Research Report 222
SOME THERMODYNAMIC RELATIONSHIPS
FOR SOILS AT OR BELOW THE
FREEZING POINT

2: EFFECTS OF TEMPERATURE AND PRESSURE
ON UNFROZEN SOIL WATER

by

Philip F. Low, Pieter Hoekstra,
and

Duwayne M. Anderson

JULY 1967

U.S. ARMY MATERIEL COMMAND
COLD REGIONS RESEARCH & ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE

DA Task IVO14501B52A02

Distribution of this document is unlimited

PREFACE

This report was prepared by Dr. Philip F. Low, * Expert; and Dr. Pieter Hoekstra and Dr. Duwayne Anderson, Earth Sciences Branch, Research Division (Mr. James A. Bender, Chief), U. S. Army Cold Regions Research and Engineering Laboratory.

Part I of this report on the thermodynamics of frozen soil, "Freezing Point Depression and Heat Capacity," was published as USA CRREL Research Report 222 (December, 1966).

USA CRREL is an Army Materiel Command laboratory.

* Department of Agronomy, Purdue University.

CONTENTS

Preface-----	Page
Summary -----	ii
Literature cited -----	iv
	5

ILLUSTRATIONS

Figure

1. Adsorption isotherms of liquid water on Na-bentonite at two external pressures and high relative humidities -----	3
2. Adsorption isotherm for liquid water on Na-bentonite at -5°C and atmospheric pressure -----	4

TABLES

Table

I. Increase in unfrozen water (ΔW) in Na-bentonite caused by in- creasing the pressure from 1 to 100 atm at different tem- peratures -----	4
--	---

SUMMARY

Thermodynamic methods are presented for calculating, from the water adsorption isotherms, the change in unfrozen water content of a partially frozen soil with temperature at a constant pressure or with pressure at a constant temperature. Then, using pertinent experimental data for Na-Wyoming bentonite, the increase in unfrozen water caused by a confining pressure of 100 atm is obtained as a function of temperature. Such information is shown to be relevant to the mechanical properties of frozen soils under stress.

SOME THERMODYNAMIC RELATIONSHIPS FOR SOILS AT OR BELOW THE FREEZING POINT: II. EFFECTS OF TEMPERATURE AND PRESSURE ON UNFROZEN SOIL WATER

by

Philip F. Low, Pieter Hoekstra and Duwayne M. Anderson

In an earlier paper (Low, Anderson and Hoekstra, 1966), an equation was derived that relates the relative partial molar free energy and relative partial molar heat content of the water in a soil to its freezing point depression. By using pertinent experimental data for Na-Wyoming bentonite and given certain assumptions, it was shown how this equation can be used to determine unfrozen water in a soil at different temperatures. In the present paper, a description will be given of the way in which another equation, derived in the same paper, can be used for this purpose. In addition, equations will be derived that can be used with supplementary data to calculate the effect, at a given temperature, of confining pressure on unfrozen water.

The effect of temperature on the activity of liquid water in the soil is given by eq 23 of the previous paper (Low, Anderson and Hoekstra, 1966), viz.,

$$(\ln a_l)_{T=T_a} - (\ln a_l)_{T=T_f} = \frac{(H_l^\circ - \bar{H}_l)}{R} \left(\frac{T_a - T_f}{T_a T_f} \right) \quad (1)$$

where a_l is the activity of water in the liquid phase in the soil, T_a is any temperature of interest, T_f is the freezing temperature, H_l° is the molar heat content of pure liquid water (the standard state), $\bar{H}_l$ is the partial molar heat content of the water in the liquid phase in the soil and R is the molar gas constant. Because of the choice of standard state for the water, a_l can be replaced by p/p° , i.e., by the ratio of the vapor pressure of liquid water in the soil to the vapor pressure of pure liquid water at the same temperature. Hence, if p/p° and $(H_l^\circ - \bar{H}_l)$ are known as functions of water content at $T=T_a$, p/p° can be calculated and plotted as a function of water content for $T=T_f$. However, when water in the liquid phase is in equilibrium with that in the ice phase $p/p^\circ = p^\square/p^\circ$, where $p^\square$ is the vapor pressure of the ice. Now assume that, at atmospheric pressure and a given temperature, the activity of the liquid water in the soil is a single-valued function of the liquid water content and that the ice in the soil has the properties of pure bulk ice. The validity of these assumptions has been discussed previously (Low, Anderson and Hoekstra, 1966). Then $p^\square/p^\circ$ can be obtained for atmospheric pressure at the appropriate value of T_f from tables given by Dorsey (1940). This value of $p^\square/p^\circ$ can be referred to the water adsorption isotherm where p/p° is plotted versus water content to obtain the corresponding value of the water content. The latter value may be regarded as being that of the unfrozen water in the partially frozen system.

The procedure just described for obtaining unfrozen water at any temperature and atmospheric pressure can be used as an alternative to that described in the previous paper (Low, Anderson and Hoekstra, 1966). The two procedures give the same results.

Next, consider the thermodynamic equation

$$\bar{F}_l - F_l^\circ = RT \ln p/p^\circ \quad (2)$$

2 EFFECTS OF TEMPERATURE AND PRESSURE ON UNFROZEN WATER

where $\bar{F}_l$ is the partial molar free energy of liquid water in the soil, F_l° is the molar free energy of water in the standard state and T is any temperature of interest. This equation can be differentiated with respect to the pressure, P , to yield

$$\left(\frac{\partial \bar{F}_l}{\partial P}\right) - \left(\frac{\partial F_l^\circ}{\partial P}\right) = RT \left[\frac{\partial \ln p/p^\circ}{\partial P} \right] \quad (3)$$

if the temperature and composition are held constant. But, we have

$$\left(\frac{\partial \bar{F}_l}{\partial P}\right) = \bar{V}_l; \quad \left(\frac{\partial F_l^\circ}{\partial P}\right) = V_l^\circ \quad (4)$$

in which $\bar{V}_l$ and V_l° are the partial molar volume of the liquid water in the soil and of pure liquid water, respectively. Consequently, we can write

$$RT \left[\frac{\partial (\ln p/p^\circ)}{\partial P} \right] = \bar{V}_l - V_l^\circ. \quad (5)$$

At constant temperature and composition (the ratio of liquid water to clay), eq 5 can be integrated between the limits of atmospheric pressure, P_a , and any other pressure, P , to give

$$(\ln p/p^\circ)_{P=P} - (\ln p/p^\circ)_{P=P_a} = \frac{(\bar{V}_l - V_l^\circ)}{RT} (P - P_a) \quad (6)$$

if the water is regarded as being essentially incompressible. Thus, if we know $(\bar{V}_l - V_l^\circ)$ and p/p° as a function of water content at atmospheric pressure and a given temperature, we can get p/p° as a function of water content at any other pressure and the same temperature. It should be noted here that, if the soil is wet enough for $\bar{V}_l = V_l^\circ$, pressure has no effect on p/p° .

If we let $\bar{F}_s$ represent the partial molar free energy of water in ice and $p^\square$ the vapor pressure, we can write

$$\bar{F}_s - F_l^\circ = RT \ln p^\square/p^\circ. \quad (7)$$

The same operations can be performed on this equation as were performed on eq 2, with the result that

$$(\ln p^\square/p^\circ)_{P=P} - (\ln p^\square/p^\circ)_{P=P_a} = \frac{V_s - V_l^\circ}{RT} (P - P_a) \quad (8)$$

which is analogous to eq 6. In the above equation V_s is the molar volume of pure water in the ice form. Using eq 8 and data for $p^\square/p^\circ$ and $(V_s - V_l^\circ)$ at atmospheric pressure, $p^\square/p^\circ$ can be determined at any other pressure.

As has been mentioned before, $p/p^\circ = p^\square/p^\circ$ when ice and water are in equilibrium in the soil. Therefore, if the assumptions invoked previously are valid, i. e., that the activity (and hence p/p°) is a single-valued function of the liquid water content and that the ice in the soil has the properties of pure bulk ice at the existing pressure, the unfrozen water in the soil can be determined at any pressure in the following way. First, a curve of p/p° is plotted against water content for the pertinent value of T_f . This curve may have to be obtained from data at another temperature, T_a , and atmospheric pressure, as described earlier. Next, the curve is corrected to the pressure of interest by utilizing

the appropriate data in eq 6. Then $p^{\square}/p^{\circ}$ is determined for the required temperature and pressure by obtaining $p^{\square}/p^{\circ}$ at this temperature and atmospheric pressure from the tables given by Dorsey (1940) and correcting the same to the required pressure by means of eq 8. The resulting value of $p^{\square}/p^{\circ}$ is then referred to the (corrected) curve of p/p° versus water content to obtain the corresponding water content. This water content represents the liquid interfacial water in the partially frozen soil.

To illustrate the application of the concepts and methods described above, the following example is presented. From the swelling pressure, π , of Na-Wyoming bentonite (Warkentin et al., 1957; Koenigs, 1961) the value of p/p° at atmospheric pressure was calculated for each of several water contents by the relationship

$$RT \ln p/p^{\circ} = - \bar{V}_l \pi \quad (9)$$

in which $\bar{V}_l$ was assigned the value for normal water. Then the resulting data were combined with the adsorption data of Mooney et al. (1952) and plotted as shown by the solid line in Figure 1. Since, at the water contents included in the figure, $(H_l^{\circ} - \bar{H}_l)$ in eq 1 becomes very small, the adsorption isotherm changes little with temperature. Hence, the solid line in Figure 1 represents the adsorption isotherm of water, some of it supercooled, on Na-bentonite at atmospheric pressure and at temperatures in the range of 0 to about -10°C. If the system freezes, the isotherm is truncated at a relative humidity given by the ratio of the vapor pressure of ice to that of pure supercooled water at the given temperature. For example, at -5°C the vapor pressure of ice is 3.013 mm Hg and that of supercooled water is 3.163 mm Hg (Dorsey, 1940). The resulting relative humidity is 0.9526. The clay will adsorb 0.35 g of water per g of clay at this relative humidity. Adsorbed water in excess of 0.35 g water per g clay will freeze to ice unless it supercools. Thus the continuation of the adsorption isotherm at -5°C beyond a relative humidity of 0.9526 represents the adsorption of supercooled water on the clay. If the water does not supercool, the isotherm will rise vertically at this relative humidity because the relative humidity is constant regardless of the amount of ice present in the system.

Figure 1. Adsorption isotherms of liquid water on Na-bentonite at two external pressures and high relative humidities. (Reference state = pure liquid water.)

4 EFFECTS OF TEMPERATURE AND PRESSURE ON UNFROZEN WATER

Figure 2. Adsorption isotherm for liquid water on Na-bentonite at -5°C and atmospheric pressure. (Reference state = pure ice.)

If pure bulk ice is chosen as the standard state instead of pure bulk water, the relative humidity is the ratio of the vapor pressure of the adsorbed water to that of ice at the given temperature. In this case the adsorption isotherm at -5°C is of the form shown in Figure 2. The unfrozen water now corresponds to a relative humidity of 1.0.

The adsorption isotherm at -10°C and a pressure of 100 atmospheres is given by the dashed line in Figure 1. To obtain this isotherm from the one at atmospheric pressure, it was necessary to have values of $\bar{V}_l$ at the different water contents to use in eq 6. These values were estimated from the results of Anderson and Low (1958) and ranged from 0.01876 to 0.01846 liters per mole. The handbook value (0.01805 liters per mole) was used for $\bar{V}_l^\circ$.

The value of the relative humidity of ice, and hence of frozen Na-Wyoming bentonite, at -3°C and atmospheric pressure is 0.9714. This value can be obtained, as before, from values of $p^\square$ and p° given by Dorsey (1940). Increasing the pressure to 100 atm increases the relative humidity to 0.9794. The latter value was calculated by using the values of V_s and $\bar{V}_l^\circ$ reported by Dorsey (1940, p. 199 and 462) in eq 8. As shown by reference to Figure 1, the content of unfrozen water in the clay at atmospheric pressure and a relative humidity of 0.9714 is 0.43 g/g; the content of unfrozen water at 100 atm and a relative humidity of 0.9794 is 0.47 g/g. Thus, increasing the pressure from 1 atm to 100 atm at -3°C increased the unfrozen water by 0.04 g/g clay.

Presented in Table I are data, calculated by the method just described, on the increase of unfrozen water in Na-bentonite caused by increasing the pressure from 1 to 100 atm at different temperatures. These data are in qualitative agreement with those of Tsytoich (1958) who found large increases of unfrozen water in clay soils subjected to external pressures. They are also in qualitative agreement with the observation of Vialov (1959) that, under non-uniform loading, ice laminae will shift from regions of relatively high stress to regions of relatively low stress. Thus they may help to explain some important mechanical processes that occur in frozen soils under loading, eg., creep.

Table I. Increase in unfrozen water (ΔW) in Na-bentonite caused by increasing the pressure from 1 to 100 atm at different temperatures.

Temp ($^\circ\text{C}$)	ΔW (g/g clay)	Temp ($^\circ\text{C}$)	ΔW (g/g clay)
-1.5	0.18	-5	0.02
-2	0.10	-6	0.01
-3	0.04	-7	0.01
-4	0.04	-8	0.005

LITERATURE CITED

- Anderson, D.M. and Low, P.F. (1958) The density of water adsorbed by lithium-, sodium-, and potassium-bentonite, Soil Science Society of America, Proceedings, vol. 22, p. 99.
- Dorsey, N.E. (1940) Properties of water-substance. New York: Reinhold Publishing Co., 3rd edition.
- Koenigs, F.F.R. (1961) The mechanical stability of clay soils as influenced by the moisture conditions and some other factors, Versl. Landbouwk, Onder, Nr. vol. 67, p. 7.
- Low, P.F.; Anderson, D.M. and Hoekstra, P. (1966) Some thermodynamic relationships for soils at or below the freezing point. 1. Freezing point depression and heat capacity, U. S. Army Cold Regions Research and Engineering Laboratory (USA CRREL) Research Report 222. Also Journal of Geophysical Research 1968.
- Mooney, R.W.; Keenan, A.C. and Wood, L.A. (1952) Adsorption of water by montmorillonite. I Heat of adsorption and application of BET theory, American Chemical Society, vol. 74, p. 1367.
- Tsyтовich, N.A. (1958) Bases and foundations on frozen soils, H. R. B. Special Report 58.
- Vialov, S.S. (1959) Rheological properties and bearing capacity of frozen soils, USA CRREL Translation 74, 1965.
- Warkentin, B.P.; Bolt, C.H. and Miller, R.D. (1957) Swelling pressures of montmorillonite suspensions, Soil Science Society of America, Proceedings, vol. 21, p. 495.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H.		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE SOME THERMODYNAMIC RELATIONSHIPS FOR SOILS AT OR BELOW THE FREEZING POINT: II. EFFECTS OF TEMPERATURE AND PRESSURE ON UN- FROZEN SOIL WATER			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Research Report			
5. AUTHOR(S) (First name, middle initial, last name) Philip F. Low, Pieter Hoekstra, and Duwayne M. Anderson			
6. REPORT DATE July 1967	7a. TOTAL NO. OF PAGES 9	7b. NO. OF REFS 8	
8a. CONTRACT OR GRANT NO. b. PROJECT NO. c. DA Task 1VO14501B52A02 d.		9a. ORIGINATOR'S REPORT NUMBER(S) Research Report 222, Pt. 2	
		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
10. DISTRIBUTION STATEMENT This document is available to U.S. government agencies and their contractors from: Defense Documentation Center. Microfilm or photocopy of this document is available at cost of reproduction from: Clearinghouse for Federal Scientific and Technical Information.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U. S. Army Cold Regions Research and Engineering Laboratory	
13. ABSTRACT Thermodynamic methods are presented for calculating, from the water adsorption isotherms, the change in unfrozen water content of a partially frozen soil with tem- perature at a constant pressure or with pressure at a constant temperature. Then, using pertinent experimental data for Na-Wyoming bentonite, the increase in un- frozen water caused by a confining pressure of 100 atm is obtained as a function of temperature. Such information is shown to be relevant to the mechanical properties of frozen soils under stress.			

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