CALCULATION OF INITIAL FREEZING POINT, EFFECTIVE MOLECULAR WEIGHT AND UNFREEZABLE WATER OF FOOD MATERIALS FROM COMPOSITION AND THERMAL CONDUCTIVITY DATA[1]

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ABSTRACT

A procedure was developed for simultaneous determination of the effective molecular weight, unfreezable water, and initial freezing point of foods based on composition and thermal conductivity data. Freezing properties were determined by trial and error and optimized by minimizing the difference between calculated and reported values of thermal conductivity. The procedure involved determination of the ice fraction at several temperature levels. Corresponding thermal conductivity values at each temperature level were then calculated. Results showed that calculated values of effective molecular weight, unfreezable water, and initial freezing point for various types of meat and fish are comparable to those published. The parallel-perpendicular model was found an excellent predictor of thermal conductivity of frozen meat and fish with muscle fibers oriented toward the direction of the heat flow.

INTRODUCTION

During freezing and thawing process operations, high moisture foods are exposed to temperatures that can make them susceptible to microbial growth. To determine if a food material has reached critical conditions during freezing and thawing, information is needed on temperature distribution as a function of time. In frozen particles, temperature distribution can be determined by numerical modeling, which requires data on freezing and thermal properties; however, data

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on these properties for various foods are seldom available. In this study, a method is proposed for the calculation of initial freezing point (T_f), unfreezable water (b), and effective molecular weight (ω_e) of frozen materials from thermal conductivity (k) and composition (X^W) data. Conversely, thermal conductivity can be calculated if those three freezing properties are known.

Freezing proceeds gradually, and in the presence of solutes the freezing point of the unfrozen fraction drops as the amount of water in the system decreases. The relationship between freezing point (T_f) and the amount of unfrozen water in the system can be expressed with the following (Heldman 1974):

$$\frac{L_f \omega_w}{R}\left[\frac{1}{T_{fw}} - \frac{1}{T_f}\right] = \ln(X_a) \tag{1}$$

The left-hand side of Eq. (1) is derived from the summation of chemical potentials of different phases of matter in the system, and the right-hand side is the mole fraction of the unfrozen water (X_a). The mole fraction of water in a solution depends on the weight fractions of unfrozen water (X_w^w) and dissolved solids (X_{ds}^w) in the system and their corresponding molecular weights (ω_w and ω_{ds}), respectively. The X_a is calculated by the following equation:

$$X_a = \frac{X_w^w}{X_w^w + X_{ds}^w(\omega_w/\omega_{ds})} \tag{2}$$

If all solids in the system are dissolved, the ω_{ds} can be computed from the weight fractions and molecular weights of all the solute in the system. This assumption was made in several previous freezing studies because dissolved solids are difficult to identify and quantify; however, it is unrealistic since only a fraction of the total solids actually dissolves in the unfrozen water. To account for the undissolved solids, Heldman (1974) suggested using total solids in the calculation and a parameter called effective molecular weight (ω_e), which serves as a correction factor for using total solids instead of undissolved solids in the equation. By replacing ω_{ds} with ω_e, Heldman (1974) calculated ω_e from Eq. (1) and (2) using the moisture content (MC) and the T_f of the system, and concluded that his procedure for calculating the ω_e is valid only in systems without a significant amount of unfreezable water. Other studies have used the concept of effective molecular weight and suggested several other methods for calculating it. Table 1 shows the published ω_e for some materials used in this study.

The definition of unfreezable water is often interchanged with that of bound water (Chen 1985). Unfreezable water has been defined as the amount of unfrozen water in the system at -40C. In contrast, bound water is the amount of water left in the system after drying. Pham (1987) and Chen (1985) reported that the wide ranges of both bound and unfreezable water overlap each other. They are assumed equal in this study because the difference in their values has not been clearly established in the literature. The literature values of bound water for various food materials are listed in Table 2.

Several workers including Choi (1985) and Murakami and Okos (1988) have proposed the modeling of thermal conductivity (k) of foods based on composition. Choi (1985) reported that the k of food materials can be determined from the major components, such as protein, carbohydrates, fats, ash, water, and ice. He developed empirical equations of thermal properties for each food component as a function of temperature.

The objective of this study was to develop a method for calculating initial freezing point, effective molecular weight, and unfreezable water of food materials from composition and thermal conductivity data. This study will increase the database of food properties that are useful in numerical modeling of heat transfer in frozen foods.

TABLE 1.
LITERATURE VALUES OF ω_e FOR VARIOUS FOOD MATERIALS AT SPECIFIED LEVELS OF MOISTURE AND FAT CONTENTS

	MC (% wb)	Fat (%)	ω_e
Lean beef	74	---	662[a,b], 677[c], 724[d]
	50	---	677[c], 701[b], 702[a], 1071[d]
Cod fish	82	---	466[a,b], 494[d], 519[c]
	50	---	509[a,b], 519[c], 810[d]
Lamb kidneys	79.8	2.9	416[e]
Lamb loin	64.9	11.7	1023/684[f,e]
	52.5	28.4	1993[e], 779[e,f]
	44.4	39.4	3711[e], 1078[e,f]
Calf veal	77.5	4.4	1091[e]

[a] Heldman 1974; Chen 1985.
[b] Bartlett 1944; Chen 1985.
[c] Schwartzberg 1976; Chen 1985.
[d] Chen, 1985.
[e] Schwartzberg 1976.
[f] Based on nonfat solids.

TABLE 2.
LITERATURE VALUES OF b FOR VARIOUS FOOD MATERIALS

	b (sb)	References
Meat, fish	0.24-0.27	Duckworth (1971); Schwartzberg (1976)
	0.143-0.318	Pham (1987)
Lean beef[a]	0.34, 0.36	Reidel (1951,1957,1959); Chen (1985)
	0.25	Schwartzberg (1976); Chen (1985)
	0.06, 0.054	Bartlett (1944); Chen (1985)
	0.31, 0.389	Chen (1985)
Cod fish[b]	0.364, 0.39	Reidel (1951,1957,1959); Chen (1985)
	0.25	Schwartzberg (1976); Chen (1985)
	0.082, 0.075	Bartlett (1944); Chen (1985)
	0.342, 0.419	Chen (1985)

[a]Corresponding MC = 74 and 50% wb, respectively.
[b]Corresponding MC = 82 and 50% wb, respectively.

MATERIALS AND METHODS

Calculation of Parameters

Ice Fraction. In the proposed procedure, the amount of ice in the system (X_i^w) at any temperature is calculated from Schwartzberg's (1976) equation. Since unfreezable water is not available for the freezing process, Schwartzberg (1976) modified Heldman's (1974) equation by subtracting the amount of unfreezable water (bX_s^w) from the unfrozen fraction (X_w^w). The resulting equation is:

$$X_a = \frac{X_w^w - bX_s^w}{(X_w^w - bX_s^w) + (18/\omega_e)X_s^w} \tag{3}$$

Then, X_i^w is calculated from the following:

$$X_i^w = MC - X_w^w - bX_s^w \tag{4}$$

Note that at above freezing temperatures, MC is equal to X_w^w. Schwartzberg (1976) agreed with Heldman (1974) that the effective molecular weight (ω_e) serves as a correction factor for using the weight fraction of the total solids.

Thermal Conductivity. Modeling of thermal conductivity based on composition requires a structural model to relate the various food components (Murakami and Okos 1988). The two basic structural models are the parallel and perpendicular models. In the parallel model, all food components are assumed to be arranged parallel to the direction of heat flow. In the perpendicular model, they are perpendicular to the heat flow. In this study, it was found that the published thermal conductivity values for frozen meat were lower than those calculated with the parallel model and higher than those calculated with the perpendicular model. For example, Pham and Willix (1989) reported that the thermal conductivity of lamb kidneys at -40C is 1.65 W/m-K. The predicted values are 0.64 W/m-K using the perpendicular model and 2.06 W/m-K for the parallel model. The predicted values using the parallel model are high since components with high thermal conductivity (i.e., ice and liquid water) can compensate for those with low thermal conductivity (i.e., protein and fat). In the perpendicular model, the total conductive heat has to pass through each component. Thus, the components with low thermal conductivity can serve as insulators. In this study, the structural model chosen for frozen foods is a parallel-perpendicular model, which combines the two basic structural models. In this model, frozen food materials are assumed as 2-phase systems of liquid and solid, which are arranged perpendicular to the direction of heat flow. Then, the solid phase is made up of the ice fraction and other nonwater components which are arranged parallel to the heat flow. The parallel-perpendicular model is expressed in the following equation:

$$\frac{1}{k}=\frac{(1-X_l^v)}{k_s}+\frac{X_l^v}{k_l} \qquad (5)$$

where:

$$k_s=\frac{\Sigma X_n^v k_n}{\Sigma X_n^v} \qquad (6)$$

A parallel-perpendicular model with the solid and liquid phases in parallel arrangement and the solid phase components in perpendicular arrangement was also evaluated. This model was found to give high standard errors. The k model (Eq. 5 and 6) requires the volume fraction (X^v) of the components rather than their weight fractions (X^w). Because data on food composition are usually available in terms of weight fractions, the equivalent volume fractions must be calculated. Volume fractions can be calculated from weight fractions and densities (ρ) by the following conversion equation:

$$X_m^v = \frac{X_m^w/\rho_m}{\sum_{n=1}^{N}(X_n^w/\rho_n)} \qquad (7)$$

Initial Freezing Point. The presence of ice in frozen foods dramatically increases the k of the system. Since the k of ice is as much as four times that of water, the accuracy of k models for frozen foods depends largely on the accuracy of ice content prediction. Figure 1 illustrates how the initial freezing point (T_f) influences the temperature-thermal conductivity (T-k) curve of a material. This figure was calculated using the parallel-perpendicular model used in this study and it is consistent with the figures published by Heldman and Gorby (1975) and Pham and Willix (1989). Figure 1 shows that when the system temperature drops below the T_f, its k increases rapidly. The higher the T_f, the sooner the ice forms, and consequently the higher is the k of the system. We used the T-k curve to estimate the starting values for T_f.

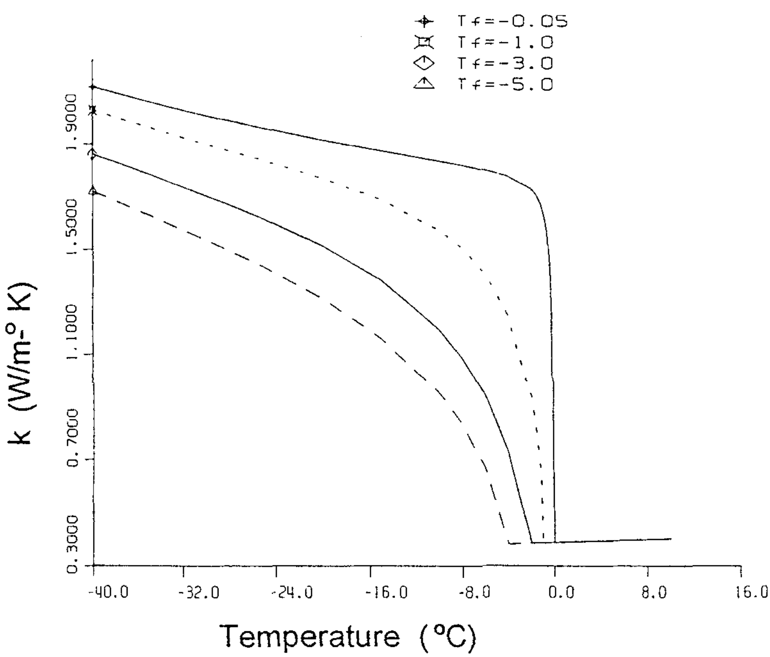

FIG. 1. CALCULATED k AS INFLUENCED BY T_f

Unfreezable Water. The effect of unfreezable water (b) on k is demonstrated in Fig. 2. This figure was derived by calculating Eq. (3), (5) and (6) at several values of b. As the b of the system increases, the slope of the T-k curve at the subfreezing temperatures decreases. Figure 2 shows that the difference between T-k curves with different values of b increases as the system temperature decreases; thus, if the b value is inaccurate, the error in the calculated k increases as the temperature decreases. The T-k curves were used to determine the starting values of b in the proposed procedure.

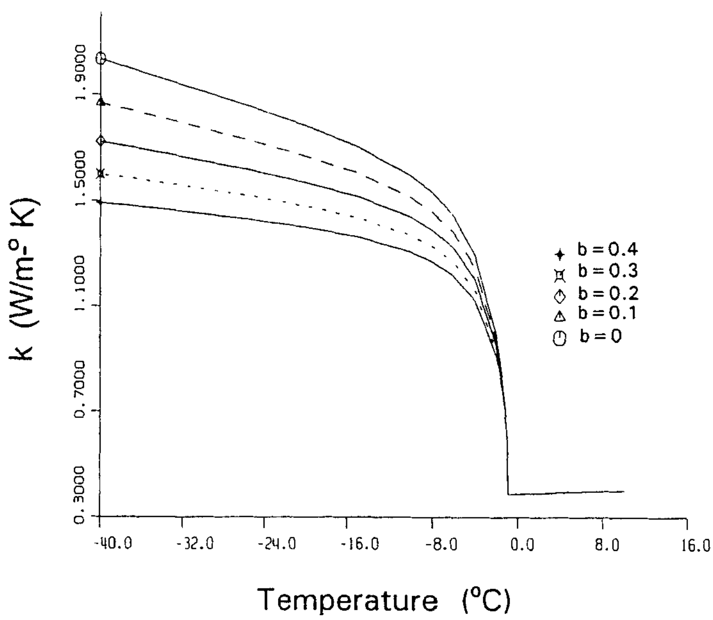

FIG. 2. EFFECT OF b ON THE k OF FROZEN FOODS

Food Composition. Published studies of food properties seldom include complete information on food composition. In this study, alternative sources for composition data were handbooks published by the U.S. Department of Agriculture (USDA) (Watt and Merrill 1975; Adams 1975). However, since the data on composition from these sources are not specific to the materials used in this study, they are referred to as the reference composition. Published data on food properties may be available for levels of moisture, protein, fat content, or other components ($X_{j,f}$) that differ from those in the reference composition ($X_{j,o}$). The weight fractions of the remaining components which are not given in the literature ($X_{m,f}$) were adjusted from their corresponding values in the reference composition ($X_{m,o}$) by the following equation:

$$X_{m,f}^{w} = \frac{X_{m,o}^{w}}{(1-\Sigma X_{j,o}^{w})}\left[1-\Sigma X_{j,f}^{w}\right] \tag{8}$$

For example, the reference composition of haddock is MC = 80.2% wb, proteins = 18.3%, fats = 0.1%, and ash = 1.4%. If a published study on the k of haddock uses materials with MC = 83.6% wb and fat = 0.08%, then their calculated protein and ash contents are 15.16 and 1.16%, respectively. Another importance of Eq. (8) is that the composition of foods at various MC levels can be determined even if proximate analysis is done at only one MC level.

The proximate analysis of materials used by Pham and Willix (1989) did not total 100% because of experimental errors. This was corrected by adjusting the MC so that the sum of the components was 100%, and the corrected proximate analysis was used as the reference composition.

Standard Error. To compare the predicted values ($\hat{k}_n$) to literature data (k_n) of thermal conductivity at various temperatures, we used the standard error (E) as a measure of fit. They were evaluated from the following equation (Choi 1985):

$$E = 100\left[\frac{\sum_{n=1}^{N}(k_n-\hat{k}_n)^2}{N}\right]^{1/2} \Bigg/ \left[\frac{\sum_{n=1}^{N}(K_n)}{N}\right] \tag{9}$$

In this study, E values $<10\%$ were considered acceptable.

Literature Data

Thermal conductivity data used in the study were obtained from the literature. Data were found for fresh lamb meat and offal, pork, veal, beef, turkey, fish, and liquid foods in frozen states. Initial results of modeling in this study showed that the parallel-perpendicular model had unacceptably high standard errors when used in frozen liquids (i.e., 18% for sucrose solution, 20% for sugar solution and 12% for orange juice) and inconsistent results in frozen meats with fibers perpendicular to heat flow (i.e., 22% for pork and 6% for pork leg). The parallel-perpendicular model is inappropriate for frozen liquid foods since the solid phase (i.e., ice and fiber) is randomly arranged relative to the liquid phase, which is contradictory to the assumption of the parallel-perpendicular model. In the case of frozen meats with fiber perpendicular to the heat flow, the parallel-perpendicular model matches the physical configuration of the muscle and the spaces between them in which ice can form. However, there is insufficient data in the literature to evaluate the effectiveness of the model for these type of materials. Therefore, the food materials included in this study were limited to meat and fish with fibers parallel to the heat flow and those without specification of fiber orientation. Data on lamb meat and offal were generated from regression equations published by Pham and Willix (1989) (Table 3). Specific equations for various parts of lamb were chosen over the generalized equation because they provided more accurate values. Between -2.0 and 0C, the k values were calculated at an interval of 0.1C, since the T_f is most likely to fall within this range. Thirty-one data points were generated at T <0C. For other meats, the number of k data from the literature at freezing temperatures (N_{kf}) was limited, between 2 and 4 data points (Table 4). Data for meat other than lamb were those taken from Morley (1972), which he tabulated from several publications; those for fish were taken mostly from Jason and Long (1955). Pham (1990) suggested that at least two data points, both above and below the freezing point, were sufficient to make trend assessments.

TABLE 3.
CALCULATED VALUES OF T_f, b AND ω_e OF LAMB MEAT AND OFFALS (THE k VALUES WERE CALCULATED FROM THE REGRESSION EQUATIONS OF PHAM AND WILLIX 1989)

	MC (% wb)	Fat (%)	b (sb)	T_f (°C)	ω_e	E (%)
Leg	73.6	4.8	0.40	-1.1	704	6.6
Leg, minced	73.9	4.9	0.40	-1.1	703	7.1
Hearts	69.8	13.0	0.40	-1.2	833	4.8
Hearts, minced	68.8	14.5	0.40	-1.1	972	2.5
Livers	68.9	7.1	0.40	-1.1	931	4.6
Livers, minced	67.7	4.5	0.40	-1.0	1097	3.5
Brains	79.0	8.3	0.40	-0.9	620	4.7
Kidneys	79.9	3.3	0.40	-0.9	560	4.3
Thymus	79.2	6.0	0.40	-0.8	714	4.9
Thymus, minced	75.9	9.1	0.30	-0.9	754	3.5

TABLE 4.
CALCULATED T_f, b AND ω_e OF VARIOUS MEAT PRODUCTS

	MC (% wb)	Fat (%)	N_{kf}	b (sb)	T_f (°C)	ω_e	E (%)	Ref.
Pork leg	75.1	7.8	4	0.27	-1.03	694	2.4	a
	72.0	6.1	3	0.20	-0.6	1048	0.8	b
Lamb leg	71.0	9.6	4	0.30	-1.2	710	6.2	a
Veal leg	75.0	2.1	4	0.25	-0.8	916	2.0	a
Beef, inside round	78.7	1.4	2	0.25	-1.6	420	2.2	a
	76.5	2.35	4	0.30	-1.8	383	4.6	a
Beef, sirloin	75.0	0.009	3	0.30	-0.9	785	2.6	b
Turkey breast	74.0	2.1	4	0.15	-1.2	586	0.8	c
Turkey leg	74.0	3.4	3	0.30	-1.3	540	1.3	b

a. Hill *et al.* 1967, as tabulated by Morley 1972.
b. Lentz 1961, as tabulated by Morley 1972.
c. Digitized from Lentz 1961.

A major problem in modeling studies that depend on literature data is assessing the accuracy of the models and data. In most cases, data for the same materials are an aggregate from several sources, causing possible test sample incompatibility. Moreover, since information on data precision is seldom reported, evaluation of predictive model accuracy is difficult with respect to the original data. This problem was also recognized by Heldman and Gorby (1975). In this study, most of the data on freezing and thermal properties were taken from different studies, except those taken from Pham and Willix (1989), which reported both k and freezing properties. Most literature data on unfreezable water and effective molecular weights were calculated from various mathematical models.

Calculation Scheme

The calculation procedure for initial freezing point, effective molecular weight, and unfreezable water combines both numerical and graphical techniques. Figure 3 illustrates the flow diagram of the proposed technique. The procedure is a numerical iteration in which k is calculated from assumed values of T_f and b; the calculation stops when the difference between the calculated and literature values of k is within a defined maximum limit. The data required are food composition and thermal conductivity values at both the freezing and nonfreezing temperatures. The k values at $T > T_f$ are used to establish visual trends for estimating the T_f and b.

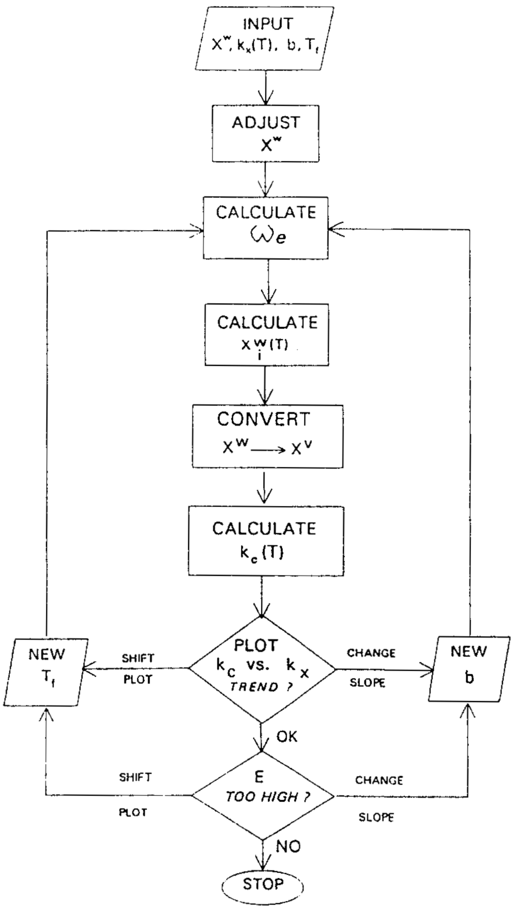

FIG. 3. FLOW DIAGRAM FOR CALCULATING ω_e, b, AND T_f.

The calculation is initiated by adjusting the reference composition to match the composition of the food material used in the published k data. The first values of T_f and b are visually estimated from the T-k curve. Then the effective molecular weight is evaluated from Eq. 1 and 3 by assuming that the amount of unfrozen water is equal to the initial moisture content. After the ice fraction is calculated at various temperatures, the k values as a function of temperature are calculated. The calculation is repeated with a new value of T_f until the optimum value of T_f is found. The optimum value of T_f is determined by using an optimization procedure based on the observation that when the T_f is underestimated, the sum of the experimental k is greater than the sum of the calculated k, and when the T_f is overestimated, the calculated k values are higher than the experimental values. After the optimization, if the standard error between the calculated and literature k values is $< 10\%$, the calculation stops; otherwise, the calculation procedure restarts using new values of b and T_f, which are obtained graphically by comparing the T-k plots of the literature values and calculated values of k. The calculated k values are determined by using the latest values of b and T_f. If the calculated values of k are initially lower and cross those of the literature data, a higher value of unfreezable water is used. If the calculated T-k plot is always lower than the literature T-k, a lower value of T_f is chosen.

RESULTS AND DISCUSSION

Calculated Freezing Properties

Lamb. Tables 3-5 list the calculated ω_e, T_f and b of fresh lamb and offal, other assorted meats, and fish. The fat content of the products is given to allow calculation ω_e and b based on nonfat solids. For fresh lamb and offal, mincing did not affect b and T_f values, except for minced thymus, b = 0.3 (Table 3). The result that the calculated b value of minced thymus is lower than the thymus gland is consistent with the findings by Pham and Willix (1989). The ω_e of the minced products was higher than that of those not minced. The biggest difference was found in liver, where the ω_e increased by 17.9% after mincing. The fat content of the minced livers was almost half that of those not minced (see Food Composition section for calculation). Although their moisture content was almost identical, the measured protein content of the livers increased from 22.3 to 25.4% after mincing. Consequently, the minced livers may have more soluble proteins, and since proteins have high molecular weights, their presence increased the ω_e. The highest standard error among lamb meat and offal was 7.1%; the average error was 4.8%. In comparison, the general equation for lamb meat and offal developed by Pham and Willix (1989) had an error of $\pm$ 8%. Although their error may be calculated differently, the error comparison indicates that accuracy of the predicted k values in this study was within the range of the literature data.

Meat and Poultry. The b values for other meats ranged from 0.15 to 0.30 (Table 4). Turkey breast had the lowest b value at 0.15. The b values of pork legs and beef inside round increased with increasing fat content. The calculated T_f for assorted nondehydrated meats ranged from -0.6 to -1.3C, which is within the reported values for nondehydrated meat. The ω_e ranged from 383 to 1048.

Values for beef inside round, which has low fat content, were the lowest. The calculated b, T_f and ω_e values between the two samples of pork legs are different although their moisture contents are almost identical. The reason is the differences in their reported thermal conductivity values. For example, at -13.2C, Hill *et al.* (1967) and Morley (1972) reported that the thermal conductivity of pork leg is 1.42 W/m-K while Lentz (1961) and Morley (1972) reported that at -8.5C, it is 1.41 W/m-K. This can be attributed to the differences in either the fat contents of the sample or the accuracies in the published data. Nevertheless, it is found in this study that the standard errors for these two samples are low. Overall, the standard errors for the various types of meat products ranged from 0.8 to 6.2% (Table 4).

Fish. The unfreezable water in fish varies more than that in meat products, from 0.1 to 0.3 per solids basis (Table 5). Trout and catfish have the lowest value of unfreezable water; red fish has the highest. Therefore, in fish with high moisture content, e.g., red fish and haddock, a larger fraction of their water cannot be frozen. The calculated T_f and k for all fish are almost identical in spite of the wide differences in their moisture content. These values could be attributed to high moisture contents; the differences in the MC among fish were too small to influence the values of T_f and k. The standard error for all fish was between 1.9 and 2.7%.

TABLE 5.
PREDICTED T_f, b AND ω_e FOR VARIOUS FISH SAMPLES

	MC (%wb)	Fat (%)	N_{kf}	b (sb)	T_f (°C)	ω_e	E (%)	Ref.
Catfish	77.8	3.29	5	0.10	-0.8	693	2.4	a
Haddock	83.6	0.08	5	0.25	-0.7	517	2.7	a
Perch	79.1	0.90	5	0.15	-0.8	757	2.2	b
Red fish	84.7	0.80	5	0.30	-0.7	520	1.9	a
Trout	78.1	2.04	5	0.10	-0.8	703	2.4	a

a. Jason and Long 1955.
b. Lusk *et al.* 1964.

Comparison with Literature Values

Unfreezable Water. The proposed technique was validated by comparing the calculated ω_e, T_f, and b values to those reported in the literature (Tables 6-8). The ratio of calculated values to literature data indicates the accuracy of the proposed procedure. For unfreezable water, calculated values for fish and meat are within the range of the published values (Table 6). The calculated

TABLE 6.
COMPARISON BETWEEN THE CALCULATED AND LITERATURE VALUES OF b FOR VARIOUS MEAT AND FISH SAMPLES

	Calc.	Lit.	Calc./Lit.[a]	Ref.
Meat	0.2-0.3	0.143-0.36	1.0	TABLE 2
Fish	0.15-0.30	0.143-0.39	1.2	TABLE 2
Beef	0.25-0.30	0.219-0.318	1.0	TABLE 2
Lamb kidney	0.40	0.466	0.9	Pham 1987
Calf veal	0.25	0.29	0.9	Pham 1987
Haddock	0.25	0.143	1.7	Pham 1987
Perch	0.15	0.205	0.7	Pham 1987
Lamb Muscle	0.433-0.492	0.303-0.494[b]	1.2	Pham 1987
	0.3-0.4	0.144-0.31	1.5	Pham 1987; Pham and Willix 1989

[a] Based on median values.
[b] Calculated based on nonfat solids.

values for haddock and perch are not in agreement with those published by Pham (1987), which were calculated from enthalpy-temperature data. However, the b values calculated for these two fish species are within the generally recommended range for all fish and meat. For fresh lamb and offal, Pham and Willix (1989) recommended an unfreezable water of 0.4 based on protein content, in which the per solids equivalent would be lower than the calculated b values. Pham (1987) also suggested that the b value be calculated on the basis of nonfat solids, which actually bind the water in the system. This method can reduce incompatibility caused by difference in fat content. Using this method, Pham (1987) reported that the unfreezable water of lamb loin is between 0.303 and 0.494. In comparison, the calculated values for lamb leg in this study were between 0.433 and 0.492. Pham's (1987) lamb had fat contents of 11.7-9.4%, whereas the lamb legs used in this study had 4.8-9.6% fat.

Effective Molecular Weight. Table 7 compares the calculated and literature values of ω_e for various meats. In beef, the lower limit of the calculated values was lower than that of published values, whereas its upper limit was slightly higher. The ratio of calculated to published values is 0.8, and the difference in their medians is small. The worst ratio is 0.3 for lamb muscle, and the difference in their medians is 1660. The meats used in this comparison are the same as those used in the b comparison. Schwartzberg (1976) observed the same wide variations of the ω_e for various parts of lamb meat and calf veal and suggested that the ratio should be calculated by disregarding the fat content.

TABLE 7.
COMPARISON BETWEEN THE CALCULATED AND LITERATURE VALUES OF ω_e FOR VARIOUS FOOD MATERIALS

	Calc.	Lit.	Calc./Lit.[a]
Beef	383 - 785[b]	662 - 724[c,d]	0.8
Fish	517 - 757[e]	466 - 519[d,f]	1.3
Lamb muscle	703 - 710[g]	1023 - 3711[h,i]	0.3
	578 - 582[g,j]	684 - 1078[h,i,j]	0.7
Lamb kidney	560	416[i]	1.3
	474[j]	356[i,j]	1.3
Calf veal	916	1091[i]	0.8
	839[j]	878[i,j]	1.0

[a] Based on median.
[b] Sirloin and inside round, ave. MC=76.8% wb.
[c] Lean beef, MC=74% wb.
[d] Chen 1985.
[e] Catfish, Haddock, Perch, Red Fish & Trout.
[f] Cod.
[g] Lamb leg, fat=4.8%.
[h] Lamb loin, fat=11.7-39.4%.
[i] Schwartzberg 1976.
[j] Nonfat solids only.

When the effective molecular weights were recalculated on the basis of only nonfat solids, the ω_e ratio improved to 0.7 and the difference of their medians decreased to 301. In lamb kidneys, calculation of the ω_e from nonfat solids did not improve the comparison ratio, as the difference in the fat content among the products was very small (0.4%). In calf veal where the fat contents were 4.4 and 2.1%, the ω_e ratio improved to 1.0 when ω_e was calculated from nonfat solids.

Freezing Point. Table 8 compares the calculated and literature values of T_f. T_f values were calculated for materials that had an MC comparable to those used in the literature. The T_f were determined from the ω_e and b values calculated from this study (Table 8). Most of the literature data were evaluated from the equation of Chang and Tao (1981), the calculations of Chen (1985), Pham (1987), Succar and Hayakawa (1990), and the Mollier diagram of Riedel (Chen 1985). For nondehydrated materials, the biggest difference among the published values was < 0.2C, which was small for practical purposes. In general, the calculated freezing points were higher than those evaluated with Chang and Tao's (1981) equation but lower than published values. Haddock and cod, which have similar compositions, were compared at 82% wb. At the lower MC levels, haddock and the "lean fish meat" of Succar and Hayakawa (1990) were compared. The calculated freezing points of haddock were within the range of published values of the respective fish. In beef, the calculated values for sirloin

TABLE 8.
COMPARISON BETWEEN THE CALCULATED AND LITERATURE VALUES OF T_f FOR VARIOUS MEAT AND FISH PRODUCTS

	MC (% wb)	Calc. (°C)	Literature	Calc./Lit.
Fish	82.0	-0.83[a]	0.87[h,c], 0.9[h,d],-0.7[e],-0.8[f]	0.92-1.17
	75.0	-1.23	-0.82[e], -1.0[f],-1.29[g]	0.95-1.5
	66.0	-1.98	-1.95[f],-1.96[g]	1.0
Lean beef	80.0	0.64[h]	0.73[i],-0.74[e]	0.86-0.88
	74.0	-0.92[h]	1.0[d,j],-0.98[c,j]-1.0[i,j],-0.83[e]	0.92-1.11
	70.0	-1.19	-1.01[f],-1.20[g]	1.0-1.18
	63.0	-1.72	-1.63[g],-1.76[f]	0.98-1.06
	50.0	-3.24[h]	-2.6[c,j],-2.8[d,j],-3.6[i,j]	0.9-1.25
Calf veal	77.5	-0.63	-0.68[i],-0.78[e]	0.81-0.93
Haddock	83.6	-0.73	-0.89[i],0.69[e]	0.82-1.1
Perch	79.1	-0.68	-0.86[i],-0.76[e]	0.79-0.9

[a] Reference material is haddock, MC=83.6% wb.
[b] Cod.
[c] Chen 1985.
[d] Mollier Chart of Riedel as reported by Chen 1985.
[e] Chang & Tao (1981).
[f] Succar & Hayakawa (1990).
[g] Calc. by Succar & Hayakawa (1990) using Chen's (1985) procedure.
[h] Reference sample is beef sirloin, MC=75% wb and fat=0.9%.
[i] Pham 1987.
[j] Lean beef.

were compared with published values for lean beef. Except for beef at MC = 50% wb, the T_f values found in this study were close to those reported in the literature. Although the ω_e and b of beef and fish were evaluated at high MC, the calculated T_f for dried products is still within the reported values. For beef at 50% wb, the result is inconclusive because the reported values differ by 1.0C.

Sensitivity Analysis

Because ω_e is calculated from T_f and b, their influence on its value is important. A sensitivity analysis was done for three representative foods. Beef sirloin represented lean beef, haddock represented all fish, and lamb liver represented all non-muscle materials (Table 9). Results indicated that regardless of food type, the effect of T_f on the calculated ω_e was more than that of b. Moreover, the magnitude of influence of each parameter was not affected by material type. The average change in ω_e per unit change of b is $\pm$ 300, whereas for every 1.0C change of T_f ω_e changed by $\pm$ 1300. Because the accuracy of most temperature transducers is $\pm$ 0.5C, the calculated ω_e can vary by $\pm$ 650 due to error in temperature. Therefore, since the differences among the ω_e

values listed in Tables 4-6 are within this limit of error, it can be concluded that the calculated ω_e for fresh lamb and offal, and assorted meat and fish are not significantly different from one another.

TABLE 9.
SENSITIVITY ANALYSIS OF THE ω_e AND E AS AFFECTED BY T_f AND b

			$[E/E_o]$			
	$[\Delta\omega_e/\Delta T_f]$[a]	$[\Delta\omega_e/\Delta b]$[b]	$(T_f$-0.5)	$(T_f$+0.5)	(b-0.15)	(b+0.15)
Beef sirloin	1229	283	3.6	3.8	2.8	2.2
Haddock	1597	113	3.2	3.1	3.0	2.0
Lamb liver	1066	510	4.0	2.5	2.1	1.6

[a] Calculated at ± 0.5C of the tabulated T_f in Tables 4-6.
[b] Calculated at ± 0.15 of the tabulated b in Tables 4-6.

The effect of the accuracy of T_f and b on the standard error (E) of the calculated k was also analyzed (Table 9). E values were calculated for T_f values ± 0.5C and b values ± 0.15 of the values listed in Tables 3-5. These E values were then divided with the respective E values (E_o) for the tabulated values of b and T_f. On the average, a ± 0.5C error in the T_f value can cause E values to increase by 3.4 times, whereas an error of ± 0.15 in b can result in an increase in standard error of 2.3 times. Thus, an error of ± 0.5C in T_f is equivalent to ± 0.22 error in b. Since the average E of all the materials in Tables 3-5 is <4% and the accuracy of thermocouples is typically ± 0.5C, the tolerable E for k modeling can be as high as 14%. This finding indicates that all the predicted values in this study (Tables 3-5) are within an acceptable limit.

CONCLUSIONS

Based on the findings in this study, the following conclusions are drawn:

(1) The proposed calculation procedure for effective molecular weights, unfreezable water, and initial freezing point from thermal conductivity and food composition produces acceptable results (E <10%). The accuracy of this procedure depends largely on the accuracy of the thermal conductivity data.

(2) For a group of foods with large differences in fat content, the ratio of calculated values to literature values improved (closer to 1.0) when unfreezable water and effective molecular weight were calculated from nonfat solids. The ratio did not improve when variation of fat content of different foods in the group was small.

(3) Because standard errors for the foods studied were < 10%, the parallel-perpendicular model is an adequate structural model for predicting the thermal conductivity of frozen meat with fibers that are parallel to heat flow.

(4) The calculated effective molecular weights of fresh lamb and offal, assorted meats, and fish are not significantly different from one another.

(5) Considering the accuracy of thermocouples, standard errors of up to 14% may be acceptable for thermal conductivity models for frozen foods.

NOMENCLATURE

b	Unfreezable water or bound water, based on fraction of solids (sb)
E	Standard error based on k values (%)
k	Thermal conductivity (W/m-°K)
k_n, $\hat{k}_n$	Literature and calculated values of k at various temperature levels, respectively
L_f	Latent heat of fusion (333.8 m^3-Pa)
MC	Moisture content (% wet basis or % wb)
N, N_{kf}	Total number and N of k data at $T < T_f$
R	Universal gas constant (8.314 m^3-Pa/g-mole-°K)
T	Temperature
T_f, T_w	Initial freezing point (°C or °K) and freezing point of pure water (273.15°K)
X_a	Mole fraction of unfrozen water
X^w, X^v	Weight and volume fractions, respectively (decimal or %)
$X_{j,f}$	Values of certain food component of the material used in the measurement of thermal and freezing properties
$X_{j,o}$	Corresponding reference values of the $X_{j,f}$ components
$X_{m,f}$	Calculated values of the non $X_{j,f}$ components
$X_{m,o}$	Reference values of the non $X_{j,f}$ components
ω, ω_w	Molecular weight and molecular weight of water (18)
ρ	Density (kg/m^3)

Subscripts

c	Calculated
ds	Dissolved solids
e	Effective
I	ice
l	Liquid
n	Dummy
p	Protein
uf	Unfrozen water
s	solids or solutes
w	Water
o	Optimum
x	Experimental or literature

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