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Using Equivalent Volumetric Enthalpy Variation to Determine the Freezing Time in Foods

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ABSTRACT

Total freezing time calculations have been carried out by considering two partial times; the precooling, corresponding to the time from the initial temperature to the initial solidification temperature, and the tempering, from the initial solidification temperature to the final temperature. The samples having a slab geometry were the Karlsruhe Test Substance (methyl cellulose gel) and different kinds of meats. The calculation method used the closed form solution for the precooling period and Plank's equation with the equivalent volumetric enthalpy variation for the tempering time. Some hypotheses were adopted to simplify the temperature distribution in the sample at the end of the two periods and to use the same thermophysical properties for each group of samples. The accuracy obtained makes this method valuable enough for many practical uses in freezing time calculations of foods.

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NOTATION

Bi Biot number $Bi = \alpha R/k_1$ (dimensionless)
c_1 Specific heat of the unfrozen zone (J/kg °C)
c_2 Specific heat of the freezing zone (J/kg °C)
E_1 Linear equivalent volumetric enthalpy variation (J/m^3)
E_q Quadratic equivalent volumetric enthalpy variation (J/m^3)
Δh Volumetric enthalpy increment (J/m^3)
k_1 Thermal conductivity of the unfrozen zone (W/m °C)
k_2 Thermal conductivity of the freezing zone (W/m °C)
L Latent heat (J/kg)
L_{ef} Effective latent heat (J/kg)
R Half thickness of the slab (m)
SD Standard deviation
S_t Stefan's number $S_t = c(T_f - T_s)/L$ (dimensionless)
t Time (s)
t_e Experimental freezing time (h)
t_f Freezing time (h)
t_1 Freezing time considering linear temperature (h)
t_q Freezing time considering quadratic temperature (h)
T_a Air temperature (°C)
T_c Final freezing temperature of the thermal centre (°C)
T_f Initial solidification temperature of the thermal centre (°C)
T_i Initial temperature of the food (°C)
T_s Surface temperature (°C)
x Position (m)
X Freezing front position (m)

α Heat transfer coefficient (W/m^2 °C)
ε Percentage of relative error (%)
ρ Density (kg/m^3)
ψ Water content (%)

INTRODUCTION

Refrigeration has been an accepted method of food preservation since the turn of the century. Freezing time prediction is important in determining the final quality of foods and the economics of the process. It is also of interest when controlling freezing processes or when designing a satisfactory freezing process as it facilitates the calculation of the refrigeration loads.

The term 'freezing time' is the elapsed time between the beginning of the process and when the thermal centre reaches the desired final temperature. Determining this value for foodstuffs, which freeze progressively over a certain temperature range, requires the solution of a complex heat transfer problem. While freezing foodstuffs, non-linear heat conduction is combined with a progressive phase-change and this process depends on the boundary conditions: geometry, composition, etc. There are two main approaches to the evaluation of freezing time. The first uses analytical methods and the second graphical and numerical methods, mainly finite difference and finite element methods. Finite difference methods have limitations for irregularly shaped or non-homogeneous products. Finite element methods require complex calculations and computer facilities to solve even a very simple problem although they are effective for irregularly shaped and non-homogeneous products. The accuracy depends on the simplifications introduced and on the adequacy of the thermal property data (Cleland & Earle, 1984; Cleland *et al.*, 1987; Salvadori & Mascheroni, 1989).

The earliest analytical solution for heat conduction equations involving a phase-change was obtained by Neumann and can be found in Lunardini (1991). Among the analytical methods developed (Plank, 1941; Salvadori & Mascheroni, 1991) the most used is Plank's equation, which is simple in construction and can be used in pure substances when the Stefan number, S_t, is small. When freezing non-pure substances, the phase-change covers a wide temperature range and the latent heat corresponding to the phase-change occurring at a single temperature is not a good concept for a rigorous study. This is the case for foodstuffs, binary eutectic mixtures or model materials such as the Karlsruhe Test Substances (KTS). However, Plank's equation has a strong theoretical basis and has been adopted for most freezing time calculations in foods. Many workers have modified the basic formula by introducing some correction factors, often semi-empirical, to allow for variations from the oversimplified initial assumptions of Plank's equation (Le Blanc *et al.*, 1990; Chung & Merrit, 1991; Hossain *et al.*, 1992). In general the correction factors are not constant but rather depend on the size of the product or other factors like composition, solidification temperatures and/or the Biot number, etc. When the initial temperature of the sample is higher than that of the onset of solidification, there exist two different periods; from the sample's initial temperature to the temperature corresponding to the beginning or onset of solidification, and from there to the final temperature. This paper predicts the total freezing time in a model system (KTS) and meats by considering both the precooling and the tempering times. In calculating the latter time, Plank's original equation is used, replacing the latent heat with the equivalent volumetric enthalpy variation using the hypotheses of linear and quadratic temperature changes in the freezing zone. It was also assumed that a uniform temperature exists in the sample at the limit of each period considered.

THEORY

Precooling time

The precooling time is considered to be the cooling time needed to change the temperature of a sample which has a half thickness R and an initial uniform temperature T_i, to the initial uniform solidification temperature T_f. There is a third boundary condition during cooling and the air temperature T_a is constant:

$$t>0 \quad -k\frac{\partial T}{\partial x}=\alpha(T-T_s) \quad x=0 \tag{1}$$

where α is the heat transfer coefficient. The precooling time is obtained (Chung & Merrit, 1991; Kakaç & Yener, 1985) by solving

$$\frac{T-T_{\mathrm{a}}}{T_{\mathrm{i}}-T_{\mathrm{a}}}=2\sum_{n=1}^{\infty}\frac{\sin\beta_n\exp\left[-\beta_n^2\left(\frac{k_1 t}{\rho c_1 R^2}\right)\right]}{\beta_n+\sin\beta_n\cos\beta_n} \tag{2}$$

where ρ, c_1 and k_1 are the density, specific heat and thermal conductivity of the unfrozen zone, T denotes temperature, t is the time and β_n is the nth root of the equation:

$$Bi=\beta_n\tan\beta_n \tag{3}$$

in which $Bi=\alpha R/k_1$. In our calculations, up to seven first roots of eqn (3), obtained by iteration, were used to solve eqn (2). For practical purposes precooling time can also be obtained with little error, from the usual graphs of temperature versus time for heat conduction without phase-change.

Tempering time

The tempering time is the time needed to change the temperature of the sample with the initial uniform temperature T_{f}, to the final temperature of the thermal centre T_{c}. If Stefan's number S_t is small, a quasi-steady linear solution for the temperature change as a function of the position in the freezing zone is obtained, as described in Lunardini (1991) and Mihori and Watanabe (1994). When the slab is being frozen from both sides, Plank's equation is obtained (Cleland & Earle, 1977).

$$t_{\mathrm{f}}=\frac{\rho L}{T_{\mathrm{f}}-T_{\mathrm{a}}}\left(\frac{1}{2}\frac{2R}{\alpha}+\frac{1}{8}\frac{(2R)^2}{k_2}\right) \tag{4}$$

This equation is commonly used in practical calculations of freezing or thawing times in foods (Cleland & Earle, 1984). The quasi-steady system in eqn (4) neglects specific heat and the only energetic term is the latent heat, L. In order to take specific heat into account, Janson (1963) developed an appropriate method which maintained the simplicity of Plank's approach. This approach considers the quasi-steady solution and defines an effective latent heat, L_{ef}, including the latent heat, L, and the specific heat, c_2, of the frozen zone,

$$L_{\mathrm{ef}}=L+\frac{c_2(T_{\mathrm{f}}-T_{\mathrm{a}})}{2} \tag{5}$$

When a non-pure substance is subjected to a freezing or thawing process, a fixed phase-change temperature does not exist because the phase-change transition takes place over a wide temperature range. Thus, the latent heat concept is not valid and a temperature dependent specific heat, over the temperature range of phase-change, can be considered (Mascheroni & Calvelo, 1982).

One way to take this into account is to consider the equivalent volumetric enthalpy variation. From Ramos *et al.* (1994), if a linear temperature distribution in the freezing zone is considered, its value is:

$$E_l = \frac{1}{T_f - T_c} \int_{T_c}^{T_f} \Delta h(T)\,dT \tag{6}$$

When the temperature distribution in the freezing zone is quadratic, its value is:

$$E_q = \frac{1}{2\sqrt{T_f - T_c}} \int_{T_c}^{T_f} \frac{\Delta h(T)}{\sqrt{T - T_c}}\,dT \tag{7}$$

MATERIALS AND METHODS

Experimental values for freezing times for KTS and meat samples were taken from the literature (Cleland & Earle, 1977; Mascheroni & Calvelo, 1982; De Michelis & Calvelo, 1983; Hung & Thompson, 1983; Bazán & Mascheroni, 1984). KTS, defined as a 23% methylcellulose gel, is frequently used in heat transfer problems of cooling and freezing of foods because of the very similar thermal properties between KTS and foods (Bonacina *et al.*, 1974; Cleland & Earle, 1977). The study related to KTS was based on two experimental studies, the first one on 43 cases (Cleland & Earle, 1977), and the second one on 23 cases of varying water content (Hung & Thompson, 1983). Tables 1 and 2 compare the predicted times with the experimental data from the two sources. Table 3 gives a similar comparison for the seven studies related to meat; five experiments with lean beef from De Michelis and Calvelo (1983), six with minced beef from Cleland and Earle (1977), four experiments with mutton from Bazán and Mascheroni (1984), nine experiments with lean beef from Hung and Thompson (1983), six experiments with semi-membranous muscle and heat transfer perpendicular to the fibres (SMPEF) from Mascheroni and Calvelo (1982) and three experiments with semi-membranous muscle and heat transfer parallel to the fibres (SMPAF) from Macheroni and Calvelo (1982). The slab thickness $2R$ ranged from 0·014 to 0·100 m, air temperature, T_a, from -19 to $-44{\cdot}7$°C, initial temperature, T_i, from 2·9 to 34·5°C and surface heat transfer coefficients, α, from 8·5 to 430 W/m^2 K (it is generally not specified how α was obtained). With these parameters the experimental freezing times obtained ranged from a few minutes to more than 15 h.

RESULTS AND DISCUSSION

The thermophysical properties of the model substance KTS are quite well defined (Riedel, 1960; Cleland & Earle, 1984). Although, in general, different water contents will produce different calculated freezing times (Ramos *et al.*, 1994) and in spite of the fact that the experimental samples of Hung and Thompson (1983) do not always have the same (but similar)

TABLE 1
Experimental Data from Cleland and Earle (1977) and Predicted Freezing Times for KTS

$2R$ (m)	α (W/m^2 K)	T_i (°C)	T_a (°C)	$t_e \pm err$ (h)	t_l (h)	ε_l (%)	t_q (h)	ε_q (%)
0·100	320	28·0	−20·0	4·28 ± 0·18	4·98	−16·4	5·19	−21·4
0·100	310	3·0	−23·0	3·46 ± 0·15	3·15	9·1	3·33	3·6
0·072	410	3·0	−22·0	1·92 ± 0·09	1·70	11·3	1·80	6·0
0·072	330	10·5	−24·5	1·82 ± 0·09	1·87	−2·5	1·96	−7·8
0·072	90	11·0	−21·7	3·02 ± 0·14	3·01	0·3	3·18	−5·3
0·072	51·9	30·0	−40·0	2·62 ± 0·10	2·85	−8·8	2·98	−13·7
0·072	51·9	30·0	−20·0	4·80 ± 0·22	5·00	−4·3	5·26	−9·6
0·072	51·9	10·0	−40·0	2·22 ± 0·10	2·31	−4·2	2·44	−10·0
0·072	51·9	10·0	−20·0	4·50 ± 0·20	4·18	7·1	4·43	1·5
0·072	21·6	30·0	−40·0	4·74 ± 0·18	4·87	−2·8	5·12	−8·0
0·072	21·6	30·0	−20·0	8·96 ± 0·38	8·78	2·0	9·26	−3·4
0·072	21·6	10·0	−40·0	4·02 ± 0·17	4·01	0·3	4·25	−5·8
0·072	21·6	10·0	−20·0	7·96 ± 0·34	7·46	6·3	7·94	0·2
0·072	16·7	28·0	−26·7	8·50 ± 0·35	8·22	3·3	8·67	−2·0
0·072	13·6	3·0	−26·0	8·42 ± 0·33	7·69	8·7	8·24	2·2
0·0485	410	11·0	−21·0	1·00 ± 0·05	1·00	0·0	1·05	−5·3
0·0485	360	3·0	−23·5	0·88 ± 0·05	0·81	8·0	0·85	2·5
0·0485	90	34·5	−22·0	2·04 ± 0·08	2·00	2·1	2·09	−2·6
0·0485	90	13·7	−24·3	1·54 ± 0·07	1·54	−0·2	1·63	−5·7
0·0485	30·6	20·0	−30·0	2·74 ± 0·12	2·70	1·4	2·85	−4·2
0·0485	30·6	20·0	−30·0	2·74 ± 0·12	2·70	1·4	2·85	−4·2
0·0485	30·6	20·0	−30·0	2·74 ± 0·12	2·70	1·4	2·85	−4·2
0·0485	30·6	20·0	−30·0	2·70 ± 0·12	2·70	−0·0	2·85	−5·7
0·0485	30·6	20·0	−30·0	2·66 ± 0·12	2·70	−1·6	2·85	−7·3
0·0485	16·7	15·3	−25·3	5·26 ± 0·20	4·87	7·5	5·17	1·7
0·0485	13·6	28·6	−29·5	5·82 ± 0·23	6·15	−5·6	6·50	−11·7
0·0485	13·6	3·0	−26·0	5·34 ± 0·20	4·88	8·7	5·23	2·0
0·025	430	3·0	−19·0	0·34 ± 0·03	0·29	13·6	0·31	8·1
0·025	400	21·6	−22·0	0·32 ± 0·03	0·34	−8·0	0·36	−13·2
0·025	90	28·0	−24·0	0·68 ± 0·04	0·69	−1·9	0·73	−7·3
0·025	90	11·0	−20·0	0·74 ± 0·04	0·70	5·6	0·74	−0·3
0·025	51·9	30·0	−40·0	0·64 ± 0·04	0·67	−4·7	0·70	−10·1
0·025	51·9	30·0	−20·0	1·26 ± 0·07	1·21	3·7	1·28	−1·6
0·025	51·9	10·0	−40·0	0·56 ± 0·04	0·55	1·6	0·59	−4·8
0·025	51·9	10·0	−20·0	1·12 ± 0·07	1·03	7·7	1·10	1·7
0·025	21·6	30·0	−40·0	1·42 ± 0·07	1·37	3·6	1·44	−1·6
0·025	21·6	30·0	−20·0	2·74 ± 0·14	2·52	7·9	2·67	2·6
0·025	21·6	10·0	−40·0	1·26 ± 0·07	1·13	10·0	1·21	4·1
0·025	21·6	10·0	−20·0	2·44 ± 0·13	2·17	11·2	2·31	5·2
0·025	16·7	28·7	−26·0	2·68 ± 0·13	2·50	6·6	2·65	1·2
0·025	16·4	3·0	−24·5	2·40 ± 0·11	2·06	14·0	2·22	7·6
0·025	13·6	22·0	−25·3	3·10 ± 0·12	2·96	4·6	3·14	−1·2
0·025	13·6	5·8	−29·6	2·32 ± 0·10	2·17	6·5	2·32	−0·2

TABLE 2
Experimental Data from Hung and Thompson (1983) and Predicted Freezing Times for KTS

$2R$ (m)	α (W/m^2 K)	T_i (°C)	T_a (°C)	t_e (h)	t_l (h)	ε_l (%)	t_q (h)	ε_q (%)
0·013	9	5·1	−19·9	3·07	2·36	23·3	2·53	17·6
0·028	11·5	18·3	−25·0	5·03	3·83	23·8	4·07	19·0
0·013	9	2·9	−30·1	2·03	1·53	24·6	1·65	18·9
0·048	11	3·7	−30·1	6·23	5·12	17·9	5·48	12·0
0·012	11	29·6	−30·1	2·30	1·51	34·5	1·59	30·7
0·047	11	30·2	−20·4	13·18	9·12	30·8	9·65	26·8
0·029	108	3·5	−29·3	0·55	0·48	12·1	0·51	6·3
0·011	110	26·3	−32·4	0·21	0·16	24·0	0·17	19·9
0·045	108	29·6	−29·3	1·46	1·26	14·0	1·31	10·0
0·012	108	16·8	−30·9	0·22	0·17	21·3	0·18	16·7
0·048	108	4·2	−29·4	1·22	1·02	16·7	1·08	11·5
0·011	106	4·4	−25·7	0·21	0·16	23·5	0·17	18·2
0·010	104	30·2	−20·3	0·33	0·23	30·8	0·24	26·9
0·048	104	4·5	−20·0	1·85	1·46	21·1	1·55	16·0
0·011	104	4·4	−20·1	0·27	0·21	24·2	0·22	18·8
0·011	69	3·8	−30·6	0·25	0·19	22·8	0·21	17·3
0·044	68	18·0	−25·6	1·93	1·57	18·8	1·65	14·3
0·027	68	30·9	−24·9	1·23	0·92	25·5	0·96	21·6
0·030	67	17·4	−20·1	1·55	1·15	25·5	1·22	21·1
0·027	68	17·3	−25·0	1·03	0·82	20·2	0·87	15·5
0·027	68	17·3	−24·7	1·03	0·83	19·3	0·88	14·6
0·027	68	17·4	−25·2	1·00	0·82	18·3	0·86	13·5
0·028	68	17·9	−25·1	1·12	0·86	22·9	0·91	18·4

water content, a water content of 77% has been used for the both families of KTS experimental data (Cleland & Earle, 1977; Hung & Thompson, 1983). The thermophysical values used to solve eqns (2) and (3) are given in Table 4 where the equivalent volumetric enthalpy variation values are obtained by considering that a linear, E_1, or a quadratic, E_q, temperature distribution exists in the freezing zone, and considering T_s almost equal to T_a to obtain eqns (6) and (7) (Ramos *et al.*, 1994). These values are approximately $2{\cdot}09 \times 10^8$ and $2{\cdot}26 \times 10^8$ (J/m^3). The first value is used in the literature (Hung & Thompson, 1983; Cleland & Earle, 1984; Pham, 1984) for freezing calculations, and the second one when thawing KTS (Cleland *et al.*, 1986). In both cases they are used over a large range of experimental conditions.

When studying the different kinds of meat, because of the variety, types and compositions, there is no possibility of using a unique value for each thermophysical property for all cases. Often there is no information to relate the data to the water content of the sample, the thermal conductivity when it is freezing, or other thermophysical properties of interest. Therefore, in order to use an average value, $\psi = 0{\cdot}75$ has been chosen for the water content of all the meat samples. The solidification temperature, T_f was obtained from Sanz *et al.* (1989) and Salvadori and Mascheroni (1991) for

TABLE 3
Experimental Data and Predicted Freezing Time for Meat

$2R$ (m)	α (W/m^2 K)	k_1 (W/mK)	T_i (°C)	T_a (°C)	T_c (°C)	$t_e \pm error$ (h)	t_l (h)	ε_l (%)	t_q (h)	ε_q (%)
Lean beef[a]										
0·06	168·5	0·48	18·3	−38·7	−18	1·30	1·17	9·8	1·23	5·0
0·06	146·9	0·48	18·0	−33·3	−18	1·52	1·40	7·6	1·48	2·5
0·06	88·1	0·48	17·8	−39·9	−18	1·57	1·47	6·5	1·54	1·4
0·06	72·2	0·48	22·0	−27·3	−18	2·47	2·37	3·7	2·51	−1·7
0·094	120·5	0·48	8·0	−36·5	−18	2·83	2·66	6·0	2·82	0·5
Minced meat[b]										
0·072	220·0	0·44	28·0	−25·0	−10	2·32 ± 0·12	2·38	−2·5	2·50	−7·9
0·072	51·9	0·44	3·0	−23·9	−10	3·84 ± 0·18	3·55	7·5	3·79	1·2
0·0485	90·0	0·44	30·0	−25·4	−10	1·68 ± 0·08	1·74	−3·4	1·83	−9·0
0·0485	21·6	0·44	3·0	−28·4	−10	3·30 ± 0·17	3·30	0·1	3·53	−6·9
0·025	30·6	0·44	28·6	−25·7	−10	1·54 ± 0·07	1·87	−21·3	1·96	−27·2
0·025	16·7	0·44	16·5	−28·8	−10	2·34 ± 0·12	2·22	5·1	2·36	−1·0
Mutton[c]										
0·06	79·5	0·495	10·6	−37·0	−18	1·90	1·55	18·6	1·64	13·7
0·06	99·58	0·495	9·6	−40·15	−18	1·47	1·28	13·0	1·35	7·9
0·06	120·53	0·495	10·3	−33·15	−18	1·92	1·42	26·1	1·50	21·7
0·06	102·89	0·495	9·4	−39·9	−18	1·65	1·26	23·3	1·34	18·8
Lean beef[d]										
0·030	107	0·51	30·8	−28·0	−18	0·97	0·72	25·6	0·76	21·7
0·048	106	0·51	17·4	−25·2	−18	1·80	1·47	19·1	1·55	14·4
0·019	104	0·51	4·8	−20·3	−18	0·54	0·45	16·6	0·48	11·0
0·047	69	0·51	4·3	−27·6	−18	1·75	1·45	17·3	1·54	11·8
0·014	68	0·51	29·8	−25·8	−18	0·58	0·41	29·3	0·43	25·4
0·036	67	0·51	17·9	−20·8	−18	1·97	1·53	22·0	1·63	17·3
0·014	8·5	0·51	17·2	−30·3	−18	2·72	2·20	19·0	2·33	14·1
0·033	8·5	0·51	4·8	−25·2	−18	6·50	5·70	12·3	6·09	6·2
0·047	10·5	0·51	30·8	−20·7	−18	15·77	10·17	35·5	10·75	31·8

TABLE 3 *contd.*

2R (m)	α ($W/m^2 K$)	k_1 (W/mK)	T_i (°C)	T_a (°C)	T_c (°C)	$t_e \pm error$ (h)	t_l (h)	ε_l (%)	t_q (h)	ε_q (%)
Semi-membranous muscle (perpendicular to the fibres)[e]										
0·061	217·7	0·48	14·1	−36·2	−18	1·40	1·17	16·4	1·23	11·8
0·062	161·7	0·48	17·0	−39·0	−18	1·33	1·25	5·8	1·32	0·8
0·060	156·3	0·48	12·0	−44·2	−18	1·07	1·02	3·9	1·08	−1·5
0·060	137·9	0·48	19·7	−39·0	−18	1·17	1·28	−9·9	1·35	−15·7
0·060	138·1	0·48	11·4	−44·7	−18	1·13	1·05	7·0	1·11	1·8
0·060	143·5	0·48	19·9	−40·6	−18	1·22	1·22	0·3	1·28	−5·0
Semi-membranous muscle (parallel to the fibres)[e]										
0·060	96·9	0·51	19·4	−43·9	−18	1·07	1·29	−19·8	1·35	−26·2
0·094	22·76	0·51	16·0	−42·0	−18	5·50	5·65	−2·7	5·97	−8·6
0·080	120·5	0·51	21·0	−33·0	−18	2·85	2·46	13·7	2·59	9·1

[a] From De Michelis and Calvelo (1983).
[b] From Cleland and Earle (1977).
[c] From Bazán and Mascheroni (1984).
[d] From Hung and Thompson (1983).
[e] From Mascheroni and Calvelo (1982).

TABLE 4
Thermophysical Properties of KTS

Property	*KTS*
k_1 (W/m °C)	0·55
k_2 (W/m °C)	1·65
c_1 (J/m^3 °C × 10^{-6})	3·71
ρ (kg/m^3)	1006
T_f (°C)	−0·6
E_l (J/m^3 × 10^{-8})	2·16
E_q (J/m^3 × 10^{-8})	2·33

each case as

$$T_f = \frac{1-\psi}{0{\cdot}06908 - 0{\cdot}4393\psi} \tag{8}$$

A mean value of the thermal conductivity $k=(k_1+k_2)/2$ was used for calculations of the precooling time. Thermal conductivity of the freezing region was evaluated as $T=(T_f+T_a)/2$. If the heat transfer direction during freezing was not specified in the experimental data, a mean thermal conductivity value was calculated from that parallel to and perpendicular to the fibres. When heat transfer was parallel to the fibres:

$$k_1 = 0{\cdot}1075 + 0{\cdot}501\psi + 5{\cdot}052\ 10^{-4}\psi T \quad T \geq T_f \tag{9}$$

$$k_2 = 0{\cdot}398 + 1{\cdot}448\psi + \frac{0{\cdot}985}{T} \quad T < T_f \tag{10}$$

When heat transfer was perpendicular to the fibres

$$k_1 = 0{\cdot}0866 + 0{\cdot}501\psi + 5{\cdot}052 \times 10^{-4}\psi T \quad T \geq T_f \tag{11}$$

$$k_2 = 0{\cdot}378 + 1{\cdot}376\psi + \frac{0{\cdot}930}{T} \quad T < T_f \tag{12}$$

The volumetric enthalpy variation, Δh, and density ρ, are

$$\Delta h = (T+40)(3{\cdot}874 - 2{\cdot}534\psi) - 902{\cdot}893(1-\psi)\left(\frac{1}{T} + \frac{1}{40}\right) \tag{13}$$

and

$$\rho = \frac{1053}{0{\cdot}98221 + 0{\cdot}11310\psi + \dfrac{0{\cdot}25746(1-\psi)}{T}} \tag{14}$$

respectively. In the same way as in the KTS case, $2{\cdot}22 \times 10^8$ and $2{\cdot}39 \times 10^8$ (J/m^3) are the calculated values in the linear, E_l, and the quadratic, E_q, equivalent volumetric enthalpy variation, respectively. Literature data (Hung

& Thompson, 1983; Cleland & Earle, 1984; Cleland & Cleland, 1986) for the change in enthalpy or the latent heat of lean, minced and ground beef are $2{\cdot}09 \times 10^8$, $2{\cdot}30 \times 10^8$ and $1{\cdot}88 \times 10^8$ (J/m^3), respectively. As these are close to the values obtained for both the linear and the quadratic equivalent volumetric enthalpy variation cases, the calculated values for E_1 and E_q were used in all the meats studied.

A given freezing time, t_c, from T_i to T_c in the thermal centre, can be divided for calculation purposes into two partial times: precooling and tempering times, or into three partial times: precooling, phase-change and tempering times. Both have been extensively used (Mascheroni & Calvelo, 1982; Bazán & Mascheroni, 1984; Pham, 1984; Chung & Merrit, 1991). In this paper the first type of calculation is used and a final temperature $T_c = -18°C$ has been adopted in accordance with some international regulations on frozen foods (Bazán & Mascheroni, 1984). Therefore, two partial times have to be added to predict the total experimental freezing time t_e. As defined above, the total freezing is the sum of the times given by eqns (2) and (4) with the latent heat value, L, replaced by the linear equivalent volumetric enthalpy variation, E_1, and by the quadratic one, E_q, to give the corresponding freezing times t_1 and t_q.

The best way to check the accuracy of any calculation method is to compare its results with experimental values. However there are not many useful data in the literature to carry out this task, because often, experimental values are not accompanied by their corresponding experimental errors. One case where experimental freezing time and corresponding experimental error for KTS, Table 1, and minced meat, Table 3, are given is in Cleland and Earle (1977): Fig. 1 gives the predicted freezing time t_1 versus experimental freezing time t_e for these 43 samples of KTS, using E_1 instead of L in eqn (4). The diagonal line passes near or crosses (in almost all cases) the experimental freezing time error band, indicating that good precision is obtained in these cases. Numerical values and the results of the predicted freezing times for this case and that when E_q is used in eqn (4), are given in Table 1. Figure 2 gives the predicted freezing time t_1 versus experimental freezing time t_e for the six cases of minced meat given by Cleland and Earle (1977) and here also good precision is obtained. These numerical values and the results of the predicted freezing time when E_q is used in eqn (4) are given in Table 3.

Considering only the central value of the experimental freezing times (without the corresponding experimental errors), the percentage of relative error ε can be defined as

$$\varepsilon_i = 100 \frac{(t_{ei} - t_{ci})}{t_{ei}} \tag{15}$$

where c represents either $c=1$ and $c=q$. Mean values of ε_i and their standard deviations are given for all cases studied in Table 5. For the two cited cases from Cleland and Earle (1977), KTS and minced meat, the mean percentage of errors ε obtained are $\leq \pm 3\%$a and $< \pm 8{\cdot}5\%$, respectively. Disagreement with the experimental freezing time for KTS (Table 2) and lean beef (Table 3) from Hung and Thompson (1983) are greater (more than 17%) but here no experimental errors were reported. Also the four

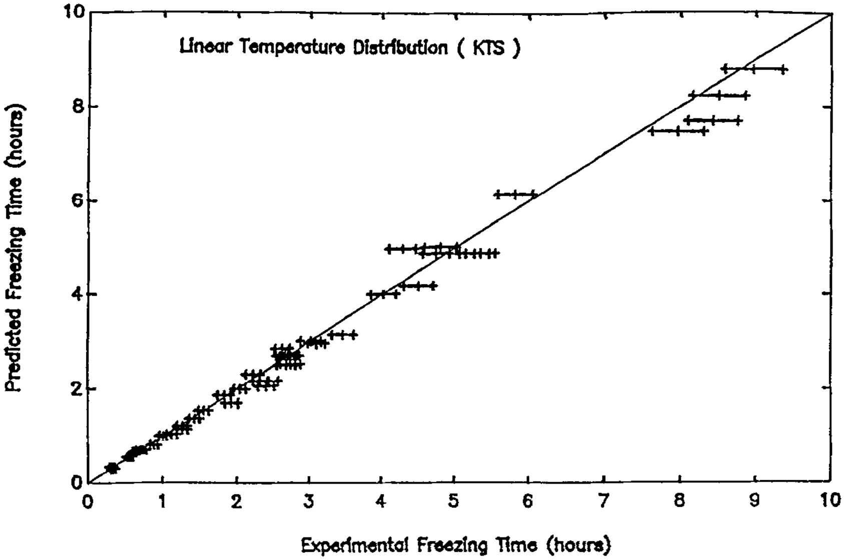

Fig. 1. Freezing times for KTS; experimental, from Cleland and Earle (1977), and predicted considering a linear temperature profile in the freezing zone.

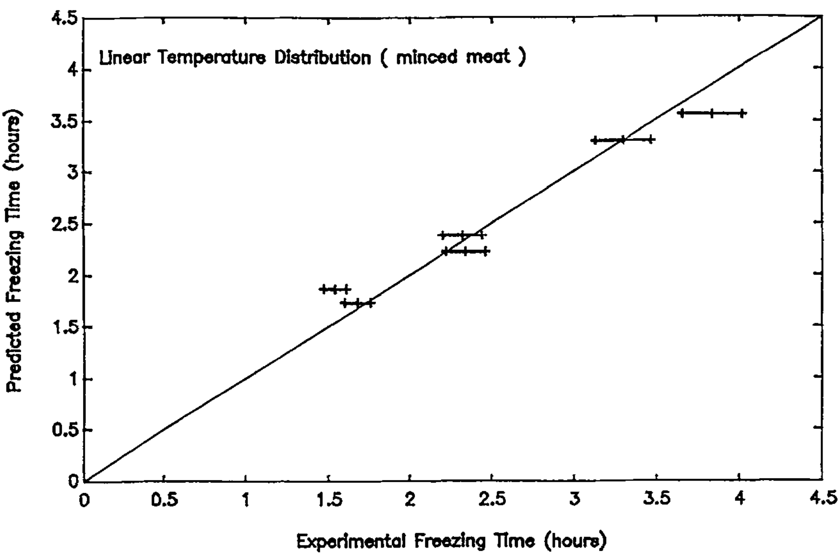

Fig. 2. Freezing times for minced meat; experimental, from Cleland and Earle (1977), and predicted considering a linear temperature profile in the freezing zone.

cases of mutton give important errors between experimental and predicted freezing times, Tables 3 and 5. Regarding mutton, the composition can be very different from the rest of the meats studied and therefore its thermophysical properties also differ from the calculated values.

TABLE 5
Summary of Percentage Differences between Experimental and Predicted Freezing Time for KTS and Meat

	Percent relative error ε							
	Linear temp. distr.				*Quadratic temp. distr.*			
	Mean (%)	*SD (%)*	*Min (%)*	*Max (%)*	*Mean (%)*	*SD (%)*	*Min (%)*	*Max (%)*
KTS[a]	2·6	6·4	−16·4	14·0	−3·0	6·2	−21·4	8·1
KTS[b]	22·4	5·2	12·2	34·5	17·7	5·5	6·4	30·7
Lean beef[c]	6·7	2·2	3·7	9·8	1·6	2·5	−1·7	5·0
Minced meat[a]	−2·4	10·2	−21·3	7·4	−8·4	10·1	−27·2	1·2
Mutton[d]	20·2	5·7	13·0	26·1	15·6	6·1	7·9	1·2
Lean beef[b]	21·9	7·2	12·3	35·5	17·1	8·0	6·2	31·8
SMPEF[e]	3·9	8·6	−9·9	16·4	−1·3	9·0	−15·7	11·8
SMPAF[e]	−2·9	16·8	−19·8	13·7	−8·6	17·6	−26·2	9·1

[a] From Cleland and Earle (1977).
[b] From Hung and Thompson (1983).
[c] From De Michelis and Calvelo (1984).
[d] From Bazán and Mascheroni (1984).
[e] From Mascheroni and Calvelo (1982).

In general, working with higher initial temperatures will probably increase errors (producing greater differences between experimental and predicted values) than with similar experimental conditions but lower initial temperatures, Tables 1–3. Other errors would appear (Hung & Thompson, 1983) because volume and size increase when the phase changes from liquid to solid. This could produce, in any meat product, an increase in the freezing time not accounted for in the prediction procedure. Slight deviations from symmetric conditions (de Michelis & Calvelo, 1983; Bazán & Mascheroni, 1984) or the evaporation of water from the product during freezing also affects that prediction. The influence of the specific composition and temperature of each sample on the thermal conductivity and specific heat also affects the freezing time prediction. In relation to this, it should be noted that only one equation was used to determine each thermophysical property for all the different kinds of meats studied here. Anywhere, average errors of ± 10–15% are acceptable in many engineering applications (Cleland *et al.*, 1982). In the majority of the cases studied this error range is higher than that obtained with the method developed in this paper. Both hypotheses, linear and quadratic temperature changes, provide good predictions.

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