

Models of Phase Equilibrium of Water in Ideal Models of Rock at Negative Temperatures

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Abstract – The article analyzes models of phase equilibrium of water in rocks, where a mineral matrix is treated as an assembly of particles with a determined effective molar mass, depending on dispersibility and surface properties of the mineral matrix. This provides an opportunity to develop a model of phase equilibrium for detached water in rocks at negative temperatures. Models allow studying the commonality of phase equilibrium for detached water with maximum simplification.

Keywords – rocks; models of phase equilibrium of water; ideal system; two-component system; three component system; the amount of unfrozen water; detached water.

I. INTRODUCTION

Rocks are multicomponent systems, consisting of a hard matrix, water, and dissolved matter. Water is the main factor influencing on rock properties [1, 2] in general and processes that take place in it [3–5], especially at negative temperatures [6, 7] when ice appears.

The specificity of studying phase transformations of detached water, such as freezing and defrosting, allows to distance from analyzing geochemical processes that happen in

the solid part of rocks. These processes can be eliminated from our research, thus simplifying the details of a thermodynamic system in question. The use of simple models is a key to eliminating errors and allows to evaluate the influence of stated assumptions on the result of modeling [8].

II. RESULTS

The ideal two-component model of rock consists of a mineral matrix and detached water. The isotherm equation of water absorption for this model is deduced from the equality of the chemical potentials of water and equilibrium vapor in a system [9].

$$W = \frac{M_w P}{M_{sc} P_0} = \frac{M_w P}{1 - \frac{P}{P_0} M_{sc} (P_0 - P)}, \quad (1)$$

where P is equilibrium pressure of water vapor; P_0 is the pressure of saturated vapor; M_w and M_{sc} are molar masses of water and solid matrix respectively; W – humidity. Hereinafter indices indicate: sc – solid matrix of rock; w – water.

The graph, calculated based on the formula (1), is slack and rising steadily, which corresponds to the III type of isotherms (Fig. 1) [10]. The isotherms of a III type have a convex form

with respect to the horizontal axis P/P_0 throughout the entire length. They are observed on porous and non-porous objects.

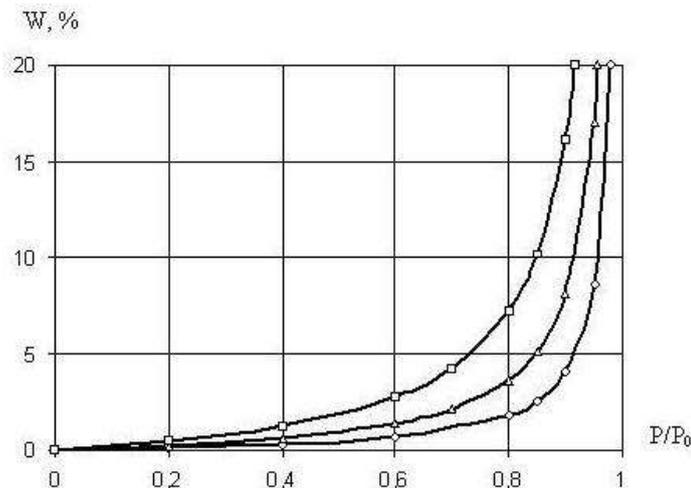


Fig. 1. The isotherm of water absorption in the ideal model of rock, consisting of a mineral matrix and detached water with a mass of mineral matrix equal to: □ – 1000 g/mole; △ – 2000 g/mole; ○ – 4000 g/mole.

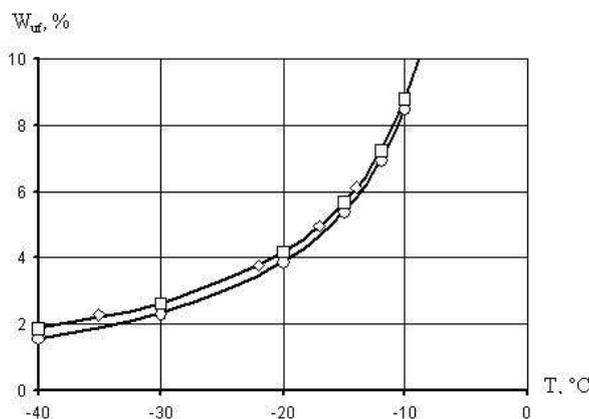


Fig. 2. The dependence between unfrozen water content and temperature in an ideal model of rock at $M_{sc}=2000$ g/mole: ◇ – based on the formula (2); □ – with a constant difference of water and ice thermal capacities $c_i - c_w = const$; ○ – calculation with the assumption that $c_i - c_w = 0$.

The isotherm of a III type is quite often used to describe the adsorption of water. For example, the work [10] contains the isotherm of water adsorption on earth silicon and on organic high-molecular polymers (polytetrafluorethylene, polyethylene), that show strong isotherms of a III type.

Thus, the comparison of water adsorption isotherms in an ideal system that are described with the formula (1) and the experimental isotherms of water [10] allows supposing the possibility of using ideal system models in cases of weak interaction between water and solid matrix.

The work [9] reviews an ideal two-component system, consisting of a mineral matrix and water, at negative

temperatures and represents the relationship between the amount of unfrozen water and temperature as:

$$W_{uf} = \frac{\frac{M_w}{M_{sc}} \exp \left[\frac{L_{cr}(T - T_0) + T_0 \int_{T_0}^T (c_i - c_w) dT - TT_0 \int_{T_0}^T \frac{c_i - c_w}{T} dT}{RTT_0} \right]}{1 - \exp \left[\frac{L_{cr}(T - T_0) + T_0 \int_{T_0}^T (c_i - c_w) dT - TT_0 \int_{T_0}^T \frac{c_i - c_w}{T} dT}{RTT_0} \right]}, \quad (2)$$

where W_{uf} – is the content of unfrozen water; L_{cr} – the crystallization heat of volumetric water; T – temperature; T_0 – freezing temperature of volumetric water; R – gas constant; c_i и c_w – molar heat capacities of ice and water respectively.

Fig. 2 represents the family of graphs showing the temperature dependence of unfrozen water content, calculated based on the formula (2) and provided $c_i - c_w = const$ and $c_i - c_w = 0$, at $M_{sc} = 2000$ g/mole.

It is clear that there is some difference in the results of calculations based on the formula (2) provided $c_i - c_w = 0$. The difference in the results of calculations based on the formula (2) provided $c_i - c_w = const$ at the temperature above -40 °C is not significant.

Let's review an ideal three-component system, consisting of a mineral matrix, water, and dissolved matter.

The theory of phase equilibrium for detached water is one of the most difficult problems in thermodynamics of phase transfers for water in rocks. The phase equilibrium of detached water in saline soils is described with the temperature dependence of unfrozen water content for non-saline soils, usually using two approaches [3, 11, 12].

To calculate the freezing temperature of detached water in °C the first approach uses the formula

$$T = T_1 + T_2, \tag{3}$$

where T is the freezing temperature of detached water; T_1 is the freezing temperature of water in non-saline soil; T_2 is the freezing temperature of volumetric water (calculated on the basis of nonsolvent volume).

The work [3] indicates that appearing ions increase the dispersibility of a system, the size of the active surface and the amount of unfrozen water. Then the conclusion is made without any justification that it is possible to calculate the freezing temperature as additive value, in particular as a sum of ΔT_1 that determines the impact of the surface force and ΔT that determines the impact of osmotic force.

The second approach assumes that unfrozen water content is additive [12]. In this case, the content of unfrozen water in saline soil at temperature T is represented as the sum of

$$W = W_1 + W_2, \tag{4}$$

where W_1 is the unfrozen water content in non-saline soil at temperature T ; W_2 is the addition to the unfrozen water content, caused by dissolved substances. Note that W_2 is determined based on conditions of phase equilibrium in volumetric water.

The unfrozen water content as the function of temperature and salinity [9]

$$W_{uf} = \frac{\left(\frac{M_w}{M_{sc}} + \frac{ZM_w}{M_s}\right) \exp\left[\frac{L_{cr}(T-T_0) + (c_i - c_w)(T-T_0)T_0 - (c_i - c_w)RT_0 \ln(T/T_0)}{RTT_0}\right]}{1 - \exp\left[\frac{L_{cr}(T-T_0) + (c_i - c_w)(T-T_0)T_0 - (c_i - c_w)RT_0 \ln(T/T_0)}{RTT_0}\right]}, \tag{5}$$

where Z is salinity; M_s is the molar mass of dissolved matter.

Salinity remains constant when there is no replacement of components during freezing and defrosting. That's why the formula (5) describes the changes in unfrozen water content at constant salinity for a particular system – rocks with a particular salinity depending on the temperature.

The feasibility of conditions (3) and (4) was assessed in ideal systems. The results are shown in Fig. 3 and 4

Fig. 3 shows the results of water content calculation in two-component systems: in volumetric solution (water and dissolve matter) and non-saline rock (solid matrix and water) as well as three-component system (solid matrix, water and dissolved matter). Fig. 3 also shows a graph, obtained by summing the temperatures of equilibrium phase of water in two-component systems (volumetric solution and non-saline rock) with equal content of unfrozen water. To satisfy the condition (3) this graph should coincide with the temperature dependence of unfrozen water in a three-component system. Fig. 3 shows that this doesn't happen, i.e. the condition (3) is generally not met in ideal systems.

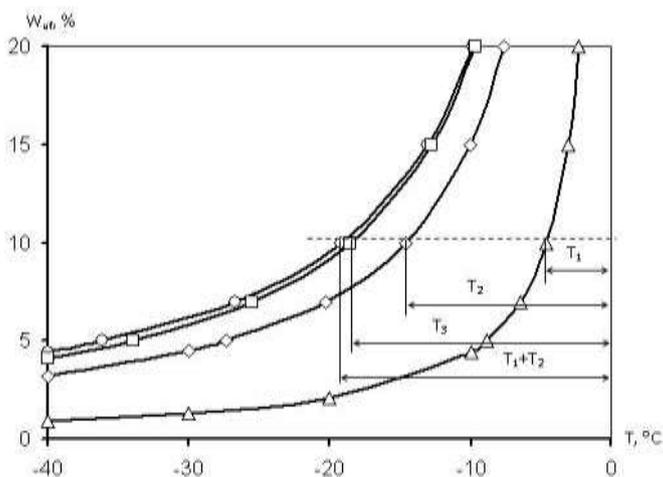


Fig. 3. The temperature dependence of unfrozen water content in an ideal system: □ – in a three-component system – saline rock; ◇ – in a two-component system – volumetric solution; △ – in a two-component system – non-saline rock; ○ – the result of a calculation based on $T = T_1 + T_2$.

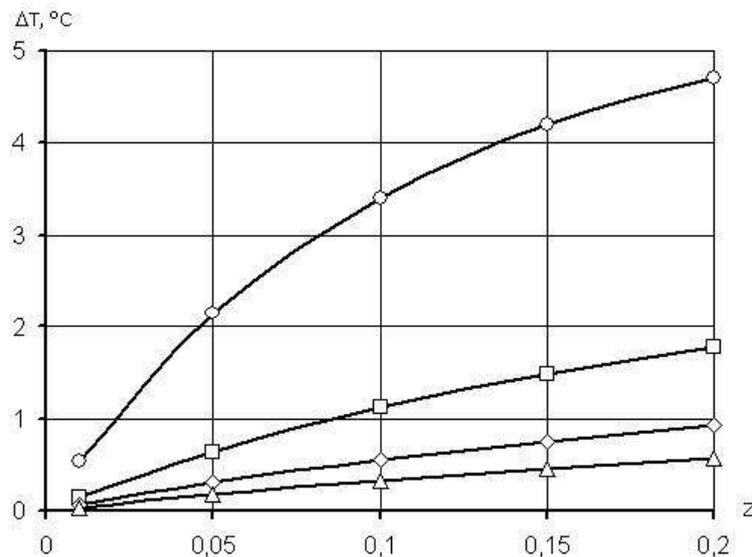


Fig. 4. The dependence of ΔT from salinity with unfrozen water content equal to \circ – $W_{uf}=5,0\%$; \square – $W_{uf}=10,0\%$; \diamond – $W_{uf}=15,0\%$; \triangle – $W_{uf}=20,0\%$. $M_{se}=4000$ g/mole.

It is clear that with assumed original data graphs in question almost converge at high levels of unfrozen water. The formulas show that variance between these two graphs, in this case, is influenced by the level of salinity, the content of unfrozen water and molar masses of components.

Fig. 4 shows the influence of salinity at different unfrozen water contents on the variance between two graphs, defined as $\Delta T = T_1 + T_2 - T_3$, where T_1 , T_2 и T_3 are explained in Fig. 3.

It is clear (Fig. 4) that when salinity decreases and the content of unfrozen water ΔT increases, the compared graphs come closer to each other. Thus it is possible to use formulas (3) in cases of high unfrozen water content and low levels of salinity.

Condition (4) is met in models of ideal systems. This can be seen by comparing expressions for unfrozen water. This is connected with the fact that all component particles in ideal system models are identical, i.e. Only mole concentrations of components are used in equations, describing the state of ideal systems as only the number of particles has importance, but not their properties.

III. CONCLUSION

1. By using the theory of ideal systems the article describes models of phase equilibrium for detached water in rocks at negative temperatures. Models allow studying the commonality of phase equilibrium for detached water with maximum simplification.

2. The feasibility of models is assessed by the comparison of calculation results with adsorption isotherms, the content of unfrozen water with experimental data and empirical formulas.

3. The research also analyzed the conditions for using assumptions based on superposition principle that allow calculating the properties of multicomponent systems (saline

rocks) based on the properties of binary systems (non-saline rocks and volumetric solutions).

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