TEMPERATURE DEPENDENCE OF THE HEAT OF CRYSTALLIZATION OF WATER

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Results of a comparative analysis of thermodynamic relationships are presented, permitting calculation of the temperature dependence of the heat of crystallization of water.

Free water at atmospheric pressure freezes at a temperature of 0°C with liberation of 334 kJ/kg of heat. Water sometimes supercools significantly, but freezing of supercooled water is as a rule accompanied by an abrupt increase (discontinuous) in temperature to 0°C. Thus, the question of temperature dependence of the heat of crystallization does not arise in connection with supercooling.

The freezing point of any material depends on pressure. Thus, an increase in pressure to 13.3 MPa decreases the freezing point of water by approximately 1°. Consequently, one may speak of the temperature dependence of heat of crystallization of free water acted upon by excess pressure. At high pressures (above 216 MPa) ice I transforms into other denser modifications, the melting points of which, on the contrary, increase with increase in pressure. Apparently, the freezing point of water can be reduced by pressure application only to −22°C, which corresponds to the point of transition from ice I to ice III in the water phase diagram.

We will now consider thermodynamic relationships which permit calculation of the temperature dependence of the heat of phase transition. Strictly speaking, the Kirchhoff equation $(\partial \Delta H/\partial T)_p = \Delta c_p$ cannot be used for precise determination of the temperature dependence of the heat of phase transition, since in contrast to chemical reactions phase transitions of the first sort cannot occur at different temperatures and constant pressure (volume). However, we can use the following relationships for this purpose [1]:

1) the Clapeyron–Clausius equation

$$\frac{\partial p}{dT} = \frac{L}{T\Delta v}, \tag{1}$$

2) the equation for the difference between the equilibrium specific heats of the corresponding phases

$$c''_{\mathrm{equ}} - c'_{\mathrm{equ}} = \frac{dL}{dT} - \frac{L}{T} \tag{2}$$

(displacement along the phase equilibrium curve is accompanied by simultaneous change in p and T; therefore, the specific heat corresponding to phase equilibrium c_{equ} differs from c_p and c_v);

3) we may also use the equation

$$\frac{\partial L}{\partial T} = \Delta c_p + \frac{L}{T} - L\left(\frac{\partial \ln \Delta v}{\partial T}\right)_p. \tag{3}$$

Equations (1)-(3) are universal, and applicable to phase equilibrium curves of any homogeneous substances. Given appropriate data, they may be used to precisely calculate the temperature dependences of heats of evaporation, sublimation, and crystallization. However, due to lack of complete data, determination of L(T) from Eqs. (1)-(3) is often difficult, so that for practical calculations approximate equations are often used. For example, on the basis of Eq. (3), we may write [2]

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$$\Delta L = \left[\Delta c_p + \frac{L_0}{T_0} - L_0\left(\frac{\partial \ln \Delta v}{\partial T}\right)_p\right]\Delta T. \tag{4}$$

For solids and liquids at temperatures sufficiently removed from the critical point, taking $c_{equ} \approx c_p$ in Eq. (2), or neglecting the quantity $(\partial \ln\Delta v/\partial T)_p$ in Eq. (3), we obtain [1]

$$\frac{\partial L}{\partial T} = \Delta c_p + \frac{L}{T}. \tag{5}$$

Equation (5) can be used for calculation of the heat of crystallization (fusion), while for approximate calculation of the heat of evaporation (sublimation), neglecting the liquid (crystal) volume and assuming the vapor to be an ideal gas, we obtain from Eq. (3):

$$\frac{\partial L}{\partial T} = \Delta c_p. \tag{6}$$

Under the condition that Δc_p = const the solutions of Eqs. (5) and (6) have the form

$$L(T) = L_0\frac{T}{T_0} + \Delta c_p T \ln\frac{T}{T_0}, \tag{7}$$

$$L(T) = L_0 + \Delta c_p \Delta T. \tag{8}$$

If for Δc_p we take the difference in specific heats of water and ice (L_0 = 334 kJ/kg), Eqs. (6) and (8) give the difference in their enthalpies. In this case, the enthalpy difference does not characterize the heat of crystallization of water, since no corresponding equilibrium phase transition exists. As was noted above, for approximate calculation of the temperature dependence of heat of crystallization of water under high pressure, Eqs. (5) and (7) should be used.

We will estimate the quantity $(\partial L/\partial T)$ using Eqs. (5) and (6):

$$\frac{\partial L}{\partial T} \approx \Delta c_p + \frac{L_0}{T_0} = 3.32 \ \text{kJ/(kg·K)}, \quad \frac{\partial L}{\partial T} \approx \Delta c_p = 2.09 \ \text{kJ/(kg·K)}.$$

It is evident that the divergence between these values is about 60%. Consequently, use of Eqs. (6) and (8) for calculation of the heat of crystallization of water can lead to significant errors.

In the majority of cases the need for data on the temperature dependence of the heat of crystallization of water is related to phase transition of pore water in hygroscopic materials, which, as is well known, freezes over a wide range of negative temperatures (determination of the amount of unfrozen water by the calorimetric method, solution of a wide class of thermophysical problems involving freezing and thawing of moist media, etc.).

It is generally accepted that the physical state of the unfrozen water is similar to that of bound water in the melting material; the stronger the bond, the lower the temperature at which freezing occurs. As is well known, bound water has physical properties which differ from those of free water: increased density, viscosity, thermal conductivity; reduced heat capacity, electrical conductivity, dielectric permittivity, solvent capability, vapor pressure, freezing point, etc. Consequently, the heat of phase transition of bound water may differ from that of free water. However, at the present time the question of the heat of phase transition of the bound material has yet to be answered decisively. It is clear only that it differs from the heat of phase transition of the substance in a volume. This is also indicated by experimental data. Thus, it was shown in [3, 4] that the heat of fusion of adsorbed material, calculated by graphical integration of thermal conductivity curves in the region of their maxima, is less than the heat of fusion of the material in volume. For example, their difference in the adsorption system n-hexane–silica gel is equal to 7-13% [3]. The heat of fusion of the adsorbed monolayer (two-dimensional state of the material) comprises about half the heat of fusion of the volume adsorbate [4]. The water formed upon fusion of ice flowing over the surface of the material releases a heat of wetting, which also contributes to the total amount of heat absorbed [4].

The reduction in heat of crystallization of bound water can be explained by the fact that its absorption is accompanied by liberation of heat [5] and an increase in the degree of molecular ordering [6], i.e., the freezing portion of the bound water apparently occupies an energy state intermediate between ice and free water. Thus, freezing of bound water

TABLE 1. Heat of Crystallization of Water (kJ/kg) vs. Temperature

Temperature, °C								$(\partial L/\partial T)_m$, kJ/(kg·K)	Notes
0	−5	−10	−15	−20	−30	−40	−50		
334	309	285	262	242				4,60	(1) [11, 12]
334	318	302	286	270				3,18	(4) [2]
334	318	301	285	269				3,24	(5)
334	323	311	298	286	257	224	189	2,89	(6) [13]
333	323	313	301	288	264	236	210	2,47	(6) [10, 14]
334	324	313	303	292	271	250	229	2,09	(6) [15]
333	317	300	282	263	226	187	143	3,81	(10, 11)[10]
333	317	300	285	267	232	196	162	3,43	(10, 12)[10]

over a wide spectrum of negative temperatures at constant pressure occurs because of its energy inhomogeneity and structural changes. The temperature and heat of crystallization then depend on the quantity of liquid phase water (its binding energy), i.e., in the given case we have physically a completely different process than freezing of free water upon reduction in temperature.

In the theory of bound water adsorption, capillary, and osmotic forms of binding are distinguished [7, 8]. Only adsorbed water is physically (molecularly) bound to the solid skeleton of the material. Therefore, it may develop that the heat of crystallization of bound water will depend on the form of binding as well as the temperature. For example, for one and the same temperature the freezing of adsorbed water may be accompanied by liberation of a smaller quantity of heat than freezing of water bound in other forms. Thus, the following hypotheses may be proposed regarding the heat of crystallization of bound water:

1) the heat of crystallization of bound water is a unique function of temperature;

2) the heat of crystallization of bound water depend not only on temperature, but on the form of bonding.

It is not justifiable to apply the equations considered above for calculation of the temperature dependence of the heat of crystallization of bound water. Here the problem is not only lack of appropriate data, but mainly the inapplicability of the equations themselves for description of the gradual freezing at constant (atmospheric) pressure of energetically inhomogeneous bound water. For example, the Clapeyron–Clausius equation can be used to describe phase equilibrium of bound water only at a fixed film thickness (binding energy).

To calculate the heat of crystallization of bound water, Chistotinov [9] proposed use of the equation

$$L_b(T) = L^\infty(T) + \Delta\mu - T\left(\frac{\partial\Delta\mu}{\partial T}\right)_p. \tag{9}$$

Neglecting the third term on the right, the value of which is approximately 1/20 of the second term, we obtain

$$L_b(T) = L^\infty(T) + \Delta\mu \tag{10}$$

[where $L^\infty(T)$ is the heat of crystallization of bound water].

To find $\Delta\mu$ the equation

$$\Delta\mu = \frac{1}{\ln T_0/T + 1}\int_T^{T_0}\frac{L^\infty(T)}{T}\,dT \tag{11}$$

may be used, or the widely known [9, 10] simpler expression

$$\Delta\mu = L_0\Delta T/T_0. \tag{12}$$

It should be noted that in Eqs. (9)-(11) the quantity $L^\infty(T)$ should properly be termed not the heat of crystallization of the free water, but the difference between the enthalpies of supercooled water and ice.

An equation similar to Eq. (9) can be obtained by using another approach. On the basis of Hess's law, for the heat of transition of water from the adsorbed layer into the crystalline phase we may take the difference between the heats of sublimation of ice and evaporation of bound water

$$L_b(T) = L_s - Q_a = \Delta H_w - q_a. \quad (13)$$

The heats Q_a and q_a, being functions of the moisture content of the material, must correspond to the quantity of unfrozen water in the specimen at the given temperature T.

Inasmuch as $q_a = -\Delta\mu + T(\partial\Delta\mu/\partial T)_{W_p}$ (calculated from equilibrium specific moisture content isotherms) [8], we obtain an equation analogous to Eq. (9). The differential heat of adsorption depends on the form of the material [8]; therefore, in determining $L_b(T)$ with Eq. (13) an unambiguous temperature dependence is not obtained (corresponding to the second hypothesis). This difference develops because of neglect of the temperature coefficient of the chemical potential in Eq. (9). In the moisture state where the moisture exceeds the maximum hygroscopic value the heat of crystallization of pore moisture does not differ from the heat of crystallization of free water. Table 1 presents values of the heat of crystallization of water as a function of temperature, taken from various studies. The notes column indicates equation numbers (in parentheses) and citations from the literature.

The mean temperature coefficient $(\partial L/\partial T)_m$ varies significantly depending on the form of the equation and original data used: from 2.09 to 4.6 kJ/(kg·K). Only the last two lines of the table refer directly to bound water. The first three lines are heats of phase transition of free water under excess pressure, while lines 4-7 are the differences between the enthalpies of supercooled water and ice. It is quite interesting that the temperature coefficients calculated with the bound water model prove to be close to the results obtained for reduced freezing point of free water under the action of excess pressure (see Table 1). This result is apparently not a random one, but reflects a deep internal relationship. It is appropriate here to recall the model in which the action of adsorption forces is compared to high pressure [16].

In summation it should be stressed that the temperature coefficient of the heat of crystallization of water is significant, and must be considered in practical calculations. For approximate calculation of the heat of crystallization of free water located under high pressure, Eq. (5) or Eq. (7) should be used. Use of Eq. (6) or Eq. (8) for this purpose is improper, as was shown above. For unfrozen bound water Chistotinov's expression or Eq. (13) is preferable, since they directly consider the bound state of the water.

NOTATION

T, temperature; p, pressure; ΔH, enthalpy difference; L, heat of phase transition; Δv, difference between specific volumes of phases; c_p, c_v, c_{equ}, specific heat at constant pressure, constant volume, and in equilibrium; Δc_p, difference between specific heats of phases; L_0, heat of phase transition at temperature T_0 = 273.15°K (for water); $\Delta T = T - T_0$; $L_b(T)$, heat of crystallization of bound water; Δμ, chemical potential of bound water; L_s, heat of sublimation of ice; Q_a, heat of evaporation of bound water; ΔH_w, difference between enthalpies of supercooled water and ice; q_a, differential heat of adsorption; W_p, equilibrium specific moisture content of material.

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A UNIFIED METHOD OF NUMERICAL CALCULATION OF THE CONJUGATE PROBLEM OF HEATING BODIES BY LIQUIDS IN CONCURRENT FLOW AND COUNTERFLOW

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A unified algorithm is proposed for the solution of conjugate problems of heat exchange in one-sided and two-sided heating of solid bodies in concurrent flow and counterflow.

In connection with the development of the parameters of the heat-transfer agents used in modern heat exchangers, it becomes necessary to increase the accuracy of calculation of the temperature fields in their elements. Therefore, it is preferable to solve heat-exchange problems in a conjugate statement. In the creation of heat exchangers this makes it possible to reduce their energy capacity and metal content and to increase their productivity by an average of 10% [1].

The mathematical formulation of the problem in a conjugate statement includes the energy equation for the heat transfer agent and the heat-conduction equation for the solid body, as well as, apart from the usual boundary conditions, the conditions at the surface of the body bathed by the heat-transfer agent (the internal boundary conditions). The semidetailed and the detailed conjugate problems of heat exchange should be distinguished. In the first case the temperature field in the heat-transfer agent is described by a quasi-one-dimensional energy equation and the internal boundary conditions have the form of boundary conditions of the third kind. In the second case, two- and three-dimensional energy equations are considered and the internal boundary conditions are boundary conditions of the fourth kind.

Major progress has now been achieved in the solution of conjugate problems of heat exchange through the use of modern numerical and analytic methods. This pertains primarily to problems of heating of bodies in one-sided and two-sided concurrent flow over them [2-5]. At the same time, methods of solving conjugate problems of heat exchange between solid bodies and heat-transfer agents in counterflow are less well developed. The existing semianalytic methods [6-8] have limited application and, in addition, they reduce the problem to an infinite-

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