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Original scientific paper

A CALCULATION MODEL FOR THE HEAT CAPACITY OF BEEF WITH DIFFERENT MOISTURE DURING FREEZING TAKING INTO ACCOUNT FREE WATER CRYSTALLIZATION

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Abstract

The paper proposes a model for the process of free moisture crystallization in beef within the framework of the Debye concept with establishment of dependencies of model parameters on the initial moisture content. Model adequacy was validated by comparison of the calculation results with the results of the experiments on determination of values of heat capacity and phase transition enthalpy in beef with different initial moisture obtained by the differential scanning calorimetry method. It is shown that the end of free water phase transition in beef with initial moisture in a range of 37% to 80% occurs at a temperature of 243 K. Calculation dependencies of parameters of the model used for calculation of beef heat capacity are presented.

Introduction

The knowledge of product thermophysical properties is extremely important in designing and realization of processes of their transportation, storage and technological processing linked with freezing and thawing. This determines a large number of studies conducted by several foreign and national scientists [1,2,3,4,5,6,7,8,9,10,11,12,13] and summarized largely in [14]. Meat is one of such products. Meat freezing is accompanied by crystallization of water contained in it. From the viewpoint of studying heat exchange processes in meat refrigerated processing, it is conventional to classify water contained in it into free and bound. There is still no strict definition of the term "bound water" [13]. It is noted that bound water does not freeze at a temperature of minus 40 °C. It is shown in [2,15] that freezing of free water and, consequently, crystallization are ended when refrigerating at minus 30 °C (beef) and minus 31 °C (pork) (243.15 K and 242.15 K, respectively). Riedel pointed at this fact for the first time by the example of beef [2].

When studying the process of phase transition, the basic thermophysical characteristics of a product are the cryoscopic temperature T_f and initial moisture content w. At the cryoscopic temperature in a range of 273 K to 268 K, the crystallization process is accompanied by the release of 90% of latent heat of crystallization [12]. Specific isobaric heat capacity measured in this area is a sum of heat capacities: true heat capacity [11] and heat capacity conditioned by released latent heat of crystal formation [15].

It is generally agreed that the most reliable results are obtained upon measurement using a low-temperature adiabatic vacuum calorimeter [8,16,17]. Figure 1 presents a graph of the dependence of beef heat capacity measured using such instrument according to the data obtained by Latyshev [8].

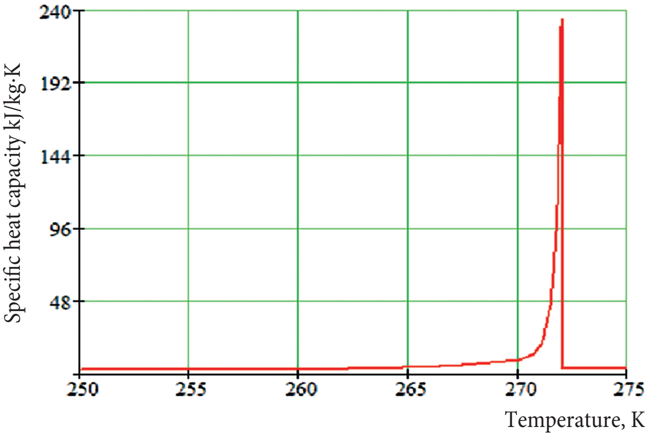

Figure 1. Dependence of beef specific heat capacity measured using a low-temperature adiabatic vacuum calorimeter [8]

Peculiar features of the indicated measurements are discreteness and duration of the measurement process upon the absence of the possibility to manage the rate of refrigeration. Due to this, discreteness of results, as a rule, is equal to or higher than 1 K.

The studies appeared that noticed the significance of the effect of physico-chemical processes occurred in meat in a range of the subcryoscopic temperatures ($T_{kr} \pm 0.5$ K) on its consumer properties [18]. For such investigations of meat refrigeration in a narrow range of the subcryoscopic temperatures, higher frequency of temperature measurement using the DSC method is necessary [16,17,19].The use of the differential scanning calorimetry method allows minimizing discreteness for specific heat capacity calculation.

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At present, however, there is no method that enables predicting the character of meat heat capacity dependence on a temperature in a range of the phase transition temperatures.

Several studies of the crystallization process consider two phenomena: the crystal growth and diffusion of the intercrystalline liquid phase to the crystal surface. With that, they analyze the crystal growth rate, which changes the sizes of channels between them and hydrodynamics of the intercrystalline liquid flow. This approach is realized in [20,21,22]. The calculated dependencies presented in these studies are markedly inconsistent with the data obtained using an adiabatic calorimeter [8]. A significant difference in the nature of these processes from meat free water crystallization does not allow using any elements of these studies in this research.

The aim of this research is to develop a model for crystallization process based on the Debye concept, which enables predicting by calculation the specific isobaric heat capacity depending on a temperature and initial moisture as applied to beef freezing.

Materials and methods

The development of a model for free water crystallization in beef is based in this study on the publication [19], in which the authors (being also the authors of the present paper) showed the possibility to use the Debye concept by the example of NOR beef. The dependence has the following form:

$$c = 3\mu \cdot N \cdot k \cdot \left(\frac{\theta}{T_{kr} - T + \delta}\right)^2 \cdot e^{-\left(\frac{\theta}{T_{kr} - T + \delta}\right)} + B \cdot 10^{-3} \cdot T, \qquad (1)$$

where

c is meat specific heat capacity, kJ/kg·K;

3 is the nondimensional coefficient;

$\mu \cdot N$ is the number of crystallization centers in a meat sample;

$N = 10^{25}$ kg^{-1} is the order of determining the number of crystallization centers;

$\mu = 0.0725 \div 1.035$ is the coefficient that depends on the sample moisture content;

T_{kr} is the beef cryoscopic temperature (the temperature of the beginning of free water freezing with crystal formation);

$\theta = h\nu/k$, K is the characteristic temperature;

h is the Planck constant, $h = 6.626 \cdot 10^{-34}$ J · s;

ν is the vibration frequency of atoms in a crystal, s^{-1};

k is the Boltzmann constant, J/K; $k = 1.38 \cdot 10^{-23}$ J/K;

T is Kelvin temperature;

δ is the coefficient corresponding to a deviation of the temperature of the water crystallization onset in the process of transformation into ice from the temperature of the heat capacity peak in the process of phase transition, K;

B is the coefficient characterizing the contribution of heat capacity of components not containing free water, $B = 7.5 \cdot 10^{-3}$ kJ/kg·K.

By investigating beef heat capacity in a wide range of moisture (37% — 75%), the possibility to use dependence (1) to calculate specific isobaric heat capacity using the calculated dependencies of the parameters μ, θ, δ and T_{kr} obtained below is shown in this paper.

The most important characteristic of the crystallization process is the cryoscopic temperature T_{kr}. Methods for measuring this parameter are given in [15, 19]. For beef, the temperature, when free water is finally frozen out, is 243 ±0.25 K (–30.15 ±0.25 °C), which corresponds to the end of free water phase transition in beef. The above mentioned paper [19] presents dependence (2) by the results of the experimental study of a decrease in heat capacity of a frozen sample lower than the temperature of the end of phase transition.

$$c_{fr.b.} = 0{,}548 + 1{,}85 \cdot 10^{-3} \cdot T + 1.68 \cdot 10^{-5} \cdot T^2, \qquad (2)$$

where $c_{fr.b.}$ is specific heat capacity of frozen beef not including heat capacity determined by latent heat of crystallization (melting) kJ/kg · K.

It is necessary to note that the intersection point of the phase transition curve (1) with curve (2) corresponds to the end of moisture crystallization process in beef. Fulfilment of the indicated statement by dependence (1) for different moisture levels in beef can be another criterion of the model adequacy to the real process of phase transition.

The experimental base of this study aimed at validation of the dependence (1) adequacy are the results of the detection of heat capacity of beef with different moisture content obtained by the differential scanning calorimetry (DSC) method using a DSC204 F1 NETZSCH instrument.

Detection of phase transition enthalpy in beef freezing by the indicated method ensured the error of not more than ± 3%. When processing the results of the DSC experiments with the method of τ — R correction [17], dependencies of beef heat capacity on temperature were practically in the complete agreement with the data on heat capacity obtained using the adiabatic instrument by Latishev at a meat moisture level of 74.1% [8].

Latent heat of water crystal formation in the samples was calculated as the integral difference of total heat capacity of the sample $c_{TS.S}$ and specific heat capacity of the frozen sample $c_{fr.b.}$ by (2):

$$\Delta H_{LH} = \int_{T_1}^{T_2} (c_{TS.S} - c_{fr.b.})\, dt \qquad (3)$$

where:

ΔH_{LH} — enthalpy (latent heat) of crystallization of free water in a beef sample, J/kg;

T_1, T_2 are temperatures of the beginning and end of the melting peak, respectively ($T_1 = 243$ K; $T_2 = T_{kr}$ is the cryoscopic temperature) °C;

$c_{fr.b.}$ is the line determined by the values of beef specific heat capacity by (2);

$c_{TS.S}$ is the line that characterizes total (effective) specific heat capacity of a sample.

The method of heat capacity determination proposed in the work [19] in correspondence with the concept of heat capacity by Debye can be used for analysis of the association of obtained dependency (1) parameters with indicators of the freezing regime and different meat initial moisture.

Different moisture content in the samples was achieved by freeze drying, after which they were placed into a crucible for DSC measurements. After DSC measurements of heat capacity values, the crucibles were opened and moisture of the samples was determined by drying in a thermostat at an air temperature of 100oC and the following weighing.

Values of the cryoscopic temperature necessary for investigations were detected using an osmometer-cryoscope OSCR-1. The instrument was entered into the RF State Register of measuring instruments under the number of 42519-09. The technical characteristics are given in Table 1.

The absolute thermodynamic scale, according to which T = 273.15 K + t °C [14], is used in the work.

Table 1. Main specifications of OSKR-1

Parameter	Error
Range of freezing temperature measurement:	**0 to –3.720 °C**
Limits of allowable fundamental absolute error in temperature measurement	
— in the range of 0 to –0.930 °C:	**±0.002 °C**
— in the range of –0.930 to –3.720 °C:	**±0.010 °C**
Sample volume, not less than:	**0.3 ml**

The development of the model of heat capacity by (2) in dependence on a temperature and moisture of the studied beef sample is realized by selection of the model parameter investigation depending on the initial moisture by minimizing the integral dependencies (3) and (4). The results are given in table 2, as well as in the form of polynomial dependencies (6–10). The final correction of correspondence of the calculated values of beef specific heat capacity to the values obtained by the empirical way is carried out using the coefficient B.

The parameter T_{kr} was determined using the above mentioned instrument with account for the instrument error and random errors with the overall error of ± 0.05 K.

The parameters μ; θ; and δ were found based on the following considerations:

1 — It has been noticed that the parameter μ is determined by the maximum value of the peak of the experimental curve of heat capacity, which enables using this parameter as a reference point when determining the parameter μ. The sequence of these points obtained at different moisture levels in beef can be described as a polynomial of type (8), Figure 3.

2 — The characteristic temperature θ, as was shown above upon its definition, depends on the character of heat removal (the phonon flow according to Debye with the frequency of $\nu \sim 10^{11}$); with that, the value of the parameter θ increases with reduction of the water content in a sample; several reference points of the parameter θ value for the experimental curves of beef heat capacity allowed obtaining the empirical polynomial dependence of the parameter on moisture (9), Figure 6.

3 — The parameter δ (see the definition above). This value practically compensates errors in the measurement of the cryoscopic temperature and corrects the position of the peak of the heat capacity curve in the area of phase transition. The sequence of values of this parameter obtained upon correction by bringing into proximity the position of the empirical peak of the phase transition curve to the calculated one by dependence (2) is approximated by dependence (10), Figure 5.

Verification of the obtained calculated expressions of specific heat capacity for samples with all moisture levels was carried out by several criteria:

1 — minimization of the difference between the calculated and experimental values of phase transition enthalpy; that is, minimization of the difference between the results of the calculation by (3) and calculation of enthalpy using dependencies (1) and (2):

$$\Delta H_{LH}^{exp} - \Delta H_{LH}^{calc} = \int_{T_1}^{T_2} (c_{TS.S} - c_{fr.b.})\, dt - \int_{T_1}^{T_2} (c_1 - c_2)\, dt, \tag{4}$$

where: c, $c_{fr.b}$ are specific heat capacities calculated by dependencies (1) and (2).

2 — minimization of the difference between the sequence of measurement results for specific heat capacity by the DSC method and by equation (1).

$$\Delta c = c_1 - F(T_{DSK}), \tag{5}$$

See Figure 2. The experimental curves of heat capacity $F(T_{DSK})$ are marked in the figure by the numbers with the 'e' index.

Results and discussion

In the final form, the mathematical model of free water crystallization upon beef freezing is a system of equations (1), (2), (6–10) plus correcting equation (11).

Approximating dependencies of the parameters T_{kr}, ΔH, μ, θ, δ on the initial moisture content in beef have the following form (6–10):

$$T_{kr}(w) = 257.1 + 34 \cdot w - 18 \cdot w^2;\ \Delta_{error} \leq 0{,}1\% \tag{6}$$

$$\Delta H_{LH} = L \cdot w \cdot (1 - 0{,}35 \cdot (1 - w)/w);\ \Delta_{error} \leq 5\% \tag{7}$$

$$\mu(w) = 0{,}014 + 1{,}85 \cdot w^4 + 3 \cdot w^5;\ \Delta_{error} \leq 14\%; \tag{8}$$

$$\theta(w) = 3{,}66 - 4{,}35 \cdot w;\ \Delta_{error} \leq 20\% \tag{9}$$

$$(w) = 1{,}94 - 2{,}25 \cdot w;\ \Delta_{error} \leq 10\%. \tag{10}$$

It is necessary to note that the error of dependence (7) in the area of low moisture levels (< 60%) is ± 5%, in the area of >60% of moisture, the deviation of calculated values is ~3%. The use of dependence (7) by Riedel [2] to calculate beef enthalpy is significantly easier than the use of dependencies (1 and 2) without decreasing accuracy.

Dependencies of beef heat capacity by equation (1) using the experimental data presented in Table 2 are given in a form of graphic dependencies in Figure 2. It is necessary

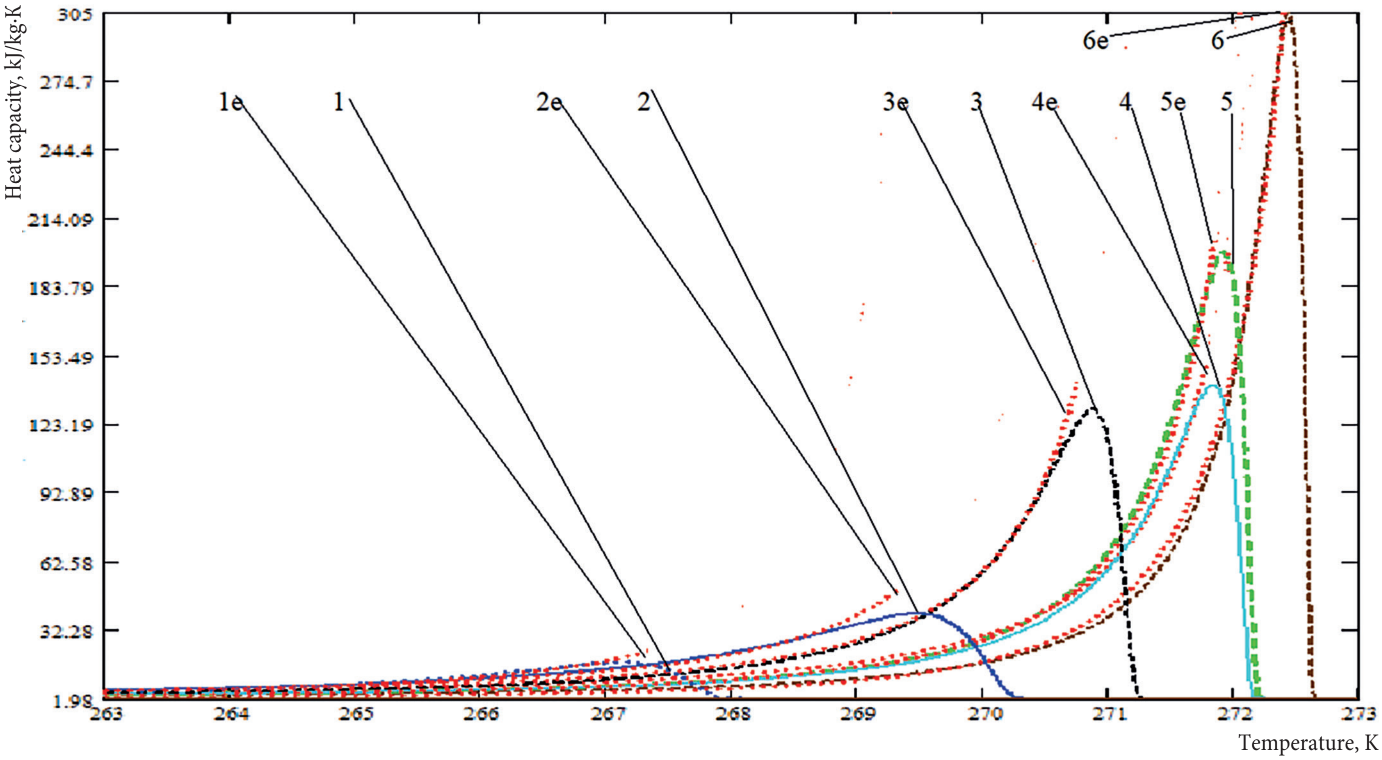

Figure 2. Dependencies of beef heat capacities at different initial moisture levels presented in Table 2

Table 2. Moisture, cryoscopic temperature, enthalpy and parameters μ, θ, δ of the equation of phase transition in beef samples

Number of meat samples	Initial beef moisture w, mass fraction	T_{kr} ±0.05 K	H_{LH}, by (3) (exp.) kJ/kg	H_{LH} (calc.) by (1), kJ/kg	H_{LH}, (calc.) by (5) kJ/kg	μ, non-dimensional	θ, K	δ, K
1	0,370	267,14	45	44.998	49,843	0,0725	2,130	1,100
2	0,450	269.14	91	90,136	85,850	0,2980	1,800	0,96
3	0,600	270,73	interp. 155	155,420	153,364	0,6300	0,920	0,600
4	0,651	271.84	168,5	169.837	169,837	0,7130	0,820	0,400
5	0,700	271,85	198	198.213	198,213	0,8780	0,710	0,416
6	0,751	272,4	220	220.07	220,007	1,0350	0,497	0,28

to take into account that all calculations are true in a range of 243 K ≤ T_{kr} K.

Numbers of curves correspond to the sequential numbers of the rows in Table 2; with that, the numbers with the "e" index correspond to approximations of the experimental values of heat capacities and without the index to calculated values by equation (1).

Figures 3–7 present the graphs of dependencies (6–10) with account for data of Table 2.

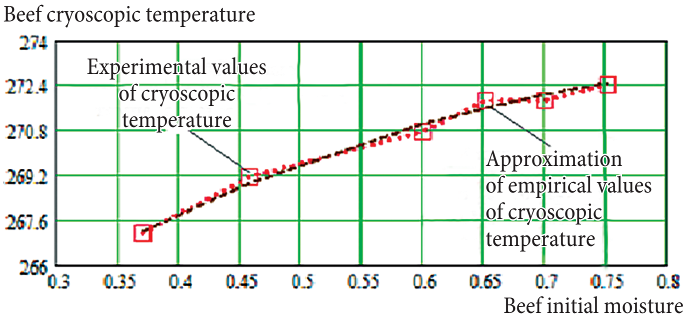

Figure 3. Dependence of the beef cryoscopic temperature by the experimental results and by approximating equation (6)

Upon condition of postulation of the circumstance that at the temperature of the end of phase transition all curves by equation (1), which were calculated for different moisture levels by equations (6–10), should converge in one intersection point at $T_{kr} = 243$ K with the freezing curve of a beef frozen sample (11) (Figure 8), calculated by equation (2), it is necessary to assign a value to constant B that ensures the condition of the postulate in equation (1) for each moisture level. Table 3 gives these values and the polynomial approximation of the set of values (11).

Table 3. Adjusted values of the parameter B for equation (1)

w	0.37	0.45	0.600	0.625	0.700	0.752
$B·10^{-3}$. J/kg·K	7.55	6.911	7.197	7.385	7.325	7.557

$$D(w) = 9{,}125 - 8{,}5w + 8{,}5w^2,\ (\Delta_{error} \pm 5\%) \qquad (11)$$

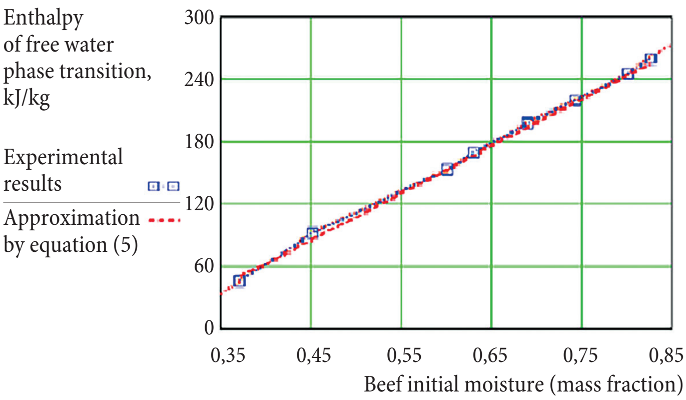

Figure 4. Dependence of enthalpy of phase transition (crystal formation) on the initial moisture of the beef sample by equation (7)

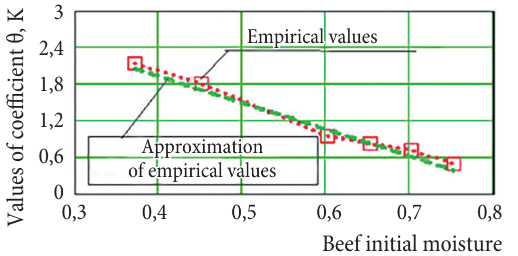

Figure 6. Dependence of the characteristic temperature θ on the initial moisture of beef sample, approximation by equation (9)

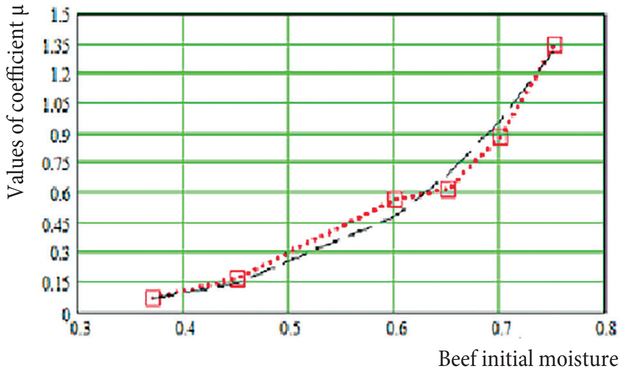

Figure 5. Dependence of the coefficient μ, which characterizes the number of crystals in the mass unit of freezing water, on the initial moisture content by equation (8)

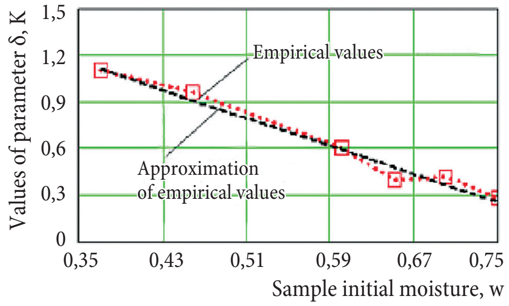

Figure 7. Empirical values of the parameter δ and their approximation depending on the beef initial moisture by equation (10)

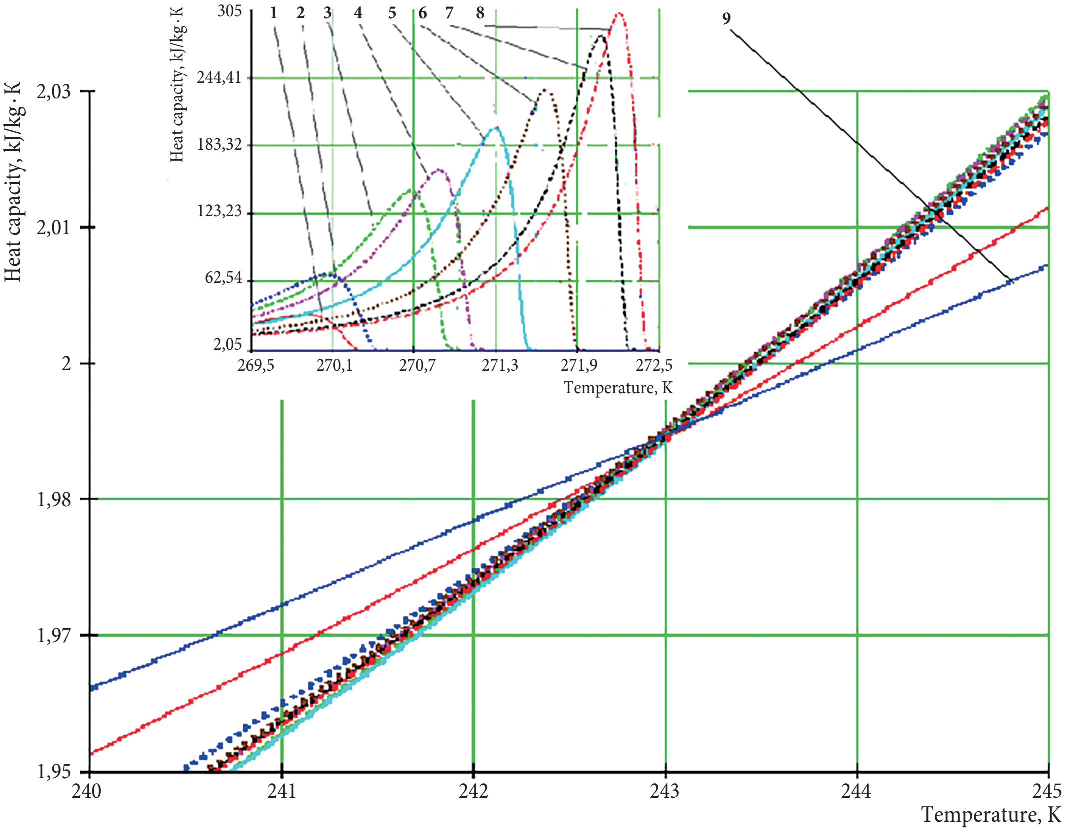

Figure 8. The intersection point of phase transition curves according to equation (1) with account for dependencies (6–10) with freezing curve of beef frozen sample (11) by equation (2)

Conclusion

The calculated model was developed for the beef freezing process in a range of temperatures of free water phase transition realized by the way of crystallization described by the system of equations (1–2, (6–11), linking beef specific heat capacity, temperature and initial moisture.

The proposed model allows predicting beef heat capacity values in a range of the most energy-intensive freezing process.

The development method can be used for similar computational simulation of freezing processes for other meat raw materials and semi-finished products as well as fish.

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