DEPRESSION OF FREEZING TEMPERATURE OF WATER AND WATER SOLUTIONS IN POROUS MATERIALS

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In porous materials filled with water or water solutions of inorganic salts, water freezes at lower temperatures than under normal conditions; the reason is the decrease of water vapor tension above the convex meniscus of liquid in pores. The freezing point depression is not very significant in pores with radii from 0·05 μm to 10 μm (about 0·01—2·5 K). Only in smaller pores, especially when filled with inorganic salt solutions, this depression is important.

Frost resistance of porous materials is a very important property for assessing their suitability for architecture and art works. Water vapor from air can condense in porous materials even at low air humidities. In frosty weather, ice is formed from condensed water; because of the lower ice density forces can evolve which may affect the material strength.

In this connection the knowledge of the effect of pore size on the freezing behavior of water and water solutions in pores is essential. It follows from thermodynamics that, under equilibrium conditions, the freezing (solidification) temperature of a liquid in a capillary (pore) is lower than of a liquid with flat liquid–vapor interface. It is also known that freezing temperature decreases when salts are dissolved in the liquid. The aim of this paper is to predict quantitatively the decrease of freezing point of water under conditions of no heat and mass transport resistances, i.e. in physical equilibrium.

Pore structures (i.e. pore shapes, pore sizes and interconnections of pores) are highly diversified. Because perfect defining and describing of pore structure is not feasible with todays knowledge, it is necessary to start with idealized and simplified model structures; the most frequently applied model visualizes pores as a bundle of straight cylindrical, nonintersecting capillaries (cylindrical pore model). This model forms the basis for evaluation of pore size distributions from intrusion of mercury (mercury porosimetry) and from physical adsorption of inert gases (i.e. nitrogen adsorption at liquid nitrogen boiling point — BET method). Therefore, the evaluation of freezing temperature depression was performed for the cylindrical pore model.

In the freezing temperature depression two factors play a role:

1) Because porous materials are usually perfectly wetted by water, a semispherical liquid mensicus (with radius equal to the pore radius, r — see Fig. 1) is formed in a pore partly filled with water solution. It is well known from the thermodynamics, that water vapor tension, p, over a convex water surface with radius r is lower than the corresponding vapor tension over a flat surface, p_∞. Vapor tensions p and p_∞ are related by the Kelvin equation[1]

$$\ln\left(p/p_\infty\right) = -2\gamma\mathscr{V}/(rRT)\,, \tag{1}$$

where γ denotes the water surface tension, $\mathscr{V}$ the molar volume of water, R the gas constant and T the temperature (K).

Because at water freezing temperature (or, more correctly, at triple-point temperature) water in liquid phase, vapor phase and solid (ice) phase are in mutual equilibrium, the ice vapor tension, p_{ice}, must equal the liquid water vapor tension above the convex meniscus, p.

2) Water vapor tension over a water solution of nonvolatile inorganic salts, with a flat surface, p_∞, is related to vapor tension of pure water, p_∞^0, by the Raoult law[1]

$$p_\infty = p_\infty^0 y\,, \tag{2}$$

where y denotes the mole fraction of water in the solution. In determining y it is necessary to take into account dissociation of inorganic salts in solutions. E.g. for water solution of the completely dissociated sodium sulfate $Na_2SO_4 (2\,Na^+ + SO_4^{2-})$ with weight concentration c (wt. %), the water mole fraction y is given by

$$y = \frac{(100 - c)/18{\cdot}02}{(100 - c)/18{\cdot}02 + 3c/142{\cdot}04} \tag{3}$$

(18·02 and 142·04 in Eq. *(3)* are the molecular weights of water and sodium sulfate [g/mole], respectively, and the numerical coefficient 3 gives the number of ions into which sodium sulfate in water solution dissociates). For illustration, Table I shows the water mole fractions in solutions of sodium, magnesium and potassium sulfates with weight concentration c (wt. %).

Thus, equilibrium between liquid water, water vapor and ice is attained at such temperature T, for which Eq. *(4)* is satisfied:

$$\ln\left[p_{ice}/(y p_\infty^0)\right] = -2\gamma\mathscr{V}/(rRT)\,. \tag{4}$$

Temperature T then represents the water freezing point. In solving Eq. *(4)* it is necessary to take into account the temperature dependence of water surface tension, γ, of water molar volume, $\mathscr{V}$, of vapor tensions of ice, p_{ice}, and liquid water, p_∞^0.

By numerical solution of Eq. (4), for different radii of semispherical meniscus (and, thus, for different pore radii), temperature dependences of physical properties in the following forms were used:

$$1/\mathscr{V} = A_1 + B_1(T - 273\cdot15)$$

$$\gamma = A_2 - B_2(T - 273\cdot15)$$

$$\ln p_{ice} = A_3 - B_3/(T - 43)$$

$$\ln p^{\circ}_{\infty} = A_4 - B_4/(T - 43)\,.$$

TABLE I
Water mole fractions, y, in solutions of completely dissociated sulfates

c, wt. %	0·1	0·5	1	5	10	20
$100y$ (Na_2SO_4)	99·96	99·8	99·6	98·0	95·9	91·3
$100y$ ($MgSO_4$)	99·97	99·85	99·7	98·5	96·8	93·0
$100y$ (K_2SO_4)	99·96	99·81	99·6	98·1	96·0	91·4

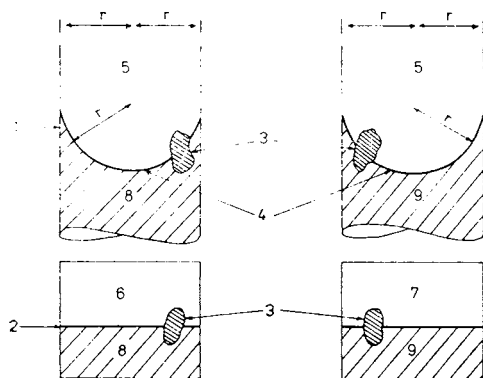
FIG. 1

Situation in a partly filled pore at the beginning of water freezing. 1 Pore, 2 flat interface, 3 ice (vapor tension p_{ice}), 4 semispherical meniscus, 5 water vapor (vapor tension p), 6 water vapor (vapor tension p°_{∞}), 7 water vapor (vapor tension p_{∞}), 8 water, 9 water solution
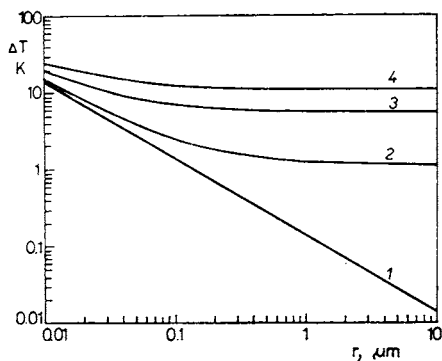
FIG. 2

Depression of freezing temperature of water and water solutions (ΔT) in pores of different sizes (radius r). Water mole fraction, y: 1 1·00 (no dissolved salts), 2 0·99, 3 0·95, 4 0·90

The adjustable constants A_i and B_i $(i = 1, 2, 3, 4)$ were determined from values of water molar volume, surface tension, ice vapor tension and liquid vapor tension in temperature range $-15 - 0°C$ (ref.[2]).

The obtained results are summarized in Fig. 2, in which the decrease of water freezing temperature (ΔT) is plotted versus the pore radius (r) for water solutions with water mole fractions (y) between $y = 1$ (no dissolved salts) and $y = 0.90$. It can be seen that the decrease of water freezing point for pure water is higher than 1 K only in pores with radii smaller than $0.1 \, \mu m$. Considering that salt solutions in pores are only moderately concentrated (concentration of sodium sulfate solutions would probably not exceed 5 wt. %, i.e. $y > 0.98$, cf. Table I) the decrease of water freezing temperature in pores with radii larger than $1 \, \mu m$ will not exceed 2 K.

In very narrow pores the decrease of freezing point is significant, particularly in pores filled with salt solutions. However, even in this case the freezing point of solutions with water mole fraction $y = 0.98$ (corresponding to 5 wt. % of Na_2SO_4) will not be lower than $-5°C$ unless the pore radii are smaller than $0.045 \, \mu m$ $(45 \, nm)$. Water from this solution does not freeze at $-10°C$ only in pores with r smaller than $0.017 \, \mu m$ $(17 \, nm)$.

It follows from the literature (e.g.[3]) that frost resistance of porous materials, which represents one of the most significant criteria for application, depends rather on the pore size distribution than on the total porosity. It turns out, however, that speculations of different authors, who ascribe the frost resistance to pores in some size ranges, are oversimplified (e.g.[4]); usually the shape and interconnection of pores are not taken into account, and, in particular, the depression of water freezing point due to the presence of curved water solution meniscus is overemphasized. From the results obtained here it follows that the decrease of pure water freezing temperature can be significant only in pores smaller than $0.05 \, \mu m$ $(50 \, nm)$ and that the effect of meniscus curvature on freezing point depression is not very large even with solutions of mineral salts.

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