Estimating the initial freezing point of foods from composition data

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Summary The initial freezing point of food was estimated from the mole fractions of individual solutes in the aqueous phase (ions, sugars, acids and alcohol), derivable from information given in nutritional tables. Predicted values were compared with experimental measurements taken from the literature. Predicted and experimental values generally agreed to within 1 °C, despite the solute concentrations of the measured foods being assumed to be those of the average compositions given in nutritional tables. The effects of the addition of salt to meat and of dehydration of various foods on freezing point depression, and the effect of temperature on the ice content of frozen foods were also successfully predicted.

Keywords Acid, alcohol, freezing point depression, ice content, ions, sugar.

Introduction

When a frozen food is heated quasi-statically, the temperature at which the last infinitesimal trace of ice melts, is called the initial freezing point. Alternative names include: transition temperature, final melting point, or simply freezing point. The initial freezing point is one of an important group of related properties which includes: boiling point, osmotic pressure and water activity. Knowledge of any one of these allows estimation of the others. For example, the magnitude of the freezing point depression (or the elevation of boiling point) defines the water activity (e.g. Ferro Fontan & Chirife, 1981) and thereby indicates the susceptibility of the food to microbial growth (e.g. Corry, 1987 and Mossel *et al.*, 1995). The lower the initial freezing point, the more microbiologically stable the food, the lower the water activity, the higher its boiling point and the slower the ice content increases as the temperature is lowered. In conjunction with the water and unfreezable water contents, knowledge of the initial freezing point allows estimation of the ice content of a frozen product at any temperature (Heldman, 1974; Miles, 1974a) and hence estimation of many other properties which are highly dependent on the ice content such as: thermal conductivity, enthalpy, density, heat capacity, coefficient of cubical expansion and compressibility (e.g. Miles, 1974b; Schwartzberg, 1976; Miles & Morley, 1978; Miles, 1991). Consequently the initial freezing point is a key characteristic for predicting the physical and microbiological properties of food.

Previous attempts at estimating the initial freezing point of foods have been based on either statistical relationships with the mass fractions of water or semi empirical relations with the concentration of solutes (see for example the review by Rahman, 1995). In the equations of Schwartzberg (1976) and Chen (1987) and Chen & Nagy (1987), for example, the mass fraction of solutes is used with an effective molecular weight of the solutes to calculate the freezing point from an equation derived on the basis of a modified Raoult's Law. The different contributions of each

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solute is not allowed for on an individual basis. Instead the effective molecular weight of the solutes has to be determined for each food empirically (Schwartzberg, 1976; Chen, 1986) by reference to the observed freezing point depression. While this logic appears circular, it has considerable advantages in that it can be used to calculate the change in freezing point caused by drying (such as effectively occurs in the freezing process), without introducing any further assumptions or unnecessary errors of prediction. However, the purpose of the present paper is to investigate the possibility of using details of the concentrations of individual chemical components, published in nutritional tables such as McCance and Widdowson's *Composition of Foods* (Paul & Southgate, 1978) to estimate the initial freezing point of foods, with sufficient accuracy for some engineering calculations, without recourse to measurement.

It is odd that, to our knowledge, this has not been attempted before. We aimed to develop a means for estimating the initial freezing point of any food, not solely for a specific group of foods, and decided to use Raoult's Law to do some prescreening to select a list of the likely key components responsible for the majority of the freezing point depression. Having selected a list, we could use statistics to allow for non-ideal behaviour, interactions and curvature, etc. It turned out that the available data did not warrant this second stage.

Model development

The starting equation for this work is the relation between ΔT, the depression of the freezing point of an ideal solution, and the mole fraction of solute, X_m:

$$\Delta T = \frac{RT_0{}^2}{\Delta H_{melt,m}} X_m \tag{1}$$

(see any physical chemistry text, e.g. Atkins, 1978). Here R is the gas constant, T_0 is the temperature (in K) of fusion of pure ice in pure water and $\Delta H_{melt,m}$ is the molar enthalpy of fusion of ice. Although using molar concentration simplifies equations, it is more practical to use mass concentrations since these are directly available from nutritional tables. The mole fraction of solute, X_m, may be written in terms of the mass fractions of water, x_w, and solute, x_s, as:

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

where M_s and M_w are the molecular masses of the solute and water, respectively.

The total mole fraction of solutes governs the initial freezing point of a mixture of non-interacting solutes and eqn 1 may be generalised to:

$$\Delta T = \frac{RT_0^2 \sum \dfrac{x_i}{M_i}}{\Delta H_{melt,m}\left[\dfrac{x_w}{M_w} + \sum \dfrac{x_i}{M_i}\right]} \tag{3}$$

where x_i is the mass fraction of the ith component and M_i is its molecular mass. If, as in a food, some of the water is unfreezable, x_w is replaced by $x_w - x_b$, where x_b is the mass fraction of unfreezable water. We also generalise the equation to include factors τ_i to allow for molecular dissociation and other non-ideal behaviour and the freezing point depression is finally given by:

$$\Delta T = \frac{RT_0^2 \sum \dfrac{\tau_i x_i}{M_i}}{\Delta H_{melt,m}\left[\dfrac{x_w - x_b}{M_w} + \sum \dfrac{\tau_i x_i}{M_i}\right]} \tag{4}$$

x_b is comprised of water that is bound to components of the food, such as protein or starch, and can be estimated from the proximate analysis by use of the equation:

$$x_b = \sum \sigma_r x_r \tag{5}$$

where the coefficients σ_r are component-specific constants. The predictions were mainly rather insensitive to the precise choice of coefficients and for the purpose of this work only two components were used in the estimation: carbohydrate and protein. A review of the literature suggested mean σ_r coefficients of 0.3 and 0.45, respectively.

Assumptions

1 Foods consist of such varied components in so wide a range of complex organisations that the precise use of eqn 4 is not practical. Fortunately, simplification and approximation is possible. The soluble components such as various sugars, ions and acids and soluble proteins, will contribute to the freezing point depression, while the insoluble components such as fat and the insoluble proteins will not. Furthermore some components, such as protein and starch, have such high molecular masses that their contribution to the mole fraction of solutes is negligible; it is the small molecules such as sugars, ions and acids which contribute appreciably, and in this work we attempt to estimate the effect of these components only as an approximation.

2 For freezing point analysis, sugars can be divided into three groups of molecule: monosaccharides (e.g. glucose, fructose and galactose) which all have the same molecular mass of 180 and are therefore predicted by this theory to have an equal effect on the initial freezing point; disaccharides (e.g. sucrose, lactose and maltose) which also have the same molecular mass (342) and contribute equally; and the higher order sugars, the oligosaccharides (trisaccharides, tetrasaccharides and pentasaccharides) which generally exist in rather low concentrations in foods and because of their high molecular mass their effect is slight. Furthermore oligosaccharides are rarely individually specified in nutritional tables. Consequently for the purpose of this paper their contribution has been neglected.

3 The metallic elements sodium, potassium, calcium, magnesium and iron are assumed to exist mainly in the form of single positive ions and that chloride and phosphate ions are the major inorganic negative ions. Sulphur, although present in quite high concentrations in protein-rich foods is mainly associated with the amino acid cysteine and, as a first approximation, has therefore been assumed not to contribute to the freezing point depression. Other specific ions such as carbonate and nitrate or nitrite may be important in some foods but for the purpose of this paper have not been included in the calculations since they are rarely quoted in nutrition tables, and only sodium, potassium, calcium, magnesium, iron, chlorine and phosphorus as given in McCance and Widdowson's composition tables (Paul & Southgate, 1978) have been used. By dividing the mass fraction of each mineral element by its atomic mass we estimate the number of moles of ions containing that element per unit mass of food. This calculation assumes that there is only a single atom of the element per ion. The calculation also assumes that all the ions are completely dissociated (if strong electrolytes).

4 In contrast, the major organic acids in foods (acetic, citric, malic, lactic, tartaric and oxalic) are weak and for the purpose of the calculations in this paper are considered to be undissociated. It is emphasised that this is a first approximation, that the degree of dissociation is low but that some dissociation does occur. For example Matsuoka (1992) measured the freezing point depression of aqueous solutions of organic acids (citric, malic and tartaric) and compared measurements with those calculated on the basis of Raoult's law. From the appreciable deviation in one direction, it may be concluded that these acids must have dissociated. Equally Pitzer & Brewer (1961) showed that the degree of dissociation of acetic acid was concentration-dependent and small (<10%). In an actual food the situation is complicated by the presence of ions such as phosphate which may be protonated to different extents (e.g. $H_2P0_4^-$ & $HP0_4^{2-}$, see Lehninger, 1982), and consequently affect the hydrogen ion concentration. In this work the protonated forms of ions are not distinguished; each ion contributes equally to the freezing point depression.

By the above means a list of components that may be important in governing the initial freezing point of foods was identified (Table 1), and for the reasons outlined above a value of 1 was assigned to each τ_i as a first approximation. Data for the initial freezing points of foods was then extracted from the literature and their composition noted from nutritional tables. Accordingly it was possible to compare predictions made on the basis of eqn 4 with actual measurements.

Collection of data

Four groups of data were analysed:

(a) Data for the initial freezing point of foods were collected from review papers and monographs. The water content of the food was usually recorded by the authors and this was noted, but rarely was a detailed composition given. Reference was then made to two standard references for the composition of foods (Paul &

Table 1 The components and their molecular masses used for predicting the initial freezing point of food from equation 4. For the calculations in this paper all the coefficients, τ_i, were taken to equal 1

Component	M_i
Water	18
Monosaccharide	180
Disaccharide	342
Lactic acid	90
Malic acid	134
Citric acid and isocitric acid	192
Acetic acid	60
Tartaric acid	150
Oxalic acid	90
Alcohol	46
Na	23
K	39
Ca	40
Mg	24
Fe	56
P	31
Cl	35.5

Southgate, 1978; Souci *et al.*, 1989) and the composition data which most closely matched the measured food water content was noted alongside the freezing point. In this way a matrix was established consisting of the initial freezing point and the mass fractions of water, fat, protein, monosaccharide sugar, disaccharide sugar, oligosaccharide sugar, starch and elements: K, Na, etc. This matrix consisted of 211 rows, each row representing a published measurement of the initial freezing point for a particular food. However, this data set was further reduced by selecting only those foods in which the water contents of the measured sample and that given in nutritional tables were within 0.5% point of each other.

(b) Our own data (Sheard *et al.*, 1990) for the initial freezing point of minced beef containing different quantities of sodium chloride and sodium polyphosphate were re-analysed to estimate a full proximate analysis at each salt/polyphosphate concentration by adjustment of McCance and Widdowson's data (Paul & Southgate, 1978) for raw beef.

(c) the mass fraction of ice (x_{ice}) of several specific foods at different levels of dehydration has been measured by Riedel down to −40 °C, and recorded in the form of an empirical equation (Riedel, 1978):

$$x_{ice} = \frac{s + x_w - 1}{s} \tag{6}$$

where

$$s = \frac{t}{a + bt + ct^2 + dt^3} \tag{7}$$

The coefficients a, b, c and d are food-specific constants (see Table 2).

The temperature (t °C) at which these equations yield an ice content of zero represents the initial freezing point which may be obtained by selecting the appropriate numerical solution of the equation, $x_{ice} = 0$.

In this way the initial freezing point of the foods analysed by Riedel (1978) was determined over a range of hydrations. These were matched with the proximate analysis data of the native food and the effect of dehydration on the proportions of non-aqueous components was calculated from:

$$x_i = \frac{1 - x_w}{1 - x_{w0}} x_{i0} \tag{8}$$

Here, x represent mass fractions, w denotes water, i the ith component and x_{io} and x_{wo} refer to the mass fractions before dehydration/rehydration to any arbitrary level x_w.

Hence a complete matrix of initial freezing point and composition data was obtained for each food measured by Riedel, each row representing a measurement at a different level of hydration.

(d) Pham (1987) predicted the initial freezing point of various foods by finding the point of intersection of published enthalpy data in the frozen and unfrozen states. These data were matched to composition data by the method (a), above, if the food was native and by (c), above, if the food was dehydrated.

Table 2 Numerical values of the coefficients used in Riedel's empirical equations (6, 7) for the ice content of low-fat foods. Data taken from Riedel (1978)

Food	a	b	1000c	1000d
Beef	−2.51	1.262	+2.2	+0.09
Saltwater fish	−3.62	1.160	−6.2	−0.03
White of egg	−2.94	1.164	−5.5	−0.03
Low-fat cheese	−3.37	1.071	−5.1	−0.01
Baker's yeast	−3.13	1.225	+3.7	+0.11

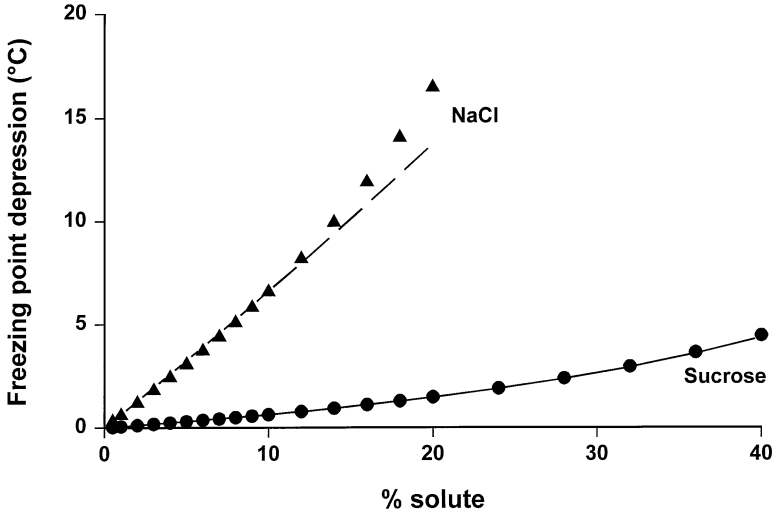


Figure 1 Initial freezing point of sucrose and salt solutions. Data taken from Weast (1988–89). Lines drawn using eqn 4. (% solute is by mass).

Results

Equation 4 predicted the initial freezing point of sodium chloride and sucrose solutions quite precisely over the concentration range observed in most foods (Fig. 1). The data and predictions followed non-linear concave upward loci which agreed very well over the entire concentration range in sucrose solutions, but at high concentrations of sodium chloride, the measured depression was higher than predicted. This latter effect was not caused by the logarithmic approximation used in the derivation of the original equation, which represented an error of only a few percentage at most, but was possibly caused by interaction between the water molecules and the ions (effectively causing an unfreezable water content term, which was assumed to be zero in this calculation).

Morley's measurements (Sheard *et al.*, 1990) of the initial freezing point of beef in the absence of salt and polyphosphate was within 0.1 °C of the predicted value (Fig. 2). The addition of 1 and 4% sodium chloride had a very marked effect on the initial freezing point (Fig. 2) and was predicted

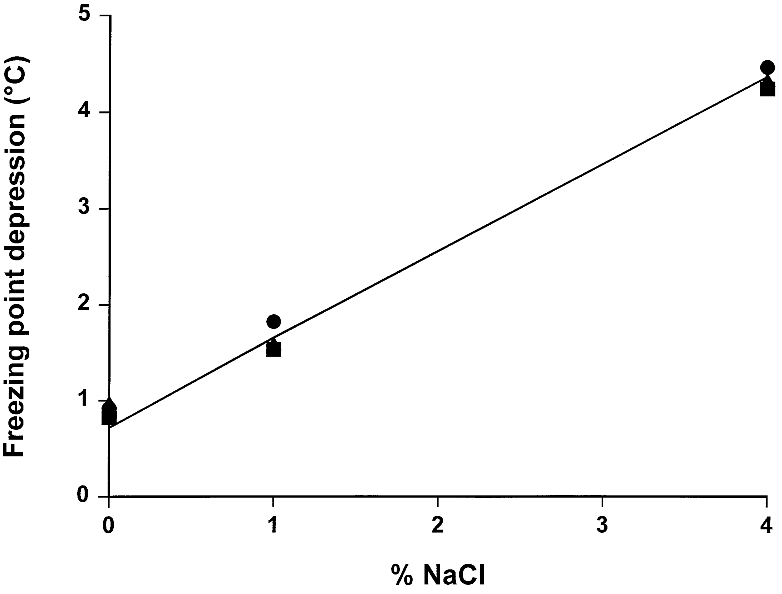


Figure 2 Effect of additions of salt and polyphosphate on the initial freezing point of beef. Initial freezing point data of Sheard *et al.* (1990). Lines drawn using McCance and Widdowson's sample 237 adjusted for the appropriate additions of sodium, chlorine and phosphate. ■: 0% sodium polyphosphate; ▲: 0.25% sodium polyphosphate; ●: 0.5% sodium polyphosphate. (% salt is by mass).

quite accurately by the equation (errors of the order of only 10%). The equation also predicted the absence of a substantial change on adding up to 0.5% polyphosphate, a component which has a marked effect on the myofibrillar lattice and consequently the water-holding capacity of the meat (Sheard *et al.*, 1990).

In foods that were progressively dehydrated, the predicted freezing point depression decreased with increasing water content and displayed concave upward loci (Fig. 3), and this behaviour was predicted by eqn 4. In some foods, e.g. saltwater fish, beef and cheese, the absolute agreement was good (within 1 °C over most of

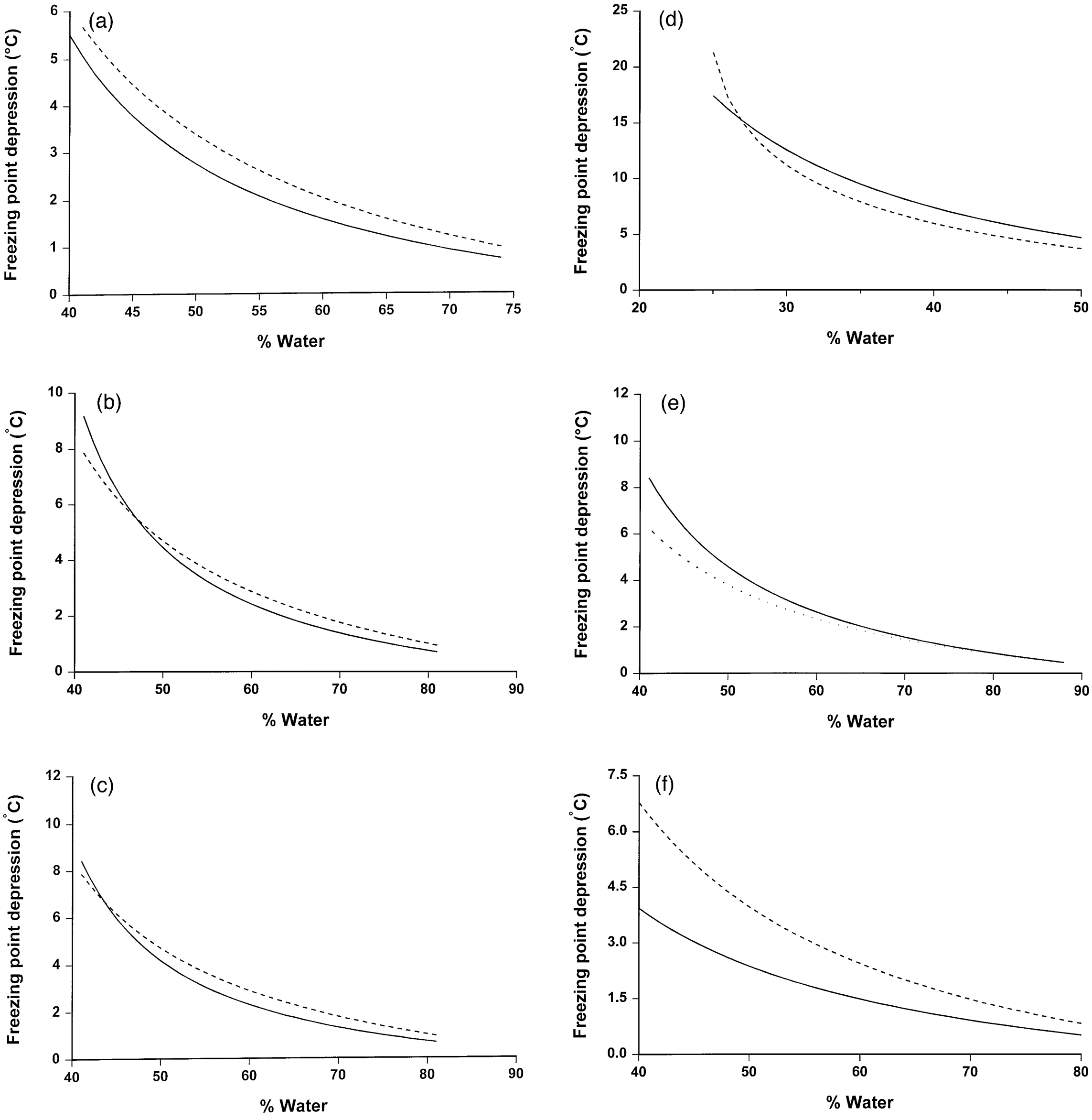
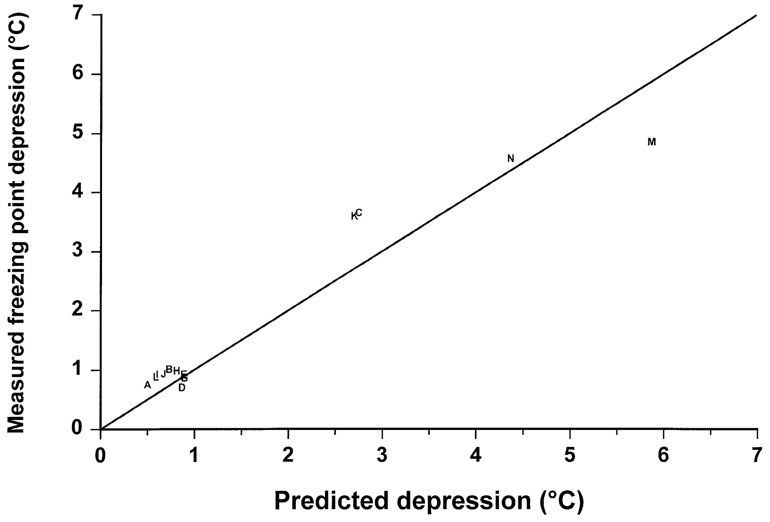


Figure 3 Comparison of the effect of dehydration on the initial freezing point of various foods. Empirical equation of Riedel (see eqns 6 and 7 and Table 2) compared with that predicted by eqn 4 using the composition data of the given reference number. (a) Beef CW(237); (b) Cod SFK(333); (c) Haddock CW(451); (d) Edam cheese CW(154); (e) Egg white CW(166); (f) Baker's yeast CW(968). Solid line: current predictions based on eqn 4; dashed line: Riedel's equation (see text). CW = McCance and Widdowson's Tables (Paul & Southgate, 1978); SFK = Souci *et al.* (1989). (% water is by mass).



Symbol (Letter)	Food	Type	Freezing point reference	Composition Reference	% Moisture
A	Beef	lean	Riedel (1957a)	calculated from CW(237)	80
B	Beef	lean	"	calculated from CW(237)	74
C	Beef	lean	"	calculated from CW(237)	50
D	Beef	veal	Fleming (1969)	CW(312)	77.5
E	Lamb	lean	"	CW(390)	64.9
F	Lamb	medium fat	"	calculated from CW(390)	52.5
G	Lamb	very fat	"	calculated from CW(390)	44.4
H	Lamb	kidney	"	CW(477)	79.8
I	Cod	muscle	Riedel (1956)	Calculated from SFK(333)	82
J	Cod	muscle	"	Calculated from SFK(333)	80.3
K	Cod	muscle	"	Calculated from SFK(333)	50
L	Haddock	muscle	"	CW(451)	83.6
M	Bread	white	Riedel (1959)	CW(33)	37.3
N	Bread	wholewheat	"	CW(56)	42.4

Figure 4 Initial freezing point of various foods. Freezing point data taken from Pham (1987). Composition data correspond to reference number codes: CW = Paul & Southgate (1978), SFK = Souci *et al.* (1989).

the temperature range) (Figs 3a–d). The fits for egg white and baker's yeast were not so precise (Figs 3e and f).

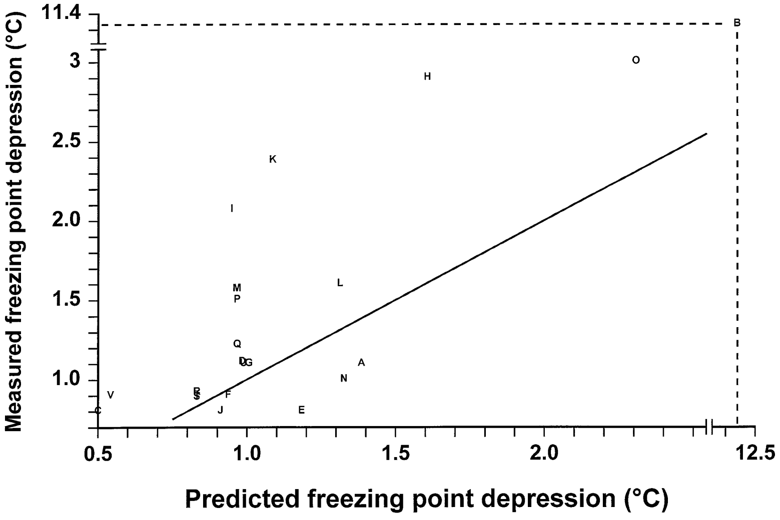
Pham's data for various foods also fitted the predictions within about 1 °C (Fig. 4), and so did the literature data for fruit (Fig. 5) with the exceptions of data for oranges, lemons and morello cherries.

The data for vegetables appeared to be scattered mainly above the predicted level (Fig. 6). As there was relatively little variation in the data, the correlation between measured and predicted freezing points was also poor. Even so, only one datum (for okra) was over 1 °C different from that predicted (Fig. 6).

Discussion

This work has clearly shown that usefully accurate predictions of the initial freezing point of foods can be made on the basis of the known chemical composition. Equation 4 thus provides a means for estimating the initial freezing point of those foods with appropriate composition data published in nutritional tables. In particular it allows the effect of the addition of salt to meat and of dehydration of meat, fish and cheese to be predicted with useful precision.

Some of the unexplained variance in the initial freezing point is no doubt caused by errors of temperature measurement. Errors of the order of 1 °C are not uncommon in values quoted in the litera-



Symbol (Letter)	Food	Type	Freezing point Reference	Composition Reference
A	Apple	flesh	R	SFK(737)
B	Apple Juice	concentrate	R	calculated from SFK(896)
C	Aubergine	flesh	R	SFK(649)
D	Bilberries	whole fruit	R	SFK(772)
E	Blackberries		R	SFK(767)
F	Cranberries	whole fruit	R	SFK(785)
G	Grapefruit		R	SFK(829)
H	Cherries	sour, morello	F&F	SFK(751)
I	Lemons	whole	C&M	SFK(864)
J	Melons		R	SFK(862)
K	Oranges	flesh	C&M	SFK(808)
L	Pears	flesh	R	SFK(742)
M	Peaches		C&M	SFK(756)
N	Pineapple		R	SFK(805)
O	Pomegranate		R	SFK(828)
P	Raspberry	whole	C&M	SFK(776)
Q	Raspberry	whole	R	SFK(776)
R	Strawberry	whole	C&M	SFK(769)
S	Strawberry		R	SFK(769)
T	Strawberry		R	SFK(769)
U	Tangerine		W&B	SFK(845)
V	Rhubarb		R	SFK(621)

Figure 5 Initial freezing points of various fruits. Freezing point data taken from the noted review/monograph: R = Rao (1992); C&M = Cubik & Maslov (1965); W&B = Woolrich & Bartelett (1965); F&F = Fikiin, A. G. & Fikiin, K. A. (Personal communication, Technical University of Sofia, Bulgaria.); SFK = Souci *et al.* (1989). Composition data correspond to the stated reference number codes.

ture. For example the freezing points of unadulterated raw meats are often quoted in engineering texts as −2 °C or lower (see ASHRAE, 1985) whereas there is overwhelming evidence (Riedel, 1957a; Fleming, 1969; Miles,1974a; Sheard *et al.*, 1990) that, when measured with care, the initial freezing point is much nearer to −1 °C. Equally, the composition figures used in our calculations were not of the samples of food in which the freezing point was actually measured, but were average values of other samples quoted in nutritional tables. While use of such data for lean beef or fish is unlikely to cause large errors, it is clearly undesirable. But when the data are applied to manu-

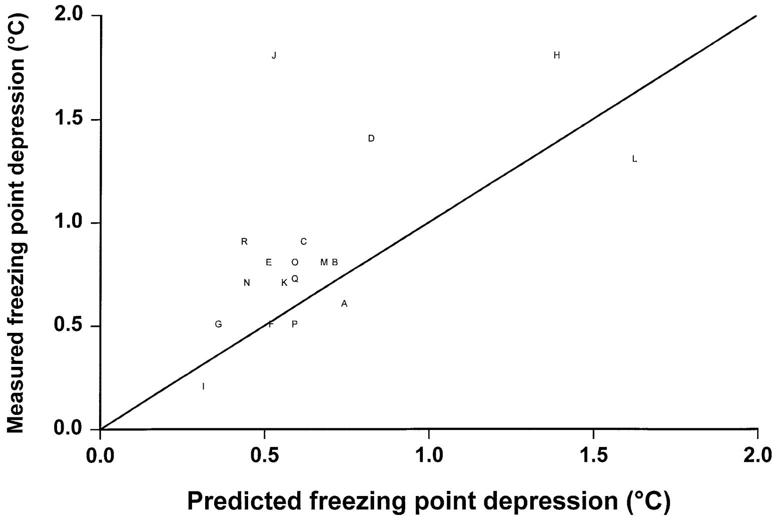


Figure 6 Initial freezing points of various vegetables. Freezing point data taken from the noted review/monograph. Composition data correspond to the stated reference number codes. Reference codes as Fig. 5.

Symbol (Letter)	Food	Type	Freezing point Reference	Composition Reference
A	Broccoli		R	SFK(595)
B	Brussels sprouts		R	SFK(623)
C	Cabbage		R	SFK(626)
D	Carrots		R	SFK(562)
E	Cauliflower		R	SFK(592)
F	Celery	stem	R	SFK(590)
G	Cucumber	flesh	R	SFK(656)
H	Horseradish	flesh	R	SFK(560)
I	Lettuce	head	R	SFK(612)
J	Okra		R	SFK(851)
K	Potatoes		R	SFK(542)
L	Potatoes	sweet	R	SFK(539)
M	Pumpkin		R	SFK(659)
N	Radishes		R	SFK(573)
O	Tomatoes		F&F	SFK(664)
P	Tomatoes		R	SFK(664)
Q	Tomatoes	pulped	R	SFK(664)
R	Mushroom		R	SFK(718)

factured foods such as bacon, cheese, bread, bakers yeast, egg white powder, which may be produced using different recipes and consequently contain different quantities of key components like sugar and salt, the errors could be large. It is noticeable that the most successful use of eqn 4 was for foods in the former category and where particular care was taken to determine the initial freezing point precisely (e.g. the data of Riedel, 1956;1957ab, 1959, 1968, 1976, 1978; Pham, 1987; & Sheard *et al.*, 1990). In order to progress with this approach, it is essential that reliable data for the initial freezing point are obtained on foods with precisely measured compositions.

The effect of variations in the proportions of any individual component can be estimated by partial differentiation of eqn 4. For example if the mass fraction of the jth component increases by δxj, while all other relevant mass fractions remain constant, the increase in ΔT is given by:

$$\delta(\Delta T)_j = \frac{\tau_j R T_0^2 \dfrac{\delta x_j}{M_j}\left(\dfrac{x_w - x_b}{M_w}\right)}{\Delta H_{melt,m}\left[\dfrac{x_w - x_b}{M_w} + \sum \dfrac{\tau_i x_i}{M_i}\right]^2} \qquad (9)$$

Corresponding changes due to deviations in the mass fractions of water and bound water are given, respectively, by:

$$(\Delta T)_w = -\frac{RT_0^2 \frac{\delta x_w}{M_w} \sum \frac{\tau_i x_i}{M_i}}{\Delta H_{melt,m}\left[\frac{x_w - x_b}{M_w} + \sum \frac{\tau_i x_i}{M_i}\right]^2} \qquad (10)$$

and

$$\delta(\Delta T)_b = \frac{RT_0^2 \frac{\delta x_b}{M_w} \sum \frac{\tau_i x_i}{M_i}}{\Delta H_{melt,m}\left[\frac{x_w - x_b}{M_w} + \sum \frac{\tau_i x_i}{M_i}\right]^2} \qquad (11)$$

The total change in the depression of the freezing point due to small changes in any number of the components may be determined by adding the individual changes calculated from equations (9–11).

As a food freezes, pure ice crystallizes out of solution thereby increasing the concentration of solutes in the residual aqueous phase and depressing its freezing point further. Thus, left at a constant temperature, t, an equilibrium will establish between the ice and the aqueous phase. As t is lowered, the mass fraction of ice, x_{ice}, increases. Rewriting the freezing point depression as $-t_f$ in °C:

$$t_f = -\frac{RT_0^2 \sum \frac{\tau_i x_i}{M_i}}{\Delta H_{melt,m}\left[\frac{x_w - x_b}{M_w} + \sum \frac{\tau_i x_i}{M_i}\right]} \qquad (12)$$

and the temperature, t, at which the mass fraction of ice is x_{ice} as:

$$t = -\frac{RT_0^2 \sum \frac{\tau_i x_i}{M_i}}{\Delta H_{melt,m}\left[\frac{x_w - x_b - x_{ice}}{M_w} + \sum \frac{\tau_i x_i}{M_i}\right]} \qquad (13)$$

Equations 12 and 13 yield the ice content in terms of t and t_f:

$$x_{ice} = (x_w - x_b)\left(1 - \frac{t_f}{t}\right) \qquad (14)$$

provided $\sum \frac{\tau_i x_i}{M_i} \ll \frac{x_w - x_b}{M_w}$, a low concentration assumption implicit in the use of eqn 1 on which this analysis is based. Equation 14 has been found to fit experimental data for the ice content of beef, lamb, pork and cod (Miles, 1974a). The same temperature dependence has been reported for the ice content of other foods, including fruit and vegetables (van Beek, 1979; Mellor, 1978) and is proposed in the Ryutov (1976) equation. The equation of Schwartzberg (1976) also reduces to this equation at low concentrations (Miles, 1991). Although the equation is derived on the basis of low concentrations, it yields the correct asymptotic value for the ice content as t→–∞. The equation presented here is therefore compatible with the known relation between temperature and ice content of frozen foods.

The separate contribution of each food component, i, to the freezing point depression may be rewritten from eqn 4 as:

$$\Delta T_i = \frac{RT_0^2 \sum \frac{\tau_i x_i}{M_i}}{\Delta H_{melt,m}\left[\frac{x_w - x_b}{M_w} + \sum \frac{\tau_i x_i}{M_i}\right]} \qquad (15)$$

For example, in apples, 90% of the predicted depression was caused by monosaccharide sugar and in apple juice concentrate the corresponding proportion was 80%. The acid concentration in fruits may also be important. For example, McCance and Widdowson report that citric acid could comprise as much as 6% of the mass of a lemon. This corresponds to a depression of 0.66 °C due to citric acid alone. While the average citric acid content of lemon is quoted at 4.92% by Souci *et al.* (1989), the samples measured ranged from 3.5–7.2%. This translates into an estimated difference in initial freezing point due to citric acid concentration variation alone of 0.41 °C (by use of eqn 15). Disaccharide sugars on the other hand contributed ≈50% of the depression in milk, with sodium, potassium, phosphorus, chloride and calcium all contributing about 10% each. Salt appears to be the major contributor to the freezing point depression in cheese and variations in the quantity introduced in the cheese-making process may be expected to cause substantial deviations from the mean. Minerals are the major freezing point depressants in raw beef. Potassium contributed about 0.25 °C and lactic acid would also contribute about 0.16 °C in a sample comprising 0.5% lactic acid by mass (Souci *et al.*, 1989). However, the lactic acid content of raw meat may be subject to considerable variation (Souci *et al.* record a range from 0.2% to 0.8% by mass) dependent on the glycogen reserves in the muscle at death (e.g.

Lawrie, 1966). The variation in lactic acid quoted by Souci *et al.* (1989) corresponds to a difference in initial freezing point of 0.19 °C (eqn 9). This study therefore indicates that there should be a correlation between the freezing point depression in raw meat and its pH. This variation could be a cause of the differences in freezing point that can be resolved by careful measurement of different samples (Miles, 1974a).

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