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# Prediction of Calorimetric Properties and Freezing Time of Foods from Composition Data

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## ABSTRACT

*Simple relationships were found for predicting the enthalpy–temperature curve of foods over the range −40–+40°C from composition data, using Schwartzberg's bound water model. The specific heats above and below freezing were found by adding the component specific heats, while empirical equations were used to calculate freezing point and bound water content. The model produced predictions of acceptable engineering accuracy (±10% errors in freezing time and heat load) for meats (including cooked and cured meats), fish (including surimi), fruits and cheese, as well as Tylose gels. Additional terms were used to account for the heat of solidification of fats, however, more study is needed on how to correlate accurately this effect. Copyright © 1996 Elsevier Science Limited*

## NOTATION

| | |
|---|---|
| $a_w$ | Water activity |
| $Bi$ | Biot number, $hr/k_F$ |
| $\Delta c$ | Difference in specific heat between water and ice, J kg$^{-1}$ K$^{-1}$ |
| $c_F$ | Specific heat of frozen food, J kg$^{-1}$ K$^{-1}$ |
| $c_U$ | Specific heat of unfrozen food, J kg$^{-1}$ K$^{-1}$ |
| $c_x$ | Apparent specific heat due to fat solidification, J kg$^{-1}$ K$^{-1}$ |
| $h$ | Heat transfer coefficient, W m$^{-2}$ K$^{-1}$ |
| $H$ | Enthalpy, J kg$^{-1}$ |
| $\Delta H$ | Enthalpy change, J kg$^{-1}$ |
| $H_x$ | Heat of solidification of fat at freezing point, J kg$^{-1}$ |
| $k_F$ | Thermal conductivity of frozen food, W m$^{-1}$ K$^{-1}$ |
| $L$ | Latent heat of freezing, J kg$^{-1}$ |
| $L_0$ | Latent heat of freezing at 0°C, J kg$^{-1}$ |
| $M$ | Molecular weight, kg kmol$^{-1}$ |

| | |
|---|---|
| $r$ | Half-thickness of slab, m |
| $R$ | Gas constant, J kmol$^{-1}$ K$^{-1}$ |
| $t$ | Freezing time, s |
| $T$ | Absolute temperature, K |
| $T_0$ | Freezing point of water in Kelvins |
| $\theta_A$ | Environment temperature, °C |
| $\theta_C$ | Final product centre temperature after freezing, °C |
| $\theta_E$ | Final product temperature, °C |
| $\theta_F$ | Initial freezing temperature, °C |
| $\theta_{Fm}$ | 'Mean' freezing temperature, °C |
| $\theta_I$ | Initial product temperature, °C |
| $\Delta\theta$ | Difference between mean product temperature and environment temperature, °C |
| $x$ | Mass fraction |
| $\rho$ | Density, kg m$^{-3}$ |
| *Subscripts* | |
| a,b,f,i,o,p,s,w | Ash, bound water, fat, ice, other components, protein, solutes, water |
| 1 | Precooling period |
| 2 | Freezing period (after precooling) |

## INTRODUCTION

In order to design freezing equipment and processes, it is important to have accurate information on the enthalpy–temperature ($H$–$T$) relationship of the food being processed. This data is best obtained by an adiabatic calorimeter (Riedel, 1957; Fleming, 1969; Pham *et al.*, 1994; Lindsay & Lovatt, 1994), although differential scanning calorimeters (DSC) have also been used.

Foods do not have a sharp freezing point like water; latent heat is released gradually over a large range of temperature. Using Raoult's law Bartlett (1944) suggested that the frozen fraction varies as $(1-T/T_F)$. Schwartzberg (1976) improved the relationship by introducing a bound water fraction $x_b$, which will not freeze at any temperature. Although it is unclear what 'bound water' actually means in physical terms, the concept is useful in practice and was developed further by Chen (1985) and Pham (1987). Chen compared the model's prediction with the data then available. For many foods, composition data did not exist and he had to use empirical equations. The COST project (Miles *et al.*, 1983) also used a variation of Schwartzberg's model.

The objectives of this study are (a) to fit Schwartzberg's model to enthalpy–temperature data for a range of foods; (b) to derive simplified relationships for predicting the enthalpy–temperature curve of foods over the range $-40$–$+40$°C from composition; (c) to curve-fit empirical equations that enable the parameters of Schwartzberg's model to be calculated from composition data; and (d) to see whether the unified approach allows freezing time and product heat load to be accurately calculated.

## THEORY

### Enthalpy–temperature relationship

Food can be considered as a mixture of water, dissolved matter and undissolved solids. During freezing, the remaining solution becomes more and more concentrated and obeys the freezing point depression equation (Bartlett, 1944)

$$\frac{\mathrm{d}(\ln a_w)}{\mathrm{d}T} = \frac{M_w L}{RT^2} \tag{1}$$

Assuming Raoult's law, the water activity is given by

$$a_w = \frac{x_w}{x_w + \dfrac{M_w}{M_s} x_s} \tag{2}$$

Schwartzberg (1976) modifies this equation by introducing bound (unfreezable) water:

$$a_w = \frac{x_w - x_b}{x_w - x_b + \dfrac{M_w}{M_s} x_s} \tag{3}$$

Substituting for $a_w$ from the above equation into eqn (1) leads to an equation for the rate of ice formation. Further assuming that heat of solution effects are negligible, an expression for the apparent specific heat $c_{app}$ (which includes latent heat effects) is obtained:

$$c_{app} = c_U + (x_b - x_{wo})\Delta c + \frac{M_w x_s a_w}{M_s(1-a_w)}\left[\Delta c + \frac{M_w L^2}{(1-a_w)RT^2}\right] \tag{4}$$

Schwartzberg showed that this equation can be approximated to within 0·03% by

$$c_{app} = c_U + (x_b - x_{wo})\Delta c + \frac{M_w x_s a_w}{M_s}\left[\frac{RT_0^2}{M_w \theta^2} - 0{\cdot}8\Delta c\right] \tag{5}$$

Integration leads to an equation of the form

$$\text{for } \theta \leq \theta_F\text{: } H = A + c_F\theta - B/\theta \tag{6}$$

$$\text{for } \theta \geq \theta_F\text{: } H = D + c_U\theta \tag{7}$$

$A$ is an arbitrary parameter related to the reference point for enthalpy, while $B$, $c_F$ and $c_U$ are the parameters of Schwartzberg's model. $D$ can be calculated in terms of the other parameters since the above two expressions must be equal at the freezing point $\theta_F$, resulting in

$$\text{for } \theta \geq \theta_F\text{: } H = A + c_F\theta_F - B/\theta_F + c_U(T - T_F) \tag{7a}$$

Pham (1987) showed that the bound water content $x_b$ can be found from data by determining $B$ by regression and using

$$B = (x_w - x_b) L_0 \theta_F \tag{8}$$

while the freezing point $\theta_F$ can be determined from the intersection of the lines represented by eqns (6) and (7). Since $\theta_F \approx -1°C$ for most fresh foods, an error as small as 0·1°C would mean a percentage error of $\approx 10\%$ in $\theta_F$, which is unacceptable. The intersection method used in this work minimises this error because it determines $\theta_F$ from information over the entire $H$–$T$ curve, rather than measuring $\theta_F$ directly.

Assuming that the enthalpy–temperature curve follows Schwartzberg's relationship, it can be calculated from $x_w$, $x_b$, $c_F$, $c_U$ and $\theta_F$. This paper will attempt to find out whether these quantities can be predicted from composition.

## Freezing time and heat load calculations

In most freezing applications, a convective boundary condition is assumed. Plank's (Plank, 1941) equation is usually taken as the starting point for calculating the freezing time. This equation is exact for the case of zero sensible heat, sharp phase change and one-dimensional shape (slab, cylinder or sphere). Many approximate equations have since been proposed to correct for the assumptions underlying Plank's equation. Hossain *et al.* (1989) showed that the effect of shape can be considered separately by first calculating the freezing time for a slab then multiplying it by an analytically derived shape factor. To correct for the effect of sensible heat during precooling and subcooling and for the gradual release of latent heat, the following method of Pham (1986) has been shown to be simple and accurate. The total freezing time from a uniform temperature $\theta_I$ to a final centre temperature $\theta_C$ for a slab is given by

$$t = \frac{\rho r}{h}\left(\frac{\Delta H_1}{\Delta\theta_1} + \frac{\Delta H_2}{\Delta\theta_2}\right)\left(1 + \frac{Bi}{4}\right) \tag{9}$$

where $\Delta H_1$ is the difference in enthalpy between temperatures $T_I$ and $T_F$, and $\Delta H_2$ the difference in enthalpy between temperatures $T_F$ and $T_E$. The equation indicates that the effect of any uncertainties in calorimetric properties can be isolated in the second factor, $\Delta H_1/\Delta\theta_1 + \Delta H_2/\Delta\theta_2$. Equation (9) was derived from the assumption that the rate at which heat is extracted from the product is proportional to the difference $\Delta\theta$ between environment temperature and air temperature. The second factor can thus be generalised into

$$\left(\frac{\Delta H}{\Delta\theta}\right)_m = \int_{\theta_C}^{\theta_I} \frac{dH}{\theta - \theta_A} \tag{9a}$$

which will be used in the evaluation of errors in process time due to calorimetric properties.

## Additive model for specific heats

For the specific heats $c_U$ and $c_F$, an alternative approach is to use the additive model,

$$c_{\mathrm{mixture}} = \sum c_j x_j \tag{10}$$

where $c_j$ are the specific heats of the various food components. Values of $c_j$ in kJ kg$^{-1}$ K$^{-1}$, listed by Choi & Okos (1986) are, for a temperature of 20°C: $c_w = 4177$, $c_f = 2012$, $c_p = 2032$, $c_a = 1129$, $c_o = 1587$. The value for $c_o$ was based on carbohydrates. The additive model provides an alternative approach for calculating specific heats when regression against composition is unsuccessful due to experimental errors.

## MATERIALS AND METHOD

Rahman (1994) compared literature data on freezing point (an important parameter in the prediction of $H$–$T$ curves) of meat to various correlations. Although all equations had empirical parameters that were found by regression, and only meat was considered, mean deviations of about 50% were found for all models. Even when only beef was considered (34 data points), mean deviations ranged from 24 to 43%. This illustrates the importance of being highly selective with the data.

In the present work, only the data gathered by Fleming (1969), Pham *et al.* (1994) and Lindsay & Lovatt (1994) will be used for the analysis. These authors obtained complete $H$–$T$ and composition data over the range −40 to +40°C for 43 food materials. The reason for being so selective is that, to the author's knowledge, this is the only body of data with complete enthalpy and composition information. (Riedel obtained authoritative calorimetric data but did not provide complete information on material composition; in most cases only moisture content was given.) Furthermore they were all obtained by using adiabatic calorimetry, which is a fundamental steady-state measurement method and can better deal with inhomogeneous foods than differential scanning calorimetry, because it uses larger sample sizes. The equipment used had been carefully calibrated and all calibration data have been published. DSC relies on the assumption that the sample attains thermal equilibrium instantaneously, which may not be true. When phase change occurs, the latent heat peak obtained by DSC tends to be smeared out, which indicates that there is a significant thermal lag.

The calorimetric apparatus used for Fleming's (1969) dataset was similar to that used for Pham *et al.*'s (1994) and Lindsay and Lovatt's (1994) datasets, except that the latter used a stirrer motor that was completely immersed in the calorimeter liquid, resulting in less uncertainty in the heat input. Calibration tests on water showed agreements of ±0·1% for the specific heats of ice and water and 0·6% for the latent heat, compared with previous literature values (Pham *et al.*, 1994). The materials measured include meats (beef, chicken, lamb, pork; lean of fat; fresh, cooked or cured), fish and surimi, animal fats, butter, cheese, icecream and Tylose (methylcellulose) gels.

For the data analysis, the parameters $c_U$, $c_F$ and $B$ of eqns (6) and (7) are found by multilinear regression against the $H$–$\theta$ data, after which bound water and freezing point are found as described in the theory section. The parameters of the model ($c_U$, $c_F$, $\theta_F$, $x_b$) are then regressed against composition using a stepwise regression method where explanatory (independent) variables are removed if they alter the $F$-

statistic by less than 2. Both component mass fractions $x_i$ and the mass ratios of components to water $x_i/x_b$ were tried as variables in the regression.

## RESULTS AND DISCUSSION

### Calorimetric parameters for individual components

The specific heats $c_U$, $c_F$, initial freezing points $\theta_F$ and bound water contents $x_b$ were calculated for all materials and are tabulated in Table 1. These parameters are sufficient to re-create the entire regressed $H$–$T$ curves. From Table 1, the parameters listed above were regressed against composition.

**TABLE 1**
Bound Water for Various Materials

| *Material* | $c_U$ | $c_F$ | $\theta_F$ | $x_b$ | *Material* | $c_U$ | $c_F$ | $\theta_F$ | $x_b$ |
|---|---|---|---|---|---|---|---|---|---|
| (Pham *et al.*, 1994) | | | | | (Lindsay & Lovatt, 1994) | | | | |
| Tylose (76·1% water) | 3·809 | 1·905 | −0·797 | 0·084 | Tylose | 3·720 | 2·320 | −0·580 | 0·125 |
| Tylose (76·9% water) | 3·784 | 2·308 | −0·615 | 0·123 | Butter unsalted | 4·210 | 2·140 | −1·120 | 0·026 |
| Lamb lean | 3·679 | 2·118 | −0·803 | 0·054 | Butter salted | 3·940 | 1·670 | −6·250 | −0·052 |
| Beef lean | 3·644 | 2·159 | −0·732 | 0·050 | Cheddar cheese | 3·410 | 1·650 | −5·930 | 0·026 |
| Chicken lean | 3·706 | 2·063 | −0·806 | 0·049 | Mozzarella cheese | 3·530 | 2·120 | −2·350 | 0·055 |
| Chicken fat | 3·451 | 2·291 | −0·344 | −0·066 | Icecream | 4·070 | 2·870 | −2·390 | −0·020 |
| Mutton cooked | 3·660 | 2·092 | −0·948 | 0·044 | Lean pork | 3·650 | 2·090 | −0·820 | 0·031 |
| Butter | 3·971 | 1·675 | −4·809 | −0·093 | Venison | 3·980 | 2·540 | −1·100 | −0·014 |
| Butter unsalted | 4·440 | 2·324 | −0·728 | −0·038 | Pork sausage meat | 3·810 | 1·930 | −2·230 | −0·012 |
| Peas frozen | 4·166 | 2·339 | −0·783 | 0·019 | Beef sausage meat | 3·790 | 1·950 | −2·340 | 0·003 |
| Mutton liver | 3·840 | 2·168 | −0·894 | 0·032 | Beef mince | 3·620 | 2·040 | −0·780 | 0·056 |
| Mutton kidney | 3·939 | 2·215 | −0·665 | 0·025 | Beef fat | 3·840 | 1·750 | −1·950 | −0·04 |
| Ham cooked | 3·510 | 1·803 | −3·283 | −0·005 | Pork kidney fat | 4·060 | 1·760 | −0·800 | −0·058 |
| Hamburger patties | 3·525 | 1·664 | −1·897 | −0·013 | Surimi | 3·530 | 2·210 | −1·860 | 0·025 |
| Kiwifruit | 3·832 | 2·408 | −1·332 | 0·030 | Apple (red delicious) | 3·850 | 2·300 | −1·270 | 0·009 |
| Venison | 3·687 | 2·141 | −0·863 | 0·044 | | | | | |
| Mutton brains | 3·719 | 2·101 | −0·592 | 0·018 | (Fleming, 1969) | | | | |
| Gurnard | 3·777 | 2·057 | −0·786 | 0·040 | Lamb loin lean | 3·383 | 1·880 | −0·896 | 0·071 |
| Terakihi | 3·679 | 2·054 | −0·817 | 0·049 | Lamb loin medium | 2·944 | 1·754 | −0·842 | 0·080 |
| Pork lean | 3·620 | 2·060 | −0·790 | 0·034 | Lamb loin fat | 3·340 | 1·579 | −0·841 | 0·080 |
| Beef fat | 3·680 | 1·600 | −2·690 | −0·093 | Lamb kidney | 3·929 | 2·313 | −0·957 | 0·094 |
| Beef lard | 3·700 | 1·600 | −3·390 | −0·069 | Calf veal | 3·535 | 1·847 | −0·682 | 0·065 |
| Pork fat | 3·620 | 1·640 | −1·870 | −0·124 | | | | | |

## Preliminary data analysis

When a preliminary regression analysis was carried out on the foods studied (Tylose was excluded from all following analyses), it quickly became apparent that some foods behaved differently from others. Fat materials (animal fats, butter) did not correlate well with other foods, because the *H–θ* curve above 0°C contains phase change transitions due to melting and the (water) freezing point was not always clearly determined, due to the low water content. A somewhat more surprising trend is that non-fat dairy foods (cheese and icecream) also behaved differently from the other foods: they all contain a substantial amount (10–30%) of dairy fats, which melts substantially in the range 0–40°C.

Unless otherwise indicated, the following analyses will not include Tylose, fats and dairy foods. This leaves 27 food materials which comprise meats (fresh, cooked and cured), fish and fruits.

## Unfrozen specific heat (meat, fish and fruit)

As mentioned earlier, all fats and dairy foods are excluded from this analysis. Because of the limited data, regression analysis on the present data failed to produce a physically plausible relationship, with some coefficients being negative. It was decided therefore to calculate $c_U$ from the additive model (eqn (10)) and then to compare the theoretical values to the data. Results are shown in Figure 1. There is reasonable correlation between theoretical and measured values ($R^2 = 0{\cdot}60$) and the errors statistics were: mean error 3·3%, s.d. 5·5%, range −6 to +16%.

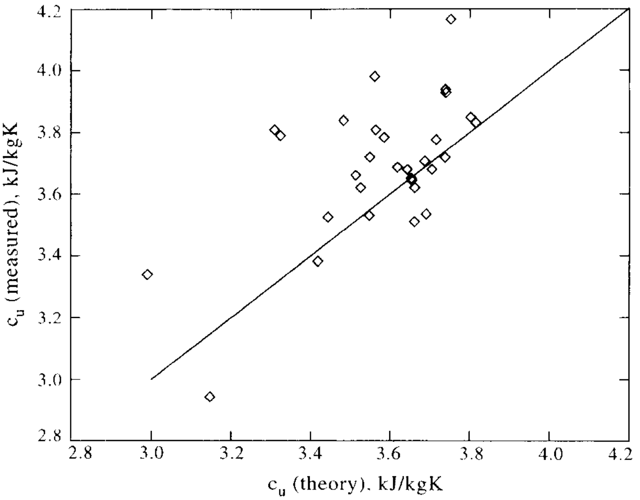

**Fig. 1.** Measured specific heat of unfrozen foods vs those predicted from the additive model (<FDR10</FDR).

## Freezing point (meat, fish, fruit and non-fat dairy foods)

After trying various combinations of variables using Minitab's stepwise regression procedure (which automatically eliminates variables with non-significant effects), the following regression equation was obtained:

$$\theta_F = -0{\cdot}141 - 4{\cdot}36x_o/x_w - 43{\cdot}5x_a/x_w \tag{11}$$

$$R^2(\text{adj}) = 91{\cdot}6\%$$

Since the constant is insignificant ($t$-ratio $= -1{\cdot}55$) it can be eliminated, giving an alternative regression equation which is more theoretically satisfying:

$$\theta_F = -4{\cdot}66x_o/x_w - 46{\cdot}4x_a/x_w \tag{12}$$

Measured and regression values for $\theta_F$ are plotted in Figure 2, showing good agreement. Also shown are predictions from Chang and Tao's (Chang & Tao, 1981) equation, using the empirical coefficients of Rahman (1994). Rahman found that this is the best of the six equations he tested, yet it can be seen that it is much poorer than eqn (12), even for meat.

In this case, $x_o$ probably represents mainly the sugar content while $x_a$ represents the salt content. Using Raoult's law, estimates of the molecular weight of the ash can be made. The resulting equivalent weight is 40 and assuming a monovalent salt, the 'effective' molecular weight is 80, which is somewhat higher than the molecular weight for sodium chloride (58·45). The effective molecular weight of 'other' is 794. This appears very high since the molecular weights of various fruit and dairy sugars were in the range 180–350 (Weast, 1985; Chen, 1986). However, not too much significance should be attached to the value found here because the number of data is limited and the value of $x_o$ very low.

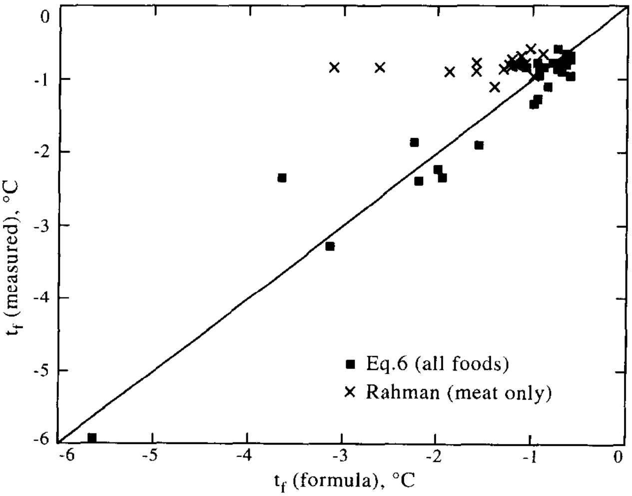

**Fig. 2.** Measured initial freezing points vs those calculated from eqn (12).

## Bound water (meat, fish, fruit and non-fat dairy foods)

Apart from the initial freezing point, bound (unfreezable) water is the most crucial factor influencing calorimetric data, because it directly affects latent heat. The bound water fraction $x_b$ was calculated using eqn (8) and is shown in Table 1. Regression analysis was used to find a relationship between bound water content and composition. To be acceptable, the equation must predict that as $x_w$ tends to zero so does $x_b$; therefore, $x_b/x_w$ was used as the dependent variable. The following regression equation was found (Figure 3)

$$x_b/x_w = 0{\cdot}3407 - 0{\cdot}344x_w - 4{\cdot}51x_a + 0{\cdot}167x_p \tag{13}$$

$$R^2(\text{adj.}) = 73{\cdot}7\%$$

Since the constant (0·3407) and the coefficient of $x_w$ (0·344) are within 1% of each other, they can be equated:

$$x_b/x_w = 0{\cdot}342(1 - x_w) - 4{\cdot}51x_a + 0{\cdot}167x_p \tag{14}$$

This equation correctly predicts that $x_b$ tends to zero when $x_w$ tends to zero *or* unity (i.e. pure water). Also plotted in Figure 3 is the empirical equation used by Miles *et al.* (1983):

$$x_b = 0{\cdot}3x_p + 0{\cdot}1x_c \tag{15}$$

where $x_c$, the carbohydrate mass fraction, is taken to be $x_o$ in this work.

## Frozen specific heat (meat, fish and fruit)

Regression of frozen specific heat $c_F$ vs composition did not yield any sensible correlation. Using the additive model (eqn (10)) also yielded poor predictions, with a correlation coefficient of −0·240 between theory and data, and relative errors of

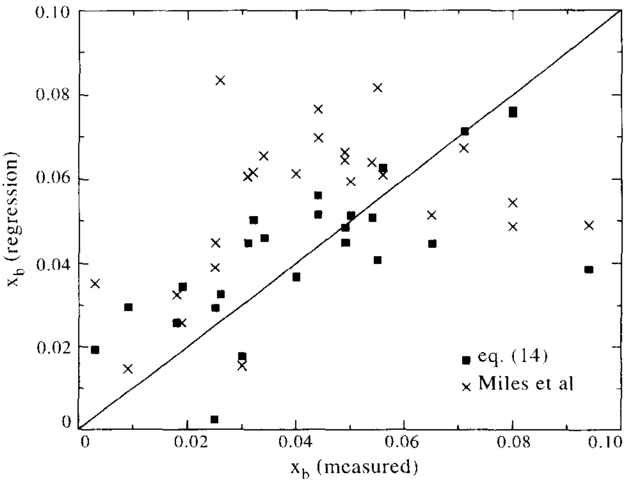

**Fig. 3.** Calculated vs measured bound water content.

16 to 28%. Because the effect of $c_F$ is small compared to that of latent heat, it was decided not to pursue the matter further and the additive model was used in spite of its poor fit.

In summary, the additive model (eqn (10)) was used for the specific heats $c_F$, $c_U$ while empirical regression equations were used for $\theta_F$ (eqn (12)) and $x_b$ (eqn (14)).

### Expected errors in freezing time and heat load due to calorimetric property formulae

From the engineering point of view, the real test of a food enthalpy model is whether it will allow accurate prediction of freezing times and heat loads. Food freezing operations, however, take place over a wide range of conditions: overall heat transfer coefficients, initial and final product temperatures, environment temperature, product size and shape. By using eqn (9a), the effect of uncertainties in calorimetric properties can be isolated and estimated.

The relative errors in $\Delta H$ (i.e. errors in heat load) and in process time (from eqn (9a), were calculated for various foods and shown in Table 2. Two initial temperatures, 30 and 0°C, and two freezing medium temperatures, −25 and −35°C, were used to cover the range normally encountered in practice. The final product temperature was assumed to be −20°C in all cases. The errors are acceptable in engineering terms (about ±10% or less) for meat (fresh and cooked), fish, fruit, cheese and Tylose gels, but large errors are found for icecream and fats.

Errors for fat are largely attributable to latent heat of fat solidification. To account for this effect, the standard enthalpy–temperature model was modified by adding the following term to the enthalpy when $\theta$ exceeds $\theta_F$:

$$H = H_{\mathrm{model}} + x_f[H_x + c_x(\theta - \theta_F)], \ \theta \theta_F \tag{16}$$

with $H_{\mathrm{model}}$ being the enthalpy predicted by eqns (6) and (8), $H_x = 28978$ J kg$^{-1}$ and $c_x = 1892$ J kg$^{-1}$ K$^{-1}$ (found by averaging over 10 fatty materials). For low-fat materials this correction does not significantly affect the accuracy of the predictions, while for predominantly fatty materials it reduced the mean errors to mostly acceptable levels (Table 3). However, the spread is still quite wide, particularly for freezing

TABLE 2

Percentage Errors (Calculated–Measured) in Heat Load and Freezing Time Due to Uncertainties in Estimating Calorimetric Properties (Mean ± s.d.). Freezing is Assumed to Stop at −20°C

| | *Meat & fish (24 matls)* | *Fruit (3 matls)* | *Fats (10 matls)* | *Tylose gels (3 matls)* | *Cheese (2 matls)* | *Icecream (1 matl)* |
|---|---|---|---|---|---|---|
| $\Delta H(-20\text{–}0°\mathrm{C})$ | 1·1 ± 3·7 | −1·7 ± 2·3 | −27·2 ± 10·6 | 2·5 ± 0·8 | −0·5 ± 3·5 | −14·3 |
| $\Delta H(-20\text{–}30°\mathrm{C})$ | −0·4 ± 3·6 | −2·8 ± 3·1 | −34·4 ± 7·6 | −0·6 ± 0·8 | −9·9 ± 0·1 | −16·5 |
| $t_F$ ($T_I$ = 0°C, $T_A$ = −25°C) | 0·8 ± 4·6 | −4·4 ± 1·7 | −23·3 ± 7·6 | 9·2 ± 1·0 | 4·4 ± 1·1 | −16·6 |
| $t_F$ ($T_I$ = 30°C, $T_A$ = −25°C) | −0·0 ± 4·2 | −4·5 ± 1·0 | −29·0 ± 5·5 | 6·4 ± 1·0 | −1·1 ± 1·8 | −17·4 |
| $t_F$ ($T_I$ = 0°C, $T_A$ = −35°C) | 0·8 ± 4·2 | −3·3 ± 1·2 | −25·5 ± 8·6 | 7·0 ± 1·1 | 2·6 ± 0·5 | −15·6 |
| $t_F$ ($T_I$ = 30°C, $T_A$ = −35°C) | −0·2 ± 3·8 | −3·7 ± 1·4 | −31·5 ± 6·4 | 4·0 ± 1·0 | −4·1 ± 0·8 | −16·7 |

TABLE 3

Percentage Errors in Heat Load and Freezing Time for Freezing 10 Animal Fats (mean ± s.d.), Using Model Corrected for Fat Solidification. Freezing is Assumed to Stop at −20°C

| *Quantity* | *% errors (calc-meas)* |
|---|---|
| $\Delta H$ (−20–0°C) | $-7{\cdot}1 \pm 15{\cdot}7$ |
| $\Delta H$ (−20–30°C) | $-0{\cdot}7 \pm 5{\cdot}4$ |
| $t_F$ ($T_I = 0$°C, $T_A = -25$°C) | $-6{\cdot}7 \pm 8{\cdot}6$ |
| $t_F$ ($T_I = 30$°C, $T_A = -25$°C) | $-4{\cdot}6 \pm 5{\cdot}4$ |
| $t_F$ ($T_I = 0$°C, $T_A = -35$°C) | $-5{\cdot}1 \pm 9{\cdot}7$ |
| $t_F$ ($T_I = 30$°C, $T_A = -35$°C) | $-3{\cdot}2 \pm 5{\cdot}5$ |

from an initial temperature of 0 to −20°C. This is because fats are complex mixtures whose components solidify at a different temperature, while eqn (16) does not take these variations into account.

As an illustration, enthalpy–temperature curves calculated from the model (with correction for fat solidification) for a representative of each type of food are shown in Figure 4 together with the data. The latter have been smoothed to fit the Schwartzberg model used in this paper.

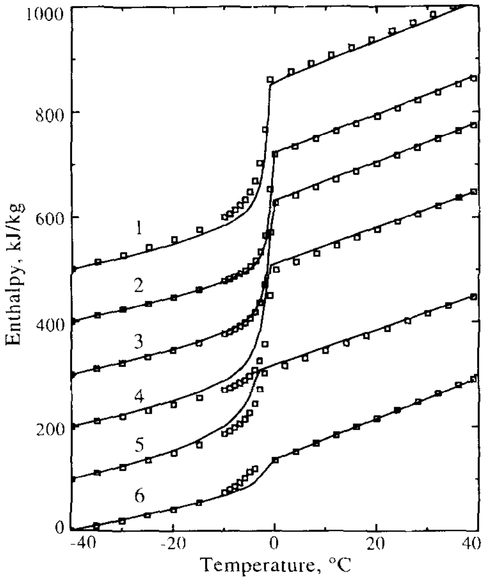

**Fig. 4.** Calculated enthalpies vs smoothed data. 1: kiwifruit, 2: lean beef, 3: gurnard, 4: Tylose, 5: mozzarella cheese, 6: butter.

## CONCLUSIONS

In summary, the calorimetric properties of foods can be calculated from composition using Schwartzberg's model, combined with eqn (12) for the initial freezing point, eqn (14) for the bound water content, the additive model (eqn (10)) for specific heats both above and below freezing, but with an additional factor for the latent heat of fat melting as shown in eqn (16). Because the amount of data considered was not large while foods vary greatly in compositions and properties, we should not draw strong sweeping conclusions. However, some general trends have been observed and point the way to further research. The additive model for the unfrozen specific heat is satisfactory, but more data is needed on the melting latent heats and temperature of fats. Below the freezing point, Schwartzberg's bound water model can predict enthalpies with acceptable engineering accuracy, except for fats and icecream. From a fundamental point of view, further investigation is needed to derive a model for predicting bound water from basic principles rather than regression.

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