

## Chapter 2

# Heat Transfer Coefficient and Physical Properties

### 2.1 Introduction

Before freezing time and heat load can be calculated, the physical parameters or inputs must be available. These can be classified into two groups: environmental factors and food properties. The former comprise the environment temperature and the heat transfer coefficient. The latter is often difficult to determine and its calculation is a vast subject, but only a brief treatment will be given in this work.

The relevant physical properties of the food are the freezing point, enthalpy, specific heat, density and thermal conductivity. The last four properties are functions of temperature and there is usually a discontinuity or large change around the freezing point. If data are available, we still have to put them in a usable form by using some curve-fitting (regression) equation. If reliable data on the properties are not available, we have to estimate them from composition data. This chapter describes some of the ways this can be done. The property prediction methods described in this chapter are certainly not the only ones and not necessarily the most advanced available, and there will be methods more suited to specific types of foods, but they are conceptually simple and will in most cases provide satisfactory answers. A more comprehensive review may be obtained from Gulati and Datta (2013).

### 2.2 Heat Transfer Coefficient

The heat transfer coefficient  $h$  is the ratio of heat flux  $q$  (heat flow per unit area) to the difference between the temperature  $T_s$  of the surface and that of the cooling medium,  $T_a$ :

$$h = \frac{q}{T_s - T_a} \quad (2.1)$$

Its inverse  $1/h$  is termed the surface resistance to heat transfer. For an unwrapped product in air,  $h$  includes contributions from convection, radiation and evaporative cooling (see e.g. Davey and Pham 1997) and will be denoted by the symbol  $h_{surf}$ :

$$h_{surf} = h_{conv} + h_{rad} + h_{evap} \quad (2.2)$$

The inverse of  $h_{surf}$  measures the resistance to heat transfer at the food–fluid interface. The convective contribution depends on the geometry of the product, the properties of the surrounding fluid, the flow pattern and the degree of turbulence. For many frequently occurring configurations the convective heat transfer coefficient can be calculated from empirical correlations. It can also be calculated by computational fluid dynamics, provided a suitable turbulence model is used (Hu and Sun 2001; Pham et al. 2009). The radiative contribution depends on the temperature and emissivity of the product surface and those of the radiation source or sink (such as the surrounding walls). The evaporative cooling contribution depends on the temperature and humidity at the product surface and those of the surroundings. In immersion freezing the radiation and evaporative cooling contributions can be neglected.

If the product is wrapped, heat from the product must be released by passing it through layers of trapped air (if any), wrapping materials and the boundary layer at the fluid–solid interface; therefore the effective heat transfer coefficient will be given by

$$h = \left( \frac{\delta_{air}}{k_{air}} + \frac{\delta_{wrap}}{k_{wrap}} + \frac{1}{h_{surf}} \right)^{-1} \quad (2.3)$$

where  $\delta$  is the thickness of the trapped air or wrapping.

The heat transfer coefficient is frequently the most uncertain parameter in a freezing calculation. However, errors in  $h$  are not serious if the Biot number is large, which indicates that internal resistance to heat transfer rather than  $h$  is the controlling factor (more of this in Sect. 3.2.3). For most of the non-numerical methods covered in this work,  $h$  is assumed to be constant throughout the cooling and freezing process, although in practice it may vary.

The heat transfer coefficient is highly dependent on process conditions and its estimation is a vast and complex subject. The reader is referred to Kondjoyan (2006) for a review in the food refrigeration field. Becker and Fricke (2004) presented some experimental values. Typical ranges are shown in Table 2.1.

## 2.3 Density

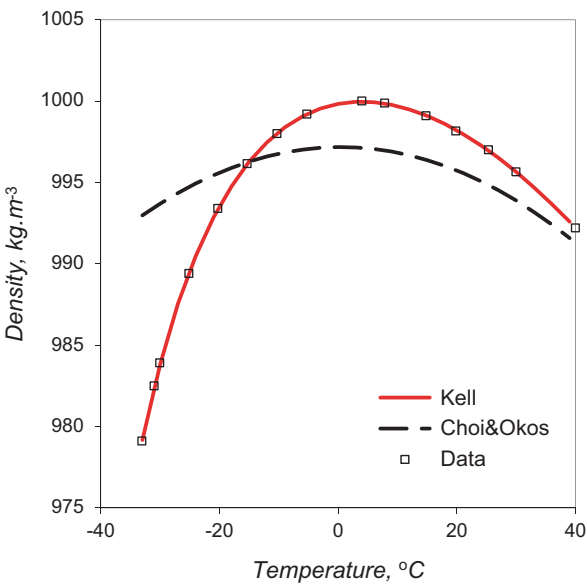
In one unit mass of a composite material, each component  $i$  contributes mass  $X_i$  and volume  $X_i/\rho_i$ . The density of the material is therefore the total mass (1) divided by the total volume:

$$\rho = \frac{1}{\sum_i \frac{X_i}{\rho_i}} \quad (2.4)$$

**Table 2.1** Typical heat transfer coefficients for common equipments. (Source: Karel and Lund 2003; Sinha 2011; Pham unpublished)

Type of equipment	Heat transfer coefficients (W·m <sup>-2</sup> K <sup>-1</sup> )
Still air chillers and freezers	5–10
Air blast chillers and freezers	15–30
Impingement chillers and freezers	50–200
Fluidized bed chillers and freezers	50–250
Immersion chillers and freezers	100–300
Plate chillers and freezers	500–1000

**Fig. 2.1** Density of liquid water at atmospheric pressure: Kell (Eq. 2.5), Choi & Okos’s equation and data from Hare and Sorensen (1987), Sotani et al. (2000) and Lide (2009)



Polynomial expressions for the density of food components as functions of temperature were presented by Choi and Okos (1986) and the coefficients are shown in Table 2.2. For water, Choi & Okos’s coefficients are given only for completeness, as the equation is not very accurate. Values for the density of water are available in the CRC Handbook (Lide 2009), on the NIST website (2013a) and in Wagner and Pruss (2002). An accurate regression equation for water density at atmospheric pressure down to  $-30^{\circ}\text{C}$  was given by Kell (1975) (Fig. 2.1):

$$\rho_{\text{wv}} = \frac{a_0 + a_1\theta + a_2\theta^2 + a_3\theta^3 + a_4\theta^4 + a_5\theta^5}{1 + b\theta} \tag{2.5}$$

where  $a_0=999.83952$ ,  $a_1=16.945176$ ,  $a_2=-7.9870401\times10^{-3}$ ,  $a_3=-4.6170461\times10^{-5}$ ,  $a_4=1.0556302\times10^{-7}$ ,  $a_5=-2.8054253\times10^{-10}$ ,  $b=0.016879850$ .

**Table 2.2** Coefficients of the equation  $\rho = A + B\theta + C\theta^2$  for the dependence of density on temperature (Choi and Okos 1986) and predicted values at  $-40$ ,  $-20$  and  $20^\circ\text{C}$ . Predictions from Eq. 2.5 (recommended) for water are also included

Component	$A$	$B$	$C$	Value at $-40^\circ\text{C}$	Value at $-20^\circ\text{C}$	Value at $20^\circ\text{C}$
Water	997.18	$3.1439 \times 10^{-3}$	$-3.7574 \times 10^{-3}$	(991)	(996)	(996)
Water (Eq. 2.5)	—	—	—	962	994	998
Ice	916.89	$-1.3071 \times 10^{-1}$	0	922	920	—
Protein	1329.9	$-5.1840 \times 10^{-1}$	0	1351	1340	1320
Fat	925.59	$-4.1757 \times 10^{-1}$	0	942	934	917
Carbohydrate	1599.1	$-3.1046 \times 10^{-1}$	0	1612	1605	1593
Fibre	1311.5	$-3.6589 \times 10^{-1}$	0	1326	1319	1304
Ash	2423.8	$-2.8063 \times 10^{-1}$	0	2435	2429	2418

## 2.4 Calorimetric Properties

The freezing behaviour of a real food is different from that of water. Pure water has a sharp freezing point at  $0^\circ\text{C}$ , where all the phase changes and latent heat releases take place. The moisture in foods contains various solutes such as salts and sugars; therefore its freezing point is lower than that of pure water, about  $-1^\circ\text{C}$  for fresh foods, lower still for processed foods (salted, cured etc.). After the first ice crystals have appeared, the remaining solution becomes more concentrated and its freezing point is further depressed according to the thermodynamics of solutions. Therefore, the latent heat is released over a range of temperature. Figure 2.2 illustrates the differences in the calorimetric properties (apparent specific heat and latent heat) of pure water and water-rich foods. The term *apparent* specific heat implies that latent heat is included in the specific heat.

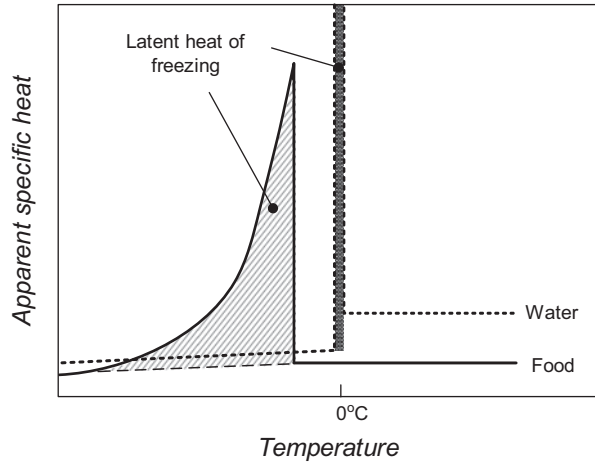
### 2.4.1 Freezing Point

Because phase change in food freezing takes place over a range of temperature, we also use the term *initial freezing point* to refer to the temperature where the ice crystal first appears (in the absence of supercooling). It can be calculated from the concentration of solute using the thermodynamic relationship

$$-\ln a_w = \frac{M_w \lambda_f}{R_g} \left( \frac{1}{T_f} - \frac{1}{T_0} \right) \quad (2.6)$$

where  $a_w$  is the water activity,  $M_w$  the molar mass of water ( $18.02 \text{ kg}\cdot\text{kmol}^{-1}$ ),  $\lambda_f$  the latent heat of freezing per unit mass of water ( $334 \text{ kJ}\cdot\text{kg}^{-1}$ ),  $R_g$  the gas constant ( $8.314 \text{ kJ}\cdot\text{K}^{-1}\text{kmol}^{-1}$ ),  $T_f$  the freezing point of the solution and  $T_0$  that of pure water

**Fig. 2.2** Apparent specific heat of water–ice and foods



(273.15 K). For dilute solutions, Raoult's law applies, and water activity can be calculated from

$$a_w = 1 - ix_{sol} \quad (2.7)$$

where  $x_{sol}$  is the solute mole fraction in the solution and  $i$  the van't Hoff factor, which accounts for molar or ionic dissociation in the solution. The solute mole fraction  $x_{sol}$  can be calculated as follows. Let  $X_s$  be the mass fraction of total solids,  $X_w$  that of water and  $X_{sol}$  that of solutes. In the widely used bound water model, some of the water is bound to the solid phase and does not participate in the solvation or freezing process (Schwartzberg 1976), while the rest is *free water*. Let the mass fraction of bound water (as a fraction of total food mass) be  $X_b$ , then that of free water will be  $X_w - X_b$ . The solute mole fraction in the free water will therefore be

$$x_{sol} = \frac{\frac{X_{sol}}{M_{sol}}}{\frac{X_{sol}}{M_{sol}} + \frac{X_w - X_b}{M_w}} \quad (2.8)$$

Schwartzberg et al. (2007) showed that Eq. 2.6 can be well approximated by

$$\theta_f \approx -\frac{R_g T_0^2}{M_w \lambda_f} \frac{\frac{M_w}{M_{sol}} i X_{sol}}{X_w - X_b + \frac{1}{2} \frac{M_w}{M_{sol}} i X_{sol}} \quad (2.9)$$

where  $\theta_f \equiv T_f - T_0$  is the freezing point in °C and  $M_{sol}$  is the molecular mass of solute. For low solute concentrations the last term in the denominator can be neglected to give

$$\theta_f \approx -\frac{R_g T_0^2 i X_{sol}}{\lambda_f M_{sol}} \frac{1}{X_w - X_b} \quad (2.10)$$

Since Raoult's law holds only for dilute solutions, a correction for deviations from Raoult's law has been proposed (van der Sman and Boer 2005; van der Sman 2008) using the Pitzer equation, which should be used for processed meats which frequently have salt added. However the subsequent treatment in this chapter will assume Raoult's law.

If the composition of a food is accurately known, Eq. 2.9 or 2.10 will give accurate freezing time predictions (Miles et al. 1997). Reasonable predictions can also be obtained from the following empirical equation (Pham 1996), based on available data for meat, fish, fruit and non-fat dairy foods:

$$\theta_f \approx -\frac{1}{X_w} (4.66 X_{other} + 46.4 X_{ash}) \quad (2.11)$$

where  $X_{ash}$  is the ash (mineral) mass fraction in the food and  $X_{other}$  is the mass fraction of components (such as carbohydrates) other than ash, water, fat or proteins.

## 2.4.2 Bound Water

Bound water may be calculated from

$$X_b = b X_{ds} \quad (2.12)$$

where  $X_{ds}$  is the total dry solids mass fraction and  $b$  is the bound water to solids mass ratio. According to Duckworth (1971)  $b$  ranges from 0.24–0.27 for meat and fish muscle. Pham (1987a) found the following mean (minimum, maximum) values for  $b$ : for meat and fish, 0.217 (0.143, 0.318); for egg, 0.106 (0.103, 0.109); for bread, 0.127 (0.111, 0.143); for Tylose (a methyl cellulose gel often used as a meat analogue in freezing experiments), 0.402 (0.352, 0.430). Fikiin (1998) reported  $b$  values of 0.257 for meat, 0.270–0.280 for fish, 0.275 for egg white, 0.167 for yeast, 0.080 for green peas, 0.117 for spinach.

More accurate predictions may be obtained by taking into account the composition of the food solids. Pham (1987a) found that for meat the bound water/protein ratio is about 0.4. Miles et al. (1997) and van der Sman and Boer (2005) proposed

$$X_b = 0.3 X_{prot} + 0.1 X_{carb} \quad (2.13)$$

Pham (1996) proposed

$$\frac{X_b}{X_w} = 0.342(1 - X_w) - 4.51X_{ash} + 0.167X_{prot} \quad (2.14)$$

The last equation has the advantage of correctly predicting that  $X_b \rightarrow 0$  when  $X_w$  tends to 0 or unity (pure water).

### 2.4.3 Frozen Fraction

As we have seen earlier, after the food passes through its initial freezing point, ice continues to form as temperature falls, leaving behind a more and more concentrated solution. This solution is in thermodynamic equilibrium with the ice and therefore its freezing point will be  $T$  or  $\theta$ . Thus the solution's concentration and its activity are related to temperature by the same equations that determine initial freezing point (Eq. 2.6, 2.9 or 2.10), with  $T_f$  or  $\theta_f$  replaced by  $T$  or  $\theta$  and  $X_w$  replaced by  $X_w - X_{ice}$ , where  $X_{ice}$  is the mass fraction of ice. For example, Eq. 2.10 becomes:

$$\theta \approx -\frac{R_g T_0^2 i X_{sol}}{\lambda_f M_{sol}} \frac{1}{X_w - X_{ice} - X_b} \quad (2.15)$$

Then dividing Eq. 2.10 by Eq. 2.15 and re-arranging gives

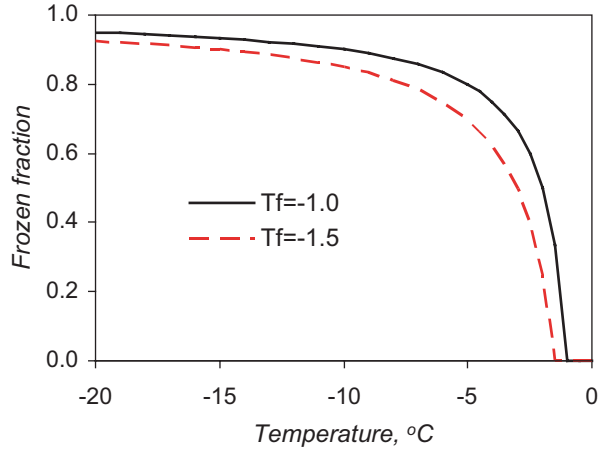
$$X_{ice} \approx (X_w - X_b) \left( 1 - \frac{\theta_f}{\theta} \right) \quad (2.16)$$

Although this equation is accurate only at temperatures not far below the freezing point, it is often used to estimate the ice fraction and hence enthalpy due to its simplicity. For processed foods with salts added, van der Sman's approach (van der Sman and Boer 2005; van der Sman 2008), which corrects for deviations from Raoult's law, can be used.

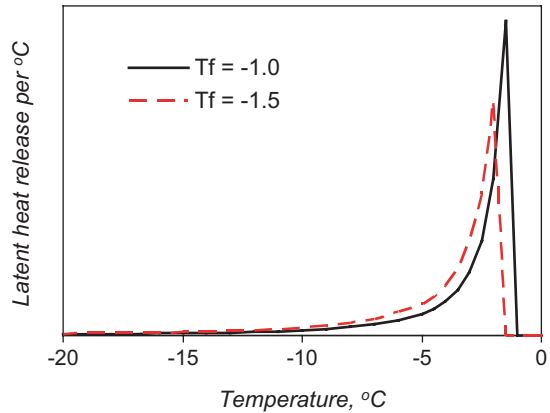
Others have proposed empirical equations derived from fitting experimental data. Fikiin (1998) recommended the following equation by Tchigeov (1956, 1979) for meat, fish, milk, eggs, fruits and vegetables, which requires only the freezing point and total moisture content and can thus be used when full composition is not known:

$$X_{ice} = \frac{1.105}{1 + \frac{0.7138}{\ln(\theta_f - \theta + 1)}} X_w \quad (2.17)$$

**Fig. 2.3** Frozen fraction for two foods with freezing points differing by 0.5 K



**Fig. 2.4** Latent heat release rate for two foods with freezing points differing by 0.5 K



The equation is reported to be satisfactory for  $-45^{\circ}\text{C} \leq \theta \leq \theta_f$  and  $-2^{\circ}\text{C} \leq \theta_f \leq -0.4^{\circ}\text{C}$ .

*Errors due to uncertainty in freezing point* Often the freezing point  $T_f$  or  $\theta_f$  is only known to within  $\pm 0.5$  K, so there is a large relative uncertainty in the last term in Eq. 2.16 and hence in the ice content and resulting enthalpy and specific heat curves (Figs. 2.3 and 2.4). It is possible to estimate the effect of this uncertainty on freezing time and heat load calculations. If freezing is stopped at a final product temperature  $\theta_e = -18^{\circ}\text{C}$ , the total latent heat load will be proportional to the amount of ice formed at  $\theta_e$ , i.e. proportional to  $1 - \theta_f/\theta_e$ . If the uncertainty in  $\theta_f$  is  $\delta\theta_f$ , the relative error in the total latent heat load will be  $(\delta\theta_f/\theta_e)/(1 - \theta_f/\theta_e)$ . For  $\theta_f = -1.0^{\circ}\text{C}$ ,  $\delta\theta_f = 0.5$  K,  $\theta_e = -18^{\circ}\text{C}$ , the latent heat error will be around 3%. The error in the total heat load (including sensible heat) will be somewhat smaller.

Again ignoring sensible heat, the instantaneous rate of heat removal is inversely proportional to the temperature difference between the food and its surroundings,



$\theta - \theta_a$ , therefore the freezing time is proportional to  $\int_{\theta_f}^{\theta_e} \frac{dX_{ice}}{\theta - \theta_a}$ , i.e. to  $\int_{\theta_f}^{\theta_e} \frac{d(1 - \theta_f / \theta)}{\theta - \theta_a}$

or  $\int_{\theta_f}^{\theta_e} \theta_f \frac{d(1/\theta)}{\theta - \theta_a}$  from Eq. 2.16. Integration shows that for  $\theta_f = -1.0^\circ\text{C}$ ,  $\delta\theta_f = 0.5\text{ K}$ ,

$\theta_e = -18^\circ\text{C}$ ,  $\theta_a = -30^\circ\text{C}$ , the freezing time error will be around 1.3 %. If sensible heat is taken into account the error will be smaller still. The lowering of the freezing point tends to increase freezing time, but this is compensated by a lesser latent heat load, therefore the freezing time error is small. In conclusion we can say that errors in the initial freezing point are likely to have only a small effect on freezing time.

#### 2.4.4 Enthalpy

Enthalpy  $H$  ( $\text{J}\cdot\text{kg}^{-1}$ ) is the heat content per unit mass of food at a given temperature. It is measured from an arbitrary reference temperature, since in all calculations we are concerned only with changes in enthalpy. In freezing calculations the usual reference temperature is  $T_{ref} = -40^\circ\text{C}$ .

Once the ice content has been calculated as shown in the previous section, the food's enthalpy can be obtained simply by adding those of the components:

$$H = X_{uw}H_{uw} + X_{ice}H_{ice} + X_{prot}H_{prot} + X_{fat}H_{fat} + X_{carb}H_{carb} + X_{fib}H_{fib} + X_{ash}H_{ash} \quad (2.18)$$

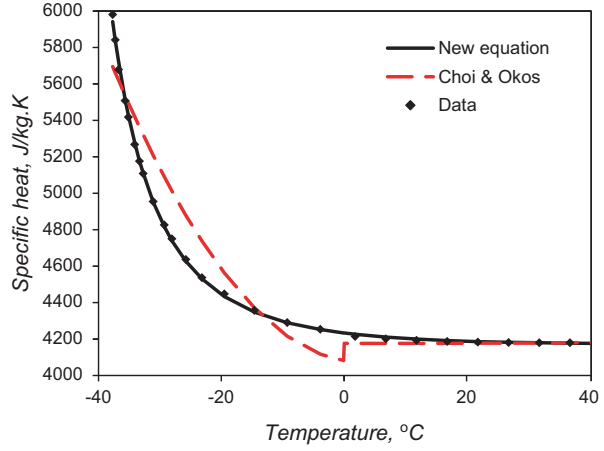
where for each component  $i$  apart from water:

$$H_i = \int_{T_{ref}}^T c_i dT \quad (2.19)$$

where  $c_i$  is the specific heat ( $\text{J}\cdot\text{kg}^{-1}\text{K}^{-1}$ ) of component  $i$ . Equation 2.19 assumes that the mixture is ideal, i.e. that there is no heat of mixing effect. The enthalpy of unfrozen water  $H_{uw}$  is calculated differently from that of the other components, because water exists in two phases and we have taken ice at  $T_{ref}$  to be the reference state. Since liquid water at temperature  $T$  can be obtained by taking ice at the reference temperature, heating it to  $T_0$  ( $0^\circ\text{C}$ ), melting it, then bringing the liquid water to temperature  $T$ , its enthalpy will be given by:

$$H_{uw} = \int_{T_{ref}}^{T_0} c_{ice} dT + \lambda_{f0} + \int_{T_0}^T c_{uw} dT \quad (2.20)$$

**Fig. 2.5** Specific heat of water according to Eq. 2.21, Choi and Okos's equation and averaged experimental data (Wagner and Pruss 2002; Holten et al. 2013).



where  $\lambda_{f0}$  is the latent heat of freezing at 0 °C. Values of specific heats for water, ice, proteins, fat, carbohydrates, fibre and ash are listed by Choi and Okos (1986) as second-order polynomial functions of  $T$ , which can be readily integrated to yield enthalpy values according to the above equations. The coefficients of the functions are given in Table 2.3 together with typical values. For liquid water there is a step jump at 0° and the equation does not agree well with accepted values (Fig. 2.5), therefore the following equation should be used instead:

$$c_{uw} = 6.6353 \times 10^5 x^2 - 1.2132 \times 10^4 x + 4231.0 \quad (2.21)$$

where  $x = 1/(\theta + 54.15)$ . This agrees with accepted values (Wagner and Pruss 2002; Holten et al. 2013) for  $-40^\circ\text{C} \leq \theta < 100^\circ\text{C}$  to within 1 %.

Over a limited temperature range the specific heats of the components are often assumed to be constant, and if furthermore Raoult's law holds (solution is ideal) the following approximate equations are obtained (Schwartzberg 1976; Pham 1987a):

$$H(T \leq T_f) = A + c_f \theta - \frac{B}{\theta} \quad (2.22)$$

$$H(T > T_f) = H_{T=T_f} + c_u (\theta - \theta_f) \quad (2.23)$$

where  $A$  is an arbitrary constant and

$$B = -(X_w - X_b) \lambda_{f0} \theta_f \quad (2.24)$$

**Table 2.3** Coefficients of the equation  $y = A + B\theta + C\theta^2$  for the dependence of specific heat on temperature (Choi and Okos 1986) and predicted values at  $-40$ ,  $-20$  and  $20^\circ\text{C}$ . Predictions from Eq. 2.21 (recommended) for water are also included

Component	$A$	$B$	$C$	Value at $-40^\circ\text{C}$	Value at $-20^\circ\text{C}$	Value at $20^\circ\text{C}$
Water ( $-40$ to $0^\circ\text{C}$ )	4081.7	$-5.3062$	$9.9516 \times 10^{-1}$	5886	4586	—
Water ( $0$ to $150^\circ\text{C}$ )	4176.2	$-9.0864 \times 10^{-2}$	$5.4731 \times 10^{-3}$	—	—	4177
Water (Eq. 2.21)	—	—	—	6688	4445	4188
Ice	2062.3	6.0769	0	1819	1941	—
Protein	2008.2	1.2089	$-1.3129 \times 10^{-3}$	1958	1983	2032
Fat	1984.2	1.4733	$-4.8008 \times 10^{-3}$	1918	1953	2012
Carbohydrate	1548.8	1.9625	$-5.9399 \times 10^{-3}$	1461	1507	1586
Fibre	1845.9	1.8306	$-4.6509 \times 10^{-3}$	1765	1807	1881
Ash	1092.6	1.8896	$-3.6817 \times 10^{-3}$	1011	1053	1129

The parameters of Eq. 2.22 and 2.23 can be derived from composition (Pham 1996) or by curve-fitting experimental data. Pham (1987a) tabulates values of the parameters  $A$ ,  $B$ ,  $\theta_f$  and  $c_f$  for several types of foods.

Due to the limitations of Raoult's law, the above enthalpy equations may not always agree well with experimental data for temperatures below freezing. Furthermore, although the moisture content can easily be measured, full composition is not always available. Fikiin and Fikiin (1999) proposed the following empirical equation which only requires the freezing point and total moisture content to be known:

$$H(T \leq T_f) = -C(T_f - T)^D \quad (2.25)$$

where  $C = 225.25X_w - 13.105$ ,  $D = \frac{0.046}{X_w} + 0.122$ .

### 2.4.5 Sensible Specific Heat

Some analytical and approximate methods for calculating freezing/thawing times and heat loads require values of the sensible or “true” frozen and unfrozen specific heats  $c_f$  and  $c_u$  (excluding latent heat of phase change) at certain temperatures. These can be calculated from

$$c_f = X_{uw}c_{uw} + X_{ice}c_{ice} + X_{prot}c_{prot} + X_{fat}c_{fat} + X_{carb}c_{carb} + X_{fib}c_{fib} + X_{ash}c_{ash} \quad (2.26)$$

$$c_u = X_{uw}c_{uw} + X_{prot}c_{prot} + X_{fat}c_{fat} + X_{carb}c_{carb} + X_{fib}c_{fib} + X_{ash}c_{ash} \quad (2.27)$$

where  $X_{uw}$  and  $X_{ice}$  can be calculated from the equations in Sect. 2.4.3 and the components'  $c$ -values from those in Sect. 2.4.4.

### 2.4.6 Apparent Specific Heat

The derivative of enthalpy,  $c_{app} \equiv dH/dT$ , is termed the apparent (or effective) specific heat of the food, because it includes latent heat effects. The most general way to compute it is by numerical differentiation of the enthalpy–temperature function:

$$c_{app} = \frac{H(T + \delta T) - H(T - \delta T)}{2\delta T} \quad (2.28)$$

where  $\delta T$  is a small temperature interval. Numerical differentiation is difficult to carry out for pure water or dilute solutions at or near the freezing point, because of the abrupt changes in enthalpy. An arbitrary smearing out of the latent heat peak (freezing temperature range) will facilitate the process.

If it is desired to calculate apparent specific heats from composition, for temperatures above freezing  $c_{app} = c_u$  as given in Eq. 2.27. Below the freezing point things get more complicated because of phase change. The contribution of water/ice to the apparent specific heat is

$$\frac{d}{dT}(X_{uw}H_{uw} + X_{ice}H_{ice}) = X_{uw}c_{uw} + X_{ice}c_{ice} + (H_{uw} - H_{ice})\frac{dX_{uw}}{dT} \quad (2.29)$$

since  $dX_{ice} = -dX_{uw}$ . From Eq. 2.20,

$$H_{uw} - H_{ice} = \lambda_{f0} + \int_{T_0}^T (c_{uw} - c_{ice})dT \quad (2.30)$$

while  $dX_{uw}/dT$  can be found, say, by differentiating Eq. 2.16:

$$\frac{dX_{uw}}{dT} = -\frac{dX_{ice}}{dT} \approx (X_w - X_b)\frac{T_0 - T_f}{(T_0 - T)^2} = (X_w - X_b)\frac{-\theta_f}{\theta^2} \quad (2.31)$$

Putting these expressions together, we obtain for the apparent specific heat below the freezing point:

$$\begin{aligned} c_{app}(T \leq T_f) = & X_{uw}c_{uw} + X_{ice}c_{ice} + X_{prot}c_{prot} + X_{fat}c_{fat} \\ & + X_{carb}c_{carb} + X_{fib}c_{fib} + X_{ash}c_{ash} + \left( \lambda_{f0} + \int_{T_0}^T (c_{uw} - c_{ice})dT \right) (X_w - X_b) \frac{-\theta_f}{\theta^2} \end{aligned} \quad (2.32)$$

The following simple approximate expressions for  $c_{app}$  can be obtained by differentiating Eq. 2.22 and 2.23:

$$c_{app}(T \leq T_f) = c_f + \frac{B}{\theta^2} \quad (2.33)$$

$$c_{app}(T > T_f) = c_u \quad (2.34)$$

*Note:* In the rest of this work the symbol  $c$  may be used to refer to the sensible specific heat (as defined in, say, Eq. 2.26, i.e. excluding latent heat of phase change) or to the apparent specific heat  $c_{app}$ , depending on context. For examples, in the heat conduction equation (Eq. 3.5)  $c$  will mean the sensible specific heat ( $c_u$  or  $c_f$ ) if latent heat is treated separately as a heat source, or the apparent specific heat if the heat source term in Eq. 3.5 is dropped. The same goes for all numerical methods used to solve the heat conduction equation. When the apparent specific heat must be used (such as in the Apparent Specific Heat Method of Sect. 5.4.1.3), the symbol  $c_{app}$  will be employed. Above the freezing point, of course,  $c = c_u = c_{app}$ .

### 2.4.7 Calorimetric Properties at High Pressure

When required for the modelling of high pressure freezing and thawing, the calorimetric properties of a food can be calculated from those at atmospheric pressure by standard thermodynamic relationships.

#### 2.4.7.1 Freezing Point at High Pressure

The freezing point depression due to pressure is given by the Clausius–Clapeyron equation

$$\frac{dP}{dT_f} = \frac{H_{ice} - H_{uw}}{T(V_{ice} - V_{uw})} = \frac{-\lambda_f}{\frac{1}{\rho_{ice}} - \frac{1}{\rho_{uw}}} \quad (2.35)$$

Density difference and latent heat change markedly at high pressure ( $>10$  MPa), therefore it is easier to rely on tabulated data for  $T_f$  vs.  $P$  (e.g. Lide 2009) or using the  $P$ – $T$  relationship for the melting curve of ice (Wagner et al. 2011). The following regression equation is probably sufficiently close to Wagner’s relationship ( $\pm 0.001$  K) for food freezing studies:

$$\theta_f = 1.8287 \times 10^{-8} z^3 - 1.5252 \times 10^{-4} z^2 - 7.4445 \times 10^{-2} z + 0.010641 \quad (2.36)$$

where  $\theta_f$  is the negative of the freezing point depression and  $z=10^{-6}$   $P$  is the pressure in MPa.

### 2.4.7.2 Enthalpy–Temperature Curve

The rate of change of enthalpy with pressure in an isothermal process is given by the thermodynamic relationship

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad (2.37)$$

where  $V=1/\rho$  is the specific volume. Putting  $(\partial V/\partial T)_P = V\beta_T$  where  $\beta_T$  is the thermal expansion coefficient and integrating this equation gives the enthalpy difference between a system at  $(T, P_1)$  and  $(T, P_2)$

$$H(T, P_2) - H(T, P_1) = \int_{P_1}^{P_2} \frac{1 - T\beta_T}{\rho} dP \approx \frac{1 - T\beta_T}{\rho_{av}} (P_2 - P_1) \quad (2.38)$$

where  $\rho_{av}$  is the average density between the two pressures. This equation enables the enthalpy–temperature curve at high pressure to be generated from that at atmospheric pressure.  $\beta_T$  can be calculated from the density–temperature relationships of the food's components (Eq. 2.5). This equation is useful only if there is no phase change during compression, i.e. if  $T \geq T_{f, P}$ , because if there is phase change  $\beta_T$  is large and varies rapidly.

To calculate  $\rho_{av}$  in Eq. 2.38 we require values of density at the lower and higher pressure. For water this can be obtained from Holten et al. (2013). For ice, density at high pressure can be calculated from the bulk modulus, which is reported as  $(8.3 \text{ to } 11.3) \times 10^3$  MPa at  $-5^\circ\text{C}$  (Gold 1958) and  $(8.65 \pm 0.2) \times 10^3$  MPa at  $-16^\circ\text{C}$  (Petrenko and Whitworth 1999).

## 2.5 Thermal Conductivity

Polynomial expressions for the dependence of the thermal conductivities of food components on temperature were presented by Choi and Okos (1986) and the coefficients are shown in Table 2.4. Predicting thermal conductivity  $k$  from composition is more difficult than predicting enthalpy or specific heat, because thermal conductivities are not additive. In a composite material the effective thermal conductivity depends on the microstructure and may also be anisotropic (dependent on direction). Many different equations of models have been proposed to predict the  $k$ -value of a composite from those of its components. Some are derived from geometric or physical considerations while others are purely empirical. The differences between

**Table 2.4** Coefficients of the equation  $y=A+B\theta+C\theta^2$  for the dependence of thermal conductivity on temperature (Choi and Okos 1986) and values at  $-40$ ,  $-20$  and  $20^\circ\text{C}$ . Note: in the original paper there was an order-of-magnitude error in the B-value for fat (M. Okos, personal communication with D. Cleland) which has been corrected here

Component	$A$	$B$	$C$	Value at $-40^\circ\text{C}$	Value at $-20^\circ\text{C}$	Value at $20^\circ\text{C}$
Water	0.57109	$1.7625 \times 10^{-3}$	$-6.7036 \times 10^{-6}$	0.490	0.533	0.604
Ice	2.21960	$-6.2489 \times 10^{-3}$	$1.0154 \times 10^{-4}$	2.632	2.385	–
Protein	0.17881	$1.1958 \times 10^{-3}$	$-2.7178 \times 10^{-6}$	0.127	0.154	0.202
Fat	0.18071	$-2.7604 \times 10^{-4}$	$-1.7749 \times 10^{-7}$	0.191	0.186	0.175
Carbohydrate	0.20141	$1.3874 \times 10^{-3}$	$-4.3312 \times 10^{-6}$	0.139	0.172	0.227
Fibre	0.18331	$1.2497 \times 10^{-3}$	$-3.1683 \times 10^{-6}$	0.128	0.157	0.207
Ash	0.32962	$1.4011 \times 10^{-3}$	$-2.9069 \times 10^{-6}$	0.269	0.300	0.356

prediction methods are particularly acute for frozen foods and porous foods, because the differences between component thermal conductivities can be very great (one order of magnitude for frozen non-porous foods, up to three orders of magnitude for frozen porous foods).

The parallel model ( $k_{par}$ ) and the series model ( $k_{ser}$ ), provide the upper and lower bounds of the thermal conductivity of a mixture:

$$k_{par} = \sum_i \phi_i k_i \quad (2.39)$$

$$k_{ser} = \left( \sum_i \frac{1}{\phi_i k_i} \right)^{-1} \quad (2.40)$$

where  $\phi_i$  are the volume fraction and  $k_i$  the thermal conductivities of pure components. The volume fraction  $\phi_i$  for a given component  $i$  can be calculated from

$$\phi_i = \frac{X_i / \rho_i}{\sum_j (X_j / \rho_j)} \quad (2.41)$$

where  $\rho_i$  is the density of component  $i$ . Since this work does not aim to make a comprehensive review of thermal properties models but only to provide some basic and useful tools for use in freezing time prediction, only a few thermal conductivity models will be mentioned. These are the Maxwell–Eucken (M-E) model, the Levy model and the effective medium theory (EMT) model. Many other equations are mentioned in the literature, but most of them involve one or more empirical curve-fitting parameters. Some are parameter-free, such as the co-continuous model (Wang et al. 2008), but lack experimental verification at this time.

- M-E model: applies to a dilute dispersion of spheres (component 2) in a continuous phase (component 1):

$$k_{M-E} = k_1 \frac{2k_1 + k_2 - 2(k_1 - k_2)\phi_2}{2k_1 + k_d + (k_1 - k_2)\phi_2} \quad (2.42)$$

- Levy model: Levy (1981) proposed a mathematical modification to the M-E model to eliminate the distinction between disperse and continuous phase, which is not always known.

$$k_{Levy} = k_1 \frac{2k_1 + k_2 - 2(k_1 - k_2)F}{2k_1 + k_2 + (k_1 - k_2)F} \quad (2.43)$$

where

$$F = \frac{1}{2} \left[ \frac{2}{G} - 1 + 2\phi_2 - \sqrt{\left( \frac{2}{G} - 1 + 2\phi_2 \right)^2 - \frac{8\phi_2}{G}} \right] \quad (2.44)$$

$$G = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2 + k_1 k_2 / 2} \quad (2.45)$$

It can be seen that the Levy model is the same as the M-E model with the dispersed volume fraction  $\phi_2$  replaced by the parameter  $F$ . It can be shown that the equation is symmetric, that is reversing indices 1 and 2 will produce the same numerical result. Wang et al. (2006) gave Levy's equation a physical basis by showing that it represents the effective conductivity of a dispersion of component 1 in component 2 co-existing with a dispersion of 2 in 1, with equal conductivities and each obeying the M-E model.

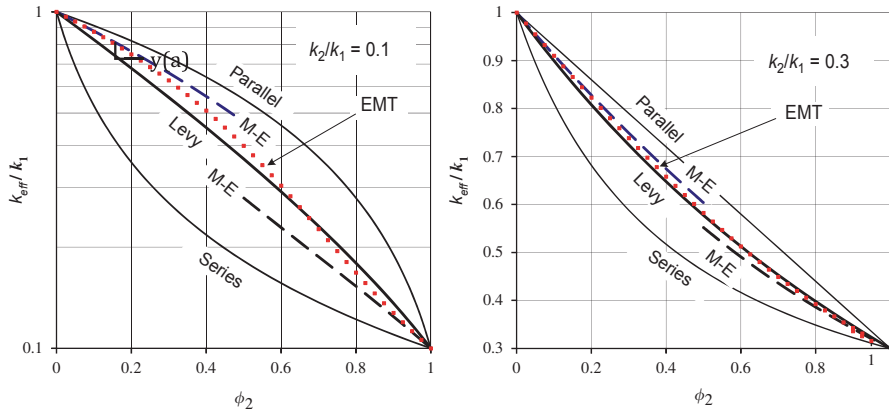
- EMT model: for a mixture consisting of  $n$  components the effective conductivity  $k_{EMT}$  is given by the implicit equation:

$$\sum_{i=1}^n \phi_i \frac{k_i - k_{EMT}}{k_i + 2k_{EMT}} \quad (2.46)$$

Of the above models, the M-E and Levy apply to pairs of components while EMT, parallel and series can apply to any number of components. To apply the M-E and Levy models to a multi-component system, we have to combine the components one by one, and the order in which they are introduced may be important.

Figure 2.6 illustrates how the different models predict variations in the thermal conductivity of the composite. It plots  $k_{eff}/k_1$  where  $k_{eff}$  is the composite's effective conductivity and  $k_1$  that of the more conducting component, against the volume fraction  $\phi_2$  of the less conducting component. The first figure is for  $k_2/k_1 = 0.1$ , a situation which typically arises in a frozen food containing ice ( $k \approx 2.2 - 2.5 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ ),





**Fig. 2.6** Ratio of effective thermal conductivity to thermal conductivity of more conducting component, as predicted by the parallel, series, Maxwell-Eucken (M-E), EMT and Levy models. The transition between the two parts of M-E is arbitrary

proteins, carbohydrates and fats ( $k \approx 0.18 - 0.19 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ ). Because the M-E equation is valid only when one component is dispersed in the other and has a low volume fraction, it is represented by two half-curves, the one on the left having component 2 as the dispersed phase and the one on the right having component 1 as the dispersed phase. The second figure assumes  $k_2/k_1 = 0.3$ , a situation which typically arises in an unfrozen food ( $k \approx 0.6 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$  for water).

If the microstructure of the food is known, the appropriate physical model should be used. For example, for porous food containing air bubbles or emulsions containing droplets, the M-E model is clearly appropriate as long as the volume fraction of the bubbles or droplets is small.

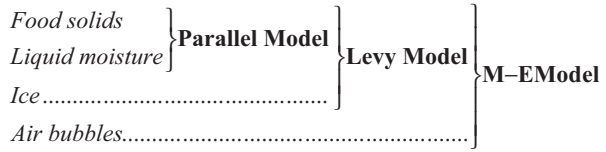
In many cases, however, the microstructure is not known and we have to rely on past experience. The following generic procedure is recommended:

- For unfrozen foods and the unfrozen phase (liquid water and food solids) of frozen foods, results predicted by the parallel, EMT, M-E and Levy models are fairly close and most workers use the parallel model, which is mathematically the simplest.
- For frozen foods, the thermal conductivity of the unfrozen phase is calculated as above, then ice and the unfrozen phase are combined using the Levy model (Pham and Willix 1989; Fricke and Becker 2001; Tarnawski et al. 2005; Pham et al. 2006a).
- For porous foods, the thermal conductivity of the dense (air-free) phase is calculated as above, then the M-E model with air as the dispersed component is used to take into account the effect of air bubbles (Wang et al. 2010).

The procedure is summarised in Fig. 2.7.

In moist porous foods, the thermal conductivity of air bubbles may be augmented by condensation–evaporation (Hamdami et al. 2003). This will be treated further in Sect. 6.2.2 (Eq. 6.23).

**Fig. 2.7** Procedure for calculating the thermal conductivity of frozen and unfrozen foods from component conductivities



If reliable experimental data for thermal conductivity at various temperatures is available, it will not be necessary to estimate  $k$  from composition and temperature. The data may be used directly by interpolating from tabulated values or by using regression equations such as (Pham and Willix 1989)

$$k = A + B\theta + \frac{C}{\theta}, \theta < \theta_f \quad (2.47)$$

$$k = D + E\theta, \theta \geq \theta_f \quad (2.48)$$

where  $A-E$  are regression coefficients. Note the similarity between the above equations with the enthalpy equations, Eq. 2.22 and 2.23, which is due to both thermal conductivity and enthalpy being dependent on the ice fraction.

Empirical equations have been proposed for specific types of foods. For some foods thermal conductivity will depend on the direction of heat flow. For example, the  $k$ -value of meat is higher along the fiber than at right angle to it (Heldman and Gorby 1975; Mascheroni et al. 1977; Pham and Willix 1989).

## 2.6 Thermal Properties of Tylose Gel

A food analogue frequently used in freezing and thawing experiments is Tylose (methyl hydroxyethyl cellulose) gel. Since experiments performed on this material are often used to compare or evaluate freezing time calculation methods, it is important to use accurate property values. Pham and Willix (1990) pointed out that previous estimates of Tylose thermal conductivity by Bonacina and Comini (1971) probably led to erroneous conclusions on the accuracy of finite difference calculations by Cleland et al. (1982). Unfortunately these erroneous data were still repeated in Otero et al. (2006).

The most accurate measurements of thermal conductivity of unsalted MH1000 Tylose gel (77% water mass fraction) were carried out by Pham and Willix (1990) using the guarded hot plate method. Calorimetric properties were determined by Riedel (1960) and Pham et al. (1994) using adiabatic calorimeters. The results are summarised in the following regression equations:

Freezing point:

$$\theta_f = -0.62 \pm 0.05^\circ\text{C} \quad (2.49)$$

Thermal conductivity:

$$k_u = 0.467 + 0.00154 (\theta - \theta_f) \quad (2.50)$$

$$k_f = 0.467 - 0.00489 (\theta - \theta_f) + 0.582 (1/\theta - 1/\theta_f) \quad (2.51)$$

(maximum error 2.5 %, mostly due to experimental scatter)

Specific enthalpy:

$$H(\theta < \theta_f) = A + c_f \theta + B/\theta \quad (2.52)$$

$$H(\theta \geq \theta_f) = H_0 + c_u \theta \quad (2.53)$$

where  $A = 82.4 \text{ kJ} \cdot \text{kg}^{-1}$ ,  $c_f = 2.31 \text{ kJ} \cdot \text{kg}^{-1} \text{K}^{-1}$ ,  $B = -133.0 \text{ kJ} \cdot \text{K} \cdot \text{kg}^{-1}$ ,  $H_0 = 299 \text{ kJ} \cdot \text{kg}^{-1}$ ,  $c_u = 3.78 \text{ kJ} \cdot \text{kg}^{-1} \text{K}^{-1}$ ,  $\theta_f = -0.62^\circ \text{C}$ . The maximum error is  $10 \text{ kJ} \cdot \text{kg}^{-1}$  except immediately (within 1 K) below the freezing point, where latent heat release causes a steep rise in the enthalpy curve and experimental data is very uncertain, since a small change in temperature will cause a very large change in enthalpy.

Otero et al. (2006) reviewed thermal property data for Tylose gel and proposed equations for extrapolating to higher pressures. Unfortunately some of the data reviewed is out of date and probably inaccurate, especially for thermal conductivity.

## 2.7 Summary and Recommendations

- The heat transfer coefficient  $h$  is frequently the most uncertain parameter in a freezing calculation. However, errors in  $h$  are not serious if internal resistance to heat transfer is the controlling factor.
- If reliable experimental data on physical properties is available at various temperatures, they should be used either by direct interpolation from tabulated data or by replacing the data with regression equations. A suitable regression equation for enthalpy below freezing is Eq. 2.22, while above freezing a constant specific heat can usually be assumed (Eq. 2.23). For thermal conductivity, Eq. 2.47 and 2.48 may be used.
- If property data is unavailable but the food's composition is known, the freezing point can be estimated from Eq. 2.11 or similar relationships. The ice fraction at various temperatures can then be estimated from Eq. 2.16. Enthalpy can then be calculated by adding component enthalpies (Eqs. 2.18, 2.19, 2.20) using the specific heat data in Table 2.3. Thermal conductivity can be calculated by the method of Fig. 2.7.
- If only the water content is available, use Eq. 2.25 for enthalpy and Eq. 2.17 for ice fraction. Thermal conductivity can then be estimated by guessing the contents of protein, fat, carbohydrate, fibers and minerals from similar products

and applying the method of Fig. 2.7. Since the thermal conductivities of likely major components except water/ice (which is usually known) and ash (which is usually present in very small amounts) are within a two-to-one range, a reasonable estimate can usually be obtained, say  $\pm 10\%$  for non-porous products. Empirical relationships may also be available for specific classes of product (meat, fish, fruit etc.) in the literature.

- Apparent specific heat can in all cases be obtained by numerical or analytical differentiation of the enthalpy–temperature relationship.
- Calorimetric properties at high pressure are readily obtained from those at atmospheric pressure by using basic thermodynamic relationships, provide the values of latent heat of freezing, density and thermal expansion coefficient are available.



## CAUTION

- In Choi and Okos (1986) there was an error in a parameter for fat thermal conductivity, which has been corrected in Table 2.3.
- For water density, Eq. 2.5 is recommended over Choi and Okos's equation.
- For water specific heat, Eq. 2.21 is recommended over Choi and Okos's equation.
- Many papers use obsolete thermal properties for Tylose gel. Those presented in Sect. 2.6 are recommended provided the composition is as described in that section.
- Specific heat may mean sensible heat only or may include latent heat depending on context. Make sure that the correct interpretation is applied.
- The prediction method given above for thermal conductivity may not work well for foods with anisotropic microstructures, such as muscle meat.

<http://www.springer.com/978-1-4939-0556-0>

Food Freezing and Thawing Calculations

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2014, XV, 153 p. 44 illus., 21 illus. in color., Softcover

ISBN: 978-1-4939-0556-0