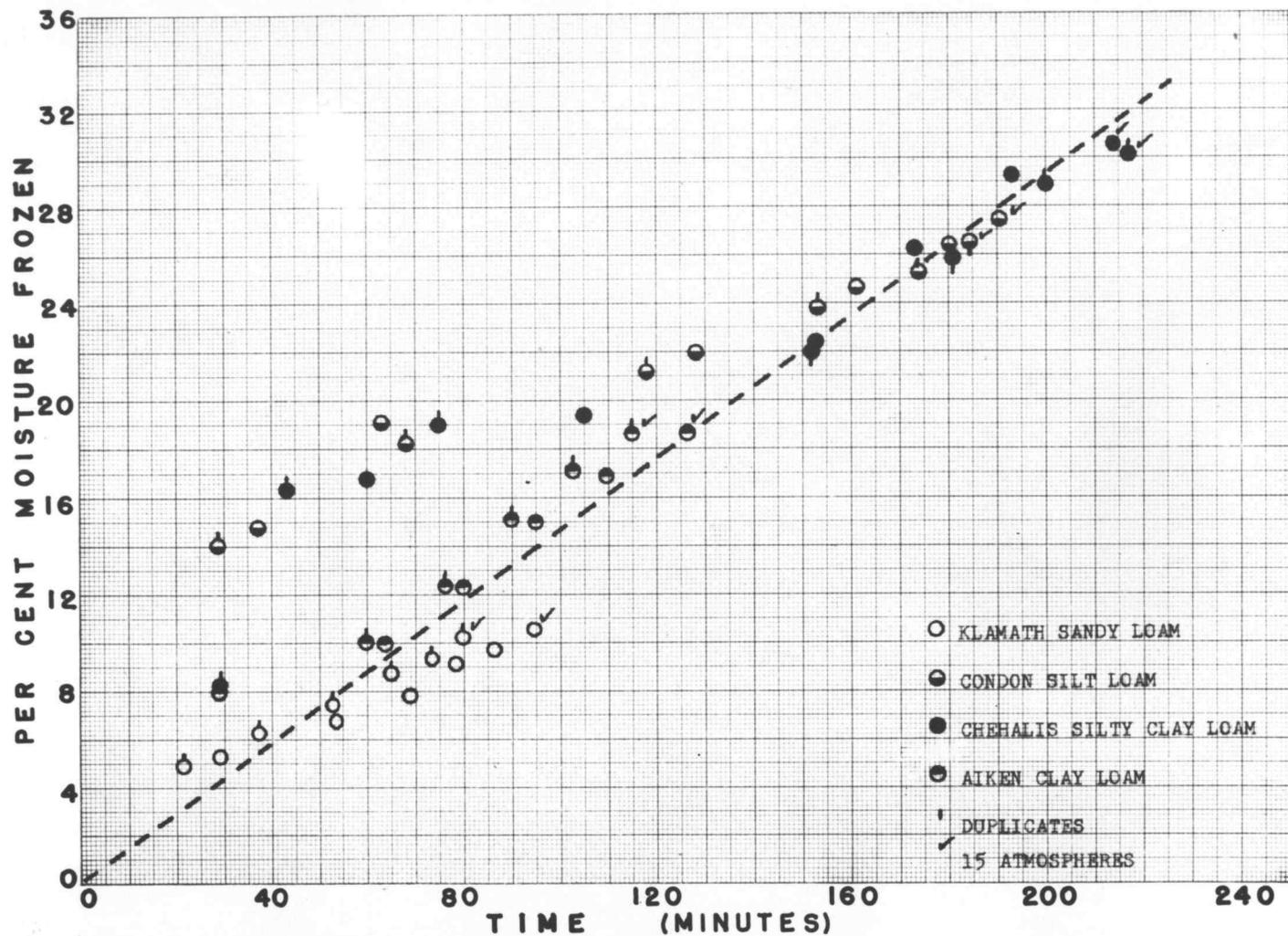


Figure 12. Same as figure 11 except that the soil samples were initially at one-tenth atmosphere tension.

difference in temperature between the sample and the bath which would tend to make the curve concave downward, and the change in heat content and heat conductivity of the sample as the moisture was transformed to ice, which would make the curve concave upward. From these results it appears that the linear relationship between ice frozen out and time may well be used in arriving at a moisture-stress curve between one and fifteen atmospheres from one soil sample.

As the results looked very promising from one atmosphere sample, one-tenth atmosphere samples were next tried. Figure 12 illustrates the results from these samples. As may be observed, the fifteen atmosphere points of all the soils fall near the line drawn through the origin. All of the points for Klamath sandy loam fall near the line, although they have apparently a slightly different slope. Those for Aiken clay loam deviate only at the lowest stress. But the points for Chehalis silty clay loam and Condon silt loam approach the line only above one or two atmospheres. These results might indicate an effect of structure on the moisture-stress characteristics at the lower stresses. The moisture-stress relationships of Klamath, being a sandy loam, and Aiken, being very well aggregated, are not influenced much by structure. The structural stability of these soils is

easily observed in a very moist sample. The Chehalis and Condon, on the other hand, very obviously lose their structure at high moisture contents and show a tendency to flow. In preparing the sample, it would appear that mechanical work serves to lower the tension somewhat of a portion of the moisture already held at a low tension.

It appears, therefore, that at the lower moisture tensions structure must be taken into consideration. An attempt at getting results from this method using samples from the pressure membrane apparatus without altering their structure might contribute to straightening out the curves. Although structure appears to be important and samples should be handled accordingly, since we can come near the correct moisture percentage at fifteen atmospheres, this method shows promise of providing moisture-tension curves from the time-temperature freezing curves of a single soil sample.

SUMMARY AND CONCLUSIONS

Vapor Pressure Control

An apparatus for controlling the water vapor pressure of a soil sample was designed and constructed for this study. The design provided for circulating moist air through a saturating chamber and a sample chamber in a closed system, with a water aspirator serving as the air pump. A rotameter-type instrument was used to control the differential pressure between the two chambers. The pressure drop, from which the relative humidity was calculated, was measured with a dibutyl phthalate manometer. The system was operated in a constant temperature bath at 30°C which was located in a constant temperature room at 22°C. The bath temperature was controlled to $\pm 0.01^\circ\text{C}$ by a thermistor-activated phase-sensitive electronic controller.

Soil samples were placed in the sample chamber and the gain or loss of moisture followed by means of a cathetometer and the Jolly balance spring by which the sample pan was suspended.

Equations were used to relate the pressure drop of the circulated air to its relative humidity and to the moisture stress in the soil sample at equilibrium. The results indicate the approach of moisture equilibrium at

much lower moisture percentages than were calculated for the soils used from the moisture-tension characteristics as obtained from the pressure membrane and pressure cooker. This was the case whether the sample was gaining or losing moisture.

Some of the reasons for failure of the sample to reach the moisture content predicted from the pressure membrane values according to the equations relating vapor pressure and stress might be listed as follows:

1. Incomplete saturation of the air with water vapor in the saturation chamber .
2. Loss of moisture at the pressure regulator, due either to pressure or temperature effects.
3. Energy intercepted by the sample to raise its temperature above that of the air passing around it.
4. Failure of the equation to be applicable in the range of soil moisture which is available to plants.

Freezing Characteristics of Soils

An apparatus for making freezing-point depression measurements has been constructed. It was essentially the same as that used by Cannell (10, pp. 1-55) and others, except for changes in the design of the thermistor probe

and in the temperature measuring circuit. The apparatus consisted of a freezing bath and sample containers, and a temperature measuring circuit containing a thermistor. The thermistor was inserted in the sample, which was placed in the containers in the bath and the temperature of the sample was followed as the sample froze.

The thermistors were calibrated by means of an equation and two known temperatures. An equation was developed for the rise in temperature of the thermistors due to self-heating. The relationship between freezing-point depression and stress was studied.

Soil samples at different stresses were frozen with a bath temperature of -2.2°C . Difficulty was encountered in arriving at the correct freezing-point, due to the necessary degree of undercooling. This method may be used to determine the soil moisture stress of a soil sample with a fair degree of accuracy, however, particularly at the lower stresses.

In an attempt to develop a complete moisture-stress curve from one soil sample, time-temperature freezing curves were drawn from saturated soil samples as they froze in a bath controlled at -8°C . An equation was developed for calculating the amount of water held between any two stress values, using the data from such time-temperature freezing curves. It was found that the K of

the equation varied throughout a curve, so an attempt was made to evaluate K. No relationship was found which could be used. Therefore, the relationship between temperature and time of freezing curves was studied, using a bath temperature of -2.2°C again. This bath temperature was used to minimize the lag of the thermistor response to the sample temperature. Soil samples of low moisture stress were used. For samples initially at one atmosphere, a linear relationship was discovered between the moisture content of the sample as calculated from the moisture-tension curve and the time associated with the freezing of the sample. This relationship was the same, regardless of the soil used.

One-tenth atmosphere samples were then studied, and a deviation from linearity at the lower tensions was found for certain soils, which indicated the effects of structure on the moisture-stress relationships. Klamath sandy loam and the well-aggregated Aiken clay loam showed a linear relationship. However, the Chehalis silty clay loam and the Condon silt loam showed the deviation from linearity at the lower stresses. Their structure is easily altered at high moisture contents, which may be the explanation for the deviation.

This method shows very good promise for ascertaining the moisture-stress relationships of various soils from

their time-temperature freezing curves, if structural effects are properly accounted for.

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