

PROPERTIES OF ICE AND PERMAFROST

PROPERTIES OF WATER IN DISPERSE ROCKS.

Part II. CRYSTALLIZATION HEAT

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The paper presents a synthesis of new data on crystallization heat of water confined in frozen porous rocks.
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INTRODUCTION

Mathematical models of complex processes in disperse (porous) materials include several related equations of transport (e.g., thermal conductivity, transport of moisture and solvents, deformation of solid, etc.) and phase equilibrium. The quality of such simulations depends on reference empirical values of parameters that characterize heat and mass transfer in disperse media and their physical (mechanical) properties. Some of these parameters have been largely measured and are available for reference, with due regard for the specificity of different materials, but some others remain poorly constrained, especially at negative temperatures. Among them is the crystallization heat of bound water, which is used in simulations of heat and mass transfer and water phase state, but the use is problematic for its uncertainty [Davidovsky and Brovka, 1985; Efimov, 1985; Brovka, 1991; Ershov et al., 1996].

Crystallization heat is one of few energy parameters of bound water that can be measured directly or inferred from adsorption experiments. It is a critical component of equations applied in calorimetry, which is still the leading way of estimating the content of liquid (unfrozen) water, though some other methods have appeared lately [Brovka, 1991; Stepanov and Timofeev, 1994]. The quality of the respective experimental results depends on whether the crystallization heat of bound water is properly expressed in heat budget equations [Kozłowski, 2003a,b]. Furthermore, the validity of its expression influences simulation results via the temperature dependence of unfrozen water contents used in models of heat and mass transfer in disperse media at negative temperatures [Permyakov, 1989].

THERMODYNAMIC STATE
OF PORE WATER AND ICE

Different equations for estimating water crystallization heat based on thermodynamic assumptions were analyzed in the reviews by Efimov [1985, 1986]. The crystallization heat of bound water most often remains beyond question in modeling being assumed equal to that of bulk water. Namely, its value used in differential scanning calorimetry (DSC) [Efimov, 1985] as well as in heat transport simulations [Permyakov, 1989; Mottaghy and Rath, 2006] corresponds to crystallization heat of bulk water at ambient pressure. Crystallization heat of pore water is most often described by the Kirchhoff equation for enthalpy difference between bulk water and ice [Gavriliev, 1970; Ershov et al., 1979; Stepanov and Timofeev, 1994; Rasmussen et al., 1997]:

$$h_w^0 - h_i = L_{cr}^0 + (C_w^0 - C_i)(T - T_0), \quad (1)$$

where h_w^0 , h_i are the enthalpies of bulk water and ice, respectively, at the temperature T ; L_{cr}^0 is the crystallization heat of bulk water at $T_0 = 273$ K; C_w^0 , C_i are the heat capacities of bulk water and ice, respectively. The bulk water-ice enthalpy difference at the same temperature is assumed in this approach to represent the crystallization heat of bound water.

The equation of state for bound water used by Ivanov [1969] defines the variations of bulk water crystallization heat along the phase equilibrium as a function of external pressure:

$$\frac{dL_{cr}}{dT} = (C_i - C_w^0) + \frac{L_{cr}}{T} - L_{cr} \left[\frac{\partial \ln(V_i - V_w)}{\partial T} \right]_P, \quad (2)$$

where L_{cr} is the crystallization heat of water, T is the water freezing point, C_w^0 and C_i are the heat capacities

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of bulk water and ice, respectively, V_w and V_i are the specific volumes of water and ice, respectively, and P is the pressure.

Thus, both equations (1) and (2) applied to crystallization of bound water refer to the properties of bulk water. It may be reasonable, and the Kirchhoff equation for bulk water may be applicable, as long as water contents strongly exceed the maximum hygroscopic moisture and the crystallization heat of bulk water covers the greatest part of bound water, which is often the case in practice. However, data obtained by various methods show that the properties of water confined in disperse systems, including crystallization heat [Anisimov *et al.*, 1981; Efimov, 1985, 1986; Brovka, 1991], differ from those of bulk water. Substituting bulk water for bound water may strongly interfere with final DSC-based calculations of liquid water contents in porous materials or with heat and mass transfer simulation results in the domain of hygroscopic moisture.

Bound water and ice are in equilibrium at the transition temperature, and the crystallization heat (L_{cr}) equals their enthalpy difference:

$$L_{cr} = h_w - h_i, \quad (3)$$

where h_w, h_i are the enthalpies of bound water and ice, respectively.

The crystallization heat L_{cr} corresponding to the water content W may be written otherwise as [Brovka, 2001]:

$$L_{cr} = L_{cr}^0 - (C_w^0 - C_i)(T_0 - T) + \mu_w - \left(\frac{\partial \mu_w}{\partial T} \right)_W T, \quad (4)$$

where L_{cr}^0 is the crystallization heat at the standard conditions; C_w^0, C_i are the heat capacities of water and ice, respectively; T_0 is the bulk water crystallization temperature; μ_w is the chemical potential of bound water.

Equations (3) and (4) are identical given that

$$h_i = -L_{cr}^0 + (C_w^0 - C_i)(T_0 - T) \text{ and } h_w = \mu_w - \left(\frac{\partial \mu_w}{\partial T} \right)_W T.$$

Note that the chemical potential terms in (4) contribute most greatly to the crystallization heat of bound water, and it is important to constrain their values at the melting temperature, i.e., the temperature dependence of $\Delta\mu$ and $\left(\frac{\partial \Delta\mu}{\partial T} \right)_W$.

Proceeding from (3), the crystallization heat of bound water is

$$L_{cr} = (h_{vw} - h_i) - (h_{vw} - h_w), \quad (5)$$

where h_w, h_i, h_{vw} are the enthalpies of bound water, ice, and bulk water, respectively.

In this equation, the bulk water-ice enthalpy difference (first brackets) is calculated by the Kirchhoff equation (1) from crystallization heat of bulk water

while the bulk-bound water enthalpy difference (second brackets) equals the net heat of adsorption.

If the enthalpies of bound water and ice at T_0 are known, (3) for the temperature T becomes

$$L_{cr} = h_w^0 - h_i^0 + (C_w - C_i)(T - T_0),$$

where h_w^0, h_i^0 are the enthalpies of bound water and ice at T_0 , C_w is the heat capacity of bound water at constant pressure and bound water content; C_i is the heat capacity of ice at constant pressure.

Hereafter the states of bound water and ice are estimated for the standard conditions (meaning that the temperature and pressure are the same for both bulk and bound water), unless specified otherwise.

Assuming that $T_0 = 273$ K,

$$h_i^0 = -L_{cr}^0,$$

where L_{cr}^0 is the crystallization heat of bulk water at a given temperature.

Therefore,

$$L_{cr} = L_{cr}^0 + h_w^0 + (C_w - C_i)(T - T_0). \quad (6)$$

This equation was given in a few publications [Efimov, 1986; Brovka, 1991], but it remains of limited use because the enthalpy and heat capacity of bound water are poorly constrained.

Among other equations more often used for this purpose, is the one suggested by Chistotinov [cited from Efimov, 1986]:

$$L_{cr}(T) = L_{cr}^0(T) + \mu_w - T \left(\frac{\partial \mu_w}{\partial T} \right)_P, \quad (7)$$

where $L_{cr}^0(T)$ is the crystallization heat of bulk water at the temperature T and μ_w is the chemical potential of bound water.

This equation coincides with (3) and (4) given

$$\text{that } h_i = -L_{cr}^0(T) \text{ and } h_w = \mu_w - T \left(\frac{\partial \mu_w}{\partial T} \right)_P.$$

If the vanishing term $T \left(\frac{\partial \mu_w}{\partial T} \right)_P$ [Efimov, 1986] is

neglected in (7), the equation becomes

$$L_{cr}(T) = L_{cr}^0(T) + \mu_w, \quad (8)$$

which means that $h_w = \mu_w$. This assumption, however, is not universally applicable and may lead to considerable errors (see below).

Or, the transition heat of different confined slit-pore materials may be found as [Gelb *et al.*, 1999]

$$L = \frac{T}{T_0} L_0,$$

where T_0 and L_0 are the temperature and melting heat of the bulk, respectively. This equation coincides with (8), provided that $\mu_w = L(T - T_0)/T_0$, but it gives L values much higher than the experimental ones [Gelb *et al.*, 1999].

**BOUND WATER/ICE PHASE CHANGE:
EXPERIMENTAL CONSTRAINTS**

Empirical equations obtained for some materials are not universal and may be inapplicable to other materials. For instance, latent heat of water freezing on silica gels depends on temperature as

$$L(T) = 7.3(T - T_0) + 334,$$

according to experimental data by *Horiguchi* [cited from *Kozłowski, 2003a, b*]. Another empirical regression equation for the temperature-dependent latent heat of fusion of water is [*Spaans and Baker, 1996*, cited from *Bittelli and Flury, 2003*]:

$$L(T) = 712.38 + 5.545T - 6.28 \cdot 10^{-3}T^2.$$

Experimental studies of the transition specific heat imply measurements of the thermal effect and amount of fused/frozen material. The former is measurable to quite a high accuracy but estimating the latter is problematic. The reason is that bound water crystallizes in a broad range of temperatures, the lower bound being unknown [*Starostin and Timofeev, 1996; Timofeev and Starostin, 2003*]. The pore size dependence of the crystallization heat of pore water was reported in many publications [e.g., *Faivre et al., 1999*] but has not been studied systematically.

The fusion (melting) heat of water (ice) confined in porous silica glass (aerosil) was estimated from temperature dependence of unfrozen water content and transition thermal effect [*Anisimov et al., 1981*] determined, respectively, by the nuclear magnetic resonance (NMR) and adiabatic calorimetry methods. The results (Fig. 1) show this heat to be much lower than that of bulk water and to have a very steep temperature dependence, as well as the unfrozen water content. The differential molar fusion heat (dQ/dm) is almost three times less than that of bulk at 271 K, but it stabilizes at 268 K and then increases at lower temperatures.

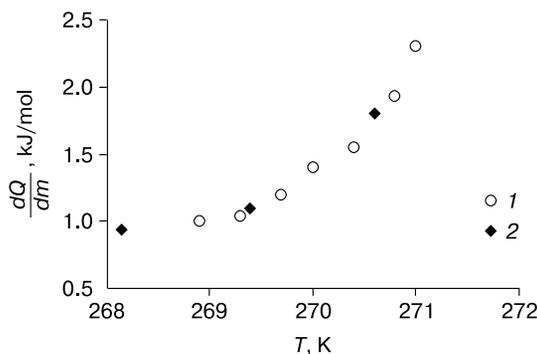


Fig. 1. Differential molar crystallization heat of water (dQ/dm) in porous silica (aerosil) as a function of temperature (T) at different water/silica concentration ratios: $H_2O:SiO_2 = 31.63$ kg/kg (1) and 4.78 kg/kg (2).

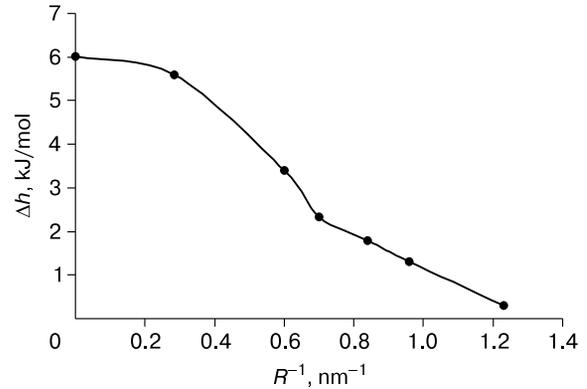


Fig. 2. Enthalpy of water (Δh) condensed in capillaries of mesoporous silica MSM-41 as a function of capillary radius (R).

The latent heat, temperature, and heat capacity of the high-temperature subsystem component turned out to be similar to the respective parameters of either bulk or zeolite water (fifty-fifty) in DSC experiments on first-kind solid-liquid phase transitions of collagen water in rat's tail tendon [*Gabuda et al., 2005a,b*]. Note however that the frozen water content was estimated approximately in that study, and the crystallization heat estimates can be only tentative.

In DSC and FT-IR (Fourier Transform Infrared Spectrometry) studies of the solid-liquid transitions of water in mesoporous MCM-41 silica gel [*Kittaka et al., 2006*], enthalpy changes upon melting of frozen water were determined as a function of pore size. The enthalpy was found to decrease with decreasing pore size (Fig. 2), and two stages of interfacial free energy change were observed below a pore size of 6.0 nm [*Kittaka et al., 2006*]. Similar DSC results were reported by [*Faivre et al., 1999*].

DSC and NMR data on ice melting in porous solids [*Rennie and Clifford, 1977*] showed that the properties of water in pores were essentially bulk properties at distances exceeding ~ 10 Å from the surface, and were influenced more by the Kelvin effect (capillarity) than by the silica surface.

Crystallization heat is sometimes estimated using variations of the melting enthalpy per gram of total water amount, which leads to underestimated values [*Faivre et al., 1999; Rault et al., 2003*]. More rigorous constraints can be obtained proceeding from the fact that the crystallization heat difference between bound and bulk water equals their evaporation heat difference [*Ershov et al., 1979; Brovka, 1991*]. Thus estimated crystallization heat for peat is within 20 kJ/kg, at 0.4 kg unfrozen water per kg of peat, or ~ 6 % of the standard value [*Brovka, 1991*]. The difference may reach 10 % in the temperature range 0 to -25 °C, which has to be taken into account in DSC

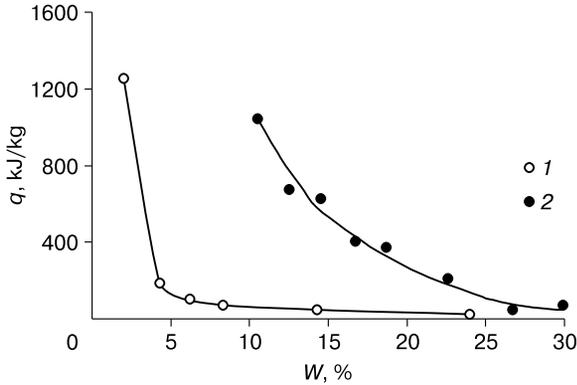


Fig. 3. Net adsorption heat of water (q) as a function of water content (W) in calcium (1) and potassium (2) bentonite (askanite) gel.

estimation of unfrozen water contents [Brozka, 1991, 2001].

The evaporation heat for adsorbed materials is often estimated using isosteric enthalpy of adsorption (Δh_a) [Gregg and Sing, 1984; Karnaukhov, 1999] found as

$$\Delta h_a = -RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_n, \quad (9)$$

where P is the equilibrium vapor pressure; T is the temperature; n is the amount of adsorbate on the adsorbent; R is the gas constant.

The reverse of Δh_a is the differential heat of adsorption, which is often called isosteric heat of adsorption (q_{st}):

$$q_{st} = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_n. \quad (10)$$

Isosteric heat of adsorption can be found by integrating (10), from experimental adsorption isotherms obtained at two or more temperature values within the range small enough to provide temperature independence. If the isotherms are obtained at two temperatures, q_{st} is [Gregg and Sing, 1984]

$$q_{st} = \left[\frac{RT_1 T_2}{T_2 - T_1} \right] (\ln P_2 - \ln P_1)_n, \quad (11)$$

where P_1, P_2 are the equilibrium vapor pressures at the temperatures T_1 and T_2 , respectively, and the amount n of adsorbate.

In the case of several temperatures, it is derived from the equation for adsorption isostere which relates P and T for the given n :

$$(\ln P)_n = -q_{st} / (RT) + \text{const}. \quad (12)$$

Then, q_{st} is estimated from the slope of the isostere plotted from a series of isotherms in rectilinear coordinates.

In order to characterize the adsorbate state relative to the parameters of bulk liquid rather than to vapor, equations (10)–(12) should use net adsorption

heat $q_{st} - q_l$ (q_l is the heat of bulk water condensation) instead of q_{st} and relative pressure P/P_0 instead of P . Note that q_{st} obtained from (10)–(12) refers to a certain n value. In general, this value influences quite strongly the adsorption heat estimates because of surface energy heterogeneity and molecular interactions in the adsorbed layer. Therefore, the curve of q_{st} as a function of n should be obtained iteratively for different n values.

Isosteric heat of adsorption has been largely studied [Raitburd, 1966; Jaycock and Parfitt, 1981; Gregg and Sing, 1984; Kiselev, 1986; Nagao et al., 1995; Vartapetyan and Voloshchuk, 1995; Khimenkov and Brushkov, 2003; Striolo et al., 2003; Hamdami et al., 2004], and the results would be useful for estimating the crystallization heat of bound water were they not fragmentary and often controversial. For instance, the energy heterogeneity of adsorbates shows up as more or less smoothly varying moisture dependence of differential adsorption heat [Raitburd, 1966] (Fig. 3). The isosteric heat of krypton adsorption on AgI studied by Jaycock and Parfitt [1981] varies in a more complex way as a function of the surface area. Furthermore, the relative error of these calculations increases at greater adsorption (in our case, at water contents about the maximum hygroscopic moisture, when net adsorption heat becomes less than 100 J/g and isosteric heat decreases). Analysis of errors in net adsorption heat estimated by (11) shows that the adsorption isotherms used for describing bound water freezing at temperatures from 0 to -30 °C have to be highly accurate. For example, equilibrium pressure errors of only 3–4 % may cause errors in net adsorption heat of bound water reaching 40–50 %. Furthermore, (11) is commonly derived from (10) assuming the same heat capacity for bound and bulk water, but this assumption is fraught with large errors. Therefore, data in this water content range are applicable only to approximate qualitative estimates of isosteric heat, and hence, crystallization heat of bound water.

The heat of water adsorption on different silica sorbent samples (Silochrom), measured by microcalorimetry [Tarasevich et al., 2001, 2005], turned out to be lower than the evaporation heat of bulk water in some adsorption capacity intervals (Fig. 4) [Tarasevich et al., 2005]. Therefore, crystallization heat of bound water can be expected to exceed that for bulk water.

This idea is supported by studies of water adsorption on the homogeneous surface of graphitized carbon black (GCB) [Kiselev, 1986]. Note that small polar molecules such as water fail to form hydrogen bonds upon interaction with GCB. The initial heat of water adsorption (Γ) on GCB is much lower than condensation heat. The values are low and grow slowly with increasing water concentration in the bulk gas phase (vapor pressure). Adsorption heat increases over the whole interval of measured adsorption val-

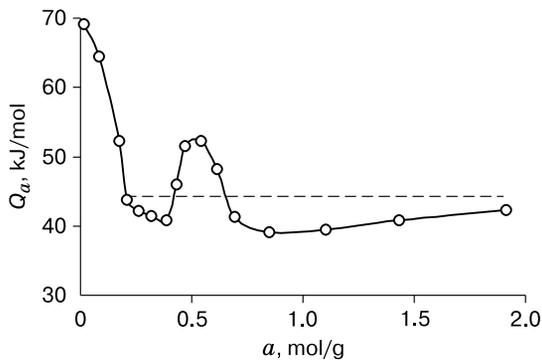


Fig. 4. Differential heat of water adsorption (Q_a) on silochrom as a function of adsorption capacity (a) at $T = 26\text{ }^\circ\text{C}$.

Dash line is the heat of bulk water evaporation.

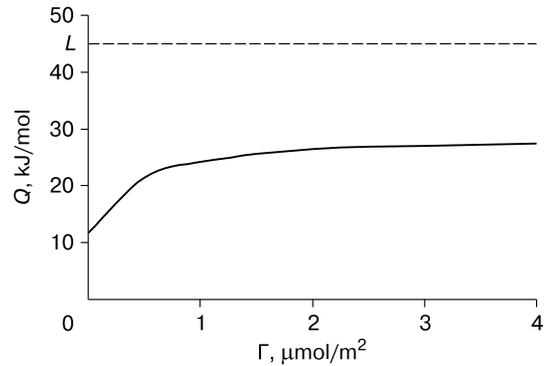


Fig. 5. Differential heat of water vapor adsorption (Q) as a function of adsorption on GCB (Γ) at 300 K .

Dash line (L) is water condensation heat.

ues but remains below condensation heat (Fig. 5). The isotherm of water adsorption is convex toward the P/P_0 axis throughout the P/P_0 interval [Kiselev, 1986], and confined water has higher crystallization heat than bulk water. Studies of melting/freezing of bulk water [Teraoka *et al.*, 2004] and water confined in different porous materials [Ishikiriya and Todoki, 1995; Olien, 1996; Hamdami *et al.*, 2004] confirm that the temperature dependence of bound water crystallization heat is not universal.

This heat equals the enthalpy difference between bound water and ice at the solid-liquid transition temperature and thus depends on the energy state of both water and ice. The properties of pore ice are commonly assumed to be the same as in bulk ice [Hoekstra, 1966; Ershov *et al.*, 1979; Deryagin *et al.*, 1989; Brovka, 1991]. This assumption, however, requires a more detailed analysis. Molecular dynamics simulation [Koga *et al.*, 2000, 2001] for the freezing of water in hydrophobic nanopores predicted formation of bilayer ice, with its crystals characterized by a hydrogen-bonding network of water molecules and each layer forming a distorted hexagonal lattice. Variations in the state of ice confined in rocks were also observed in experimental estimation of equilibrium water content in samples with different amounts of moisture at a constant negative temperature [Cheverev, 1991].

CONCLUSIONS

1. Crystallization heat of water confined in porous rocks depends on its phase composition and interaction with the solid matrix, as well as on the pore space structure. Simulations show that bound water differs from bulk water in its properties but the full picture of controls responsible for its phase equilibrium remains unconstrained.

2. Crystallization heat of bound water should be estimated simultaneously by different experimen-

tal methods which imply measurements of the thermal effect and the content of water at solid-liquid transitions. These crystallization heat estimates, however, remain controversial because of multiple controls.

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