

**Research Report 182**  
**SATURATION, PHASE COMPOSITION**  
**AND FREEZING POINT DEPRESSION**  
**IN A RIGID SOIL MODEL**

by  
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## PREFACE

This paper was presented at Session IV of the First International Conference on Permafrost held at Purdue University in November 1963. Discussions pertinent to the paper were offered in Session IV by Professor R. D. Miller of Cornell University and Dr. Duwayne Anderson of U. S. Army Cold Regions Research and Engineering Laboratory (USA CRREL). These discussions are included in this report by the kind permission of Professor Miller and Dr. Anderson. Together with the authors' closure they serve to illuminate certain research problems in phase composition of water in frozen soils.

The work was conducted by G. Robert Lange and SP4 Harlan L. McKim for the Applied Research Branch (A. F. Wuori, Chief), Experimental Engineering Division (K. A. Linell, Chief), USA CRREL.

Discussions with the following members of the USA CRREL staff have furnished many of the ideas for both the design of the experiments and the analysis and discussion of the data: Dr. Duwayne Anderson, Dr. Andrew Assur, Dr. Geoffrey Ballard, Dr. Paul Camp, Mr. Kenneth Linell, Mr. Richard McGaw, Mr. Donald Nevel, Prof. Frederick Sanger, Dr. Shunsuke Takagi, and Dr. Wilford Weeks. The authors are happy to acknowledge their assistance and encouragement.

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## SUMMARY

Two series of experiments were performed. In the first, the calorimetric method of mixtures was used to explore the effects of saturation and temperature upon the phase composition of the water at below freezing temperatures in a porcelain block with very fine pore spaces. The effect of pore size upon phase composition was held constant by use of such a rigid model. The percent of original soil water frozen was determined for a wide range of saturations and at several pertinent temperature levels. Nucleation was avoided. After about 20 hr of freezing, 64 of a total of 74 determinations showed either less than 10% or more than 70% of the water frozen. Thus, a metastable condition of saturation and temperature for guaranteed freezing was defined for the pore space model with time of freezing held constant.

In the second series of experiments, freezing point depression determinations were also made at various levels of saturation in the same porcelain blocks. A range of effective pore sizes was calculated from these data, thus characterizing the pore size distribution in the porcelain.

Both freezing point depression and guaranteed freezing data, when plotted against saturation, appear to conform to an empirical relationship of the form:  $\theta = \beta \log_e S + \epsilon$  in which  $\theta$  may be either the freezing point depression  $\Delta\theta$  or the temperature for guaranteed freezing  $\theta_f$ , and  $S$  is the saturation coefficient. The slope constant  $\beta$  has the same value (1.35) for both  $\theta_f$  and  $\Delta\theta$ .  $\epsilon$ , the temperature intercept at maximum saturation ( $S = 0.92$ ), has different values (-0.4C and -3.3C) for  $\Delta\theta$  and  $\theta_f$  respectively.

It is concluded that the phase composition of the water in frozen soils is also dependent upon the degree of saturation as well as the temperature. It is suggested that rigid models are useful tools for investigating the freezing process in soils.

# SATURATION, PHASE COMPOSITION AND FREEZING POINT DEPRESSION IN A RIGID SOIL MODEL

by

G. Robert Lange and Harlan L. McKim

## INTRODUCTION

The fact that the phase composition of the soil water is important in controlling the physical behavior of frozen soils is beginning to gain its deserved attention. It is well established that the load bearing capacity and the energy required for freezing and thawing are dependent upon the initial temperature of the soil (Lovell, 1957; Yong, 1962; Tsytoich, 1958; Williams, 1962). These and a number of other physical properties are temperature dependent chiefly because the amount of unfrozen water is also, in part, temperature dependent. Some exploratory experiments with natural soils by one of the authors have indicated that the phase composition of the soil water is also strongly dependent upon the degree of saturation. This paper is a preliminary report of the results of some experiments with an idealized soil model which illustrate the separate and combined effects of both temperature and saturation upon the phase composition of the soil water.

It has been demonstrated that cores of frozen rocks and soils may be taken from any depth below the surface and shipped to a refrigerated laboratory with very little thermal disturbance (Lange, 1963). Thermistor cables and bridge circuits that allow accurate measurement of the temperature of the rock or soil from which the core was taken are also available (Hansen, 1963). Since virtually undisturbed samples can now be examined in the laboratory, the next step towards a more complete understanding of permafrost is a quantitative description of the components of the sample.

For an undersaturated soil, there are four components: mineral grains, ice, air (or other gases), and liquid water. If the soil is fully saturated, the air is eliminated. The measurement of the amount of these components in the sample presents no special difficulties except for the differentiation between liquid and solid phases of the water. This may be accomplished by using dilatometry or calorimetry, with either the method of mixtures (Lovell, 1957) or an adiabatic calorimeter (Williams, 1962). There is reason to believe that the measurement of the dielectric constant and the a-c resistivity can eventually be used to determine the phase composition of the water. These electrical methods are especially attractive since they appear to exhibit great sensitivity; however, the present lack of an adequate theory of complex mixtures of dielectrics has discouraged their use.

While the effect of temperature upon the amount of unfrozen water has often been reported, the investigators generally worked with natural soils, which, in our experience, yield data with considerable scatter chiefly because of difficulty in remolding samples to uniform density, both from sample to sample and throughout a single sample. The effects of the degree of saturation and of pore size have not previously been thoroughly examined. The use of a rigid permeable medium such as unglazed porcelain as a model of natural soils eliminates the problem of density variations. This allows the variable of pore size to be held constant while investigating the effects of variations in saturation and temperature, since these two remaining variables are easily and accurately adjusted at will.

## EXPERIMENTAL PROCEDURE

The phase composition of the water in the unglazed porcelain was measured by the method of mixtures. The adaptation of this method to frozen soils is described by Lovell (1957), and his method was used here with the following modifications: (a) temperatures were recorded continuously using thermocouples and a millivolt recorder; (b) the change in temperature of the mixture after the introduction of the frozen sample was corrected for heat gains resulting from calorimetric inefficiencies, according to a method described by King and Grover (1941). This correction method consistently gave correct values for the heat of fusion of pure ice to  $\pm 1.0\%$ . Calorimetric inefficiency was further reduced by filling the air space between calorimeter cup and Dewar flask with styrofoam and insulating the entire calorimeter from the room temperature with a thick layer of styrofoam.

The following equation, which is usually applied to the method of mixtures, was solved for  $x$  (weight of ice) at adjusted levels of saturation and temperature:

$$\begin{aligned} (x) (C_{pi}) (\Delta t_i) + (x) (H_{fi}) + (x) (C_{pw}) (\Delta t_w) + (y) (C_{pscw}) (\Delta t_{scw}) + \\ (y) (C_{pw}) (\Delta t_w) = [(W_{cw}) (C_{pw}) (\Delta t) + (W_{ccs}) (C_{pAl}) (\Delta t) - \\ [(W_p) (C_{pp}) (\Delta t_p)] \end{aligned} \quad (1)$$

where:

- $x$  = wt of ice (g)
- $y$  = wt of unfrozen water (g)
- $x + y$  = wt of original total water substance
- $\frac{x}{x + y}$  = percent frozen
- $C_{pi}$  = specific heat of ice,  $0.496 \text{ cal g}^{-1} \text{ C}^{-1}$  at  $-5.0\text{C}$  (Chemical Rubber Pub. Co., 1953, p. 2079)
- $\Delta t_i$  = temperature change of ice ( $^{\circ}\text{C}$ ) (observed value)
- $H_{fi}$  = heat of fusion of ice ( $79.71 \text{ cal g}^{-1}$ ) (ibid.)
- $C_{pw}$  = specific heat of water ( $1.00 \text{ cal g}^{-1} \text{ C}^{-1}$ ) (ibid.)
- $\Delta t_w$  = temperature change of calorimeter water ( $^{\circ}\text{C}$ ) (observed value)
- $C_{pscw}$  = specific heat of supercooled water ( $1.01 \text{ cal g}^{-1} \text{ C}^{-1}$ ) (ibid.)
- $\Delta t_{scw}$  = temperature change of supercooled water (observed value)
- $W_{cw}$  = wt of calorimeter water (g) (observed value)
- $\Delta t$  = temperature change of calorimeter water ( $^{\circ}\text{C}$ ) (observed value)

$W_{ccs}$  = wt of calorimeter cup (Al) and stirrer (Al)(g)

$C_{pAl}$  = specific heat of Al ( $0.22 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ )(a constant of the apparatus)

$W_p$  = wt of dry porcelain model (g)

$C_{pp}$  = specific heat of dry porcelain ( $0.169 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ )(observed mean of 7 separate determinations)

$\Delta t_p$  = temperature change of porcelain ( $^\circ\text{C}$ )(observed value).

Close control of the freezing temperature was achieved by the use of a styrofoam box inside a chest-type home freezer. The freezer temperature was set at approximately  $-17^\circ\text{C}$  and was constant to within  $\pm 2.0^\circ\text{C}$ . The temperature inside the styrofoam box was controlled by a thermostatic mercury switch, a small electric heating element, and a fan. Temperature was controlled to within  $\pm 0.1^\circ\text{C}$ .

The freezing point depression for various saturation levels was measured by preparing the samples at the desired saturations in the manner described below. A thermocouple was inserted in a small hole drilled in the porcelain block and the sample and thermocouple were placed in the constant temperature cabinet. The freezing point depression data reported here were taken at a cabinet temperature of  $-9.8^\circ\text{C}$  to provide a constant cooling rate.\* Temperature vs time curves were obtained on the millivolt recorder chart. The highest temperature reached after nucleation was used as the value of the freezing point depression. Figure 1 is a plot of the data from a typical freezing point depression run. Uniformity of procedure was rigidly maintained. Only doubly distilled water (resistivity  $\sim 2.0$  megohm/cm) was used and nucleation was carefully avoided during cooling in both the calorimetric work and the freezing point depression determinations.

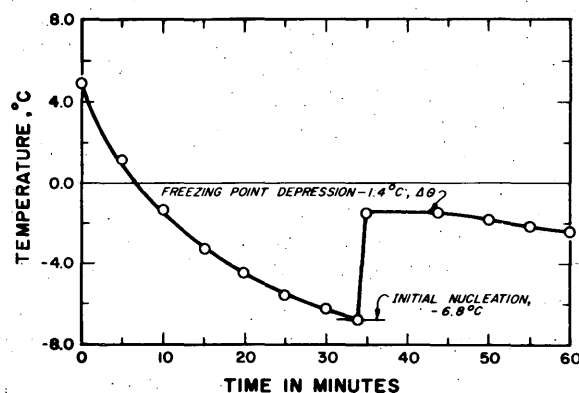


Figure 1. Typical temperature vs time curve for the determination of freezing point depression.

\*A reasonable range of cooling rates was investigated and no effect upon freezing point was observed.

## SAMPLE PREPARATION AND DESCRIPTION

An unglazed porcelain slab of the type used as a mineralogical streak plate was used. To determine whether the pore space structure would be destroyed by repeated freezing and thawing, a small piece of the slab was subjected to 20 freeze-thaw cycles at a constant freezing temperature; the coefficient of original water saturation\* was adjusted to 0.92 (which results in an ice saturation of 1.0) before the beginning of each freezing cycle. The amount of unfrozen water was measured after 5, 10, 15 and 20 freezing cycles. Since the amount of unfrozen water did not vary more than the estimated experimental error (approximately  $\pm 2.0\%$ ) it is concluded that the pore structure and size did not change during the freeze-thaw cycles. This also served as a measure of the reproducibility of the calorimetry.

To obtain an even distribution of water in the pore spaces, samples were prepared by thorough saturation and slow drying to the desired saturation level. The samples were wrapped in aluminum foil to provide a closed system. They were then immediately introduced into the constant temperature box and remained there for a period of 19 to 20 hr prior to the calorimetry. Six of the sets of data reported were taken after freezing from 50 to 65 hr and they showed that no measurable amount of additional water froze after the first few hours. The two small slabs of porcelain used in the experiments were cut to similar dimensions. The exact dimensions and properties are given in Table I.

Table I.

Sample no.	Dry weight (g)	Bulk volume (cm <sup>3</sup> )	Dry bulk density (g/cm <sup>3</sup> )	Void volume (cm <sup>3</sup> )	Porosity	Grain density (g/cm <sup>3</sup> )
2	34.81	19.34	1.80	7.48	0.387	2.94
3	35.25	19.44	1.81	7.43	0.382	2.94

It was recognized at the outset that determination of the distribution of pore sizes would be important to relate the data to natural soils. An examination of a thin section by an optical microscope at 500X failed to reveal distinct grains or pore spaces. This indicated that grain sizes and pore diameters were less than 1.0 micron. An inquiry to the manufacturer† revealed that the pore spaces were close to but less than 0.5 micron diam as measured by the bubbling pressure method. The manufacturer also felt that the pore sizes were quite uniform. A further discussion of the "mean effective" pore radii and the distribution of these sizes as calculated from the freezing point depression and capillary head measurements will be given later in this report.

## RESULTS AND DISCUSSION

Figures 2, 3, and 4 show the percent of original water that changed to ice for various saturation coefficients, at constant temperatures of -4.0C, -5.0C, and -7.5C respectively. Smoothed curves were drawn by eye. As these data were collected (without deliberate nucleation), it became clear that freezing occurred abruptly at a single, reproducible saturation level

\*Coefficient of saturation as used herein is defined as volume of water / volume of voids; i. e., 100% saturation = saturation coefficient 1.0.

†Coors Porcelain Co., Golden, Colorado.



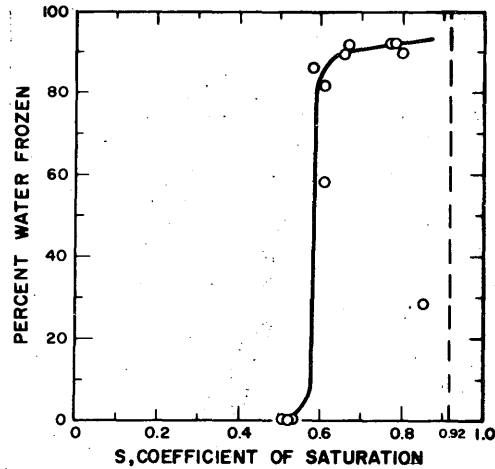


Figure 2. Percent water frozen vs coefficient of saturation at  $-4.0\text{C}$ .

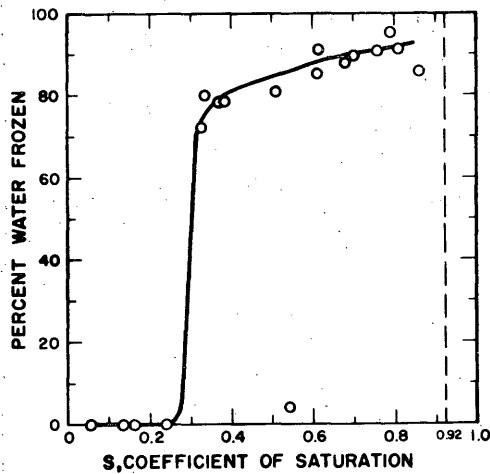


Figure 3. Percent water frozen vs coefficient of saturation at  $-5.0\text{C}$ .

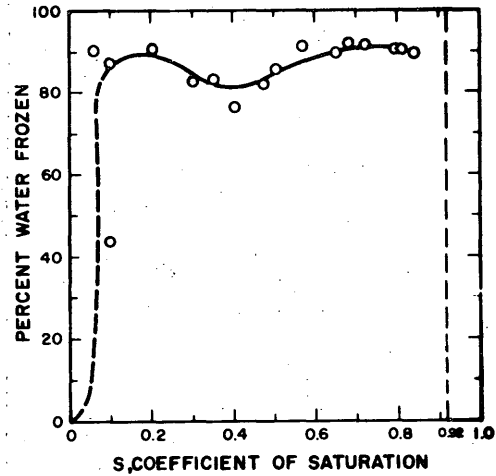


Figure 4. Percent water frozen vs coefficient of saturation at  $-7.5\text{C}$ .

for each temperature. A number of determinations were run at high levels of saturation and at temperatures of  $-1.8\text{C}$ ,  $-3.2\text{C}$  and  $-3.5\text{C}$  and at lower levels of saturation with a temperature of  $-6.0\text{C}$  to define more completely the saturation levels and temperatures required for freezing.

The effect of variations of both the degree of saturation and the temperature upon the percent of total water frozen is shown in Figure 5. In this three-dimensional plot the coefficient of saturation vs temperature was plotted on the horizontal axis and the percent of original water frozen was plotted on the vertical axis. Isopleths of equal percent original water frozen were then drawn at 10% intervals. The smoothed curves of Figures 2, 3, and 4 were also used in contouring. All of the points where data were taken are shown as small crosses.

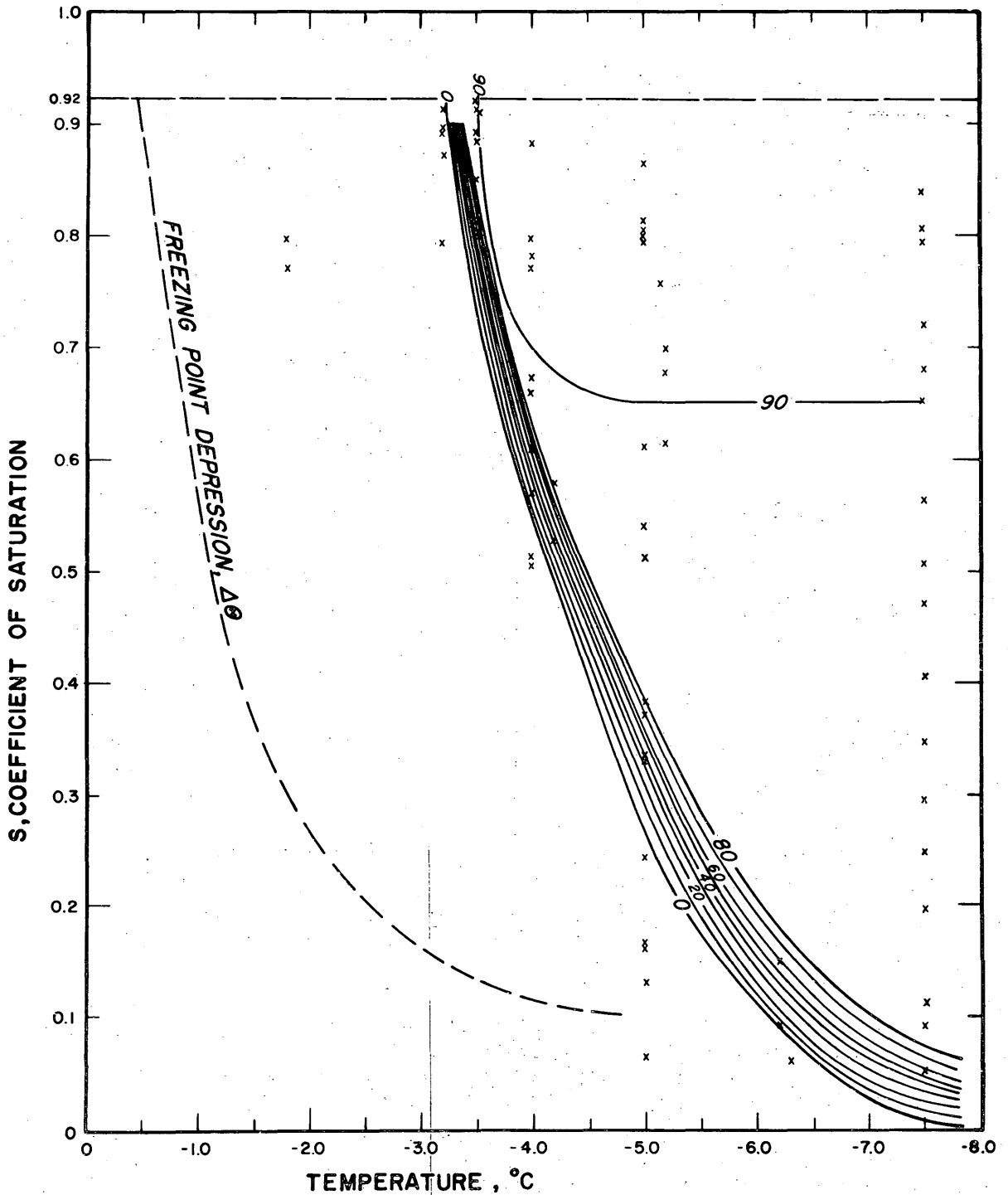


Figure 5. Effect of variation of saturation coefficient and temperature upon the percent of original water frozen; elevation is percent frozen.

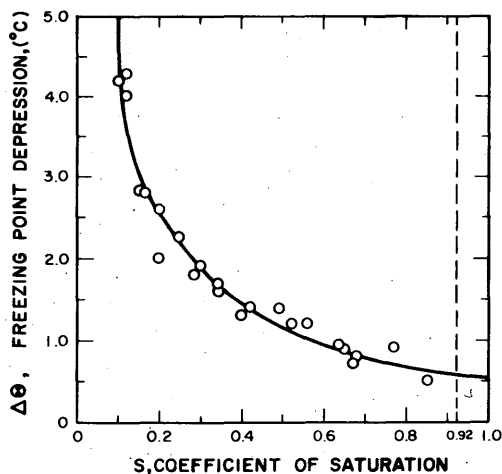


Figure 6. Freezing point depression vs saturation coefficient.

bound to the pore space walls by absorptive forces under nearly any conditions; the water that freezes abruptly upon the addition of more water (increased saturation) at the critical temperature  $\theta_f$  is considered to be the water held by meniscus forces. This water is considered to have a depressed freezing point caused by the surface tension of the meniscii (i. e., eq 2 below).

The depression of the freezing point  $\Delta\theta$  at a wide range of saturation levels was measured. A typical plot from these experiments is shown in Figure 1. This was done in an attempt to correlate freezing point depression with the location and trend of the "freezing step" that is represented by the "cliff" of Figure 5. These results are shown in Figure 6 and are also plotted as a dashed line on the three-dimensional plot of Figure 5. The temperatures of initial nucleation, as defined in Figure 1 (ranging from  $-5.2\text{C}$  to  $-7.8\text{C}$ ), were also plotted on Figure 5; however, these appeared to be more or less random in this linear plot, except that they were all temperatures lower than  $\theta_f$  at saturations above 0.2.

Determination of the freezing point depression also affords a method of characterizing the pore space geometry by use of the Gibbs-Thompson equation (Garner, 1949):

$$T_s - T_r = \frac{2\sigma T_s M}{\rho_i Q_s r} \quad (2)$$

where:

$T_s$  = normal melting point (273K)

$T_r$  = melting point ( $^{\circ}\text{K}$ ) of a nucleus of radius  $r$  (cm)

$\sigma$  = interfacial energy (air-water interface at  $S = 1.0$ ,  $71.9 \text{ erg cm}^{-2}$ )

If the coefficient of original water saturation exceeds 0.92 (the density of ice), the degree of ice saturation after freezing will exceed 1.0; i. e., ice will form outside of the pore space boundaries of the sample. This effect was actually observed in preliminary experiments and so a saturation coefficient of 0.92 was taken as a boundary condition for these experiments.

It is noted in Figures 2, 3, and 4 that only one of the many sets of data shows more than 92-93% frozen. In terms of Figure 5, this indicates that the "plateau" in the region of lower temperatures and higher saturation has relief of only 2-3% frozen and does not extend at any point above about 93% frozen. This nearly constant unfrozen fraction is that water which remains

$Q_s$  = heat of fusion ( $3.33 \times 10^9$  erg  $g^{-1}$ )

$\rho_i$  = density of solid phase ( $0.917$  g  $cm^{-3}$ )

$M$  = molecular weight of water (18).

Evaluation of the constants  $T_s$ ,  $\sigma$ ,  $Q_s$ ,  $\rho_i$ , and  $M$  allows a mean effective radius to be calculated by:

$$r_{me} = \frac{0.112}{\Delta\theta} \text{ for } r_{me} \text{ in microns}$$

where:

$$\Delta\theta = T_s - T_r \text{ or freezing point depression (}^\circ\text{C)}.$$

Pore or meniscus radii calculated in this way and the reciprocal of the calculated sizes are plotted against the natural logarithm of the corresponding coefficient of saturation in Figure 7. This is not intended as an accurate description of the pore sizes, but rather as a characterization of them. The resulting straight line gives the following equation for the mean effective radius as a function of saturation:

$$r_{me} = \frac{1}{2.0 - 11.7 \log_e S} \quad (3)$$

$r_{me}$  = mean effective pore (or meniscus) radius, in microns

$\log_e S$  = natural logarithm of the coefficient of saturation.

Equilibrium saturation values for various capillary "potentials" (or pressure heads) were measured for the porcelain model. The standard pressure membrane apparatus and procedures were used and mean effective radii calculated from these data are plotted in Figure 7. The following equation (Lambe, 1951) was used:

$$h_c = \frac{2\sigma_s}{r_{me} \gamma \cos \alpha} \quad (4)$$

where:

$h_c$  = pressure (cm of water)

$\sigma_s$  = surface tension at air-water interface ( $71.9$  dyne  $cm^{-1}$ )

$\gamma$  = density of water ( $1.00$  g  $cm^{-3}$ )

$\alpha$  = contact angle ( $\alpha = 0$ ,  $\cos \alpha = 1.0$ )

$r_{me}$  = mean effective pore radius (cm).

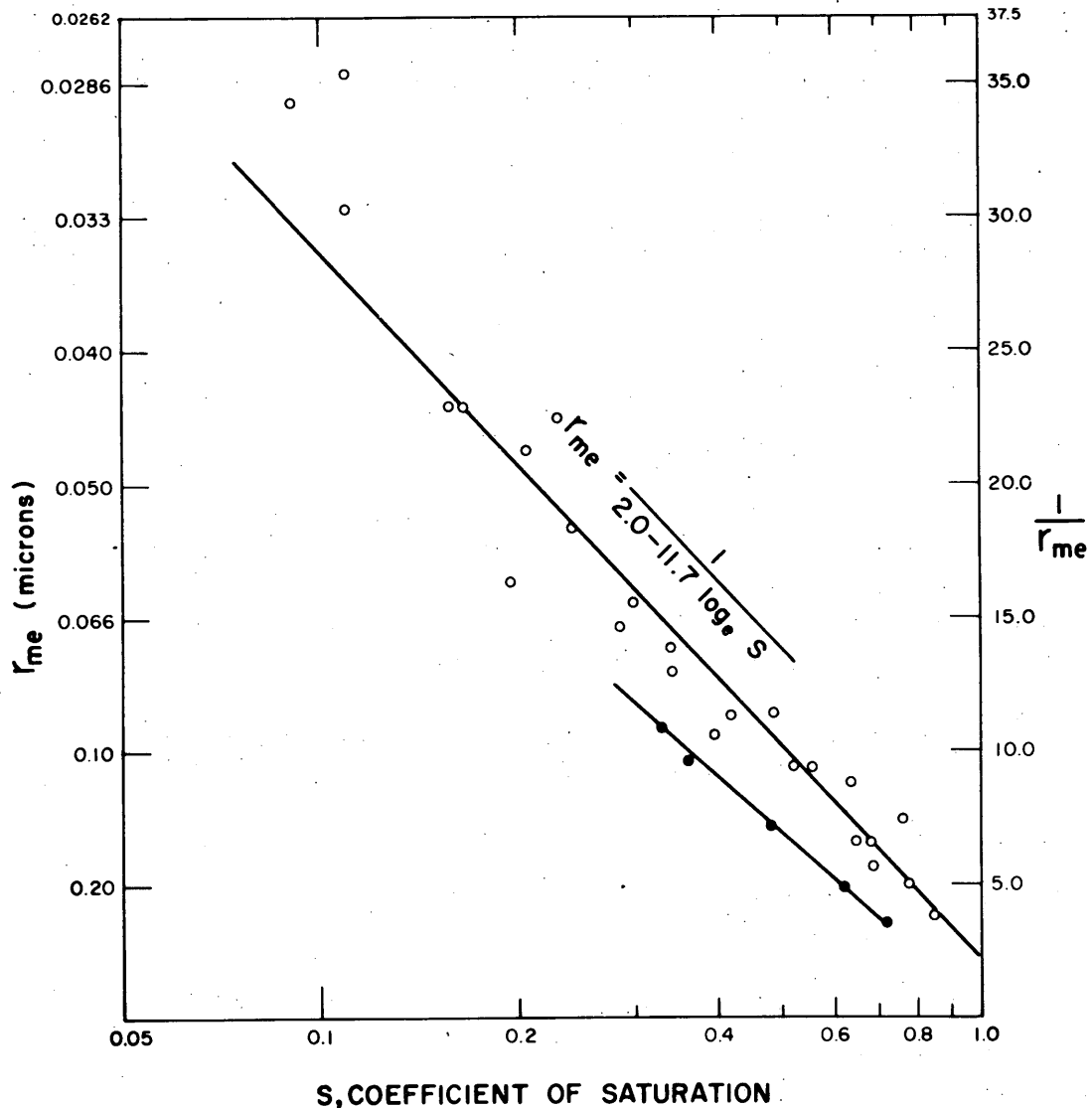


Figure 7. Pore size vs saturation calculated from freezing point depressions (o) and capillary head determinations (●).

To locate the line of the "cliff" (Fig. 5) short lines of equal temperature or of equal saturation (as were appropriate to the existing data), the ends of which represented the top and bottom of the "cliff," were drawn. These lines were then plotted against the natural logarithm of the corresponding saturation coefficient in Figure 8. The resulting straight line described the temperature  $\theta_f$  for any given degree of saturation below which freezing of most of the water in the pore spaces of the model is virtually guaranteed after 19-20 hr of freezing.

An equation may now be written of the form:

$$\theta_f = \beta \log_e S - \epsilon. \quad (5)$$

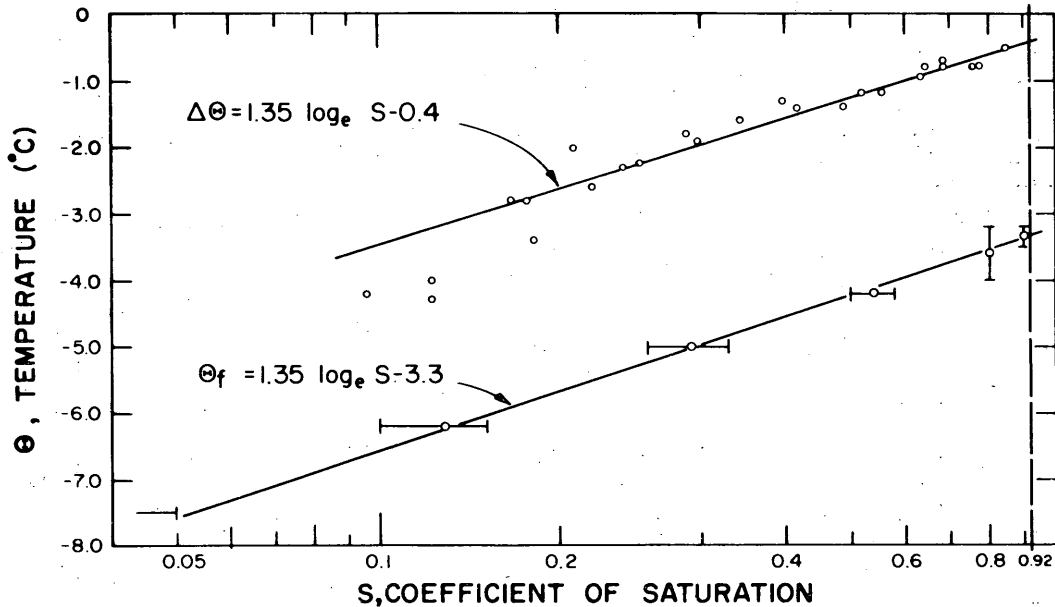


Figure 8. Freezing point depression and temperature of "guaranteed nucleation" vs coefficient of saturation.

Using values obtained from the plot for the constants  $\beta$  and  $\epsilon$ , the following is obtained:

$$\theta_f = 1.35 \log_e S - 3.4$$

where

$\theta_f$  = temperature of "guaranteed freezing" ( $^{\circ}\text{C}$ )

$S$  = coefficient of saturation

$\beta$  = slope constant

$\epsilon$  = temperature intercept.

The freezing point depression data are also plotted in Figure 8, using the same scales. These data can be described by an equation of the same form:

$$\Delta\theta = 1.35 \log_e S - 0.4 \quad (6)$$

where

$\Delta\theta$  = depression of the freezing point.

The fact that both curves have the same slope is interesting. The following explanation is tentatively proposed to describe the physical relationship between  $\Delta\theta$  and  $\theta_f$ . As the sample is slowly cooled below  $0^{\circ}\text{C}$ , deliberate nucleation will not cause freezing at temperatures above  $\Delta\theta$ ; in fact, freezing cannot occur in this region. At temperatures between

$\Delta \theta$  and  $\theta_f$  freezing can occur only if nucleation is initiated by something outside of the system such as the introduction of ice crystals or possibly physical shock. As the temperature is further reduced to the range below  $\theta_f$  the system is still not stable until nucleation and freezing occur; however, in this region nucleation is guaranteed without any outside agent if sufficient time is available. Experiments which may describe the time dependence of  $\theta_f$  are now in progress.

In our model, the temperature difference between the freezing point depression  $\Delta \theta$  and the temperature of guaranteed freezing  $\theta_f$  appears to be constant and independent of temperature and saturation, at least in the saturation range where the ratio of the amount of capillary water to the amount of adsorbed water is large. At saturations lower than 0.15 it is noted that the data appear to depart from the relationship given in eq 6; during the freezing point depression experiments it was noted that nucleation at temperatures higher than  $\theta_f$  occurred only at saturations less than 0.20. It may be that in this region of low saturation ( $S < 0.20$  to 0.15) enough of the total soil water is influenced by the adsorbed force field to cause a measurable departure from the relationships described above.

### CONCLUSIONS AND RECOMMENDATIONS

It can be concluded that the amount of the water that freezes in a frozen soil may be strongly influenced by the degree of saturation as well as by the temperature. The temperature history of a naturally occurring frozen soil may influence its phase composition and consequently its strength and effective specific heat. That is, it may be supercooled and may have suffered no accident of nucleation. The rate of advance of a nucleating front in a freezing soil has some effect on the validity of this speculation.

It is suggested that investigations of the phase composition of the soil water should be an important part of any serious engineering or scientific investigation of fine-grained frozen soils. Phase composition should be isolated as a discrete variable of strength rather than be included in the more general variable of temperature. In our opinion, if the behavior of the soil water upon freezing is investigated in a manner similar to the one that we have described, a fuller understanding of the several different (but related) aspects of the freezing behavior may be gained.

If adiabatic calorimetry is carried out in the manner described by Williams (1962) the information presented here could probably be gathered with much greater efficiency and accuracy. Further, it would seem that a method similar to the one he describes may furnish a more straightforward explanation of the relationship between the freezing point depression and the temperature of "guaranteed freezing," since both stable and metastable behavior may be described with this apparatus.

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## APPENDIX A. DISCUSSION

by

R. D. Miller\*

This paper poses a real challenge. It reminds us that we cannot say much, if anything, about the freezing of water in partially saturated soils. In this investigation, the authors used an apparently rigid and stable substrate, which is a step in the right direction; but who can say what really happens within this medium as water freezes? Does the water freeze in situ, or does it move toward the sites of nucleation until the pores in that region become saturated with water or ice or both? What is the configuration of the phase boundaries?

The authors are apparently confused in their use of eq 2. From the context, one judges that they have used the equation for the "equilibrium" temperature of an ice nucleus of radius  $r$  in water at atmospheric pressure. They ought to have used the interfacial energy of an ice-water phase boundary instead of that for air and water. If they use the latter, and take  $r$  to be the curvature of the air-water meniscus in the capillaries, they have a freezing point elevation case provided the air-ice interface is flat.

Now the strange thing, and this has been observed before, beginning with Schofield and his students, is that if one uses this equation to predict the magnitude (but not the sign) of the change in freezing point of water in soil as the soil is dried out, the results compare fairly well with "predictions" based on the desorption curve. One can rationalize this result in an unconfined specimen on the grounds that the ice segregates and forms in spaces that are large in comparison with those occupied by water and is therefore near atmospheric pressure. If the ice in Lange and McKim's experiments formed outside the block, this problem did not occur, and we have the analogue of the experiment described in Williams's contribution to this conference.

Making the indicated changes in eq 2 and assuming that ice-water = 45 dyne/cm, the upper curve in Figure 7 falls almost on top of the lower! This coincidence is hard to accept, however, for the excessive undercooling by Lange and McKim in their freezing point depression measurements means that the freezing temperatures recorded were too low, and the error increases as saturation decreases. This error arises from the fact that a finite amount of water must freeze to raise the temperature of the block to an equilibrium temperature. This fraction is a substantial portion of the total water over much of the range and, therefore, the residual unfrozen water content should have been plotted instead of the initial water content. Indeed, according to rough calculations, there was not enough water present in the drier specimens to raise the temperature more than halfway to the "predicted" equilibrium temperature.

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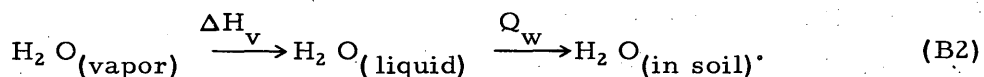
\*Cornell University.

## APPENDIX B. DISCUSSION

by

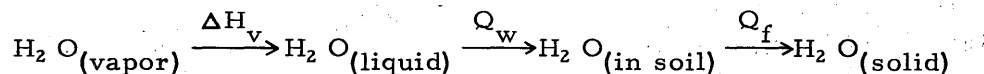
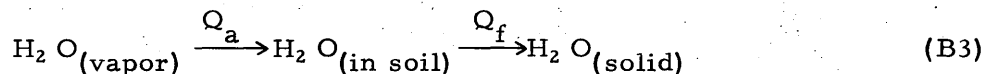
Duwayne M. Anderson\*

In the calorimetric determination of amounts of soil water remaining unfrozen at various temperatures, it has been widely assumed that the latent heat of freezing can be taken as that of an ordinary ice-water mixture (Kolaian and Low, 1963; Lange, 1963; Nersesova and Tsytoich, 1963; Vershinin et al., 1949; Lovell, 1957; Williams, 1962). Although Williams and Kolaian and Low adopted this assumption, they called attention to some of the aspects which render it questionable. Williams called particular attention to the fact that soil water exists in a lower energy state than does normal water, as evidenced by the evolution of heat when soils are wetted. Consider, at the freezing point, the transitions:

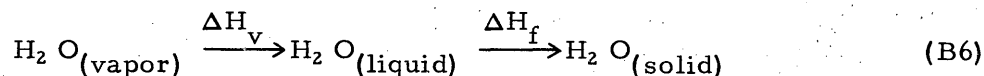


In these transitions, the subscripts denote the state of the water and the transitions may be regarded as changes in state (they may also be regarded as phase changes);  $\Delta H_v$  is the latent heat of condensation,  $Q_a$  is the differential heat of adsorption and  $Q_w$  is the differential (not the integral) heat of wetting. Here a positive sign indicates heat is evolved. If  $Q_a$  and  $Q_w$  are determined at constant pressure and in such a way that no work is done other than that due to expansion of water against atmospheric pressure, and if the initial and final states may be regarded as the same in eq B1 and B2, by the first law of thermodynamics  $Q_a$  may be regarded as equal to  $\Delta H_v$  plus  $Q_w$ .

Let us consider next the freezing of soil water. We have:



to be compared with




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in which  $Q_f$  is the heat of freezing soil water,  $\Delta H_s$  is the heat of condensation from the vapor to the solid state (the opposite of the heat of sublimation) and  $\Delta H_f$  is the latent heat of freezing.

Assuming that soil ice has the same crystallographic structure as normal ice and that it excludes solutes and foreign substances as it freezes, so that we may regard the initial and final states of eq B3, B4, B5 and B6 as being the same, it follows that:

$$Q_a + Q_f = \Delta H_s \quad (B7)$$

$$Q_w + Q_f = \Delta H_f \quad (B8)$$

It is well established that both  $Q_a$  and  $Q_w$  are continuous functions of the soil water content, increasing with decreasing soil water content in a roughly exponential fashion (Mooney et al., 1952; Janert, 1934). This being so, it follows that  $Q_f$  must in general be smaller than  $\Delta H_f$ , the difference becoming more and more pronounced at lower and lower soil water contents (or at lower unfrozen water contents).

If  $Q_a$  or  $Q_w$  is known as a function of soil water content, expressions B7 and B8 permit one to estimate  $Q_f$  for that soil at various unfrozen water contents. This information is available for a number of soil materials. As an example, from heat of desorption data for Wyoming bentonite (Mooney et al., 1952) and expression B7, the decrease in  $Q_f$  as the amount of unfrozen water in the clay is reduced is given in Table BI and shown graphically in Figure B1.\* Here negative values of  $Q_f$  mean heat must be supplied to freeze the soil water and positive values indicate that heat will be evolved on freezing. For Wyoming bentonite it appears that the transition from negative to positive values of  $Q_f$  occurs at a water content of about 10%. Assuming that this water is uniformly distributed over the enormous surface area of Wyoming bentonite ( $8 \times 10^6$  cm<sup>2</sup>/g), this corresponds roughly to a monomolecular layer.

Table BI. Heat of freezing in Wyoming bentonite computed from the differential heat of desorption (Mooney et al., 1952).

Water content (g water/g clay)	$Q_a$ (kcal/mole water)	$Q_f^*$ (kcal/mole water)
0.05	12.86	-.73
0.10	12.13	0.0
0.15	11.50	0.63
0.20	11.30	0.83
0.25	10.90	1.23
0.30	10.75	1.38

\*Taking  $\Delta H_s = 12.13$  kcal/mole.

\*The differential heats of desorption were determined at about 10C. The comparison would perhaps be more satisfying if they were available at the actual temperature of freezing; the error in this comparison, however, is certainly small.

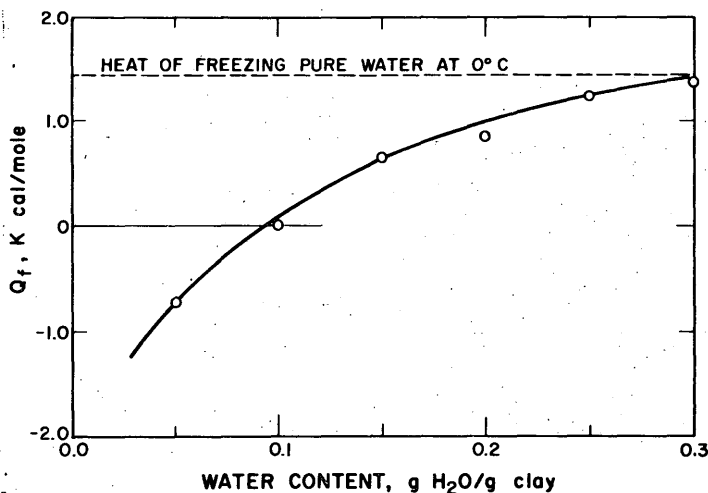


Figure B1. The heat of freezing of water in Wyoming bentonite vs water content compiled from the data of Mooney et al. and expression B7.

On the basis of this argument alone it is seen that for Wyoming bentonite, and in general for all soils, there is some water that will not freeze in the ordinary sense of the term. This conclusion also results from considering adsorption isotherms for water vapor on clays and soils. Mooney et al. (1952) report that at 0C Wyoming bentonite with a water content of 10% has a water vapor pressure of only 1.1 mm Hg compared to 4.5 mm Hg for ice. Obviously ice is not the most stable form for this clay-held water. Similar conclusions are reached on the basis of expression B8 and the heat of immersion data of Janert (1934), Zettlemoyer et al. (1955), Slabaugh (1955, 1959) and others.

The conclusion of Figure B1 is obvious: the heat of fusion of soil water must always be somewhat lower than that of pure water, the difference becoming larger the lower the unfrozen soil water content, although it is different for every soil. Attention is thus directed to the necessity of experimentally verifying this conclusion and, if it is found to be correct, of determining the heat of fusion in representative soil water systems. Since expressions B7 and B8 are based on the supposition that soil ice is no different than normal ice, it is important also to seek experimental verification of this assumption. Martynov (1959), on the basis of an X-ray study, has indicated that this supposition is true but additional work is desirable. It may be found that the ice-water interfacial energy and the energy of clay lattice expansion and swelling need to be considered, although at the present moment these are thought to be of minor importance; in any case they do not affect the main conclusion of the preceding argument. Meanwhile, the assumption of a constant heat of fusion equal to that of normal ice in calculating amounts of unfrozen water in soils from calorimetric data must be regarded as yielding erroneous results. Comparison of the areas under the curves in Figure B1 indicates the probable magnitude of the error in the case of Wyoming bentonite. From Figure B1 it is evident that the conventional computation yields amounts of unfrozen water that are too high and that the error, while it may be negligible in some instances, becomes larger the lower the unfrozen water content of the sample.

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## APPENDIX C. CLOSURE

by

G. Robert Lange and Harlan L. McKim

In his discussion of our paper, Dr. Anderson correctly points out that the latent heat of freezing measured in calorimetric determinations of the phase composition of the soil water should be corrected for the differential heat of wetting. He shows that the resulting latent heat of adsorbed soil water may be less than that normally assumed (for normal water: 79.71 cal/g).

It is clear that the heat of wetting is a phenomenon that occurs at or very near the soil water-mineral grain interface. Anderson's data for the Wyoming bentonite indicate, first, that the value of the latent heat of freezing passes through zero at water content values of less than 10% and becomes negative at lower water content values. This last, incidentally, may be taken to indicate that the remaining water (at a liquid water content of less than 10%) will not freeze at any temperature. His data further suggest that the departure from the value of the latent heat of freezing of normal water occurs at a moisture content of approximately 30%. Thus, it will be of interest to calculate the thickness of the soil water film on the bentonite particles at this critical value because, in terms of decreasing water content, apparently it is at this value that the soil water film becomes thin enough for the heat of fusion of the soil water to be appreciably influenced by the adsorptive force field of the mineral grain.

Anderson assumes the specific surface of the bentonite to be  $8 \times 10^6$  cm<sup>2</sup>/g, so we may now estimate the thickness of the soil water film at the critical moisture content:

$$\sim \frac{0.3 \text{ cm}^3}{8 \times 10^6 \text{ cm}^2} \quad (\text{per gram of dry soil})$$

$$\sim 3.7 \times 10^{-8} \text{ cm}$$

or

$$\sim 3.75 \text{ \AA} \quad (\text{Angstrom units}).$$

Recent measurements of the heat of wetting in water of the porcelain used in our work allow calculation of the specific surface. Data published by Puri and Murari\* show that the specific surface of a large number of various soils measured and calculated by four different methods agrees with the specific surface calculated from heat of wetting measurements to within a few percent. The constant that they obtained is 186.8 erg/cm<sup>2</sup> ( $\sim 4.5 \times 10^{-6}$  cal/cm<sup>2</sup>). We measured the heat of wetting of the porcelain in much the same way as the phase composition of the "soil water" in our original paper. We obtain a value for the oven dry porcelain of  $< 0.3$  cal/g. Using the constant obtained above we calculate a specific surface of  $\sim 6.7 \times 10^4$  cm<sup>2</sup>/g - approximately 100 times less than the bentonite.

\*Puri, B.R. and Murari, K. (1963) Studies in surface area measurement of soils: 1. Comparison of different methods, Soil Science, vol. 96, p. 331-336.

If we take a monomolecular layer of water to be  $\sim 2.8 \text{ \AA}$  thick, we can conclude (as Anderson does) that a moisture content of 30%, i. e.,  $\sim 3$  or  $4 \text{ \AA}$ , roughly corresponds to a monomolecular layer coating all of the bentonite surfaces. We are led (considering the curve given by Anderson in Figure B1) to the conclusion that most of the heat of wetting is generated in the first or possibly second layer of water molecules coating the mineral grains. The work of Puri and Murari (op. cit.) shows that the heat of adsorption is roughly independent of the character of the mineral surface and is approximately a constant energy value per unit of available mineral surface, for a wide range of soils:

We may now estimate the minimum critical moisture content below which the correction proposed by Anderson should be applied to calorimetric determinations of amounts of unfrozen water in any soil or soil model for which the heat of adsorption may be measured. For our porous medium:

specific surface of porcelain  $\sim 6.7 \times 10^4 \text{ cm}^2/\text{g}$

minimum critical thickness of water film  $\sim 5.6 \times 10^{-8} \text{ cm}$  ( $\sim 5.6 \text{ \AA}$ ).

Therefore, the minimum critical volume (wt) of water/gram of dry soil is:

$$(5.6 \times 10^{-8} \text{ cm}) \times (6.7 \times 10^4 \text{ cm}^2) = 3.7 \times 10^{-3} \text{ cm}^3/\text{g dry soil}$$

or  $0.00375 \text{ g water/g dry soil}$

or moisture content by wt  $\sim 0.4\%$ .

We presented phase composition data based upon calorimetry for saturation coefficients down to 0.1, which corresponds to a moisture content of 2.1%, and we commented in the original paper that the data appeared to fit our empirical relationships only down to about  $S \sim 0.15$  or  $M.C. \sim 3.2\%$ .

Since it was our purpose in this paper to pose some questions rather than to answer them, we are indebted to Professor R. D. Miller for clearly delineating these problems in his discussion. A secondary purpose of our paper was to call attention to the use of rigid models for investigations of soil water freezing phenomena. A recent paper by Corey et al.\* suggests that the lack of interconnections of pore space in a natural sandstone makes that material, at least, a poor rigid model of a soil. However, recent electron microscopy reveals that the porcelain used in our experiments is only lightly sintered and pore spaces appear to be completely connected.

Professor Miller's remarks regarding the possible movement of water towards the sites of nucleation are appropriate; however, we would like to point out that the porcelain blocks were (purposely) quite thin slabs in order to establish a minimum thermal gradient as quickly as possible after introduction into the freezing cabinet. Until an adiabatic calorimeter which incorporates some method of heating and cooling a sample with no thermal gradient becomes available, we know of no other technique for countering this valid objection. We, of course, have no knowledge of the configuration of the phase boundaries during freezing; indeed, direct observation of freezing in pore spaces would probably furnish considerable insight into these problems.

\*Corey, John C.; Nielsen, D.R.; and Biggar, J.W. (1963) Miscible displacement in saturated and unsaturated sandstone, Soil Science Society Proceedings, vol. 27, p. 258-262.

Professor Miller's argument that we should have used the interfacial energy value for an ice-water phase boundary in the Gibbs-Thompson equation (eq 2) is probably correct. Further consideration of the freezing point depression curves of temperature vs time (Fig. 1) suggests that at the time the temperature reaches the level of the freezing point depression ( $\Delta \theta$ ) there is ice present in some of the pores and it is surrounded by water.

We, too, admit to some confusion regarding the apparent paradox of the sign reversal that results when data from an experiment like ours are entered into the Gibbs-Thompson equation. We can only speculate that the values of one of the terms  $\sigma$ , interfacial energy,  $Q_s$ , heat of fusion or  $r$ , the radius, from our data should have a negative sign. Obviously, if  $\sigma$  has a negative value, then neither  $Q_s$  nor  $r$  may be negative and, if either  $Q_s$  or  $r$  is negative, then  $\sigma$  cannot be negative.

Regarding the formation of ice outside the porcelain block, we were extremely careful to discard samples where this was observed. This accounts for the paucity of data at saturation levels higher than about 0.90.

It seems unlikely to us that the freezing temperatures recorded for the freezing point depression experiments were lowered below the true equilibrium freezing temperature because long time periods of constant temperature were recorded (on the temperature vs time curves), indicating an equilibrium freezing temperature.

We are indebted to Dr. Duwayne M. Anderson for his assistance in the preparation of the first portion of this closure which relates to his discussion and to Mr. John Sayward who brought the work of Puri and Murari to our attention.



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13. ABSTRACT

Calorimetry was used to explore the effects of saturation and temperature upon the phase composition of the water at below freezing temperatures in a porcelain block with fine pore spaces. The effect of pore size upon phase composition was held constant by the rigid model. The percent of original water frozen was determined for a wide range of saturations and several temperature levels. Nucleation was avoided. After 20 hr of freezing, 64 of 74 determinations showed less than 10% or more than 70% of the water frozen. Thus, a metastable condition of saturation and temperature for guaranteed freezing was defined for the pore space model with time of freezing held constant.

Freezing points were also measured at various levels of saturation in the same porcelain blocks. A range of effective pore sizes was calculated from these data, thus characterizing the pore size distribution.

Both freezing point depression and guaranteed freezing data, when plotted against saturation, appear to conform to an empirical relationship of the form:

$$\theta = \beta \log_e S + \epsilon$$

in which  $\theta$  may be either the freezing point depression  $\Delta\theta$  or the temperature for guaranteed freezing,  $\theta_f$ , and  $S$  is the saturation coefficient. The slope constant  $\beta$  has the same value (1.35) for both  $\theta_f$  and  $\Delta\theta$ .  $\epsilon$ , the temperature intercept at maximum saturation ( $S = 0.92$ ), has different values (-0.4C and -3.3C) for  $\Delta\theta$  and  $\theta_f$  respectively.

It is concluded that the phase composition of the water in frozen soils is dependent upon the degree of saturation as well as the temperature. It is suggested that rigid models are useful tools for investigating the freezing process in soils.

14.

KEY WORDS

LINK A

LINK B

LINK C

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Phase composition of soil water  
Freezing of soil water  
Soil models