Method Article

Calculation of full process freezing time in minced fish muscle

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Abstract

The present manuscript is the expansion of the method Modelling of freezing time described in a previous paper. This modeling was used for simulating freezing times required for the inactivation of anisakids. The method described here can also be used for a number of other applications where the time or the temperature of the food needs to be modeled. In general, when a food is brought from room temperature to temperatures below −5 °C, the temperature kinetics follow three different parts which include cooling from initial temperature to the initial freezing point, freezing from the freezing point to −5 °C in the center of the food, and cooling from −5 °C to the final temperature in the center of the food. The present customized procedure is mainly based upon established estimation procedures. Following the description of the methods, an example of the calculation for freezing hake (Merluccius merluccius) mince muscle is provided for each of the phases. The method consists in the following:

- Calculation of the pre freezing and sub freezing times with a similar procedure but separately since the sample has different thermo physical properties in each stage (cooling).
- Calculation of the freezing time first for an infinite flat plate, and then a correction is applied for the actual geometry (finite cylinder).
- The total freezing time is the sum of the three separate parts of the freezing process.

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Specifications table

| Subject Area:          | Engineering                     |
|-----------------------|---------------------------------|
| More specific subject area: | Freezing of foods               |
| Method name:          | Calculation of full process freezing time in minced fish muscle |
| Name and reference of original method: | See References section |
| Resource availability: | n.a.                             |

SYMBOLS

| Symbol | Description                                      | Dimensionality |
|--------|--------------------------------------------------|----------------|
| $A_n$  | Series expansion constants                       | Dimensionless  |
| $A$    | Lag factor                                       | Dimensionless  |
| $a$    | Thermal diffusivity                              | m$^2$/s        |
| $Bi = \frac{H}{a}$ | pre freezing and sub freezing Biot number                   | Dimensionless  |
| $Bi = \frac{H}{t}$  | Freezing Biot number                              | Dimensionless  |
| $C_i$  | Volumetric specific heat of the unfrozen phase    | J/(m$^3$K)     |
| $C_s$  | Volumetric specific heat of the frozen phase and  | J/(m$^3$K)     |
| $E$    | Equivalent heat transfer dimensionality          | Dimensionless  |
| $E_1$, $E_2$ | Parameters to calculate $E$                      | Dimensionless  |
| $F_0 = \frac{a}{H}$ | Fourier number                      | Dimensionless  |
| $G_1$, $G_2$, $G_3$ | Parameters to calculate $E$                      | Dimensionless  |
| $H$    | Enthalpy of food                                 | kJ/kg          |
| $\Delta H_f$ | Volumetric difference of enthalpy                | J/m$^3$        |
| $h$    | Surface heat transfer coefficient                | J/(s m K)      |
| $K_0$  | Constant appearing in Eq. (17)                  | Dimensionless  |
| $k$    | Thermal conductivity                             | J/(s m K)      |
| $L_f = 333.6$ | Latent heat of fusion of water                   | kJ/kg          |
| $L_c$  | Shortest length of the object                    | m              |
| $P$    | Parameter in Eq. (25)                            | Dimensionless  |
| $PK = \frac{C_i(C_f-\frac{T}{T})}{\Delta H_f}$ | Plank number | Dimensionless  |
| $R$    | Parameter in Eq. (25)                            | Dimensionless  |
| $R_s$  | Semi-shortest length of the object               | m              |
| $R_n$  | Semi-length of each component                    | m              |
| $r$    | Distance to the center of the object             | m              |
| $Ste = \frac{C_i(T_f-T_{ref})}{\Delta H_f}$  | Stefan number                                    | Dimensionless  |
| $T$    | Temperature                                       | °C             |
| $T_os$ | External temperature                             | °C             |
| $T_i$  | Initial temperature in the sub process           | °C             |
| $T_0$  | Initial temperature                              | °C             |
| $T_f$  | Initial freezing temperature                     | °C             |
| $T_r$  | Reference temperature                            | °C             |
| $t_{1}$, $t_{2}$, $t_3$ | pre freezing, freezing and sub freezing times   | s, min         |
| $t = t_{1} + t_{2} + t_3$ | Time of the complete process                     | s, min         |
| $t_{flat plate}$ | freezing time for an infinite flat plate         | s, min         |
| $t_f$  | Chen's reference temperature for enthalpy        | °C             |
| $x = \frac{x}{L}$ | Dimensionless position into the object          | Dimensionless  |
| $x_a$  | Mass fraction of ash                             | %              |
| $x_b$  | Mass fraction of bound water                     | %              |
| $x_f$  | Mass fraction of fat                             | %              |
| $x_i$  | Mass fraction of ice                             | %              |
| $x_p$  | Mass fraction of protein                         | %              |
| $x_s$  | Mass fraction of solids in food                  | %              |

(continued on next page)
Method detail

In general, when a food is brought from room temperature to temperatures below −5°C, the temperature kinetics is as illustrated in Fig. 1. As the figure shows, there are three different parts: The first one is the cooling from initial temperature to the initial freezing point (temperature at which freezing begins). This is somewhat lower than the freezing point of pure water due to the components dissolved in it. The second part consists in freezing from the freezing point to −5°C in the center of the food. And the third part is the cooling from −5°C to the final temperature in the center of the food.

According to ASHRAE [1], the total freezing time is estimated by applying Eq. (1), made by three addends:

\[
t = t_1 + t_2 + t_3
\]  

![Fig. 1. Freezing kinetics.](image)
Being $t_1$, $t_2$ and $t_3$ respectively the pre freezing, freezing and sub freezing times.

The estimation of freezing times ($t_1$, $t_2$, $t_3$) depends on the initial and final temperatures of the process, as well as on the initial freezing point and the temperature where most of the water turns into ice. It is necessary to first estimate the thermo-physical properties of the food, which are a function of the food components (i.e. water, protein, fat, ash, or carbohydrate). These properties will change depending on the temperature range taken into account, and on the proportion of liquid water and ice. Thus, they will be different in the three parts of the freezing process (i.e. pre freezing, freezing and sub freezing). The dimensions of the food will also affect the freezing time. Since the estimations of the geometry parameters needed in the calculations are well known for geometries such as infinite flat plate, infinite rod, or sphere, they can be used to estimate the cooling or freezing times when the sample has regular geometries. This is the case of prism and finite cylinder, which are orthogonal intersections of the elemental geometries such as infinite flat plate and infinite rod. The surface heat transfer coefficient, which depends on the product surface, the air cooling the product, and its flux is also needed in these estimations. Both first ($t_1$) and third ($t_3$) portions may be calculated as cooling, although with quite different thermo physical properties. In this paper they were calculated according to Cuesta et al. [2] and Cuesta and Lamúa [3] whereas the freezing portion ($t_2$) was calculated according to Cleland and Earle [4,5], Cleland et al., [6,7] and ASHRAE [1].

In this work, we addressed the cooling process for a regular geometry (i.e. cylinder). In the first section, we describe the pre freezing procedure, initially for the case when the surface heat transfer coefficient is known. We then outline an indirect estimation based on experimental time-temperature data for the cases when this parameter is unknown. Next, the sub freezing estimation is described. It follows the description of the procedure to estimate the freezing time by means of the calculation for infinite flat plate to which a geometry correction is applied. The second section contains the method validation using hake (Merluccius merluccius) mince frozen in Petri dishes of known geometry as an example.

Cooling

General model

According to Carslaw and Jaeger [8], the temperature kinetics in simply-shaped, homogeneous and isotropic bodies subject to homogeneous external conditions, is given by a series of infinite terms, the general Equation of which is:

$$Y = \sum_{n=1}^{\infty} A_n \psi(\delta_n x) e^{-\delta_n^2 F_0}$$  \hspace{1cm} (2)

Being:

$$Y = \frac{T - T_{\text{ex}}}{T_0 - T_{\text{ex}}}$$, Relative difference of temperatures.  \hspace{1cm} (3)

$T$, Temperature of the object

$T_{\text{ex}}$, Temperature of the freezer

$T_0$, Initial temperature of the object

$x = \frac{r}{R}$, Dimensionless position into the object

$r$, Distance to the center of the object

$R$, Semi-shortest length of the object

$$F_0 = \frac{a t}{R^2}$$, Dimensionless time (Fourier number), \hspace{1cm} (4)

$a$, Thermal diffusivity

$A_n$, Series expansion constants (Eq. (6) below)

$$\psi(\delta_n x) = \cos(\delta_n x)$$ for flat plate

$$J_0(\delta_n x)$$ (Bessel function of the first kind and order zero) for cylinder

$$\sin(\delta_n x)/x$$ for the sphere
\[ \delta_n, \text{ } n^{th} \text{ solution to the Biot (Bi) transcendental boundary equation:} \]
\[ \left[ \frac{\partial \psi (\delta_n x)}{\partial x} \right]_{x=1} = -2Bi\psi (\delta_n) \tag{5} \]

According to Cuesta et al. [2], \( A_n \) can be written:
\[ A_n = \frac{2Bi}{\psi (\delta_n)\left[ \delta_n^2 + Bi^2 - (\Gamma - 1)Bi \right]} \tag{6} \]

\( \Gamma \), geometric constant
\( \Gamma = 0 \) for flat plate
\ 1 for cylinder
\ 2 for the sphere (Table 7)
\[ Bi = \frac{hR}{k}, \text{ Biot number,} \tag{7} \]

\( h \), Surface heat transfer coefficient
\( k \), Thermal conductivity

In elemental geometries \( \delta^2 \) can be approached by applying the following Eqs. (8) and (9) [3]:
\[ \frac{\delta_M^2}{\delta^2} = \left( 1 + \frac{2}{Bi} \right) \left( 1 + \frac{K}{0.975Bi^{1.25} + 1} \right) \tag{8} \]

Where
\[ \delta_M = \delta \text{ when } Bi \to \infty \]
\[ K = \frac{\delta_M^2}{2(\Gamma + 1)} - 1 \tag{9} \]

The maximum error detected when applying Eqs. (8) and (9) to the three elemental geometries was always less than 1.5% [3].

For compounds with regular geometries (i.e. prism and finite cylinder) which are orthogonal intersections of the elemental geometries (infinite flat plate and infinite rod), the complete solution is the product of the solutions (Eq. (2)) corresponding to these elemental geometries.

**Calculation of pre freezing cooling time**

**Thermo-physical parameters.** Thermo-physical parameters such as density, thermal conductivity, specific heat, and thermal diffusivity, can be deduced using the chemical compositions of foods from the equations of Choi and Okos collected in Tables 1 to 4 [9,10]. Thermo-physical parameters depend on temperature, and in the present paper food is cooled down from room temperature to temperatures well below 0 °C. So, in the first and third portions of the process, parameters need to be averaged for each full interval of temperatures. Thus Tables 1-4 show the mathematical models for predicting the thermal properties (temperature functions) of the food components (water, protein, fat, carbohydrate, and ash) as a function of a fixed temperature and also for a given range.

**Estimation of center cooling times.** The roots \( \delta_n \) derived from Eq. (5) are discrete values increasing with the terms of the series, so that from a certain value onwards of \( Fo \) only the first term in the series is significant and Eq. (2) may be replaced with sufficient accuracy by its first addend. This will allow us to estimate the cooling times of a regular shaped object from the first addend of the complete series (Eq. (2)) [1-4]. In fact, in the center \( x = 0 \) and \( \psi (0) = 1 \) for the three cases (infinite plate, infinite rod and sphere). Taking into account that from a certain value of \( Fo \) (generally \( Fo \sim 0.2 \) or 0.3) onwards only the first addend in the series is significant (since the roots \( \delta_n \) increase with the terms of the series and this is rapidly converging), Eq. (2) may be replaced with sufficient accuracy by Eq. (10):
\[ Y \approx A e^{-\delta^2 Fo} \tag{10} \]
\[ A = \prod_i A_i \tag{11} \]
Table 1
Thermo-physical parameters: Density $\rho_i$ of components (Tables 1-7).

| Food Component | Components Equation (kg · m$^{-3}$) |
|----------------|-------------------------------------|
| Water          | $\rho_W = 9.9718 \times 10^2 + 3.1439 \times 10^{-3} T - 7.3754 \times 10^{-3} T^2$ |
| Ice            | $\rho_I = 9.1689 \times 10^2 - 1.3071 \times 10^{-1} T$ |
| Protein        | $\rho_P = 1.3299 \times 10^2 - 5.1840 \times 10^{-1} T$ |
| Fat            | $\rho_F = 9.2559 \times 10^2 - 4.7175 \times 10^{-1} T$ |
| Carbohydrate   | $\rho_C = 1.5991 \times 10^3 - 3.1046 \times 10^{-1} T$ |
| Ash            | $\rho_A = 2.4238 \times 10^3 - 2.8063 \times 10^{-1} T$ |

From [10], chapter 19, Tables 1 and 2.

Table 2
Thermo-physical parameters: Thermal Conductivity $k_i$ of components.

| Food Component | Components Equation (W · m$^{-1}$ · K$^{-1}$) |
|----------------|-----------------------------------------------|
| Water          | $k_W = 5.7109 \times 10^{-1} + 1.7625 \times 10^{-3} T - 6.7036 \times 10^{-2} T^2$ |
| Ice            | $k_I = 2.2196 - 6.2489 \times 10^{-3} T + 1.0154 \times 10^{-4} T^2$ |
| Protein        | $k_P = 1.7881 \times 10^{-1} + 1.958 \times 10^{-3} T - 2.7178 \times 10^{-2} T^2$ |
| Fat            | $k_F = 1.8071 \times 10^{-1} - 2.7604 \times 10^{-3} T - 1.7749 \times 10^{-4} T^2$ |
| Carbohydrate   | $k_C = 2.0141 \times 10^{-1} + 1.3874 \times 10^{-3} T - 4.3312 \times 10^{-4} T^2$ |
| Ash            | $k_A = 2.2962 \times 10^{-1} + 1.4011 \times 10^{-3} T - 2.8063 \times 10^{-4} T^2$ |

*In this paper $k$ has been calculated using the perpendicular model. From [10] chapter 19, Tables 1 and 2.

$$\delta^2 = \sum \delta_n^2 \alpha_n^2$$  \hspace{1cm} (12)

$$\alpha_n = \frac{R_n}{R}, \text{ shape ratios,}$$  \hspace{1cm} (13)

$R_n$, Semi-length of each component

So, from Eq. (10), the dimensionless time required to attain a given $Y$ at the body’s thermal center is:

$$Fo \approx \frac{\ln \frac{\delta}{\delta^2}}{\delta^2}$$  \hspace{1cm} (14)

For regular geometries, when the Biot number is known (and so $\delta$), $Fo$ can be estimated by applying Eqs. (5) to (14).

The cooling time is estimated by clearing from Fourier Number (Eq. (4))

$$t = FoR^2/a$$  \hspace{1cm} (15)
Time is calculated in seconds. To calculate cooling times for other geometries, see [3].

Algorithm when the surface heat transfer coefficient is known. When the surface heat transfer coefficient, \( h \), is known the algorithm to estimate the cooling time to get the dimensionless temperature \( Y \) is as follows:

**BOX 1. Algorithm when the surface heat transfer coefficient is known**

1. Calculate the thermal properties of the product to the average of the complete temperatures interval considered (as seen in paragraph 1.2 above)
2. Determine the characteristic length of the sample \( R \) (half of the shortest of the object) and the shape ratios \( \alpha_n \) (Eq. (13))
3. Since the surface heat transfer \( h \) is known, the Biot number is calculated from Eq. (7)
4. Then, \( \delta^2 \) is determined with Eq. (12). For that, calculate the \( \delta^2_M \) values. From Table 7, \( \delta^2_M \) and \( \Gamma + 1 \) can be obtained, and then, for each component, calculate \( K \) from Eq. (9) and \( \delta^2_M \) from Eq. (8) which are used to calculate \( \delta^2 \) from Eq. (12)
5. Determine \( A_n \) for each geometry component (Eq. (6)) and then calculate \( A \), which is the product of each individual component (Eq. (11))
   - Be remembered that the function \( \psi(\delta_n) \) appearing at Eq. (6) denominator is:
     - For the infinite cylinder, \( J_0(\delta_n) \), is the Bessel function of the first kind and zero order
     - For the infinite flat plate, \( \cos(\delta_n) \) (See Table 7)
6. Estimate the cooling Fourier number (dimensionless time) by applying Eq. (14)
7. Determine cooling time by clearing from Fourier number (Eq. (15))

**Indirect estimations with unknown surface heat transfer coefficient.** The surface heat transfer coefficient can be obtained from time-temperature tables obtained experimentally. According to [11], constant \( \delta^2 \) can be estimated from these tables since Eq. (10) can be re-written as:

\[
\ln Y \approx \ln A - \delta^2 F_0
\]

By selecting the linear portion of the pre freezing part and calculating \( F_0 \) from Eq. (15), the \( \{\ln Y - F_0\} \) table (dimensionless) is made, and by linear regression of Eq. (16), \( \delta^2 \) is determined. Then, by applying next Eq. (17), \( Bi \) can be estimated:

\[
Bi \approx \delta^2 \left[ \frac{1}{\Gamma + 1} + \frac{2}{K_\delta \delta^2_M} \times \frac{\delta^2}{\delta^2_M - \delta^2} \right]
\]

Where

\[
K_\delta = \frac{\sum \delta^2_{M,n} \alpha_n^2}{\sum \delta^2_{M,n} \alpha_n^3}
\]

For elementary geometries \( K_\delta = 1 \)

And

\[
\delta^2_M = \sum \delta^2_{M,n} \alpha_n^2
\]

The particular values taken for \( \delta^2_M \) are in Table 7 (i.e. \( \delta^2_M = (\pi/2)^2 \) for infinite flat plate; \( r \) infinite circular cylinder; \( \delta^2_M = \pi^2 \) for the sphere).

\[
\Gamma + 1 = \sum \alpha_n (\Gamma_n + 1)
\]

The values for regular geometries are shown in Table 7. For other geometries:

\[
\Gamma + 1 = \frac{SV}{R}
\]

Being

\( S \), Surface

\( V \), Volume

Finally, determine the surface heat transfer coefficient, which will be needed for the calculations of the other parts of the curve, by clearing from the Biot number:

\[
h = \frac{Bi \cdot k}{R}
\]
Being \( R \) the semi-shortest length of the object.

Since \( t \) is an experimental parameter in this example, Eqs. (14) and (15) could be applied for confirmation, after the estimation of slope \( \delta^2 \) and Lag factor \( A \) from the experimental curves, an thus without the need of \( h \).

**Algorithm when the surface heat transfer coefficient is unknown.** When the surface heat transfer coefficient is not known, the algorithm to estimate it is as follows:

**BOX 2. Algorithm when the surface heat transfer coefficient is unknown**

1. Calculate the thermal properties of the product to the average of the complete temperatures interval considered (as seen in paragraph 1.2 above)
2. Determine the characteristic length of the sample \( R \) (half of the shortest of the object) and the shape ratios \( \alpha_n \)
   (Eq. (13))
3. From the experimentally obtained time-temperature data select the linear portion of the pre freezing part and make the table [\( \text{Fo} - \ln Y \)] (dimensionless)
4. Make linear regression to find the (minus) slope \( \delta^2 \)
5. Calculate the geometrical constant for parallelepiped and finite cylinder (Eq. (20)). For other geometries Eq. (21) can be applied. The particular values for simple geometries are in Table 7 (i.e. \( \Gamma + 1 = 1 \) for flat plate; \( \Gamma + 1 = 2 \) for infinite cylinder; \( \Gamma + 1 = 3 \) for sphere).
6. Calculate the maximum slope \( \delta^2_\Gamma \), For parallelepiped or finite cylinder apply the Eq. (19). For other geometries, see Cuesta and Lamúa [3]. The following particular values can be taken (Table 7): \( \delta^2_\Gamma = (\pi/2)^2 = 2.4674 \) for flat plate; \( \delta^2_\Gamma = (2.4048)^2 = 5.7832 \) for infinite cylinder; and \( \delta^2_\Gamma = \pi^2 = 9.8696 \) for the sphere.
7. Calculate constant \( K_i \) (Eq. (18)). In the case of elementary and cubic geometries (cube, cylinder of equal base that diameter or sphere) \( K_i = 1 \). For other geometries apply Eq. (18)
8. Apply Eq. (17) to estimate \( B_i \)
9. Calculate the surface transfer coefficient \( h \) applying Eq. (22)
10. Estimate the cooling time by calculating \( F_o \) (Eq. (14)) and clearing the time (Eq. (15))

**Calculation of sub freezing cooling time**

In the third portion of the complete graph (Fig. 1), the surface heat transfer coefficient need not be estimated again since it is the same as in the cooling process. Also the shape is the same but the thermo-physical parameters are some more complicated as previously. Note that the components change, since for \( T_1 < T_f \) there is a certain ice proportion.

**Thermo-physical parameters.** To estimate the mass fraction of ice, Eq. (23) is applied [10,12]:

\[
x_{ice} = \frac{1.105x_{wo}}{1 + \frac{0.7138}{\ln(t_f - T_1) + 1}}
\]  \( (23) \)

Where \( x_{wo} \) is the unfrozen mass fraction of water. Therefore, below the initial freezing temperature the mass fraction of liquid water is:

\[
x_w = x_{wo} - x_{ice}
\]  \( (24) \)

Both \( x_w \) and \( x_{ice} \) should be considered in the chemical composition and therefore in the application of the Choi & Okos equations to estimate the thermo-physical parameters.

Taking into account the mass fraction of water for the unfrozen food and the average temperature of this process, \( x_{ice} \) is calculated. The rest of the chemical components remain the same as before and can be operated as in the previous cooling example.

**Center cooling times.** The Biot number, the slope \( \delta^2 \), the lag factor \( A \), and \( F_o \) need to be calculated for this phase in the same way as for pre freezing. As in the case of \( t_1 \), this \( t_3 \) value will also be included later in Eq. (1).

**Freezing**

As stated in the Introduction, the second portion in the complete graph of the cooling process from room temperature to temperatures well below freezing temperatures is the freezing of the
food. In this section, the freezing time from initial freezing temperature \( T_f = -1.3^\circ C \) to \(-5^\circ C\) is estimated following Cleland’s method \([1,6,7]\) which estimates the freezing time for the infinite plate (or other elemental shape) and then a shape factor is applied to the actual geometry. The freezing time estimation for the infinite plate is based upon an extension of Plank’s Equation incorporating removal of sensible heat and temperature variation during freezing.

**Estimation of freezing time for the infinite plate**

The final equation is:

\[
t_{\text{flat plate}} = \frac{\Delta H_{ri}}{(T_f - T_{ex})} \left( \frac{P L_c}{h} + \frac{R L_c^2}{k_s} \right) \left[ 1 - \frac{1.65 \cdot \text{Ste} \cdot \ln \left( \frac{T - T_{ex}}{T_f - T_{ex}} \right) }{T_f - T_{ex}} \right]
\]  

(25)

\( T_r \) is the reference temperature \((-18^\circ C) \) \([1,13]\) and \( \Delta H_{ri} \) the food volumetric change of enthalpy between initial freezing temperature \( T_f = -1.3^\circ C \) and \( T_r = -18^\circ C \) \([1,6,7,14]\).

Once \( t_{\text{flat plate}} \) has been estimated, it must be divided by a geometric correction factor, called the equivalent heat transfer dimensionality \( E \):

\[
t = \frac{t_{\text{flat plate}}}{E}
\]  

(26)

Time is calculated in seconds. Factors \( P \) and \( R \) are presented in Table 5. They are functions of the Plank, Stefan and Biot numbers.

\[
Bi = \frac{h L_c}{k_s}
\]  

(27)

\[
P_k = \frac{C_i (T_i - T_f)}{\Delta H_{ri}}
\]  

(28)

\[
\text{Ste} = \frac{C_s (T_f - T_{ex})}{\Delta H_{ri}}
\]  

(29)

Where \( h \) is the surface heat transfer coefficient (estimated above), \( L_c \) is the characteristic dimension, which in this section is the shortest length (not half of the shortest length).

In our example:

- \( L_c \), height of the sample
- \( k_s \), thermal conductivity of the fully frozen food \( (T_r) \)
- \( C_i \), volumetric specific heat of the unfrozen phase (i.e. \(-1.3 \, ^\circ C\) ). For that specific heat from Choi and Okos equation (kJ·kg\(^{-1}\)·K\(^{-1}\)) must be multiplied by the corresponding density and by \(10^3\) to have \( C_i \) in J/m\(^3\) K.
- \( C_s \), volumetric specific heat of the frozen phase (i.e. \(-5 \, ^\circ C\) ), also in J/m\(^3\) K and calculated as above
- \( T_i \), initial temperature of the subprocess (i.e. \(-1.3 \, ^\circ C\) )
- \( T_f \), initial freezing temperature (i.e. \(-1.3 \, ^\circ C\) )
- \( T \), final temperature of the subprocess (i.e. \(-5 \, ^\circ C\) )

The enthalpy calculation is performed according to \([10,15]\) for temperatures below the initial freezing temperature:

\[
H = (T - T_r) \left[ 1.55 + 1.26x_s - \frac{(x_{W_0} - x_b)L_0 T_f}{T_r T} \right]
\]  

(30)

\( H \), enthalpy of food (kJ/kg)

\( T_r \), Chen’s reference temperature for enthalpy \( (T_r = -40^\circ C) \) at which enthalpy is defined to be zero \([1]\)

\( L_0 = 333.6 \, \text{kJ/kg} \), Latent heat of fusion of water

\( x_s \), Mass fraction of solids in food

\( x_b \), Bound water. According to ASHRAE \([10]\), \( x_b \) may be estimated as follows:

\[
x_b = 0.4x_p
\]  

(31)
Where $x_p$ is the protein mass fraction

Keep in mind that the $H$ value calculated in Eq. (30) is in kJ/kg, and the $\Delta H_r$ in Eq. (25) is the volumetric change of enthalpy. So the $H$ value calculated in (30) must be multiplied by the corresponding density and by $10^3$ to have $\Delta H_r$ in J/kg.

Calculation of $E$ for geometry correction

To calculate $E$ apply next Equation:

$$E = G_1 + G_2 E_1 + G_3 E_2$$  \hspace{1cm} (32)

$$E_1 = \frac{X(\varphi_1)}{\beta_1} + \left[1 - X(\varphi_1)\right] \frac{0.73}{\beta_1^{2.50}}$$  \hspace{1cm} (33)

$$E_2 = \frac{X(\varphi_2)}{\beta_2} + \left[1 - X(\varphi_2)\right] \frac{0.50}{\beta_2^{3.69}}$$  \hspace{1cm} (34)

Where $G_1$, $G_2$ and $G_3$ are given in Table 6 and the shape factors $\beta_1$ and $\beta_2$ are:

$$\beta_1 = \frac{\text{Second shortest dimension of food}}{L_c}$$  \hspace{1cm} (35)

$$\beta_2 = \frac{\text{Major dimension of food}}{L_c}$$  \hspace{1cm} (36)

The arguments $\varphi$ into the function $X(\varphi)$ in Eqs. (33) and (34) are:

$$\varphi_1 = \frac{2.32}{\beta_1^{1.77}}$$  \hspace{1cm} (37)

$$\varphi_2 = \frac{2.32}{\beta_2^{1.77}}$$  \hspace{1cm} (38)

And for both $\varphi_1$ and $\varphi_2$, the function $X(\varphi)$:

$$X(\varphi) = \frac{\varphi}{B_{ii}^{\text{34}} + \varphi}$$  \hspace{1cm} (39)

Algorithm to estimate the freezing time

For calculating the freezing time from initial freezing temperature $T_f = -1.3^\circC$ to $-5^\circC$, first, estimate the freezing time for the established interval of an infinite flat plate with the characteristic dimension $L_c$ of the actual product (the minimum of all). And secondly, estimate the freezing time for the actual solid’s using the Cleland’s number of equivalent heat transfer dimensions ($E$).
**BOX 3. Algorithm to estimate the freezing time**

Freezing time of an infinite flat plate:

1. Determine the characteristic length of the sample \( L_c \) (the shortest of the object) in m
2. Calculate thermo-physical parameters (\( \rho, k, c_p \)) at initial freezing temperature \( T_f = -1.3 \degree C \), final temperature from the freezing process \( T = -5 \degree C \) and the reference temperature \( T_r = -18 \degree C \)
3. Calculate thermo-physical parameters \( C_f \) and \( C_i \) of the frozen food (i.e. at the initial freezing temperature (-1.3\degree C) \( (C_f) \), and final freezing temperature of the subprocess (-5\degree C) \( (C_i) \).
4. The surface heat transfer coefficient \( h \) has previously been calculated
5. Calculate Enthalpy for the initial freezing temperature \( (T_f = -1.3 \degree C) \)
6. Calculate Enthalpy for \( (T_i = -18 \degree C) \)
7. Calculate \( \Delta H_f \)
8. Determine the corresponding Biot (\( Bi = \frac{hL_c}{k} \)), Plank (\( Pk = \frac{C_I(T_f-T_c)}{\Delta H_f} \)) and Stefan (\( Ste = \frac{C_I(T_f-T_a)}{\Delta H_f} \)) numbers
9. Calculate parameters \( P \) and \( R \) corresponding to the flat plate (Table 5)
10. Estimate the freezing time applying Eq. (25)

**Geometry correction:**

11. Calculate \( \beta_1 \) and \( \beta_2 \) Eqs. (35) and (36)
12. Calculate arguments \( \varphi_1 \) and \( \varphi_2 \) Eqs. (37) and (38)
13. Calculate arguments \( X(\varphi_1) \) and \( X(\varphi_2) \) (Eq. (39))
14. Obtain the \( G_1, G_2 \) and \( G_3 \) values from Table 6
15. Calculate \( E_1 \) and \( E_2 \) Eqs. (33) and (34)
16. Calculate equivalent heat transfer dimensionality \( E \) applying Eq. (32)
17. Estimate the freezing time for the actual food applying Eq. (26)

**Method validation**

To check the calculation methods, a cylindrical hake sample, 90 mm in diameter and 10 mm in height, at 18.3\degree C initial temperature, was frozen in a freezing chamber at −30\degree C. The measured chemical composition for the hake sample was: \( x_W = 0.801; x_P = 0.183; x_C = 0.004; x_A = 0.012; \) \( x_O = 0.0 \). In addition to the geometrical and compositional values, the corresponding time-temperature data for the process were obtained experimentally. These were needed for the calculation of the surface heat transfer coefficient since the air speed in the freezer was not known, and thus this parameter must be estimated indirectly.

**Example 1. Calculation of pre freezing time**

This example refers to the first portion of the complete graph: cooling from the initial temperature to the initial freezing temperature.

**Thermo-physical parameters**

These compositional data can be used to calculate the value of the thermo-physical parameters from the equations of Choi and Okos [9,10] (Tables 1 to 4). To estimate the surface heat transfer coefficient the algorithm for the indirect estimations is to be applied from the first portion of the process. Therefore, the thermal properties of the product should be calculated for the average temperature between the initial temperature and the initial freezing point temperature. From the original [time-Temperature] table, the estimated initial freezing temperature is \( T_f \approx -1.3 \degree C \).

The components are:

\[
\rho_W = 9.9718 \times 10^2 + 3.1439 \times 10^{-3} \frac{18.3^2 - (-1.3^2)}{2 \times (18.3 + 1.3)} - 3.7574 \times 10^{-3} \frac{18.3^3 - (-1.3^3)}{3 \times (18.3 + 1.3)} = 996.8 \text{ kg/m}^3
\]

\[
\rho_p = 1.3299 \times 10^2 - 5.1840 \times 10^{-1} \frac{18.3^2 - (-1.3^2)}{2 \times (18.3 + 1.3)} = 1325.5 \text{ kg/m}^3
\]

\[
\rho_f = 9.2559 \times 10^2 - 4.1757 \times 10^{-1} \frac{18.3^2 - (-1.3^2)}{2 \times (18.3 + 1.3)} = 922.0 \text{ kg/m}^3
\]

\[
\rho_A = 2.4238 \times 10^3 - 2.8063 \times 10^{-1} \frac{18.3^2 - (-1.3^2)}{2 \times (18.3 + 1.3)} = 2421.4 \text{ kg/m}^3
\]
As the porosity is assumed to be 0 ($\varepsilon = 0$), global density (see Table 1) is:

$$\rho = \frac{1}{\frac{\rho_w}{V_w} + \frac{\rho_p}{V_p} + \frac{\rho_f}{V_f} + \frac{\rho_a}{V_a}} = 1051.7 \text{kg/m}^3$$

By operating in the same way with the other parameters, we arrive at:

$$k = 0.443 \text{ W/(mK)}$$

$$c_p = 3707.2 \text{ J/kgK}$$

$$a = k\rho c = 1.13710^{-7} \text{ m}^2/\text{s}$$

**Characteristic length and shape ratios $\alpha_n$**

This is half the sample thickness:

$$R = \frac{10\text{mm}}{2} = 5.0\text{mm} = 5 \times 10^{-3} \text{m}$$

$$\alpha_H = \frac{10}{10} = 1.00$$

$$\alpha_D = \frac{10}{90} = 0.11$$

**Calculate the \{Fo – lnY\} table**

From the time-temperature data make the \{Fo – lnY\} table (dimensionless) and select the linear portion in semi logarithmic scale.

To make the \{Fo – lnY\} table be remembered that ([Eq. (3)]):

$$Y = \frac{T - T_{ex}}{T_0 - T_{ex}} = \frac{T - (-30)}{18.3 - (-30)}$$

And from [Eq. (4)]:

$$Fo = \frac{at}{R^2} = \frac{1.137 \times 10^{-7}}{(5 \times 10^{-3})^2} t = 4.546 \times 10^{-3} t$$

**Make the linear regression to find the (Minus) slope $\delta^2$**

The linear portion and the linear regression are presented in Fig. 2 and the values are:

(Minus) slope $\delta^2 = 0.076$

Lag factor $A = \exp(0.0365) = 1.037$

**Calculate the geometrical constant**

As the sample is a finite cylinder, geometrical constant is ([Eq. (20)]):

$$\Gamma + 1 = \sum \alpha_n (\Gamma_n + 1) = \alpha_H (\Gamma_H + 1) + \alpha_D (\Gamma_D + 1) = 1 \times 1 + 0.11 \times 2 = 1.22$$

**Calculate the maximum slope $\delta^2_M$**

$\delta^2_M$ is calculated by applying [Eq. (19)].

$$\delta^2_{M,H} = (\pi/2)^2 = 2.4674; \delta^2_{M,D} = (2.4048)^2 = 5.7832$$

$$\delta^2_M = \sum \delta^2_{M,n} \alpha^2_n = (\pi/2)^2 \times 1 + 5.7831 \times (0.11)^2 = 2.539$$
Calculate constant $K_\delta$

Applying Eq. (18):

$$K_\delta = \frac{\sum \delta^2_{M,n} \alpha^2_n}{\sum \delta^2_{M,n} \alpha^2_n} = \frac{2.539}{(\pi/2)^2 \times 1 + 5.7832 \times (0.11)^3} = 1.026$$

Estimating $Bi$

Applying Eq. (17):

$$Bi \approx 0.0760 \times \left[ \frac{1}{1.22} + \frac{2}{1.026 \times 2.539} \times \frac{0.0760}{2.539 - 0.0760} \right] = 0.0640$$

Clear the surface heat transfer coefficient

From Eq. (7):

$$h = \frac{Bi \cdot k}{R} = \frac{0.0640 \times 0.443}{5 \times 10^{-3}} = 5.67 \text{ W/(m}^2\text{K)}$$

Calculate the time to get the initial freezing temperature

$$T_f = -1.3^\circ \text{C}$$

$$Y_f = \frac{-1.3 - (-30)}{18.3 - (-30)} = 0.59 \text{ (Eq. (3))}$$

And Eq. (14):

$$Fo_T = \frac{\ln \frac{T_f}{Y_f}}{\delta^2} = \frac{\ln \frac{1.037}{0.039}}{0.0760} = 0.56$$

So (Eq. (15)):

$$t_1 = \frac{FoT^2}{a} = \frac{7.34(5 \times 10^{-3})^2}{1.1371 \times 10^{-7}} = 1614 \text{ s} = 26.9 \text{ min}$$

From the original $\{t-T\}$ table, the time to get $T = -1.30^\circ \text{C}$ is $t = 27.5 \text{ min}$ (deviation $-2.21\%$). This value is to be included after in Eq. (1).
Example 2. Calculation of sub freezing time

This example refers to the third portion of the complete graph: cooling from $-5^\circ C$ to $-25^\circ C$.

The surface heat transfer coefficient is the one estimated at the previous example ($h = 5.67 \text{ W/(m}^2\text{K})$). The shape is the same but the thermo-physical parameters are different, as the components change.

Thermo-physical parameters

By applying Eq. (24) the ice proportion is estimated, and with Eq. (23) the mass fraction of liquid water is calculated. Since the calculated mass fraction of water for the unfrozen fish mince is: $x_{W_0} = 0.801$, and the average temperature of this process is:

$$\bar{T} = \frac{-25 - 5}{2} = -15^\circ C$$

So:

$$x_{\text{ice}} = \frac{1.105 \times 0.801}{1 + \frac{0.7138}{m(-1.3(-15)+1)}} = 0.699$$

And:

$$x_{W} = 0.801 - 0.699 = 0.1016$$

The rest of the chemical components remain the same as before. So, the complete chemical composition for the hake sample for this interval of temperatures is:

$$x_{\text{ice}} = 0.6994; x_{W} = 0.1016 \times 0.183; x_{F} = 0.004; x_{A} = 0.012; x_{C} = 0,$$

Operating as in the previous example we get:

$$\rho_{W} = 9.9718 \times 10^2 + 3.1439 \times 10^{-3} \frac{-5^2 - (-25^2)}{2 \times (25 - 5)} = 996.2 \text{ kg/m}^3$$

$$\rho_{\text{ice}} = 9.1689 \times 10^2 - 1.3071 \times 10^{-1} \frac{-5^2 - (-25^2)}{2 \times (25 - 5)} = 918.9 \text{ kg/m}^3$$

$$\rho_{P} = 1.3299 \times 10^2 - 5.1840 \times 10^{-1} \frac{-5^2 - (-25^2)}{2 \times (25 - 5)} = 1337.7 \text{ kg/m}^3$$

$$\rho_{F} = 9.2559 \times 10^2 - 4.1757 \times 10^{-1} \frac{-5^2 - (-25^2)}{2 \times (25 - 5)} = 931.9 \text{ kg/m}^3$$

$$\rho_{A} = 2.4238 \times 10^3 - 2.8063 \times 10^{-1} \frac{-5^2 - (-25^2)}{2 \times (25 - 5)} = 2428.0 \text{ kg/m}^3$$

As the porosity is assumed to be 0 ($\epsilon = 0$), global density is:

$$\rho = \frac{1}{\frac{x_{W}}{\rho_{W}} + \frac{x_{\text{ice}}}{\rho_{\text{ice}}} + \frac{x_{P}}{\rho_{P}} + \frac{x_{F}}{\rho_{F}} + \frac{x_{A}}{\rho_{A}}} = 991.0 \text{ kg/m}^3$$

By operating in the same way with the other parameters, we arrive at:

$$k = 0.72 \text{ W/(mK)}$$

$$c_p = 2112.2 \text{ J/kgK}$$

$$a = \frac{k}{\rho c} = 3.2828 \times 10^{-7} \text{ m}^2/\text{s}$$
The characteristic length of the sample \( R \) and the shape ratios \( \alpha_n \)

The same as in example 1.

**Biot number**

The surface heat transfer coefficient has been already estimated at the example 1:

\[ h = 5.67 \, \text{W/(m}^2\text{K)} \]

So the Biot number is (Eq. (7)):

\[ Bi = \frac{h \cdot R}{k} = \frac{5.67 \times 5 \times 10^{-3}}{0.72} = 0.0394 \]

**Calculation of \( \delta^2 \)**

To estimate constants \( \delta^2 \) and \( A \) for this cylinder under this Biot number, Eqs. (12) and (11) should be taken into account, which relates the global values to their components.

The \( \delta^2 \) values for each component (infinite rod and infinite flat plate), are calculated from Eqs. (8) and (9) and then used in Eq. (12).

For elemental geometries:

\[ \frac{\delta^2_M}{\delta^2} = (1 + \frac{2}{Bi})(1 + \frac{K}{0.975Bi^{1.25} + 1}) \]  

(8)

Where

\[ K = \frac{\delta^2_M}{2(1 + 1)} - 1 \]  

(9)

For the flat plate \( \delta^2_{M,H} = \left(\frac{\pi}{2}\right)^2 \) and \( \Gamma + 1 = 1 \) (Table 7), so that:

\[ K = \left(\frac{\pi}{2}\right)^2 - 1 = 0.234 \]

And clearing from Eq. (8)

\[ \delta^2_H = \left(1 + \frac{2}{Bi}\right) \left(1 + \frac{K}{0.975Bi^{1.25} + 1}\right) = \left(1 + \frac{2}{0.0394}\right) \left(1 + \frac{0.234}{0.975 \times (0.0394)^{1.25} + 1}\right) = 0.0390 \]

By operating the same for the infinite cylinder:

\[ \delta^2_{M,D} = (2.4048)^2, \text{ and } \Gamma + 1 = 2 \]

\[ \delta^2_D = 0.0777 \]

By substituting into (12):

\[ \delta^2 = 0.0388 \times 1 + 0.078 \times 0.11^2 = 0.0397 \]

**Determine \( A_n \) for each geometry component and calculate \( A \)**

Lag factor: In order to apply Eq. (11), the values corresponding to each component need to be calculated by applying geometry Eq. (6). So, substituting into Eq. (6) for the cylinder the Biot number and \( \delta \) values corresponding to the component elementary geometries:

\[ A_D = \frac{2 \times 0.0394}{J_0(\delta_D)[0.0777 + 0.0394^2 - 0 \times 0.0394]} = 1.014 \]

\( J_0(\delta_D) \) is the Bessel function of the first kind and zero order and for the infinite flat plate function \( \psi(\delta_n) \) appearing at Eq. (6) denominator is \( \cos(\delta_H) \). The resulting \( A_H \) value is:

\[ A_H = 1.008 \]

Therefore, substituting into (11):

\[ A = A_D \times A_H = 1.022 \]
Estimate the cooling Fourier number

After estimation of $\delta^2$ and $A$, only remaining $Y$ needs to be estimated in order to apply Eq. (14). The required final temperature is $T = -25^\circ$C and the starting temperature in this third phase of the process is $T_0 = -5^\circ$C.

So (Eq. (3)):

$$Y_T = \frac{-25 - (-30)}{-5 - (-30)} = 0.20$$

And (Eq. (14)):

$$F_{or_f} = \frac{\ln \frac{A}{\delta^2}}{\ln \frac{0.102}{0.040}} = \frac{1.63}{0.040} = 41.06$$

Time to get the final temperature

So (Eq. (15)):

$$t_3 = \frac{F_{or_f}^2}{a} = \frac{41.06(5 \times 10^{-3})^2}{3.2828 \times 10^{-7}} = 3127 s = 52.12 \text{ min}$$

From the original $\{t - T\}$ table, the time elapsed between $T = -5^\circ$C and $T = -25^\circ$C is $t = 52.33 \text{ min}$ (deviation $-0.41\%$).

Fig. 3 shows both the measured and the calculated $\{\text{time} - \text{Temperature}\}$ graph for the frozen phase.

Example 3. Calculation of freezing time. As stated in the introduction there are three portions in the whole process. At example 1 the cooling time from 18.3°C to the initial freezing temperature $T_f = -1.3^\circ$C is estimated, as well as in the second example the cooling time from $-5^\circ$C to $-25^\circ$C is estimated. So, in this example the freezing time from initial freezing temperature $T_f = -1.3^\circ$C to $-5^\circ$C will be estimated following the algorithm just described above.

Estimate the freezing time of an infinite flat plate.

Characteristic length of the sample.

$L_c = 0.01 \text{ m}$
Figure 4. Measured and calculated time and temperature of the complete process.

Table 3
Thermo-physical properties: Specific heat $c_p$ of components.

| Food component | Components Equation ($kJ \cdot kg^{-1} \cdot K^{-1}$) |
|----------------|--------------------------------------------------|
| Water          | $c_{PW} = 4.1762 - 9.0864 \times 10^{-5}T + 5.4731 \times 10^{-6}T^2$ |
| (0 °C ≤ T ≤ 150 °C) | $c_{PW} = 4.1762 - 9.0864 \times 10^{-5} \frac{\Delta(T)}{\Delta T}$ + 5.4731 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Water          | $c_{PW} = 4.0817 - 5.3062 \times 10^{-3}T + 9.9516 \times 10^{-4}T^2$ |
| (-40 °C ≤ T ≤ 0 °C) | $c_{PW} = 4.0817 - 5.3062 \times 10^{-3} \frac{\Delta(T)}{\Delta T}$ + 9.9516 \times 10^{-4} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Ice            | $c_{PI} = 2.0623 + 0.6769 \times 10^{-3}T$ |
|                | $c_{PI} = 2.0623 + 0.6769 \times 10^{-3} \frac{\Delta(T)}{\Delta T}$ |
| Protein        | $c_{PF} = 2.0082 + 1.2089 \times 10^{-3}T - 1.3129 \times 10^{-6}T^2$ |
|                | $c_{PF} = 2.0082 + 1.2089 \times 10^{-3} \frac{\Delta(T)}{\Delta T} - 1.3129 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Fat            | $c_{PF} = 1.9842 + 1.4733 \times 10^{-3}T - 4.8008 \times 10^{-6}T^2$ |
|                | $c_{PF} = 1.9842 + 1.4733 \times 10^{-3} \frac{\Delta(T)}{\Delta T} - 4.8008 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Carbohydrate   | $c_{PC} = 1.5488 + 1.9625 \times 10^{-3}T - 5.9399 \times 10^{-6}T^2$ |
|                | $c_{PC} = 1.5488 + 1.9625 \times 10^{-3} \frac{\Delta(T)}{\Delta T} - 5.9399 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Ash            | $c_{PA} = 1.0926 + 1.8896 \times 10^{-3}T - 3.6817 \times 10^{-6}T^2$ |
|                | $c_{PA} = 1.0926 + 1.8896 \times 10^{-3} \frac{\Delta(T)}{\Delta T} - 3.6817 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |

From [10] chapter 19, Tables 1 and 2.

Table 4
Thermal diffusivity $\alpha_i$ of components.

| Food component | Components Equation ($m^2 \cdot s^{-1}$) |
|----------------|----------------------------------------|
| Water          | $\alpha_{PW} = 1.3168 \times 10^{-1} + 6.2477 \times 10^{-4}T - 2.4022 \times 10^{-6}T^2$ |
|                | $\alpha_{PW} = 1.3168 \times 10^{-1} + 6.2477 \times 10^{-4} \frac{\Delta(T)}{\Delta T} - 2.4022 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Ice            | $\alpha_{PI} = 1.1756 - 6.0833 \times 10^{-3}T + 9.5037 \times 10^{-5}T^2$ |
|                | $\alpha_{PI} = 1.1756 - 6.0833 \times 10^{-3} \frac{\Delta(T)}{\Delta T} + 9.5037 \times 10^{-5} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Protein        | $\alpha_{PF} = 6.8714 \times 10^{-2} + 4.7578 \times 10^{-4}T - 1.4646 \times 10^{-6}T^2$ |
|                | $\alpha_{PF} = 6.8714 \times 10^{-2} + 4.7578 \times 10^{-4} \frac{\Delta(T)}{\Delta T} - 1.4646 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Fat            | $\alpha_{PF} = 9.8777 \times 10^{-2} - 1.2569 \times 10^{-4}T - 3.8286 \times 10^{-8}T^2$ |
|                | $\alpha_{PF} = 9.8777 \times 10^{-2} - 1.2569 \times 10^{-4} \frac{\Delta(T)}{\Delta T} - 3.8286 \times 10^{-8} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Carbohydrate   | $\alpha_{PC} = 8.0842 \times 10^{-2} + 5.3052 \times 10^{-4}T - 2.3218 \times 10^{-6}T^2$ |
|                | $\alpha_{PC} = 8.0842 \times 10^{-2} + 5.3052 \times 10^{-4} \frac{\Delta(T)}{\Delta T} - 2.3218 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |
| Ash            | $\alpha_{PA} = 1.2461 \times 10^{-1} + 3.7321 \times 10^{-4}T - 1.2244 \times 10^{-6}T^2$ |
|                | $\alpha_{PA} = 1.2461 \times 10^{-1} + 3.7321 \times 10^{-4} \frac{\Delta(T)}{\Delta T} - 1.2244 \times 10^{-6} \frac{\Delta(T^2)}{\Delta T^2}$ |

From [10] chapter 19, Tables 1 and 2.
**Thermo-physical parameters.** By operating as in examples 1 and 2, but taking the equations for single T from Tables 1-3:

- \( \rho = 1052.6 \text{ kg/m}^3 \) (At \(-1.3 \, ^{\circ}C\))
- \( \rho = 997.5 \text{ kg/m}^3 \) (At \(-5 \, ^{\circ}C\))
- \( \rho = 990.6 \text{ kg/m}^3 \) (At \(-18 \, ^{\circ}C\))
- \( k_s = 0.72 \text{ J/(m s K)} \) (At \(-18 \, ^{\circ}C\))
- \( c_p = 3.66 \text{ kJ/(kg K)} \) (At \(-1.3 \, ^{\circ}C\))
- \( c_p = 2.43 \text{ kJ/(kg K)} \) (At \(-5 \, ^{\circ}C\))

Calculate \( C_i \) and \( C_s \). \( C_i = 3.857 \times 10^6 \text{ J/(m}^3\text{K)} \) (At \(-1.3 \, ^{\circ}C\))

\( C_s = 2.419 \times 10^6 \text{ J/(m}^3\text{K)} \) (At \(-5 \, ^{\circ}C\))

**Surface heat transfer coefficient.** \( h = 5.67 \text{ J/(m}^2\text{s K)} \) (from Example 1).

**Enthalpy for the initial freezing temperature \((T_f= -1.3 \, ^{\circ}C)\).** From the composition: \( x_s = 1 - x_{w0} = 0.199 \)

And (Eq. (31)):

\[ x_b = 0.4x_p = 0.0732 \]

Then (Eq. (30)):

\[ H_f = (-1.3 - (-40))\left[1.55 + 1.26 \times 0.199 - \frac{(0.801 - 0.0732) \times 333.6 \times (-1.3)}{(-1.3)(-40)}\right] = 304.6 \text{ kJ/kg} \]

**Enthalpy for \( T_r = -18^{\circ}C \).** By operating the same way:

\[ H_{Tr} = 49.3 \text{kJ/kg} \]

**Enthalpy difference per unit volume \( \Delta H_{Tr} \).** Per unit volume:

\[ \rho_f H_f = 1052.7 \times 304.6 = 3.206 \times 10^5 \text{kJ/m}^3 = 3.206 \times 10^8 \text{J/m}^3 \]

\[ \rho_r H_{Tr} = 4.880 \times 10^7 \text{J/m}^3 \]

\[ \Delta H_{Tr} = 2.718 \times 10^8 \text{J/m}^3 \]

**Biot, Plank and Stefan numbers.** \( Bi = \frac{h l_f}{k_s} = \frac{5.67 \times 0.01}{0.72} = 0.079 \) (Eq. (27))

\[ Pk = \frac{C_s(T_r-T_f)}{\Delta H_{Tr}}. \text{ As } T_i = T_f, \text{ } Pk = 0 \text{ (Eq. (28))} \]

\[ Ste = \frac{C_s(T_r-T_{ix})}{\Delta H_{Tr}} = \frac{2.419 \times 10^6 \times (-13 - (-30))}{2.718 \times 10^8} = 0.255 \text{ (Eq. (29))} \]

Calculate parameters \( P \) and \( R \) corresponding to the flat plate. Using Table 5:

\[ P = 0.5072 + 0.257\left[\frac{0.0105}{0.08} + 0.0681\right] = 0.559 \]

\[ R = 0.1684 + 0.257 \times (-0.0135) = 0.165 \]

**Estimate the freezing time for an infinite flat plate.** \( t_{flat \ plate} = \frac{2.718 \times 10^8 \times (-1.3 - (-30))}{(0.559 + 0.01)^2 + (0.165 \times 0.01)^2} \times \ln(5432.79) \text{ s (Eq. (25))} \)

**Geometric correction.**

Calculate \( \beta_1 \) and \( \beta_2 \). Using (Eq. (35) and (36)):

\[ \beta_1 = \beta_2 = \frac{0.99}{0.01} = 9 \]
Table 5
Expressions for P and R (From [1] p. 20.9).

| Shape         | P and R Expressions                  | Applicability                                      |
|---------------|--------------------------------------|---------------------------------------------------|
| Infinite Slab | $P = 0.5072 + 0.2018 \, Pk + Ste[0.3224PK + \frac{0.0005}{\text{m}} + 0.0681]$ | $10 \leq h \leq 500 \, \text{W/m}^2 \cdot \text{K}$ |
|               | $R = 0.1684 + Ste(0.2740PK - 0.0135)$ | $0 \leq D \leq 0.12 \, \text{m}$ $T_i \leq 40^\circ \text{C}$ $-45^\circ \text{C} \leq T_e \leq -15^\circ \text{C}$ |
| Infinite Cylinder | $P = 0.3751 + 0.0999 \, Pk + Ste[0.4008 \, Pk + \frac{0.0710}{\text{m}} - 0.5865]$ | $0.155 \leq Ste \leq 0.345$ |
|               | $R = 0.0133 + Ste(0.0415 \, Pk + 0.3957)$ | $0 \leq Bi \leq 4.5$ $0 \leq Pk \leq 0.55$ |
| Sphere        | $P = 0.1084 + 0.0924 \, Pk + Ste[0.231 \, Pk - \frac{0.314}{\text{m}} + 0.6739]$ | $0.155 \leq Ste \leq 0.345$ |
|               | $R = 0.0784 + Ste(0.0386 \, Pk - 0.1694)$ | $0 \leq Bi \leq 4.5$ $0 \leq Pk \leq 0.55$ |
| Brick         | $P = P_2 + P_1[0.1136 + Ste(5.766 \, Pk - 1.242)]$ | $0.155 \leq Ste \leq 0.345$ |
|               | $R = R_2 + R_1[0.7344 + Ste(49.89 \, R_k - 2.900)]$ | $0 \leq Pk \leq 0.55$ $0 \leq Bi \leq 22$ |
|               | Where                                    | $1 \leq \beta_1 \leq 4$ $1 \leq \beta_2 \leq 4$ |
|               | $P_1 = \frac{\beta_1 \beta_2}{\beta_1 \beta_2 + \beta_1 + \beta_2}$ | $1 \leq \beta_1 \leq 4$ $1 \leq \beta_2 \leq 4$ |
|               | $R_1 = \frac{1}{4}(r - 1)\frac{(\beta_1 - r)(\beta_2 - r)\ln(\frac{r}{\beta_1}) - (s - 1)(\beta_1 - s)(\beta_2 - s)\ln(\frac{r}{\beta_1}) + \beta_2}{\beta_1 \beta_2 + \beta_1 + \beta_2}$ | $1 \leq \beta_1 \leq 4$ $1 \leq \beta_2 \leq 4$ |
|               | $r = \frac{1}{4}[\beta_1 + \beta_2 + 1 + (\beta_1 - \beta_2)(\beta_1 - 1) + (\beta_2 - 1)^2]^{1/2}$ | $1 \leq \beta_1 \leq 4$ $1 \leq \beta_2 \leq 4$ |
|               | $s = \frac{1}{4}[\beta_1 + \beta_2 + 1 - (\beta_1 - \beta_2)(\beta_1 - 1) + (\beta_2 - 1)^2]^{1/2}$ | $1 \leq \beta_1 \leq 4$ $1 \leq \beta_2 \leq 4$ |

Table 6
Geometric constants.

| Geometry                | G₁ | G₂ | G₃ |
|-------------------------|----|----|----|
| Infinite Plate          | 1  | 0  | 0  |
| Infinite Cylinder       | 2  | 0  | 0  |
| Sphere                  | 3  | 0  | 0  |
| Flat Cylinder           | 1  | 2  | 0  |
| Elongated cylinder      | 2  | 0  | 1  |
| Infinite rod            | 1  | 1  | 0  |
| Rectangular parallelepiped | 1 | 1  | 1  |
| Irregular shape bi-dimensional | 1 | 1  | 0  |
| Irregular shape tri-dimensional | 1 | 1  | 1  |

Argument $\varphi$. With Eq. (37):

$$\varphi_1 = \frac{2.32}{91.77} = 0.047$$

Function $X(\varphi)$. Using (Eq. (39)):

$$X(\varphi) = \frac{\varphi}{Bi^{\frac{1}{34}}} + \varphi = \frac{0.047}{0.079^{\frac{1}{34}} + 0.047} = 0.588$$

G₁, G₂ and G₃ values. To calculate the shape factor E with Eq. (32), obtain the G₁, G₂ and G₃ values from Table 6. As it is a finite cylinder with diameter greater than height:

$G_1 = 1; \ G_2 = 2; \ G_3 = 0$
Table 7
Constant values and expressions for selected geometries.

| Constants and functions | Flat plate | Infinite cylinder | Sphere |
|-------------------------|------------|-------------------|--------|
| Geometric constant, \( \Gamma \) | 0          | 1                 | 2      |
| Maximum slope, \( \delta \) | \( (\pi/2)^2 \) | \( (2.4048)^2 \) | \( \pi n(\delta_n) / \delta_n \) |
| Function in \( A_n \), \( \psi(\delta_n) \) | \( \cos(\delta_n) \) | \( J_0(\delta_n) \) | \( \sin(\delta_n) \) |

Calculate \( E_1 \). As \( G_3 = 0 \), only \( E_1 \) must be calculated with Eq. (33).

\[
E_1 = \frac{0.588}{9} + \left[ 1 - 0.588 \right] \frac{0.73}{9^{2.50}} = 0.067
\]

Equivalent heat transfer dimensionality \( E \). Apply Eq. (32):

\[
E = 1 + 2 \times 0.067 = 1.133
\]

**Freezing time for the actual food.** Finally with Eq. (26), freezing time is estimated.

\[
t_2 = \frac{t_{\text{flat plate}}}{E} = \frac{5432.79}{1.133} = 4794 \text{ s} = 79.90 \text{ min}
\]

From the original \([t - T]\) table, the time elapsed between \( T_f = -1.3^\circ \text{C} \) and \( T = -5.04^\circ \text{C} \) is \( t = 79.17 \text{ min} \) (deviation \(-0.93 \%\)).

**Total freezing time (Examples 1+2+3)**

Thus, the total time estimated to reach \(-25^\circ \text{C} \) from \(18.3^\circ \text{C} \) is (Eq. (1)):

\[
t = t_1 + t_2 + t_3 = 26.9 + 79.90 + 52.29 = 159 \text{ min}
\]

And, from the original \([t - T]\) table, the time elapsed between \( T_0 = 18.3^\circ \text{C} \) and \( T = -25.0^\circ \text{C} \) is \( t = 159 \text{ min} \) (deviation \(-0.05 \%\)) (Figure 4).

**Additional information**

The present paper describes in full detail the method for Modelling of freezing times used in a previous paper [16]. It is well known that freezing of fish is the treatment of choice for killing *Anisakis* larvae present in muscle when the fish is being consumed raw or after cooking practices insufficient to inactivate this nematode. The need to precisely know the freezing conditions required to inactivate the larvae and at the same time preserve the quality of fish, has been postulated for a long time, since EU Regulation No 1276/2011 [17] on freezing of fish (at least \(-20^\circ \text{C}\) in all parts of the product for not less than 24 h, or \(-35^\circ \text{C} \) for not less than 15 h) in fact, covers a wide range of conditions which may have varying effects on the quality of fish. There are a number of papers that have dealt with this problem. For example, it has been shown that there are a number of freezing kinetic parameters, not only final freezing temperatures or times, which affect survival of *Anisakis* larvae [16]. When adapting these to other materials (fish species), geometries, or ambient temperatures, modeling of freezing times can help save time and efforts in finding suitable conditions, which would meet safety in terms of *Anisakis* mortality and quality of fish, as well as be in compliance with EU Regulation. For example, we showed that under this set up, doubling the thickness of the sample involved 72–74% increase in freezing time, decreasing the temperature from \(-10 \) to \(-20^\circ \text{C} \) involved an increase from 118 to 145 min, whereas increasing the fat content (from 0.7 in hake to 4.8% in mackerel) had less influence on total freezing time [16].

The modeling required to obtain experimentally-controlled time-temperature data and thus freezing experiments were performed in hake mince contained in Petri dishes as described in Sánchez-Alonso et al. [16]. Proximate analyses performed to know the thermo physical properties of fish, i.e. % protein, moisture and ash were determined according to AOAC [18], and % fat was determined according to the method of Bligh and Dyer [19].
The present model has been calculated assuming no porosity of the samples in the density functions; also the material where the mince was contained (i.e. methacrylate) was not taken into account owing to the fast heat transfer as compared to the fish mince. Despite these assumptions, the experimental and calculated results showed very good proximity, with low percentage of deviation.

In the procedure to estimate freezing times in the above examples, and for research purposes, we used relatively simple shape and boundary conditions, but conditions can be expanded to a number of other applications both for research and industrial purposes. Examples of these conditions include different fish species, different types of meat, unique products derived from fish and meat, different surface heat transfer coefficient, different shapes, etc. To calculate for different shapes, there are previous research studies available, for instance, Cleland and Earle [4,5], Cleland et al. [6,7], Cuesta et al. [2], Hossain et al. [20], Cuesta and Lamúa [3] or ASHRAE [1]. Furthermore, for references on different external cooling air conditions (temperature, moisture, velocity), see Gröber et al. [21], Rohsenow [22], Heldman and Lund [23], or ASHRAE [1,10].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi: 10.1016/j.mex.2021.101292. The Excel file containing the calculations for the complete process is available upon request (m.careche@csic.es; pacocuesta@hotmail.com).

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