Evaluation of Thermophysical Property Models for Foods

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The thermophysical properties of foods are required in order to calculate process times and to design equipment for the storage and preservation of food. There are a multitude of food items available, whose properties are strongly dependent upon chemical composition and temperature. Composition-based thermophysical property models provide a means of estimating properties of foods as functions of temperature. Numerous models have been developed and the designer of food processing equipment is faced with the challenge of selecting appropriate ones from those available. In this paper selected thermophysical property models are quantitatively evaluated by comparison to a comprehensive experimental thermophysical property data set compiled from the literature.

For ice fraction prediction, the equation by Chen (1985b) performed best, followed closely by that of Tchigeov (1979). For apparent specific heat capacity, the model of Schwartzberg (1976) performed best, and for specific enthalpy prediction, the Chen (1985a) equation gave the best results, followed closely by that of Miki and Hayakawa (1996). Finally, for thermal conductivity, the model by Levy (1981) performed best.

INTRODUCTION

Knowledge of the thermal properties of foods is required to perform the various heat transfer calculations that are involved in the design of food storage and refrigeration equipment and estimating process times for refrigerating, freezing, heating or drying of foods. The thermal properties of foods are strongly dependent upon chemical composition and temperature, and there are a multitude of food items available. It is difficult to generate an experimentally determined database of thermal properties for all possible conditions and compositions of foods. The most viable option is to predict the thermal properties of foods using mathematical models that account for the effects of chemical composition and temperature.

Composition data for foods are readily available in the literature from sources such as Holland et al. (1991) and USDA (1975, 1996). These data consist of the mass fractions of the major components found in food items. Food thermal properties can be predicted by using these composition data in conjunction with temperature-dependent mathematical models of the thermal properties of the individual food constituents.

Thermophysical properties of foods that are often required for heat transfer calculations include ice fraction, specific heat capacity, specific enthalpy, and thermal conductivity. In this paper, prediction methods for estimating these thermophysical properties are quantitatively evaluated by comparing their calculated results with an extensive, experimentally determined, thermophysical property data set compiled from the literature.

Constituents commonly found in food items include water, protein, fat, carbohydrate, fiber, and ash. Choi and Okos (1986) have developed equations presented in Tables 1 and 2 for

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Table 1. Thermal Property Equations for Food Components[a] (–40°C ≤ t ≤ 150°C)

Thermal Property	Food Component	Thermal Property Model
Thermal Conductivity, W/(m·K)	Protein	$k = 1.7881 \times 10^{-1} + 1.1958 \times 10^{-3}t - 2.7178 \times 10^{-6}t^2$
	Fat	$k = 1.8071 \times 10^{-1} - 2.7604 \times 10^{-3}t - 1.7749 \times 10^{-7}t^2$
	Carbohydrate	$k = 2.0141 \times 10^{-1} + 1.3874 \times 10^{-3}t - 4.3312 \times 10^{-6}t^2$
	Fiber	$k = 1.8331 \times 10^{-1} + 1.2497 \times 10^{-3}t - 3.1683 \times 10^{-6}t^2$
	Ash	$k = 3.2962 \times 10^{-1} + 1.4011 \times 10^{-3}t - 2.9069 \times 10^{-6}t^2$
Thermal Diffusivity, m²/s	Protein	$\alpha = 6.8714 \times 10^{-8} + 4.7578 \times 10^{-10}t - 1.4646 \times 10^{-12}t^2$
	Fat	$\alpha = 9.8777 \times 10^{-8} - 1.2569 \times 10^{-10}t - 3.8286 \times 10^{-14}t^2$
	Carbohydrate	$\alpha = 8.0842 \times 10^{-8} + 5.3052 \times 10^{-10}t - 2.3218 \times 10^{-12}t^2$
	Fiber	$\alpha = 7.3976 \times 10^{-8} + 5.1902 \times 10^{-10}t - 2.2202 \times 10^{-12}t^2$
	Ash	$\alpha = 1.2461 \times 10^{-7} + 3.7321 \times 10^{-10}t - 1.2244 \times 10^{-12}t^2$
Density, kg/m³	Protein	$\rho = 1.3299 \times 10^{3} - 5.1840 \times 10^{-1}t$
	Fat	$\rho = 9.2559 \times 10^{2} - 4.1757 \times 10^{-1}t$
	Carbohydrate	$\rho = 1.5991 \times 10^{3} - 3.1046 \times 10^{-1}t$
	Fiber	$\rho = 1.3115 \times 10^{3} - 3.6589 \times 10^{-1}t$
	Ash	$\rho = 2.4238 \times 10^{3} - 2.8063 \times 10^{-1}t$
Specific Heat, J/(kg·K)	Protein	$c_p = 2.0082 \times 10^{3} + 1.2089t - 1.3129 \times 10^{-3}t^2$
	Fat	$c_p = 1.9842 \times 10^{3} + 1.4733t - 4.8008 \times 10^{-3}t^2$
	Carbohydrate	$c_p = 1.5488 \times 10^{3} + 1.9625t - 5.9399 \times 10^{-3}t^2$
	Fiber	$c_p = 1.8459 \times 10^{3} + 1.8306t - 4.6509 \times 10^{-3}t^2$
	Ash	$c_p = 1.0926 \times 10^{3} + 1.8896t - 3.6817 \times 10^{-3}t^2$

[a]From Choi and Okos (1986).

Table 2. Thermal Property Equations for Water and Ice[a] (–40°C ≤ t ≤ 150°C)

	Thermal Property	Thermal Property Model
Water	Thermal Conductivity, W/(m·K)	$k_w = 5.7109 \times 10^{-1} + 1.7625 \times 10^{-3}t - 6.7036 \times 10^{-6}t^2$
	Thermal Diffusivity, m²/s	$\alpha_w = 1.3168 \times 10^{-7} + 6.2477 \times 10^{-10}t - 2.4022 \times 10^{-12}t^2$
	Density, kg/m³	$\rho_w = 9.9718 \times 10^{2} + 3.1439 \times 10^{-3}t - 3.7574 \times 10^{-3}t^2$
	Specific Heat, J/(kg·K)[b]	$c_w = 4.0817 \times 10^{3} - 5.3062t + 9.9516 \times 10^{-1}t^2$
	Specific Heat, J/(kg·K)[c]	$c_w = 4.1762 \times 10^{3} - 9.0864 \times 10^{-2}t + 5.4731 \times 10^{-3}t^2$
Ice	Thermal Conductivity, W/(m·K)	$k_{ice} = 2.2196 - 6.2489 \times 10^{-3}t + 1.0154 \times 10^{-4}t^2$
	Thermal Diffusivity, m²/s	$\alpha_{ice} = 1.1756 \times 10^{-6} - 6.0833 \times 10^{-9}t + 9.5037 \times 10^{-11}t^2$
	Density, kg/m³	$\rho_{ice} = 9.1689 \times 10^{2} - 1.3071 \times 10^{-1}t$
	Specific Heat, J/(kg·K)	$c_{ice} = 2.0623 \times 10^{3} + 6.0769t$

[a]From Choi and Okos (1986).
[b]For the temperature range of –40°C to 0°C.
[c]For the temperature range of 0°C to 150°C.

predicting the thermal properties of these components and ice as functions of temperature in the range of –40°C to 150°C. Choi and Okos (1986) report that the equations presented in Tables 1 and 2 produce an error of 6% or less.

Composition-based prediction methods for estimating the thermal properties of foods require detailed knowledge of the mass fractions of the various components that make up the food. Composition data for foods are readily available in the literature and can be obtained from sources such as Holland et al. (1991) and USDA (1975, 1996).

In general, the thermophysical properties of a food item are well behaved when the temperature is above the initial freezing point. However, below the initial freezing point, the thermophysical properties of a food item vary greatly due to the complex processes involved during freezing. Prior to freezing, sensible heat must be removed from the food to decrease its temperature to that at which pure ice first begins to crystallize. This initial freezing point is somewhat lower than the freezing point of pure water due to dissolved substances in the moisture within the food. At the initial freezing point, as a portion of the water within the food crystallizes, the remaining solution becomes more concentrated. Thus, the freezing point of the unfrozen portion of the food is further reduced. The temperature continues to decrease as the separation of ice crystals increases the concentration of the solutes in solution and depresses the freezing point further. The ice and water fractions in the frozen food depend upon temperature. Since the thermophysical properties of ice and water are quite different, the thermophysical properties of the frozen food vary dramatically with temperature.

PREDICTION METHODS

Ice Fraction

The thermophysical properties of frozen foods depend strongly on the fraction of ice within the food and it is necessary to determine the mass fraction of water that has crystallized. Foods can be considered to consist of three constituents: water, soluble substances, and insoluble substances. Below its initial freezing temperature, the item contains ice, unfrozen water, soluble solids, and insoluble solids. As the temperature decreases further there is an increase in the mass fraction of ice, w_{ice}, and a decrease in the mass fraction of unfrozen water, w_w. The mass fractions of ice and water are then related as follows:

$$w_{wo} = w_{ice} + w_w \tag{1}$$

where w_{wo} is the total mass fraction of water.

High moisture content food items have been modeled as ideal dilute solutions (Heldman 1974; Schwartzberg 1976; Chen 1985a, 1987, 1988; Pham 1987; Pham et al. 1994; Murakami and Okos 1996), assuming that Raoult's law is valid. The freezing point depression equation is then given by

$$\frac{d}{dT}(\ln x_w) = \frac{M_w L_o}{RT^2} \tag{2}$$

which can be integrated to yield

$$\ln x_w = \frac{M_w L_o}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right) \tag{3}$$

where x_w is the mole fraction of water in solution, M_w is the molar mass of water, L_o is the latent heat of fusion of water, R is the ideal gas constant, T_o is the freezing point of water, and T is the freezing point of the food.

In addition, the mole fraction of water in solution, x_w, is given by

$$x_w = \frac{w_w / M_w}{w_w / M_w + w_s / M_s} \tag{4}$$

An effective molar mass M_s for the solids is used since it would be difficult to determine the actual molar mass of the soluble solids. This effective molar mass is empirically determined from freezing point data so as to correlate with experimentally determined ice content data.

By manipulating Equations (1) through (4), the mass fraction of ice within high moisture content food items is obtained. Chen (1985b) proposed the following model for predicting the mass fraction of ice in a food item:

$$w_{ice} = \left(\frac{w_s R T_o^2}{M_s L_o}\right)\left(\frac{(t_f - t)}{t_f t}\right) \quad (5)$$

Based upon experimental data, Chen (1985a) developed the following equation for estimating the effective molar mass of the soluble solids in lean beef and cod muscle:

$$M_s = \frac{n}{1 - w_s} \quad (6)$$

where n = 535.4 for lean beef and n = 404.9 for cod muscle. A similar equation was developed to estimate the effective molar mass of the soluble solids in orange juice and apple juice:

$$M_s = \frac{n}{1 + 0.25 w_s} \quad (7)$$

where n = 200 for both orange juice and apple juice.

Schwartzberg (1976), however, suggested that the effective molar mass of the soluble solids within the food item can be approximated by

$$M_s = \frac{w_s R T_o^2}{-(w_{wo} - w_b) L_o t_f} \quad (8)$$

where w_{wo} is the mass fraction of water in the unfrozen food item and w_b is the mass fraction of “bound water” within the food. Bound water is that portion of the water within a food item which is bound to solids within the food, and thus is unavailable for freezing. The mass fraction of bound water may be estimated as follows:

$$w_b = 0.4 w_p \quad (9)$$

where w_p is the mass fraction of protein in the food item.

By combining Equations (5) and (8), a simple expression for predicting the ice fraction was developed (Miles 1974):

$$w_{ice} = (w_{wo} - w_b)\left(1 - \frac{t_f}{t}\right) \quad (10)$$

Equation (10) underestimates the ice fraction at temperatures near the initial freezing point and overestimates the ice fraction at lower temperatures. Tchigeov (1979) proposed an empirical relationship to estimate the mass fraction of ice:

$$w_{ice} = w_{wo}\left[\frac{1.105}{1 + \frac{0.7138}{\ln(t_f - t + 1)}}\right] \quad (11)$$

Fikiin (1996) notes that Equation (11) is applicable to a wide variety of food items and provides satisfactory accuracy.

Specific Heat

In unfrozen foods, specific heat is relatively constant with respect to temperature. However, for frozen foods, there is a large decrease in specific heat capacity as the temperature decreases. The specific heat capacity of a food item at temperatures above its initial freezing point is obtained from the mass average of the specific heat capacities of the food components:

$$c_u = \sum c_i w_i \tag{12}$$

where c_i is the specific heat capacity of the individual food components and w_i is the mass fraction of the food components. If detailed composition data are not available, a simpler equation for the specific heat capacity of an unfrozen food item, presented by Chen (1985a), can be used:

$$c_u = 4190 - 2300 w_s - 628 w_s^3 \tag{13}$$

where c_u is the specific heat capacity of the unfrozen food item J/(kg·K) and w_s is the mass fraction of the solids in the food item.

Below the freezing point the sensible heat due to temperature change and the latent heat due to the fusion of water are important. Latent heat is released over a range of temperatures, and an apparent specific heat capacity can be used to account for both the sensible and latent heat effects. Then, the specific enthalpy of a frozen food can be modeled as the sum of the constituent enthalphies:

$$h = h_s w_s + h_w w_w + h_{ice} w_{ice} \tag{14}$$

The apparent specific heat capacity, c_a, is given as

$$c_a = \frac{\partial h}{\partial T} = c_s w_s + c_w w_w + c_{ice} w_{ice} + h_w \frac{\partial w_w}{\partial T} + h_{ice} \frac{\partial w_{ice}}{\partial T} \tag{15}$$

Schwartzberg (1976) assumed that high moisture content food items can be modeled as ideal dilute solutions and developed the following equation for the apparent specific heat capacity of high moisture content food items:

$$c_a = c_u + (w_b - w_{wo})\Delta c + E w_s \left(\frac{R T_o^2}{M_w t^2} - 0.8\,\Delta c \right) \tag{16}$$

The term Δc is the difference between the specific heat capacities of water and ice ($\Delta c = c_w - c_{ice}$), E is the ratio of the molar masses of water, M_w, and food solids, M_s, ($E = M_w/M_s$), R is the ideal gas constant, T_o is the freezing point of water ($T_o = 273.2\,\mathrm{K}$), and t is the food temperature (°C).

Schwartzberg (1981) expanded his earlier work and developed an alternative method for determining the apparent specific heat capacity of a food item below the initial freezing point:

$$c_a = c_f + (w_{wo} - w_b)\left[\frac{L_o(T_o - T_f)}{T_o - T}\right] \tag{17}$$

Equation (17) has been simplified by Delgado et al. (1990) for the specific heat during thawing as

$$c_a = a' + \frac{b'}{(T_o - T)^2} \tag{18}$$

and during freezing as

$$c_a = m' + n'(T_o - T) \tag{19}$$

where the parameters a', b', m', and n' are determined via a non-linear least squares fit to empirical calorimetric measurements. Delgado et al. (1990) have determined these parameters for two cultivars of strawberries.

A slightly simpler apparent specific heat capacity equation, which is similar in form to that of Schwartzberg (1976), was developed by Chen (1985a) as an expansion of Siebel's equation (Siebel 1892) for specific heat capacity:

$$c_a = 1550 + 1260 w_s + \frac{w_s R T_o^2}{M_s t^2} \tag{20}$$

If the effective molar mass of the soluble solids is unknown, Equation (8) may be used to estimate the effective molar mass and Equation 20 becomes

$$c_a = 1550 + 1260 w_s - \frac{(w_{wo} - w_b) L_o t_f}{t^2} \tag{21}$$

Enthalpy

Above the freezing point, specific enthalpy consists of sensible energy, while below the freezing point, specific enthalpy consists of both sensible and latent energy. Equations for specific enthalpy may be obtained by integrating expressions of specific heat capacity with respect to temperature:

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \tag{22}$$

For food items that are at temperatures above their initial freezing point, the specific enthalpy may be determined by integrating Equation (12) to yield

$$h = \sum h_i w_i = \sum \int c_i w_i \, dT \tag{23}$$

Integration of Chen's (1985a) specific heat correlation yields

$$h = (t - t_f)(4190 - 2300w_s - 628w_s^3) \quad (24)$$

This equation, however, would predict zero specific enthalpy at the initial freezing point of the food item. Typically, in the literature for food refrigeration, the reference temperature for zero specific enthalpy is –40ºC. In order to make Equation (24) consistent with zero specific enthalpy at –40ºC, an additional term must be added to Equation (24):

$$h = h_f + (t - t_f)(4190 - 2300w_s - 628w_s^3) \quad (25)$$

where h_f is the specific enthalpy at the initial freezing point and may be estimated as discussed in the following section.

For food items that are at temperatures below the initial freezing point, mathematical expressions for specific enthalpy are also obtained by integrating the specific heat equations. Integration of Equation (16) between a reference temperature, T_r, and the food temperature, T, leads to the following expression for the specific enthalpy of a frozen food item (Schwartzberg 1976):

$$h = (T - T_r)\left[c_u + (w_b - w_{wo})\Delta c + Ew_s\left(\frac{RT_o^2}{M_w(T_o - T_r)(T_o - T)} - 0.8\Delta c\right)\right] \quad (26)$$

Pham et al. (1994) have rewritten Schwartzberg's specific enthalpy model, Equation (26), as follows:

$$h = A_2 + c_f t + \frac{B_2}{t} \quad (27)$$

where the specific heat is

$$c_f = c_u + (w_b - w_{wo} - 0.8Ew_s)\Delta c \quad (28)$$

$$B_2 = -Ew_sRT_o^2/M_w \quad (29)$$

and A_2 is an integration constant. Pham et al. (1994) have performed experiments to determine the specific enthalpy of 27 food items for the temperature range –40°C to 40°C and found that Equation (26) provided a good fit to their experimental data. Thus, they presented their experimental specific enthalpy data in terms of the coefficients A_2, c_f, and B_2, in Equation (27), rather than in tabular temperature-enthalpy form.

By integrating Equation (20) between a reference temperature, T_r, and the food temperature, T, Chen (1985a) obtained the following expression for specific enthalpy below the initial freezing point:

$$h = (t - t_r)\left(1550 + 1260w_s + \frac{w_sRT_o^2}{M_stt_r}\right) \quad (30)$$

By substitution of Equation (8) for the effective molar mass of the soluble solids, M_s, Equation (30) becomes

$$h = (t - t_r)\left(1550 + 1260 w_s + \frac{(w_{wo} - w_b) L_o t_f}{t_r t}\right) \quad (31)$$

Miki and Hayakawa (1996) developed a semi-theoretical equation for the specific enthalpy of frozen food items that takes the following form:

$$h = A_1\left(\frac{1}{t_r} - \frac{1}{t}\right) + B_1 \ln\left(\frac{t}{t_r}\right) + C_1 (t - t_r) \quad (32)$$

where the empirical coefficients A_1, B_1, and C_1 are given as

$$A_1 = -333\,290 w_{wo} t_f \quad (33)$$

$$B_1 = (-2088 c_w - c_{ice}) w_{wo} t_f \quad (34)$$

$$C_1 = (c_{ice} + 3.45 t_f) w_{wo} + c_s (1 - w_{wo}) \quad (35)$$

As an alternative to the specific enthalpy equations developed by integration of specific heat capacity equations, Chang and Tao (1981) developed empirical correlations for specific enthalpy. Their correlations are given as functions of water content, initial and final temperatures, and food type (meat, juice, or fruit/vegetable) and have the following form:

$$h = h_f \left\lfloor y \bar{T} + (1 - y) \bar{T}^z \right\rfloor \quad (36)$$

where $\bar{T}$ is a reduced temperature, [$\bar{T} = (T - 227.6)/(T_f - 227.6)$], and y and z are correlation parameters. In the method by Chang and Tao (1981), the reference temperature is –45.6°C (–50°F), which corresponds to zero specific enthalpy. By performing a regression analysis on experimental data available in the literature, Chang and Tao developed the following expressions for the correlation parameters, y and z, used in Equation (36) for the meats group, given as

$$y = 0.316 - 0.247(w_{wo} - 0.73) - 0.688(w_{wo} - 0.73)^2 \quad (37)$$

$$z = 22.95 - 54.68(y - 0.28) - 5589.03(y - 0.28)^2 \quad (38)$$

and for the fruit, vegetable, and juice group, given as

$$y = 0.362 - 0.0498(w_{wo} - 0.73) - 3.465(w_{wo} - 0.73)^2 \quad (39)$$

$$z = 27.2 - 129.04(y - 0.23) - 481.46(y - 0.23)^2 \quad (40)$$

Correlations were also developed for the initial freezing temperature, T_f, for use in Equation (36) as a function of water content. For the meat group,

$$T_f = 271.18 + 1.47 w_{wo} \tag{41}$$

and for the fruit/vegetable group,

$$T_f = 287.56 - 49.19 w_{wo} + 37.07 w_{wo}^2 \tag{42}$$

and for the juice group,

$$T_f = 120.47 + 327.35 w_{wo} - 176.49 w_{wo}^2 \tag{43}$$

The specific enthalpy of a food item at its initial freezing point is also required for use in Equation (36). Chang and Tao (1981) suggest the following correlation for determining the specific enthalpy of the food item at its initial freezing point:

$$h_f = 9792.46 + 405.096 w_{wo} \tag{44}$$

Thermal Conductivity

The thermal conductivity of a food item depends upon the composition, structure, and temperature of the food item. Early work in the modeling of the thermal conductivity of foods includes Eucken's adaption of Maxwell's equation (Eucken 1940). This model is based upon the thermal conductivity of dilute dispersions of small spheres in a continuous phase:

$$k = k_c \frac{1 - [1 - a(k_d / k_c)]b}{1 + (a-1)b} \tag{45}$$

In an effort to account for the different structural features of foods, Kopelman (1966) developed thermal conductivity models for both homogeneous and fibrous food items. The differences in thermal conductivity parallel and perpendicular to the food fibers are taken into account. For an isotropic, homogeneous two-component system composed of continuous and discontinuous phases, in which the thermal conductivity is independent of the direction of heat flow, Kopelman (1966) developed the following expression for thermal conductivity, k:

$$k = k_c \left[\frac{1 - L^2}{1 - L^2(1 - L)} \right] \tag{46}$$

In developing Equation (46), it was assumed that the thermal conductivity of the continuous phase is much larger than the thermal conductivity of the discontinuous phase. However, if the thermal conductivity of the discontinuous phase is much larger than the thermal conductivity of the continuous phase, then the following expression is used to calculate the thermal conductivity of the isotropic mixture:

$$k = k_c \left[\frac{1 - M}{1 - M(1 - L)} \right] \tag{47}$$

For an anisotropic, fibrous two-component system in which the thermal conductivity is dependent upon the direction of heat flow, Kopelman (1966) developed two expressions for thermal conductivity. For heat flow parallel to the food fibers, Kopelman (1966) proposed the following expression for thermal conductivity, $k_{||}$, given as

$$k_{||} = k_c\left[1 - N^2\left(1 - \frac{k_d}{k_c}\right)\right] \tag{48}$$

and for heat flow perpendicular to the food fibers where N^2 is the volume fraction of the discontinuous phase in fibrous food product:

$$k_{\perp} = k_c\left[\frac{1 - P}{1 - P(1 - N)}\right] \tag{49}$$

Levy (1981) introduced a modified version of the Eucken-Maxwell equation as follows:

$$k = \frac{k_2[(2 + \Lambda) + 2(\Lambda - 1)F_1]}{(2 + \Lambda) - (\Lambda - 1)F_1} \tag{50}$$

where Λ is the thermal conductivity ratio ($\Lambda = k_1/k_2$), k_1 is the thermal conductivity of component 1, and k_2 is the thermal conductivity of component 2. The parameter, F_1, introduced by Levy (1981) is given as

$$F_1 = 0.5\left\{\left(\frac{2}{\sigma} - 1 + 2\phi_1\right) - \left[\left(\frac{2}{\sigma} - 1 + 2\phi_1\right)^2 - \frac{8\phi_1}{\sigma}\right]^{1/2}\right\} \tag{51}$$

where

$$\sigma = \frac{(\Lambda - 1)^2}{(\Lambda + 1)^2 + \frac{\Lambda}{2}} \tag{52}$$

and ϕ_1 is the volume fraction of component 1:

$$\phi_1 = \left[1 + \left(\frac{1}{w_1} - 1\right)\left(\frac{\rho_1}{\rho_2}\right)\right]^{-1} \tag{53}$$

When foods consist of more than two distinct phases, the two-component methods for the prediction of thermal conductivity must be applied successively to obtain the thermal conductivity of the food product. For example, in the case of frozen food, the thermal conductivity of the ice and liquid water system is calculated first using one of the above mentioned methods. The resulting thermal conductivity of the ice/water system is then combined successively with the thermal conductivity predicted for each remaining food constituent to determine the thermal conductivity of the food product.

For multi-component systems, numerous researchers have proposed the use of parallel and series thermal conductivity models based upon the analogy with electrical resistance (Murakami and Okos 1989). The parallel model is simply the sum of the thermal conductivities of the food constituents multiplied by their volume fractions:

$$k = \sum_{i=1}^{n} \phi_i k_i \tag{54}$$

where the volume fraction of constituent *i* is given by

$$\phi_i = \frac{\dfrac{w_i}{\rho_i}}{\displaystyle\sum_{j=1}^{n} \frac{w_j}{\rho_j}} \tag{55}$$

The series model is the reciprocal of the sum of the volume fractions divided by their thermal conductivities:

$$k = \frac{1}{\displaystyle\sum_{i=1}^{n} \frac{\phi_i}{k_i}} \tag{56}$$

These two models have been found to predict the upper and lower bounds of the thermal conductivity of most food items. Saravacos and Kostaropoulos (1995) suggest that the parallel structural model can be used to calculate the thermal conductivity of porous food items including granular, puffed, or freeze-dried foods, while the series model can be used to calculate the thermal conductivity of low-porosity food items, including gelatinized starchy foods or high-sugar foods.

A thermal conductivity model that is intermediate to the series and parallel models can be obtained from the weighted geometric mean of the constituents as follows (Rahman et al. 1991):

$$k = \prod_{i=1}^{n} k_i^{\phi_i} \tag{57}$$

Rahman et al. (1997) have noted that the series and parallel thermal conductivity models do not take into account the natural arrangement of component phases within a food item. They developed the following model to account for the residual effects of temperature and structure of a food item:

$$\alpha = \frac{k - \phi_a k_a}{(1 - \phi_a - \phi_w) k_s + \phi_w k_w} \tag{58}$$

Rahman et al. (1997) experimentally determined the values of α for numerous fruits and vegetables and correlated them as

$$\frac{\alpha}{1 - \phi_a + \dfrac{k_a}{(k_w)_r}} = 0.996 \left(\frac{T}{T_r}\right)^{0.713} w_w^{0.285} \tag{59}$$

This model is limited to moisture content between 14% and 88%, porosity between 0.0 and 0.56, and temperature between 5°C and 100°C.

COMPARISION OF MODELS AGAINST DATA

The values from the thermophysical property models were compared with an extensive empirical thermophysical property data set compiled from the literature, shown in Table 3. The composition data for the food items listed in Table 3 were obtained from the USDA (1996).

The specific enthalpy, apparent specific heat, and ice content with respect to temperature for a variety of foods have been established by the well-known enthalpy-moisture content-temperature diagrams from Riedel (1951, 1956, 1957, 1960). Numerous researchers have used these data to validate their thermophysical property models (Chen 1985a, 1985b, Pham 1987, Schwartzberg 1976) and these data can also be found in other sources such as ASHRAE (1981), Charm (1971), and Rolfe (1968).

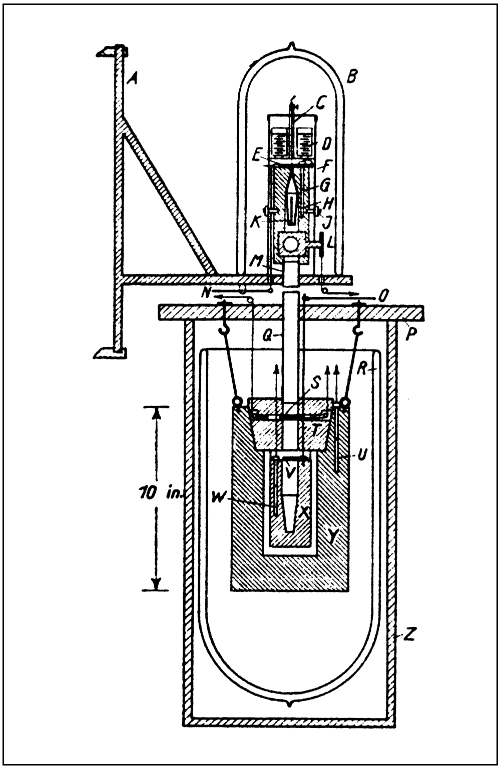

Figure 1. Calorimeter from Riedel (1951)

To obtain the enthalpy-moisture content-temperature data, Riedel (1951) constructed an elaborate calorimeter, shown in Figure 1. The upper portion of the device contains a conic copper box (K), containing a small food sample (3 to 5 g), that is brought into close contact with a copper cylinder (G). The temperature of the copper cylinder is held constant through the use of liquid air (D) and heating coils (not shown). The upper portion of the apparatus is contained within a dewar vessel (B) to ensure that it is thermally insulated from the surroundings. Once the food sample has reached the desired temperature, the small conical box containing the food sample is released into the lower portion of the calorimeter, which consists of a copper cylinder (X) in which the conical copper sample box rests.

The copper cylinder is surrounded by a large iron block (Y) that provides a constant ambient temperature and the lower portion is insulated by a large dewar vessel (R). Temperature changes of the copper cylinder are measured with a platinum resistance thermometer (U) and are used to obtain specific heat and specific enthalpy data. Riedel (1951) claims that calibration experiments performed with this calorimeter, using water as the test substance, yielded specific heat capacity and latent heat of fusion values that agreed within 0.2% of the best data given in the literature. Additional apparent specific heat data were obtained from Fleming (1969) using adiabatic calorimeter that agreed within 4% of the best data given in the literature.

The thermal conductivity data used in this evaluation were obtained from Pham (1990), who conducted a critical analysis of data available in the literature. The criteria for the selection of these data included that the product composition (or at least water content) be known, that there should be no obviously unusual trend that contradicts the majority of other data, and that the measuring equipment must have been calibrated against a material with a known thermal conductivity value. The thermal conductivity data selected by Pham were originally

Table 3. Empirical Thermophysical Property Data Set

Thermal Property	No. of Data Points	Material	Reference
Ice Fraction	13	Orange Juice (w_{wo} = 0.89)	Riedel (1951)
	14	Lean Beef (w_{wo} = 0.74)	Riedel (1957), Rolfe (1968)
	14	Cod Muscle (w_{wo} = 0.82)	Riedel (1960), Rolfe (1968)
Apparent Specific Heat Capacity	10	Cod Muscle (w_{wo} = 0.82)	Riedel (1956)
	10	Lean Beef (w_{wo} = 0.82)	Riedel (1957)
	7	Lamb Kidneys (w_{wo} = 0.798)	Fleming (1969)
	7	Lean Lamb Loin (w_{wo} = 0.649)	Fleming (1969)
	7	Moderately Fatty Lamb Loin (w_{wo} = 0.525)	Fleming (1969)
	7	Fatty Lamb Loin (w_{wo} = 0.444)	Fleming (1969)
	7	Veal (w_{wo} = 0.775)	Fleming (1969)
Specific Enthalpy	5	Apple Juice (w_{wo} = 0.872)	Riedel (1951)
	5	Orange Juice (w_{wo} = 0.89)	Riedel (1951)
	16	Cod (w_{wo} = 0.80)	Riedel (1956)
	16	Haddock (w_{wo} = 0.84)	Riedel (1956)
	16	Perch (w_{wo} = 0.79)	Riedel (1956)
	18	Lean Beef (w_{wo} = 0.74)	Riedel (1957)
	16	Cod Muscle (w_{wo} = 0.82)	Riedel (1960)
Thermal Conductivity	32	Beef	Pham (1990)
	8	Fish	Pham (1990)
	20	Lamb	Pham (1990)
	9	Poultry	Pham (1990)

obtained by either the guarded hot plate method or the line source method. The evaluation by Pham resulted in the selection of 203 thermal conductivity data points from 11 sources. These thermal conductivity measurement techniques produced an error of 5% or less with a standard deviation of 5% or less when tested with substances of known thermal conductivity.

Food composition data in the USDA Nutrient Database for Standard Reference were compiled from published and unpublished sources. Published sources include the scientific and technical literature while the unpublished data are from the food industry, other government agencies and research conducted under contracts initiated by the Agricultural Research Service (ARS) (USDA 1999). Protein content was calculated from the level of total nitrogen in the food, using conversion factors recommended by Jones (1941). Fat content was determined by gravimetric methods, including extraction methods that employ ether or a mixed solvent system consisting of chloroform and methanol, or acid hydrolysis. Carbohydrate content was determined as the difference between 100% and the sum of the percentages of water, protein, fat, and ash (USDA 1999). Although the analysis of error associated with the measurement of the composition data reported by the USDA is not complete, when such analysis is available, the error in the amount of each food constituent is generally less than 10%.

Tables 4 through 7 summarize the statistical analyses that were performed on the thermophysical property models discussed in this paper. For each of the models, the average absolute

Table 4. Statistical Analysis of Ice Fraction Models

Prediction Method	Average Absolute Prediction Error, %	Standard Deviation, %	95% Confidence Range, %	Kurtosis	Skewness
Chen (1985a)[a]	4.04	8.86	±3.00	31.2	5.44
Chen (1985b)[b]	10.6	7.45	±2.52	–1.32	0.639
Miles (1974)	10.5	7.43	±2.51	–1.32	0.653
Tchigeov (1979)	4.75	8.55	±2.89	12.7	3.60

[a]Ice fraction model of Chen (1985a) using Equations (6) and (7) to calculate molar mass.
[b]Ice fraction model of Chen (1985b) using Equation (8) to calculate molar mass.

prediction error (%), the standard deviation (%), the 95% confidence range of the mean (%), the kurtosis, and the skewness are presented.

Ice Fraction

As shown in Table 4, the method by Chen (1985b) for calculating ice fraction, in conjunction with the empirical correlations by Chen (1985a) for effective molar mass, Equations (6) and (7), produced an average absolute prediction error of 4.04%, with a 95% confidence range of ±3.00%, as shown in Table 4. In addition, the distribution of prediction errors was sharply peaked around the average absolute prediction error as evidenced by the large, positive value for the kurtosis, 31.2. The method by Chen (1985a) predicted ice fractions for beef and orange juice very well, producing average absolute prediction errors of less than 1.8%. The average absolute prediction error for the fish data set was considerably larger, 8.2%.

Using Equation (8) (Schwartzberg 1976) to approximate effective molar mass reduces the method by Chen (1985a) to that reported by Miles (1974). Thus, when using Equation (8) for effective molar mass, both the method by Chen and Miles' method produce identical results with a large average absolute prediction error of 10.6% and a 95% confidence range of ±7.45%. The average absolute prediction errors for these two methods ranged from 4.5% for the beef data set to 20% for the orange juice data.

The ice fraction equation of Tchigeov (1979) produced an average absolute prediction error of 4.75% with a 95% confidence range of ±2.89%. In addition, the distribution of prediction errors was sharply peaked around the average absolute prediction error as evidenced by the large, positive value for the kurtosis, 12.7. Tchigeov's equation performed consistently for all the food types tested. Best results were with the fish data set, producing an average absolute prediction error of 2.3%. The average absolute prediction error for the beef data set was 5.3% while for the orange juice data set, the average absolute prediction error was 7.1%.

Both Chen's method and Tchigeov's equation underestimated the ice fraction, and the error tended to decrease as the temperature of the food item decreased. The maximum error occurred near the initial freezing point of the food item. The method of Miles (1974) exhibited uniform error as a function of temperature.

The performance of both the ice fraction method by Chen (1985b) and the simple ice fraction equation reported by Miles (1974) validate the primary assumption upon which these models were derived, namely, that high moisture content food items can be considered to behave as ideal dilute solutions. Thus, these methods would be expected to produce acceptable results for foods of high moisture content.

Specific Heat

As shown in Table 5, the three apparent specific heat models produced large average absolute prediction errors along with large prediction variations. All the models produced relatively small

Table 5. Statistical Analysis of Apparent Specific Heat Capacity Models

Estimation Method	Average Absolute Prediction Error, %	Standard Deviation, %	95% Confidence Range, %	Kurtosis	Skewness
Chen (1985a)	20.5	25.6	±6.93	23.0	4.19
Schwartzberg (1976)	19.3	25.4	±6.87	24.6	4.39
Schwartzberg (1981)	19.7	25.1	±6.80	25.5	4.51

prediction errors for the fish and beef data sets and very large prediction errors for the lamb and veal data sets. The two models by Schwartzberg (1976, 1981) performed similarly, exhibiting average absolute prediction errors of approximately 20% with large standard deviations of approximately 25%. Their best performance was obtained with the fish data set, resulting in average absolute prediction errors of 10%, while their worst agreement was obtained with the veal data set, producing average absolute prediction errors of 24%. The method by Chen (1985a) produced a slightly larger average absolute prediction error of 20.5% with a standard deviation of 25.6%. The method by Chen performed best with the fish data set, producing an average absolute prediction error of 6.9% and worst with the veal data set, yielding an average absolute prediction error of 27%.

All of the apparent specific heat models exhibited large variations in prediction error, and the absolute value of the prediction error decreased as the temperature decreased. The maximum errors tended to occur near the initial freezing point of the food item.

Enthalpy

The specific enthalpy equation developed by Chen (1985a) produced an average absolute prediction error of 5.09% along with a standard deviation of 3.98%, as shown in Table 6. The average absolute prediction errors for the method by Chen method (1985b) ranged from 4.2% for the fish data set to 15% for the orange juice data set. On average, the method by Chen (1985b) tended to underpredict the specific enthalpy of foods.

The specific enthalpy equation developed by Miki and Hayakawa (1996) produced an absolute average prediction error of 5.86% and exhibited more consistency for all the food types tested as compared with the equation by Chen (1985a). For example, the specific enthalpy equation by Chen produced a very large absolute average prediction error for the orange juice data set of 15%, while the Miki and Hayakawa method predicted the orange juice data very well, producing an average absolute prediction error of 1.3%. The method of Miki and Hayakawa tended to underpredict slightly the specific enthalpy for orange juice and overpredict the specific enthalpy for all other food types tested.

The average absolute prediction error of the empirical specific enthalpy equation by Chang and Tao (1981) was found to be 7.56% and the spread of the absolute prediction errors was large, as evidenced by the relatively large standard deviation of 6.61%. The equation by Chang and Tao performed consistently for all the data sets tested.

The specific enthalpy model presented by Schwartzberg (1976) produced an average absolute prediction error of 6.48% with a moderate standard deviation of 4.64%. The model by Schwartzberg (1976) model performed consistently, with average absolute prediction errors ranging from 2.6% for the orange juice data set to 7.0% for the fish data set.

The specific enthalpy equation by Chen (1985a) produced its greatest errors near the initial freezing point and the error was reduced as the temperature decreased. The specific enthalpy equation by Miki and Hayakawa (1996) produced the greatest errors just below the initial freezing point and near –30°C. The Schwartzberg (1976) specific enthalpy model tended to underestimate near the initial freezing point and near –40°C and overestimated temperatures between

Table 6. Statistical Analysis of Specific Enthalpy Models

Estimation Method	Average Absolute Prediction Error, %	Standard Deviation, %	95% Confidence Range, %	Kurtosis	Skewness
Chen (1985a)	5.09	3.98	±0.828	4.85	1.83
Chang and Tao (1981)	7.56	6.61	±1.38	0.813	1.11
Miki and Hayakawa (1996)	5.86	3.03	±0.632	–0.232	–0.0511
Schwartzberg (1976)	6.48	4.64	±0.966	2.30	1.10

–40°C and the initial freezing point. The equation of Chang and Tao (1981), however, overestimated near the initial freezing point and near –40°C, while underpredicting at temperatures between –40°C and the initial freezing point.

The specific enthalpy equation by Chen (1985a) produced good results for apple juice, fish, and beef, but large prediction errors for orange juice. The specific enthalpy equation of Miki and Hayakawa (1996) agreed well for both apple juice and orange juice and produced good results for the fish and beef data sets. The model by Schwartzberg (1976) performed very well for both apple and orange juice. It also produced good results for the beef and fish data sets. The equation of Chang and Tao (1981) produced good results for apple juice and performed adequately for fish, beef, and orange juice.

The good agreement for the specific enthalpy models of Chen (1985a), Miki and Hayakawa (1996), and Schwartzberg (1976) validates the primary assumption upon which these models were derived, namely, that high moisture content food items can be considered to behave as ideal dilute solutions. Thus, these models would be expected to produce acceptable results for foods of high moisture content. The empirical specific enthalpy equation of Chang and Tao (1981) is based upon correlations developed from the analysis of data collected on high moisture content foods, and thus, it too would be expected to produce acceptable results for foods of high moisture content ($w_{wo} \geq 0.70$).

Thermal Conductivity

As shown in Table 7, the thermal conductivity model developed by Levy (1981) produced an average absolute prediction error of 6.86% and a standard deviation of 4.89%. The average absolute prediction errors for the method by Levy (1981) ranged from 4.4% for the lamb data set to 9.5% for the poultry data set. The model by Levy produced good results for the lamb, beef, and fish data sets.

The Kopelman (1966) isotropic model produced an average absolute prediction error of 8.08% with a 95% confidence range of ±1.47%, and this model performed consistently for all data sets except for poultry. For the poultry data set, the Kopelman (1966) isotropic model exhibited an average absolute prediction error of 12.6% while for the rest of the data sets, the model produced average absolute prediction errors of 8.3% or less.

The Kopelman (1966) perpendicular model produced an average absolute prediction error of 8.98% with a 95% confidence range of ±1.42%. Similar to the isotropic model, the perpendicular model performed consistently for all data sets except poultry. Thermal conductivity was underpredicted by 4.3% on average for the poultry data set, while overpredicting by no more than 8.5% for the rest of the data sets.

The Eucken-Maxwell (1940) model and the Kopelman (1966) parallel model performed similarly overall and these two models achieved their best results with the poultry data set. The absolute average prediction error for the poultry data set for both these models was 10%. Overall, the Eucken-Maxwell (1940) model and the Kopelman (1966) parallel model produced average absolute prediction errors of approximately 16% with a 95% confidence range of ±2.5%.

Table 7. Statistical Analysis of Thermal Conductivity Models

Prediction Method	Average Absolute Prediction Error, %	Standard Deviation, %	95% Confidence Range, %	Kurtosis	Skewness
Eucken-Maxwell (1940)	16.0	10.6	±2.55	–0.751	0.551
Kopelman Isotropic (1966)	8.08	6.12	±1.47	–0.687	0.604
Kopelman Parallel (1966)	16.4	10.4	±2.49	–0.690	0.516
Kopelman Perpendicular (1966)	8.98	5.90	±1.42	–0.117	0.564
Levy (1981)	6.86	4.98	±1.20	0.633	1.00
Parallel	21.7	13.6	±3.26	–0.900	0.354
Series	33.9	20.3	±4.87	–1.61	–0.0561

The parallel and series models produced very large average prediction errors. The parallel model overpredicted thermal conductivity for all foods tested and yielded an average absolute prediction error of 21.7%, while the series model underpredicted thermal conductivity with an average absolute prediction error of 33.9%. The spread of predictions was also quite large, with standard deviations of 13.6% and 20.3%, respectively. The large prediction errors for these models may be attributed to the fact that the direction of heat flow is not necessarily oriented with respect to the food fibers as assumed.

The Levy (1981) model and Kopelman (1996) isotropic model both tended to predict the thermal conductivity of frozen foods with less error than that of unfrozen foods. The remaining models, however, predicted unfrozen food thermal conductivity with less error than that of frozen food thermal conductivity.

CONCLUSIONS

A quantitative evaluation of selected composition-based, thermophysical property models for high moisture content foods is presented. The performance of each of the models was determined by comparing calculated results with a comprehensive empirical thermophysical property data set compiled from the literature.

For ice fraction prediction, the method by Chen (1985b) performed the best against all the food types tested. However, the method incorporates an empirical estimate for molar mass, which, at the current time, is limited to beef, cod, apple juice, and orange juice. Further development is required to extend the applicability of the method by Chen (1985) to other foods. For all the food types tested, the equation of Tchigeov (1979) performed nearly as well as the method by Chen (1985a) and has the added benefit of being easy to implement. The ice fraction equation of Miles (1974) produced the largest prediction errors.

The three apparent specific heat equations (Chen 1985a, Schwartzberg 1976, 1981) performed similarly, producing large average absolute prediction errors of approximately 20% and large prediction variations. Of the three equations tested, the Schwartzberg (1976) model yielded a slightly lower average absolute prediction error than the other two. The implementation of the Schwartzberg (1981) model could be difficult because it relies on values for the specific heat capacity of a fully frozen food item, which may not be readily available. Of the three equations tested, the equation of Chen (1985a) is the easiest to use, although it produced the largest average absolute prediction error.

The specific enthalpy equation of Chen (1985a) performed the best, while the relations of Miki and Hayakawa (1996) were nearly as good. These latter two methods are easy to implement. The performance of the specific enthalpy equations of Schwartzberg (1976) and Chang and Tao (1981) had greater error.

The thermal conductivity model of Levy (1981) exhibited the lowest average absolute prediction error. The Kopelman (1966) isotropic and perpendicular thermal conductivity models exhibited poorer agreement, but are less cumbersome to implement. The Kopelman parallel model (1966) and the Eucken-Maxwell model (1940) produced large overprediction errors, of 16% on average. The parallel and series electrical-resistance-analogy thermal conductivity models produced the largest prediction errors, with the parallel model overpredicting by 21% and the series model underpredicting by 34%.

In summary, for ice fraction prediction, the equation of Chen (1985b) performed best, followed closely by Tchigeov's (1979). For apparent specific heat, the model of Schwartzberg (1976) performed best, and for specific enthalpy prediction, the Chen (1985a) equation gave the best results, followed closely by Miki and Hayakawa (1996). Finally, for thermal conductivity, the Levy (1981) model performed best.

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NOMENCLATURE

a parameter in Equation (45): $a = 3k_c/(2k_c + k_d)$
a' parameter in Equation (18)
A_1 parameter given by Equation (32), J(K/kg)
A_2 parameter in Equation (27)
b parameter in Equation (45): $b = V_d/(V_c + V_d)$
b' parameter in Equation (18)
B_1 parameter given by Equation (32), J/kg
B_2 parameter in Equation (27)
c_a apparent specific heat capacity, J/(kg·K)
c_f specific heat capacity of fully frozen food, J/(kg·K)
c_i specific heat capacity of i^{th} food component, J/(kg·K)
c_{ice} specific heat capacity of ice, J/(kg·K)
c_p constant pressure specific heat capacity, J/(kg·K)
c_s specific heat capacity of food solids, J/(kg·K)
c_u specific heat capacity of unfrozen food, J/(kg·K)
c_w specific heat capacity of water, J/(kg·K)
C_1 parameter given by Equation (32), J/(kg·K)
E ratio of the molar masses of water and solids: $E = M_w/M_s$
F_1 parameter given by Equation (51)
h specific enthalpy, J/kg
h_f specific enthalpy at initial freezing temperature, J/kg
h_i specific enthalpy of the i^{th} food component, J/kg
h_{ice} specific enthalpy of ice, J/kg
h_s specific enthalpy of food solids, J/kg
h_w specific enthalpy of water, J/kg
k thermal conductivity, W/(m·K)
k_1 thermal conductivity of component 1, W/(m·K)
k_2 thermal conductivity of component 2, W/(m·K)
k_a thermal conductivity of air, W/(m·K)
k_c thermal conductivity of continuous phase, W/(m·K)
k_d thermal conductivity of discontinuous phase, W/(m·K)
k_i thermal conductivity of the i^{th} component, W/(m·K)
k_s thermal conductivity of food solids, W/(m·K)
$(k_w)_r$ thermal conductivity of water at the reference temperature, T_r, W/(m·K)
$k_{||}$ thermal conductivity with heat flow parallel to food fibers, W/(m·K)
$k_{\perp}$ thermal conductivity with heat flow perpendicular to food fibers, W/(m·K)
L^3 volume fraction of discontinuous phase
L_o latent heat of fusion of water at 0°C; $L_o = 333\,600$ J/kg
m' parameter in Equation (19)
M parameter in Equation (47): $M = L^2(1 - k_d/k_c)$
M_s effective molar mass of food solids (kg/mol)
M_w molar mass of water (kg/mol)
n parameter in Equations (6) and (7)
n' parameter in Equation (19)
N^2 volume fraction of discontinuous phase
P parameter in Equation (49): $P = N(1 - k_d/k_c)$

R ideal gas constant: $R = 8.314$ J/(mol·K)
t food temperature, °C
t_f initial freezing temperature of food, °C
t_r reference temperature, °C
T food temperature, K
T_f initial freezing point of food item, K
T_o freezing point of water: $T_o = 273.2$ K
T_r reference temperature, K
$\bar{T}$ reduced temperature
V_c volume of continuous phase, m^3
V_d volume of discontinuous phase, m^3
w_1 mass fraction of component 1
w_b mass fraction of bound water
w_i mass fraction of i^{th} food component
w_{ice} mass fraction of ice
w_p mass fraction of protein
w_s mass fraction of solids
w_{so} mass fraction of soluble substances
w_u mass fraction of insoluble substances
w_w mass fraction of unfrozen water
w_{wo} mass fraction of water in unfrozen food
x_w mole fraction of water in solution
y correlation parameter in Equation (36)
z correlation parameter in Equation (36)
α Rahman-Chen structural factor
Δc difference in specific heat capacities of water and ice; $\Delta c = c_w - c_{ice}$, J/(kg·K)
ϕ_1 volume fraction of component 1
ϕ_a volume fraction of air within food item
ϕ_i volume fraction i^{th} food component
ϕ_w volume fraction of water within food item
Λ thermal conductivity ratio; $\Lambda = k_1/k_2$
ρ_1 density of component 1, kg/m^3
ρ_2 density of component 2, kg/m^3
ρ_i density of i^{th} food component, kg/m^3
σ parameter given by Equation (52)

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