

Research Report 222

**SOME THERMODYNAMIC RELATIONSHIPS
FOR SOILS AT OR BELOW THE
FREEZING POINT**

**I: FREEZING POINT
DEPRESSION AND HEAT CAPACITY**

by

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SUMMARY

An extended equation was derived relating the relative partial molar free energy of water in a soil to its freezing point depression and relative partial molar heat content. The equation was used to prepare a table from which each of these three quantities can be ascertained if the other two are known. The table was used with experimental data to obtain a curve of freezing point depression versus water content for Na-Wyoming bentonite. Provided the activity of the liquid water in the clay is a single-valued function of the liquid water content and that the ice has the properties of pure bulk ice, this curve also represents the relationship between freezing point depression and unfrozen water in the partially frozen clay.

An equation for the heat capacity of a partially frozen soil was also derived. This equation was employed, in conjunction with the aforementioned curve of freezing point depression versus water content and additional experimental data for Na-Wyoming bentonite, to calculate the heat capacities of the clay at different water contents and sub-zero temperatures.

A comparison of the calculated unfrozen water contents and heat capacities of the partially frozen Na-Wyoming bentonite with the available experimental data indicated satisfactory agreement, especially as regards the unfrozen water contents.

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INTRODUCTION

Many years ago, Schofield and DaCosta (1938) published, without derivation, an equation relating the free energy of soil moisture to its freezing point depression. Subsequently, Day (1942) derived a similar equation. But these equations are valid only if the freezing point depression is small and the relative partial molar heat content of the soil water is zero. Hence, they are valid only for relatively moist soils. A more general equation is needed; such an equation is derived below.

FREEZING POINT DEPRESSION

We will let the standard state for water in both solid (s) and liquid (l) phases be pure liquid water at the temperature of the system and one atmosphere pressure. Then, for water in the solid phase,

$$\bar{F}_s - F_l^\circ = RT \ln a_s \quad (1)$$

where \bar{F}_s is the partial molar free energy of the solid water, F_l° is the molar free energy of water in the standard state, a_s is the activity of the solid water, R is the molar gas constant and T is the absolute temperature. This equation can be rearranged and differentiated with respect to T to give

$$R \left[\frac{\partial(\ln a_s)}{\partial T} \right] = \left[\frac{\partial(\bar{F}_s/T)}{\partial T} \right] - \left[\frac{\partial(F_l^\circ/T)}{\partial T} \right]. \quad (2)$$

But \bar{F} is related to the partial molar heat content, \bar{H} , and partial molar entropy, \bar{S} , by the general equation

$$\bar{F} = \bar{H} - T \bar{S}. \quad (3)$$

Also,

$$\bar{S} = - \left(\frac{\partial \bar{F}}{\partial T} \right). \quad (4)$$

Combining eq 3 and 4 and dividing by T^2 we get, after rearranging,

$$\frac{1}{T} \left(\frac{\partial \bar{F}}{\partial T} \right) - \frac{\bar{F}}{T^2} = - \frac{\bar{H}}{T^2}. \quad (5)$$

The left hand side of this expression can be obtained by taking the partial derivative of (\bar{F}/T) with respect to T . Consequently,

$$\left[\frac{\partial(\bar{F}/T)}{\partial T} \right] = - \frac{\bar{H}}{T^2} \quad (6)$$

and eq 2 can be written

$$R \left[\frac{\partial(\ln a_s)}{\partial T} \right] = \frac{(H_l^\circ - H_s)}{T^2} \quad (7)$$

(Note that the H_s is used instead of \bar{H}_s to reflect the assumption that the soil water segregates and freezes as pure, normal ice.) Now

$$H_l^\circ - H_s = \int_{T_f}^{T_0} C_s dT + L_0 + \int_{T_0}^{T_f} C_l dT = L_0 + \int_{T_0}^{T_f} (C_l - C_s) dT \quad (8)$$

where L_0 is the molar heat of fusion of pure bulk ice at T_0 , the normal melting point (273.16 K), T_f is the temperature of the frozen system and C , with the appropriate subscript, is the molar heat capacity of the component at constant pressure. Usually, C_l and C_s are expressed as functions of temperature by equations of the form

$$C_i = a_i + b_i T + c_i T^2 \quad (9)$$

where $i = l$ or s . Hence, it is convenient to write

$$C_l - C_s = \Delta a + \Delta b T + \Delta c T^2 \quad (10)$$

so that eq 8 becomes

$$\begin{aligned} H_l^\circ - H_s &= L_0 + \int_{T_0}^{T_f} (\Delta a + \Delta b T + \Delta c T^2) dT = L_0 + \Delta a (T_f - T_0) \\ &+ \frac{\Delta b}{2} (T_f^2 - T_0^2) + \frac{\Delta c}{3} (T_f^3 - T_0^3). \end{aligned} \quad (11)$$

We now define the freezing point depression of the soil water, θ , as

$$\theta = T_0 - T_f. \quad (12)$$

When eq 11 and 12 are combined we have

$$H_l^\circ - H_s = L_0 - (\Delta a + \Delta b T_0 + \Delta c T_0^2) \theta + \left(\frac{\Delta b}{2} + \Delta c T_0 \right) \theta^2 - \frac{\Delta c}{3} \theta^3. \quad (13)$$

Let

$$\left. \begin{aligned} \alpha &= -(\Delta a + \Delta b T_0 + \Delta c T_0^2) \\ \beta &= \frac{\Delta b}{2} + \Delta c T_0 \\ \gamma &= -\frac{\Delta c}{3} \end{aligned} \right\} \quad (14)$$

Then

$$H_l^\circ - H_s = L_0 + \alpha \theta + \beta \theta^2 + \gamma \theta^3. \quad (15)$$

If eq 12 and 15 are combined with eq 7 the result is

$$- \left[\frac{\partial(\ln a_s)}{\partial \theta} \right] = \frac{L_0 + \alpha \theta + \beta \theta^2 + \gamma \theta^3}{R(T_0 - \theta)^2} \quad (16)$$

In order to simplify the integration of eq 16, $1/(T_0 - \theta)^2$ is expressed as a power series, that is

$$\frac{1}{(T_0 - \theta)^2} = \frac{1}{T_0^2} \left(1 - \frac{\theta}{T_0} \right)^{-2} = \frac{1}{T_0^2} \left[1 + 2 \frac{\theta}{T_0} + 3 \left(\frac{\theta}{T_0} \right)^2 + \dots \right] \quad (17)$$

so that

$$- d(\ln a_s) = \frac{1}{RT_0^2} \left[1 + 2 \frac{\theta}{T_0} + 3 \left(\frac{\theta}{T_0} \right)^2 + \dots \right] (L_0 + \alpha \theta + \beta \theta^2 + \gamma \theta^3) d\theta \quad (18)$$

all independent variables except θ being held constant. Now $a_s = 1$ when $\theta = 0$ (because of our choice of standard states and because ice, at atmospheric pressure, having the same thermodynamic properties as pure bulk ice, is presumed to form in the soil pores). Hence, eq 18 can be integrated between these lower limits and arbitrary upper limits to give

$$\begin{aligned} - \ln a_s &= \frac{L_0 \theta}{RT_0^2} \sum \frac{n}{n} \left(\frac{\theta}{T_0} \right)^{n-1} + \frac{\alpha \theta^2}{RT_0^2} \sum \frac{n}{(n+1)} \left(\frac{\theta}{T_0} \right)^{n-1} \\ &+ \frac{\beta \theta^3}{RT_0^2} \sum \frac{n}{(n+2)} \left(\frac{\theta}{T_0} \right)^{n-1} + \frac{\gamma \theta^4}{RT_0^2} \sum \frac{n}{(n+3)} \left(\frac{\theta}{T_0} \right)^{n-1} \end{aligned} \quad (19)$$

in which n is the number of the term in the summation. Moreover, at the freezing point, the activity of the water is the same in both the solid and liquid phases since the system is at equilibrium. As a result $\ln a_s$ can be replaced by $\ln a_l$ in eq 19 to obtain

$$\begin{aligned} - \left[\ln a_l \right]_{T=T_f} &= \frac{L_0 \theta}{RT_0^2} \sum \frac{n}{n} \left(\frac{\theta}{T_0} \right)^{n-1} + \frac{\alpha \theta^2}{RT_0^2} \sum \frac{n}{(n+1)} \left(\frac{\theta}{T_0} \right)^{n-1} \\ &+ \frac{\beta \theta^3}{RT_0^2} \sum \frac{n}{(n+2)} \left(\frac{\theta}{T_0} \right)^{n-1} + \frac{\gamma \theta^4}{RT_0^2} \sum \frac{n}{(n+3)} \left(\frac{\theta}{T_0} \right)^{n-1} \end{aligned} \quad (20)$$

In equation 20, a_l is the activity of the water in the soil solution at the freezing temperature. To obtain a_l at any other temperature, T_a , we proceed as follows. Since at any temperature,

$$\bar{F}_l - F_l^\circ = RT \ln a_l \quad (21)$$

we can utilize eq 3 to 6 to obtain

$$R \left[\frac{\partial(\ln a_l)}{\partial T} \right] = \left(\frac{H_l^\circ - \bar{H}_l}{T^2} \right) \quad (22)$$

where \bar{H}_l is the partial molar heat content of the water in the soil solution. The quantity $(H_l^\circ - \bar{H}_l)$ is the negative of the relative partial molar heat content of the soil water; it can also be regarded as the negative of the differential heat of wetting. The temperature coefficients of heat content differences usually are small and since in this case there are no data to the contrary, let us assume that this quantity can be regarded as constant. If this is allowed, then integration of eq 22 between the temperatures T_f and T_a yields

$$(\ln a_l)_{T=T_a} - (\ln a_l)_{T=T_f} = \frac{(H_l^\circ - \bar{H}_l)}{R} \left(\frac{T_a - T_f}{T_a T_f} \right). \quad (23)$$

As before, eq 12 can be used to express T_f in terms of θ . When this is done, eq 23 becomes

$$(\ln a_l)_{T=T_a} - (\ln a_l)_{T=T_f} = \frac{(H_l^\circ - \bar{H}_l)}{R} \left[\frac{(T_a - T_0) + \theta}{T_a(T_0 - \theta)} \right]. \quad (24)$$

Combination of this equation with eq 20 gives

$$\begin{aligned} [\ln a_l]_{T=T_a} = & - \frac{L_0 \theta}{RT_0^2} \sum \frac{n}{n} \left(\frac{\theta}{T_0} \right)^{n-1} - \frac{\alpha \theta^2}{RT_0^2} \sum \frac{n}{(n+1)} \left(\frac{\theta}{T_0} \right)^{n-1} \\ & - \frac{\beta \theta^3}{RT_0^2} \sum \frac{n}{(n+2)} \left(\frac{\theta}{T_0} \right)^{n-1} - \frac{\gamma \theta^4}{RT_0^2} \sum \frac{n}{(n+3)} \left(\frac{\theta}{T_0} \right)^{n-1} \\ & + \frac{(H_l^\circ - \bar{H}_l)}{R} \left[\frac{(T_a - T_0) + \theta}{T_a(T_0 - \theta)} \right]. \end{aligned} \quad (25)$$

If we wish to relate the relative partial molar free energy of the soil water to θ , we can utilize eq 21 to obtain

$$\begin{aligned} [\bar{F}_l - F_l^\circ]_{T=T_a} = & - \frac{T_a L_0 \theta}{T_0^2} \sum \frac{n}{n} \left(\frac{\theta}{T_0} \right)^{n-1} - \frac{T_a \alpha \theta^2}{T_0^2} \sum \frac{n}{(n+1)} \left(\frac{\theta}{T_0} \right)^{n-1} \\ & - \frac{T_a \beta \theta^3}{T_0^2} \sum \frac{n}{(n+2)} \left(\frac{\theta}{T_0} \right)^{n-1} - \frac{T_a \gamma \theta^4}{T_0^2} \sum \frac{n}{(n+3)} \left(\frac{\theta}{T_0} \right)^{n-1} \\ & + (H_l^\circ - \bar{H}_l) \left[\frac{(T_a - T_0) + \theta}{T_0 - \theta} \right]. \end{aligned} \quad (26)$$

This is the equation which will be employed in the computations. It is important to note that, although the equation was derived for use with a soil-water system, it applies to any comparable system. For instance, it can be used to calculate the relative partial molar free energy of water in an aqueous solution; in this case, $(H_l^\circ - \bar{H}_l)$ represents the negative of the differential heat of dilution.

It is well to bear in mind the assumptions involved in the derivation of eq 26. They are:

- 1) The quantity $(H_l^\circ - \bar{H}_l)$ is independent of temperature.
- 2) The pressure on the ice is atmospheric.
- 3) The ice crystals formed in the soil are large enough that the water within them has the same thermodynamic properties as in pure bulk ice at the same external pressure and temperature.
- 4) Equations of the form of eq 9, with proper coefficients, adequately describe the specific heats of ice and water as functions of temperature.

If $T_a \approx T_0$ in eq 26, all terms beyond the first may be dropped and the reduced equation becomes the conventional equation relating the relative partial molar free energy of water to the freezing point depression.

Washburn (1924) used eq 9, with temperatures expressed in degrees centigrade, to calculate the specific heat of supercooled water. He obtained the coefficients in the equation by using the data of Barnes and Cooke (1902). Dorsey (1940) presented an analogous equation for the specific heat of ice and also corrected an error in one

of the coefficients of Washburn's equation. If we multiply their equations by the molecular weight of water and express the temperatures in °K, it becomes possible to use them to calculate the values of Δa , Δb and Δc to be inserted in eq 10. The values are found to be 71.8820, -0.40711 and 0.000648, respectively. Using these values and eq 14 we obtain -9.0358, -0.02665 and -0.000216 for α , β and γ , respectively. Consequently, the coefficients preceding the summations in eq 26 can be calculated for any value of T_a . However, the values of Δa , Δb and Δc were obtained for temperatures near 0C. It should be remembered, therefore, that the values of α , β and γ may be somewhat in error for large values of θ .

By means of a computer and a program for solving eq 26 (given in Appendix A), values of $(\bar{F}_l - F_l^\circ)$ for different assigned values of θ and $(H_l^\circ - \bar{H}_l)$ were found for $T_a = 298.16K$, a temperature for which data are available. The computer program was written so that the computations would continue until the absolute value of $(\bar{F}_l - F_l^\circ)$ for x terms in the summations equalled the absolute value of this quantity for $(x - 1)$ terms in the summations. In some cases it was necessary to let x range as high as 22. Appendix B gives the results. Values of $(\bar{F}_l - F_l^\circ)$ for unlisted values of θ and/or $(H_l^\circ - \bar{H}_l)$ can be satisfactorily obtained by linear interpolation. This is so because a straight line is obtained when $(\bar{F}_l - F_l^\circ)$ is plotted against θ at a constant value of $(H_l^\circ - \bar{H}_l)$ or when $(\bar{F}_l - F_l^\circ)$ is plotted against $(H_l^\circ - \bar{H}_l)$ at a constant value of θ .

It is evident that, with values for any two of the three thermodynamic quantities recorded in the table, a value for the third can be obtained. However, the values for the two quantities cannot be chosen arbitrarily. They must be corresponding values based on experimental evidence. Otherwise absurd values for the third quantity could result.

Equation 26 was derived to develop a deeper understanding of freezing in soil- and clay-water systems. A system of current interest is a mixture of Na-Wyoming bentonite and water, because this system is known to exhibit maximal interfacial effects. Therefore, the literature was searched for appropriate experimental data for this system to use in conjunction with Appendix B. Two general types of data were found, namely, adsorption isotherm data and swelling-pressure data. The most complete data of the former kind are those of Mooney, Keenan and Wood (1952). They reported the water adsorbed by Na-Wyoming bentonite at different relative vapor pressures (p/p°) at 0 and 20C. They also reported differential heats of desorption, calculated by means of the Clausius - Clapeyron equation. Their results were used in the following manner. First values of $(H_l^\circ - \bar{H}_l)$ at different water contents were calculated by subtracting the heat of liquefaction from the differential heats of desorption. Then these values were used, together with the adsorption data at 20C, in eq 23 to calculate corresponding values for $\ln a_l = \ln p/p^\circ$ at 25C. Finally, eq 21 was used to obtain values of $(\bar{F}_l - F_l^\circ)$ at this temperature.

To calculate $(\bar{F}_l - F_l^\circ)$ at 25C from the available swelling-pressure data, use was made of the relationship

$$(\bar{F}_l - F_l^\circ) = -\bar{v}_l \pi \quad (27)$$

where \bar{v}_l is the partial molar volume of the water in the clay and π is the swelling pressure. This equation is strictly valid only when the membrane separating the aqueous solution from the clay-water system in the pressure cell is permeable to the water and impermeable to all material suspended or dissolved in it. No membranes impermeable to dissolved ions are available, hence, strictly speaking, only data obtained in experiments with salt-free systems should be considered valid. Except for some heretofore unpublished data of the authors, however, no such data

are available. Therefore, the data of Warkentin, Bolt and Miller (1957) and of Koenigs (1961) on clays in equilibrium with 10^{-4} N and 5×10^{-4} N NaCl solutions have been used. These solutions are sufficiently dilute that the resulting errors are minor. For \bar{v}_l , a value of unity was used. According to the results of Anderson and Low (1958), this value is probably accurate to within 3%. The results of Mooney, Keenan and Wood (1952) indicate that the value of $(H_l^\circ - \bar{H}_l)$ is negligibly small at water contents above about 0.4 g H₂O/g clay. The swelling-pressure data were all obtained at higher water contents. Therefore, in using them, a value of zero was assigned to $(H_l^\circ - \bar{H}_l)$. Results thus obtained from the aforementioned sources are given in Table I. Also given in the table are values of θ obtained by using Appendix B and values of θ obtained by using the conventional equation, namely eq 26 with all but the first term omitted and $T_a = T_0$. The latter set of values is reported only for the purpose of comparison. A plot of θ (from Appendix B) against water content is shown in Figure 1.

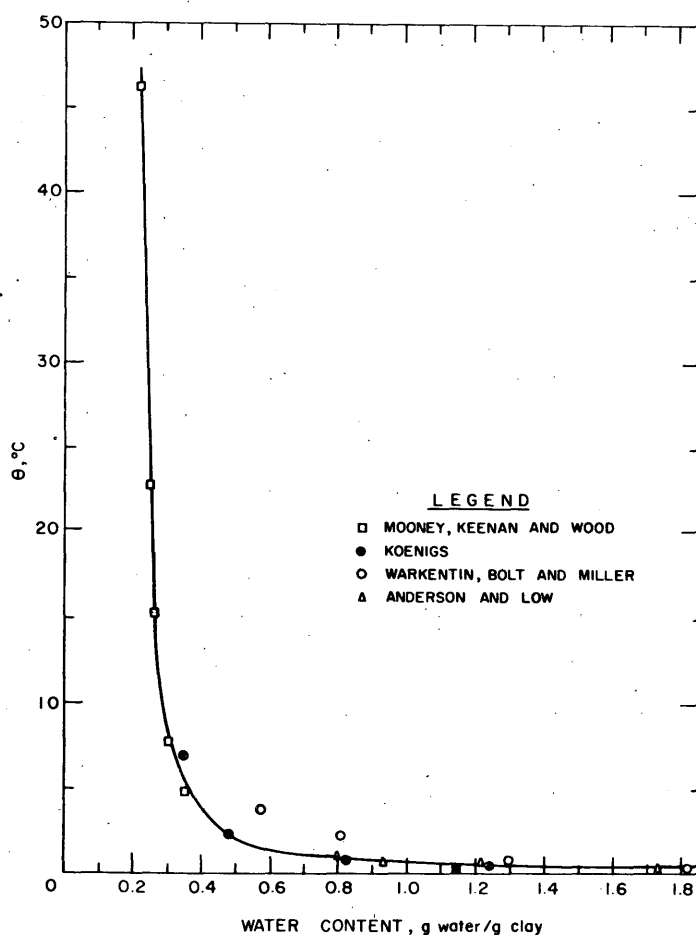


Figure 1. Relation between freezing point depression and water content for Na-Wyoming bentonite.

Although the data in Figure 1 were obtained by different investigators using different experimental methods, they conform to a single continuous curve. Hence, it is reasonable to conclude that this curve represents the relationship between freezing point depression and water content for salt-free Na-Wyoming bentonite.

The curve is useful for this reason. However, its utility is increased if it also represents the relationship between the degrees below zero and the amount of unfrozen water in the clay. Let us consider this point further.

Table I. Thermodynamic data for Na-Wyoming bentonite in water or dilute aqueous NaCl solutions.

Water Content (g H ₂ O/g clay)	(H _l [°] - \bar{H}_l) (cal/mole)	(\bar{F}_l - F _l [°]) (cal/mole)	θ^a (°C)	θ^b (°C)	Reference
0.225	420	-132.0	46.21	25.12	Mooney <u>et al.</u>
0.250	240	- 85.9	22.83	16.34	Mooney <u>et al.</u>
0.263	180	- 60.0	15.27	11.42	Mooney <u>et al.</u>
0.300	70	- 35.4	7.65	6.74	Mooney <u>et al.</u>
0.350	35	- 24.0	4.85	4.57	Mooney <u>et al.</u>
0.480	0	- 13.3	2.32	2.53	Koenigs
0.576	0	- 21.8	3.79	4.15	Warkentin <u>et al.</u>
0.794	0	- 5.69	0.99	1.08	Anderson and Low
0.808	0	- 13.07	2.28	2.49	Warkentin <u>et al.</u>
0.813	0	- 4.21	0.76	.80	Koenigs
0.925	0	- 4.39	0.76	.84	Anderson and Low
1.218	0	- 2.99	0.52	.57	Anderson and Low
1.230	0	- 2.66	0.46	.51	Koenigs
1.296	0	- 4.36	0.76	.83	Warkentin <u>et al.</u>
1.728	0	- 1.51	0.26	.29	Anderson and Low
1.816	0	- 2.18	0.38	.41	Warkentin <u>et al.</u>
2.240	0	- 1.33	0.23	.25	Koenigs
2.720	0	- 0.87	0.15	.17	Warkentin <u>et al.</u>

θ^a Obtained by using Appendix B.

θ^b Obtained by using only first term of eq 26.

Since the activity of water in pure bulk ice at atmospheric pressure is a function of temperature only, and since the activity of water in the unfrozen solution must equal that in the ice at equilibrium, we can say that the activity of the water in the unfrozen solution has a fixed value for each temperature at which the two phases are in equilibrium. But, at the equilibrium temperature and atmospheric pressure, the activity of the water in the unfrozen solution is determined by its interaction with the particle surfaces and by the number of exchangeable ions dissolved in it, i. e., by the content of liquid water, provided that the arrangement of particles is unimportant. It will be assumed that the water activity is not influenced significantly by particle arrangement. Therefore, the content of liquid water must have a fixed value for each temperature at which the two phases are in equilibrium, regardless of the amount of ice present. The net result is that Figure 1 represents not only the relationship between freezing point depression and water content, but also the relationship between freezing point depression (degrees below zero) and unfrozen

water. However, it should be noted that, for Figure 1 to represent the proposed relationships, the ice crystals that form in the clay system cannot be too small. Otherwise, the ice in them will not have the properties of pure bulk ice at atmospheric pressure. Instead, the properties of the ice will depend on the dimensions of the crystals. Then eq 26 would not be valid and, further, the content of liquid water in the partially frozen system would not have a specific value at each temperature. Fortunately, under most conditions, the ice in clay or soil systems tends to form relatively large crystals or lenses. Therefore it is believed that eq 26 is usually applicable and that Figure 1 represents the proposed relationships.

HEAT CAPACITY

If the curve in Figure 1 is an acceptable representation of the temperature-unfrozen water relationship, it can be used to calculate another important quantity, namely, the heat capacity of partially frozen clay-water mixtures. The basis for this calculation will now be developed.

Let H be the heat content of a system containing clay, ice and unfrozen water. Designate the three components by the subscripts c , s and l , respectively. Then

$$H = \bar{h}_c m_c + \bar{h}_s m_s + \bar{h}_l m_l \quad (28)$$

where \bar{h} is the partial specific heat content and m is the number of grams of the component. To obtain the heat content per gram of mixture, that is, the specific heat content, h , we divide eq 28 by $\sum m_j$, where j represents any component. The result is

$$h = \bar{h}_c \chi_c + \bar{h}_s \chi_s + \bar{h}_l \chi_l \quad (29)$$

where χ is the gram fraction. Now we differentiate this equation with respect to temperature, holding the pressure and composition constant, and find

$$\frac{\partial h}{\partial T} = \chi_c \left(\frac{\partial \bar{h}_c}{\partial T} \right) + \bar{h}_s \left(\frac{\partial \chi_s}{\partial T} \right) + \chi_s \left(\frac{\partial \bar{h}_s}{\partial T} \right) + \bar{h}_l \left(\frac{\partial \chi_l}{\partial T} \right) + \chi_l \left(\frac{\partial \bar{h}_l}{\partial T} \right) \quad (30)$$

But

$$\left(\frac{\partial h}{\partial T} \right) = c \quad (31)$$

and

$$\left(\frac{\partial \bar{h}_i}{\partial T} \right) = \bar{c}_i \quad (32)$$

where c is the specific heat capacity of the mixture and \bar{c}_i is the partial specific heat capacity of the component i . Thus,

$$c = \bar{c}_c \chi_c + \bar{h}_s \left(\frac{\partial \chi_s}{\partial T} \right) + \bar{c}_s \chi_s + \bar{h}_l \left(\frac{\partial \chi_l}{\partial T} \right) + \bar{c}_l \chi_l \quad (33)$$

However,

$$\chi_l + \chi_s = \chi_w \quad (34)$$

where χ_w is the gram fraction of the water, frozen and unfrozen, in the system. Therefore, since χ_w is constant,

$$\left(\frac{\partial \chi_s}{\partial T}\right) + \left(\frac{\partial \chi_l}{\partial T}\right) = 0 \quad (35)$$

and

$$\left(\frac{\partial \chi_s}{\partial T}\right) = - \left(\frac{\partial \chi_l}{\partial T}\right). \quad (36)$$

Combining eq 33, 34 and 36, we have

$$c = \bar{c}_c \chi_c + \bar{c}_s \chi_w + (\bar{c}_l - \bar{c}_s) \chi_l + (\bar{h}_l - \bar{h}_s) \left(\frac{\partial \chi_l}{\partial T}\right). \quad (37)$$

Now, since the ice is presumed to separate in crystals large enough to have the properties of pure bulk ice, $\bar{h}_s = h_s$. Then

$$\bar{h}_l - \bar{h}_s = \bar{h}_l - h_s = (\bar{h}_l - h_l^\circ) + (h_l^\circ - h_s). \quad (38)$$

Note that the first term on the right is the relative partial specific heat content and the second term is the heat of fusion per gram of ice at the freezing temperature, T_f . This second term can be transformed, as was done earlier for the molar heat of fusion, to

$$h_l^\circ - h_s = l_0 + \alpha' \theta + \beta' \theta^2 + \gamma' \theta^3 \quad (39)$$

in which l_0 is the heat of fusion per gram at the normal freezing point, T_0 , and α' , β' and γ' are the respective quantities in eq 14 divided by the molecular weight of water. Consequently,

$$\bar{h}_l - \bar{h}_s = (\bar{h}_l - h_l^\circ) + l_0 + \alpha' \theta + \beta' \theta^2 + \gamma' \theta^3. \quad (40)$$

Combination of this eq with eq 37 yields

$$c = \bar{c}_c \chi_c + \bar{c}_s \chi_w + (\bar{c}_l - \bar{c}_s) \chi_l - \left[(\bar{h}_l - h_l^\circ) + l_0 + \alpha' \theta + \beta' \theta^2 + \gamma' \theta^3 \right] \left(\frac{\partial \chi_l}{\partial \theta}\right) \quad (41)$$

or, since

$$\chi_i = \frac{m_i}{\sum m_j} \quad (42)$$

$$C = c \sum m_j = \bar{c}_c m_c + \bar{c}_s m_w + (\bar{c}_l - \bar{c}_s) m_l - \left[(\bar{h}_l - h_l^\circ) + l_0 + \alpha' \theta + \beta' \theta^2 + \gamma' \theta^3 \right] \left(\frac{\partial m_l}{\partial \theta}\right) \quad (43)$$

where C is the heat capacity of the mixture. The choice of eq 41 or 43 is a matter of convenience.

When the system is unfrozen $m_l = m_w$ and the third term in eq 43 drops out. Under this condition eq 43 reduces to

$$C = \bar{c}_c m_c + \bar{c}_l m_l. \quad (44)$$

Oster and Low (1964) have reported values for C and \bar{c}_l for different values of m_l in unfrozen clay-water systems in which $m_c = 1$. Their values are averages for the temperature interval 0 to 30C. Assuming that their values are approximately correct for sub-zero temperatures, the corresponding values of \bar{c}_c may be calculated

by means of eq 44. The value of \bar{c}_s can be assumed to be equal to c_s , which is obtainable, at any temperature, by means of the equation presented by Dorsey (1940), viz.,

$$c_s = 0.5057 + 0.001863 t \quad (45)$$

where c_s is expressed in calories per gram per °C and t is expressed in °C. The value of $(\bar{h}_l - h_l^\circ)$ can be obtained by dividing the values for $(H_l^\circ - \bar{H}_l)$ in Table I by the molecular weight of water and multiplying by -1. The value of l_0 is 79.62 cal/g. Values for α' , β' and γ' are -0.5019, -0.00148 and -0.000012, respectively. And values of $(\partial m_l / \partial \theta)$ are available from the curve in Figure 1. Hence, experimental values are available for every variable in eq 43.

Using the above data and eq 43 the curves in Figures 2 and 3 were obtained. In Figure 2 the temperature at which freezing begins is that temperature immediately below which a sudden rise in heat capacity occurs. When $m_w = 1$ it is -0.7°C and when $m_w = 1.8$ it is -0.4°C. These temperatures were obtained from Figure 1. At temperatures nearer zero there is no ice in the system and the last term on the right hand side of eq 43 drops out. In addition $m_l = m_w$. As a result, eq 43 reduces to eq 44. But at temperatures farther below zero, the last term in eq 43 is retained. Its magnitude is influenced largely by the value of $(\partial m_l / \partial \theta)$. Since $(\partial m_l / \partial \theta)$ is large at small values of θ , as shown in Figure 1, the heat capacity of the partially frozen clay is large at these θ values. As θ gets larger $(\partial m_l / \partial \theta)$ gets smaller, and the heat capacity falls accordingly. Thus, it is this last term that largely governs the heat capacity of a partially frozen clay. As noted from Figure 2, the effect of water content is small in comparison.

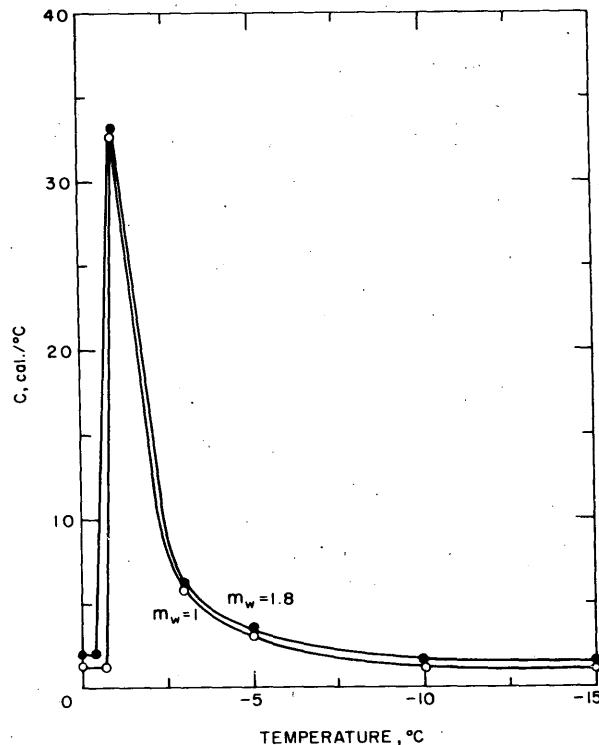


Figure 2. Relationship between heat capacity and temperature of a partially frozen Na-Wyoming bentonite.

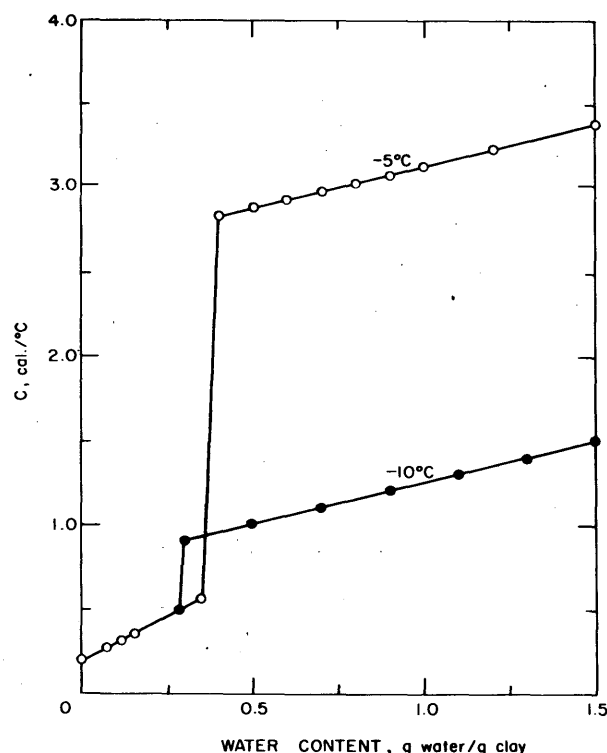


Figure 3. Relationship between heat capacity and water content of a partially frozen Na-Wyoming bentonite.

In Figure 3 the influence of the last term on the right hand side of eq 43 is again evident. A jump in heat capacity occurs when the water content attains a value at which freezing will begin. The relevant water contents in this figure, as obtained from Figure 1, are 0.350 and 0.285 g H₂O per g clay at temperatures of -5°C and -10°C, respectively. At higher water contents eq 43 obtains and, since all terms but \bar{c}_{smw} are constant, the slope of the curve is \bar{c}_s . At lower water contents eq 44 is appropriate, as before, and the slope of the curve is \bar{c}_l . The separation between the two curves at any water content is due to the difference in magnitudes of the last term of eq 43 at the two temperatures.

COMPARISON WITH EXPERIMENTAL DATA

There are few experimental data with which the calculated data in Figures 1, 2 and 3 can be compared. However, let us make those comparisons that are possible. From Figure 1, we conclude that, at temperatures as low as -40°C, there would be sufficient unfrozen water to form two complete molecular layers between adjacent clay surfaces.* This conclusion is consistent with the report of Anderson and Hoekstra (1966) that "lattice collapse beyond 16 Å could not be induced at temperatures as low as -40°C." Further, extrapolation of the curve to the temperature of liquid nitrogen (-196°C) indicates that the unfrozen water content would still be

* About 0.240 g of H₂O per g of clay is required to form a monolayer on the entire surface or two molecular layers between juxtaposed surfaces. The thickness of a monolayer is presumed to be about 3Å.

between 0.150 and 0.200 g per g of clay. This amount is in excess of that required to form a single molecular layer between adjacent clay surfaces. Hence, the separation between these surfaces should be sufficient to accommodate the molecules of an incomplete second layer. In keeping with this conclusion, Ahlrichs and White (1962) found that the $d(001)$ spacing of Na-montmorillonite in water was between 16 and 17 Å at the temperature of liquid nitrogen. According to the curve of Figure 1, there should be 0.320 g unfrozen water per g of clay at -6°C . The $d(001)$ spacing reported by Anderson and Hoekstra (1966) for Na-Wyoming bentonite at this temperature was 19 Å. Hence, if all the unfrozen water in their clay occupied interlaminar spaces, and if these spaces were completely filled, the unfrozen water amounted to 0.360 g. The fact that the interlaminar spaces were filled is suggested by the appearance of a diffuse secondary peak, corresponding to a wider interlaminar spacing, at -5°C . Therefore, agreement with experimental observation is again obtained. At temperatures higher than -5°C , the X-ray data of Anderson and Hoekstra are inconclusive, insofar as the estimation of unfrozen water is concerned, because more than one diffraction peak occurred.

The dilatometric data of Hemwall and Low (1956) and the calorimetric data of Kolaian and Low (1963) indicate more unfrozen water in Na-Wyoming bentonite at -5°C than that shown in Figure 1. The high values obtained with the dilatometric technique can be ascribed, at least partly, to the fact that adsorbed water on clays has a higher specific volume than does normal water. In calculating the unfrozen water it is assumed that the adsorbed water is normal water. The high values obtained with the calorimetric technique have been attributed by Anderson and Hoekstra (1966) to possible errors in the values assigned to the specific heat and latent heat of fusion of the clay-adsorbed water. For these quantities Kolaian and Low (1963) used values characteristic of pure bulk water. It should also be noted that another source of error in their work was the value they used for the specific heat capacity of the clay (0.75 cal. per gram per deg). As shown later by Oster and Low (1964), the correct value is 0.192. However, even when the possible errors are taken into account, a careful analysis shows that their results do not agree with those reported here. Therefore, additional research is needed to reveal the cause of the discrepancy. Such research is now in progress.

The only experimental work that has been done on the heat capacity of partially frozen Na-Wyoming bentonite is that of Anderson (1966). His work indicates that the heat capacities reported in Figures 2 and 3 are too high. For example, he reports a heat capacity of about 1.0 for Na-Wyoming bentonite containing 1 g of water per g of clay at -5°C , whereas the value reported here is about 3.0. However, recall that the heat capacities in these figures were calculated using slopes of the curve in Figure 1. These slopes were difficult to determine accurately in the range of interest. Further, only slight displacements of the curve would change the results markedly. This may explain the discrepancy between the calculated values and those reported by Anderson. Finally it should be noted here that the curve in Figure 2 is identical in form to that found experimentally for Leda clay by Williams (1964). Thus, it is likely that this curve is representative of Na-Wyoming bentonite in form but, perhaps, not in absolute position.

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APPENDIX A

The following program, written in Dartmouth BASIC, was used to compute Appendix B.

```

1 REM A1 IS -T2*L0/(TO)†2
2 REM A2 IS -T2*ALPHA/(TO)†2
3 REM A3 IS -T2*BETA/(TO)†2
4 REM A4 IS - T2*GAMMA/(TO)†2
5 REM T IS (T2-TO)
6 REM F IS (F-FO)
7 REM H IS (HO-H)
8 REM Ø IS THETA
10 DIM F(100)
15 READ A1, A2, A3, A4
20 READ TO, T
21 INPUT Ø1, Ø2, Ø3, H1, H2, H3
25 PRINT "(F-FO)", "(HO-H)", "Ø", "N"
27 PRINT
28 FOR Ø = Ø1 TO Ø2 STEP Ø3
33 FOR H = H1 TO H2 STEP H3
35 FOR X=2 TO 100 STEP 1
38 LET B1=0
40 FOR N=1 TO X Step 1
45 LET B1 = B1+(N/N)*(Ø/TO)†(N-1)
50 NEXT N
60 LET B2=A1*Ø*B1
63 LET C1=0
65 FOR N=1 TO X STEP 1
70 LET C1=C1+(N/(N+1))*(Ø/TO)†(N-1)
75 NEXT N
80 LET C2=A2*Ø†2*C1
83 LET D1=0
85 FOR N=1 TO X STEP 1
90 LET D1 = D1+(N/(N+2))*(Ø/TO)†(N-1)
95 NEXT N
100 LET D2=A3*Ø†3*D1
103 LET E1=0
105 FOR N=1 TO X STEP 1
110 LET E1=E1+(N/(N+3))*(Ø/TO)†(N-1)
115 NEXT N
120 LET E2=A4*Ø†4*E1
125 LET F(X)=B2+C2+D2+E2+H*((T+Ø)/(TO-Ø))
130 IF ABS (F(X))=ABS(F(X -1)) THEN 136
135 NEXT N
136 IF F(X)>0 THEN 155
140 PRINT F(X), H, Ø, N
145 NEXT H
155 PRINT
156 NEXT Ø
160 DATA -5.7348, .0361, .10647E-3, .8629E-6
165 DATA 273.16, 25.0
999 END

```

$(H_2 - \bar{H}_2)$

θ	0	50	100	150	200	250	300	350
5.5	-31.6222	-25.9247	-20.2272	-14.5296	-8.83212	-3.13459		
6.0	-34.504	-28.7023	-22.9005	-17.0987	-11.297	-5.49521		
6.5	-37.3869	-31.4805	-25.5741	-19.6677	-13.7613	-7.85486	-1.94847	
7.0	-40.2706	-34.2592	-28.2478	-22.2363	-16.2249	-10.2135	-4.20208	
7.5	-43.1553	-37.0384	-30.9216	-24.8048	-18.6879	-12.5711	-6.45423	-0.337393
8.0	-46.0408	-39.8181	-33.5955	-27.3728	-21.1502	-14.9275	-8.70486	-2.4822
8.5	-48.9271	-42.5983	-36.2694	-29.9405	-23.6116	-17.2828	-10.9539	-4.62501
9.0	-51.8142	-45.3787	-38.9432	-32.5078	-26.0723	-19.6368	-13.2013	-6.76578
9.5	-54.702	-48.1595	-41.617	-35.0745	-28.532	-21.9875	-15.4469	-8.90442
10.0	-57.5905	-50.9406	-44.2906	-37.6407	-30.9907	-24.3408	-17.6908	-11.0409
11.0	-63.3692	-56.5032	-49.6372	-42.7711	-35.9051	-29.039	-22.173	-15.307
12.0	-69.15	-62.0662	-54.9824	-47.8986	-40.8148	-33.7311	-26.6473	-19.5635
13.0	-74.9323	-67.6291	-60.3259	-53.0227	-45.7195	-38.4163	-31.1131	-23.8099
14.0	-80.7157	-73.1914	-65.6671	-58.1428	-50.6185	-43.0941	-35.5698	-28.0455
15.0	-86.4998	-78.7526	-71.0055	-63.2584	-55.5112	-47.7641	-40.017	-32.2698
16.0	-92.284	-84.3123	-76.3406	-68.369	-60.3973	-52.4256	-44.4539	-36.4822
17.0	-98.0679	-89.8699	-81.6719	-73.4739	-65.2759	-57.0779	-48.8799	-40.6819
18.0	-103.851	-95.4249	-86.9988	-78.5727	-70.1466	-61.7206	-53.2945	-44.8648
19.0	-109.633	-100.977	-92.3207	-83.6647	-75.0088	-66.3528	-57.6968	-49.0409
20.0	-115.412	-106.525	-97.637	-88.7493	-79.8617	-70.974	-62.0863	-53.1987
21.0	-121.189	-112.068	-102.947	-93.8259	-84.7047	-75.5835	-66.4623	-57.3411
22.0	-126.963	-117.607	-108.25	-98.8937	-89.5371	-80.1805	-70.8239	-61.4673
23.0	-132.734	-123.14	-113.546	-103.952	-94.3582	-84.7644	-75.1705	-65.5766
24.0	-138.499	-128.666	-118.833	-109.00	-99.1673	-89.3343	-79.5012	-69.6682
25.0	-144.26	-134.186	-124.112	-114.038	-103.964	-93.8895	-83.8154	-73.7412
26.0	-150.015	-139.698	-129.381	-119.064	-108.746	-98.4292	-88.112	-77.7948
27.0	-155.764	-145.202	-134.639	-124.077	-113.515	-102.953	-92.3904	-81.8282
28.0	-161.505	-150.696	-139.887	-129.077	-118.268	-107.459	-96.6496	-85.8403
29.0	-167.239	-156.18	-145.122	-134.064	-123.005	-111.947	-100.889	-89.8304
30.0	-172.963	-161.654	-150.345	-139.035	-127.726	-116.416	-105.107	-93.7974
32.0				-148.93	-137.112	-125.294	-113.476	-101.658
34.0				-158.754	-146.419	-134.085	-121.75	-109.415
36.0				-168.501	-155.64	-142.78	-129.919	-117.059
38.0				-178.16	-164.765	-151.37	-137.975	-124.58
40.0				-187.725	-173.786	-159.847	-145.908	-131.969
42.0				-197.185	-182.693	-168.201	-153.709	-139.217
44.0				-206.531	-191.476	-176.421	-161.366	-146.311
46.0				-215.752	-200.124	-184.496	-168.869	-153.241
48.0				-224.837	-208.626	-192.415	-176.205	-159.994
50.0				-233.774	-216.97	-200.166	-183.362	-166.558
55.0					-237.051	-218.716	-200.381	-182.046
60.0					-255.842	-235.904	-215.966	-196.028
65.0					-273.088	-251.47	-229.852	-208.234
70.0					-288.496	-265.115	-241.735	-218.354
75.0					-301.729	-276.497	-251.265	-226.032

 $(H_2 - \bar{H}_2)$

θ	400	450	500	550	600	650	700	750	800
5.5									
6.0									
6.5									
7.0									
7.5									
8.0									
8.5									
9.0	-0.330284								
9.5	-2.3619								
10.0	-4.39093								
11.0	-8.44093	-1.5749							
12.0	-12.4797	-5.39593							
13.0	-16.5067	-9.20348	-1.90028						
14.0	-20.5212	-12.9969	-5.4726						
15.0	-24.5227	-16.7756	-9.02844	-1.28131					
16.0	-28.5105	-20.5388	-12.5671	-4.59543					
17.0	-32.4839	-24.2859	-16.0879	-7.88992					
18.0	-36.4423	-28.0162	-19.5901	-11.164	-2.73795				
19.0	-40.3849	-31.7289	-23.073	-14.417	-5.76104				
20.0	-44.311	-35.4234	-26.5357	-17.648	-8.76038				
21.0	-48.2199	-39.0987	-29.9775	-20.8563	-11.7351	-2.61392			
22.0	-52.1107	-42.7542	-33.3976	-24.041	-14.6844	-5.32781			
23.0	-55.9828	-46.3889	-36.7951	-27.2012	-17.6073	-8.01347			
24.0	-59.8352	-50.0021	-40.1691	-30.336	-20.503	-10.67	-0.836929		
25.0	-63.6671	-53.5929	-43.5188	-33.4446	-23.3705	-13.2963	-3.2222		
26.0	-67.4776	-57.1604	-46.8432	-36.526	-26.2088	-15.8916	-5.57441		
27.0	-71.2659	-60.7037	-50.1415	-39.5792	-29.017	-18.4548	-7.89252		
28.0	-75.0311	-64.2218	-53.4125	-42.6033	-31.794	-20.9847	-10.1755		
29.0	-78.7721	-67.7137	-56.6554	-45.5971	-34.5388	-23.4805	-12.4221		
30.0	-82.488	-71.1786	-59.8691	-48.5597	-37.2503	-25.9409	-14.6314		
32.0	-89.8405	-78.0226	-66.2047	-54.3868	-42.5689	-30.7511	-18.9332	-7.11529	
34.0	-97.0801	-84.7452	-72.4104	-60.0756	-47.7407	-35.4059	-23.0711	-10.7362	
36.0	-104.198	-91.3375	-78.477	-65.6165	-52.7559	-39.8954	-27.0349	-14.1744	-1.31387
38.0	-111.185	-97.7897	-84.3945	-70.9994	-57.6043	-44.2091	-30.814	-17.4188	-4.02371
40.0	-118.031	-104.092	-90.1527	-76.2137	-62.2748	-48.3359	-34.397	-20.458	-6.51912
42.0	-124.725	-110.233	-95.7404	-81.2483	-66.7562	-52.264	-37.7719	-23.2798	-8.78767
44.0	-131.256	-116.201	-101.146	-86.0912	-71.0362	-55.9812	-40.9262	-25.8713	-10.8163
46.0	-137.613	-121.985	-106.358	-90.7299	-75.1022	-59.4744	-43.8467	-28.2189	-12.5912
48.0	-143.783	-127.573	-111.362	-95.1512	-78.9405	-62.7298	-46.5191	-30.3085	-14.0978
50.0	-149.753	-132.949	-116.145	-99.3412	-82.5371	-65.733	-48.9289	-32.1249	-15.3208
55.0	-163.711	-145.376	-127.04	-108.705	-90.3701	-72.0349	-53.6998	-35.3646	-17.0294
60.0	-176.09	-156.152	-136.214	-116.276	-96.3375	-76.3995	-56.4614	-36.5233	-16.5852
65.0	-186.616	-164.998	-143.38	-121.762	-100.144	-78.526	-56.908	-35.29	-13.672
70.0	-194.973	-171.593	-148.212	-124.832	-101.451	-78.0706	-54.69	-31.3094	-7.92879
75.0	-200.8	-175.568	-150.336	-125.104	-99.8718	-74.6396	-49.4075	-24.1754	

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13. ABSTRACT An extended equation was derived relating the relative partial molar free energy of water in a soil to its freezing point depression and relative partial molar heat content. The equation was used to prepare a table from which each of these 3 quantities can be ascertained if the other 2 are known. The table was used with experimental data to obtain a curve of freezing point depression vs. water content for Na-Wyoming bentonite. Provided the activity of the liquid water in the clay is a single-valued function of the liquid water content and that the ice has the properties of pure bulk ice, this curve also represents the relationship between freezing point depression and unfrozen water in the partially frozen clay. An equation for the heat capacity of a partially frozen soil was also derived. This equation was employed to calculate the heat capacities of the clay at different water contents and sub-zero temperatures. A comparison of the calculated unfrozen water contents and heat capacities of the partially frozen Na-Wyoming bentonite with the available experimental data indicated satisfactory agreement, especially as regards the unfrozen water contents.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
X Soils--Thermal properties X Soils--Freezing--Mathematical analysis X Soil solutions--Freezing X Soils--Moisture content--Temperature factors X Frozen ground--Unfrozen water content						

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