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WATER ACTIVITY AND INITIAL
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WATER ACTIVITY AND INITIAL FREEZING TEMPERATURE OF FOOD SYSTEMS

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ABSTRACT

WATER ACTIVITY AND INITIAL FREEZING TEMPERATURE OF FOOD SYSTEMS

By

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The application of basic thermodynamics in food research is important to the food engineer in order to solve problems related to water activity and freezing processes.

The general objective of this research is to study the application of thermodynamic concepts in determination of water activity and initial freezing temperature of food systems.

The thermodynamic relationship between water activity and initial freezing temperature in complex food systems was studied in this research. The results pointed out that the use of these expressions can be extended to solid food products such as cod, beef, pears and apples although some authors reported the application of these equations only for liquid food systems.

Studies on the liquid fraction of some food products (fruits, vegetables, beef and cod) demonstrated that the water activity and the initial freezing temperature of both the liquid fraction and the whole product are the same. These results suggest that only the soluble solids are the food components responsible for the lowering of the water activity and the initial freezing temperature of the food products.

A new procedure to determine initial freezing temperature of food products has been developed in this investigation. The method can be applied to any type of product. It has been shown that by maintaining a constant temperature difference between the cooling medium and the sample and decreasing both temperatures at the same rate, the condition of equilibrium was achieved during the latent heat removal as was evident from the horizontal plateau of the freezing curve.

Activity coefficients at subfreezing temperatures were determined for the food products. For fruits and vegetables, coefficients were between 0.923 to 1.000 and values ranged from 0.734 to 1.000 for cod and beef.

A method to determine percent unfrozen water at subfreezing temperatures was developed and compared to experimental values. The results indicated that the percent unfrozen water at subfreezing temperatures can be predicted using thermodynamic relationships.

To Maria

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LIST OF SYMBOLS

Aw	Water activity
C	Slope of isotherm
Ca	Energy constant of BET equation
C_p	Heat capacity, KJ/mole ^oC
DW	Dry weight
DM	Dry weight of a mixture
K	Norrish's constant
L_w	Latent heat of melting of ice, KJ/mole
MC	Moisture content
Me	Equivalent molecular weight of solids
R	Gas constant, KJ/mole ^oK
S	% weight of solids
SS	Soluble solids, %
T_w	Temperature as specified
T_f	Initial freezing temperature of the product
T_m	Medium temperature
TS	Total solids
T_{sc}	Temperature of maximum supercooling
T	Initial freezing temperature of water
V	Molar volume
Wm	Monolayer moisture content
X	Mole fraction

a	slope of a straight line
b	Intercept of a straight line
h	Enthalpy, KJ/mole
m	Mass fraction
mV	Microvolt
n	Number of moles
r	radius
s	seconds
μ	Chemical potential
θ	Wetting angle
γ	Activity coefficient
δ	Surface tension
ϕ	Volume fraction
β	Root of Bessel function
J	Bessel function
ℓ	Thickness, cm
α	thermal diff

Subscripts

c	calculated value
e	experimental value
i	refers to component 'i' in a mixture or food
u	unfrozen water at subfreezing temperatures
w	relative to water above freezing

1. INTRODUCTION

1.1. General Remarks

The importance of water activity in food systems is very well established. Defined as the ratio of the water vapor pressure in the food to the vapor pressure of pure water at the same temperature, water activity is the key parameter in the control of microbial growth, chemical reactions [Labuza (1980)], color and general product stability [Rockland and Nishi (1980) and Bone (1969)].

The water activity of a food product can be related to its initial freezing temperature using basic laws from thermodynamics [Denbigh (1981) and Lerici et al (1983)]. The knowledge of the initial freezing temperature of foodstuffs is essential in order to evaluate thermal properties during the freezing process. It is also used to predict freezing times and percent unfrozen water at each temperature as used in equipment design [Heldman (1974)].

Lerici et al (1983) have shown that it is possible to determine the water activity of liquid foods using the thermodynamic relationships. The water activity calculated from these equations has the inconvenience of providing its value at the initial freezing temperature instead of at room temperature, but the error introduced by this method is relatively small [Fontan et al (1981a)]. The potential use of the water activity measured at room temperature to predict initial freezing temperature and the application of these thermodynamic relationships to complex food systems (solid products) were not investigated.

The freezing of all foodstuffs can be divided into three steps: a) the removal of sensible heat until reaching the initial freezing temperature; b) the removal of latent heat over a range of temperatures; and c) the removal of sensible heat below initial freezing temperature. The reduction in product temperature below the initial freezing temperature produces ice and the remaining unfrozen portion with an increased concentration of solids. The increased concentration depresses the freezing temperature of the unfrozen solution and additional formation of ice will not occur until the temperature is lowered [Staph and Woolrich (1951) and Heldman (1974)]. Heldman (1974) developed a procedure, using this theory, to predict unfrozen water fractions during freezing of many products. His model describes the relationship for vegetables and fruits, but resulted in large deviations for beef and cod. Accurate knowledge of percent unfrozen water at each temperature allows for calculation of most factors required in the design of freezing systems.

When an experiment to measure initial freezing temperature is conducted, the product temperature usually decreases to a lower temperature (lower than the initial freezing temperature) before the first ice crystal is formed. This phenomenon is called supercooling. The experiment with any single material illustrates that the supercooling phenomena is not exactly reproducible. Even using the same specimen of a given material, a range of supercooling will be found [Knight (1967)]. Fifty measurements of supercooling temperatures for water in sealed glass bulb may give results varying over a temperature range of 10°C [Dorsey (1948)]. It is assumed that the supercooling temperature varies with product composition [Cordiez et al (1982)].

1.2. Objectives

The objectives of this research were:

1. To evaluate the contribution of the liquid fraction of foodstuffs to initial freezing temperature depression.

2. To analyze the thermodynamic expressions used to evaluate the initial freezing temperature in liquid foods and their application to complex food systems.

3. To evaluate the possibility of predicting initial freezing temperature from measurements of product water activity at ambient temperature (20°C).

4. To develop a method to measure initial freezing temperature of foods based on the supercooling phenomenon.

5. To develop expressions for the activity coefficients to use in describing freezing characteristics of complex food systems.

6. To develop a procedure to predict percent unfrozen water at subfreezing temperatures.

2. LITERATURE REVIEW

2.1. The Prediction of Water Activity

The prediction of water activity of multicomponent mixtures of dried foods was developed by Salwyn and Slawson (1959) using the individual sorption isotherms of the components according to the formula:

$$Aw = \frac{\sum DW.Aw_i.Ci}{\sum m_i.C_i} \qquad (1)$$

The Norrish (1966) equation, derived using basic thermodynamic laws, gives the following relationship for binary sugar solutions:

$$\text{Log}\ (\frac{Aw}{X_w}) = K_i.X_i \qquad (2)$$

K_i = constant obtained by plotting log Aw/X_w vs. X_i

For multicomponent systems the above equation is written as:

$$\text{Log}\ (Aw/X_w) = \sum K_i.X_i \qquad (3)$$

where: K_i is obtained as above.

Chuang and Toledo (1976) developed a relationship to predict water activity by a modification of the Norrish equation. Their equation has the following form:

$$\text{Log}\ Aw/n_i = K\ S_i/m + b \qquad (4)$$

However, according to their conclusions, the expression is limited to two components and the equation itself is too unwieldly to apply for a mixture containing more than two components.

The value of the constant K of the Norrish's equation was determined for solutions of amino acids [Chirife, Fontan and Scorza (1980)] and its value was significantly higher for diaminomonocarboxylic acids indicating that amino groups play a significant role for depressing the water activity. The length of the aliphatic chain also favours the lowering of the water activity.

Cherife et al (1980a, 1980b) calculated the constant 'K' of the Noorish's equation for binary solutions of sugars and salts. They suggested that the effect of hydrogen bonding is dominant in determining the properties of sugar solutions because of the linear relationship among polyols. The higher the number of hydroxyl groups the higher the value of 'K'. The result of the water activity using this method was always within 5% of the experimental value.

A rigorous means of calculating water activity for both simple and complex solutions is obtained by the Gibbs-Duhen equation [Ross (1975)] by the following development

$$n_i . d(\ln Aw_i) = 0 \qquad (5)$$

for a solution containing only one solute the expression can be written as follows:

$$55 . d(\ln Aw) + m_i . d(\ln Aw_i) = 0 \qquad (6)$$

In a multicomponent solution, after proper mathematical operations:

$$\ln Aw = \sum \ln Aw_i \qquad (7)$$

$$Aw = (Aw_1).(Aw_2).(Aw_3).....(Aw_i) \qquad (8)$$

where Aw_i are the water activity of each component as if they were in a binary solution.

Chirife (1978) used Ross's equation [Ross (1975)] to predict water activity in intermediate moisture foods. They have shown that it is a simple and accurate method to predict water activity in these food products. The difference between the water activity determined experimentally and the predicted value was always less than 4%.

Refinement of Ross's equation for predicting the water activity of nonelectrolyte mixtures can be found in the literature [Fontan and Chirife (1981)]. The difference of this equation from Ross's is that the water activity of each nonelectrolyte must be taken at the total molality of the mixture raised to the mi/m power (mi = molality of component 'i', and m = the total molality of the solution). The results using the modified Ross's equation had deviation from the experimental value less than 2% in most of the samples analyzed.

Electrolyte solutions behave differently from nonelectrolyte solutions such as sugars. Due to interaction of charged particles electrolytes deviate from ideal solutions [Karel (1975)] even at very low concentrations. Separate ions follow Roault's Law up to about 0.4 m [Van den Berg and Bruin (1981)].

Teng et al (1974) based on results of water activity for ternary aqueous solutions [Sangaster and Lenzi (1971)] and multicomponent electrolyte solutions [Chen et al (1973)] developed a general relationship for the prediction of water activity of nonelectrolyte and electrolyte solutions as described below:

$$Aw = 1 + B_1.m + B_2.m^2..... \quad (9)$$

where B = regression parameters

The authors listed 'B' for the solutes in question and they found no significant difference between their procedure and the experimental values.

Smith (1947) developed an expression to describe sorption of water vapor by high polymers as shown:

$$MC = a.\log(1-Aw) + b \quad (10)$$

Modification of this expression for multicomponent systems was accomplished by Lang and Steinberg (1981a, 1981b) for water activity below 0.30 and 0.95 according to the model shown below:

$$\ln (1-Aw) = (MC.DM - b_i.DW_i)/a_i.DW_i \quad (11)$$

The prediction of water activity in cook-soak equilibrated intermediate moisture meats using a modification of Grover's equation (1947) was accomplished by Webster et al (1979). However, this equation uses empirically determined constants and when the solid content is zero (water) the water activity is higher than one.

Water activity could be related to pore size of the capillaries by Labuza (1975) by the following equation:

$$\ln Aw = \frac{-\exp 2\delta \, \cos\theta \, V_w}{rRT} \quad (12)$$

but most foods have pore size between 10 and 100 μ and the water activity lowering caused by pore size is small [Labuza (1977)]. At a 100μ pore size the water activity is 0.999999 and at 10μ is 0.99999.

With macromolecules the water activity lowering can be calculated by the Flory-Huggins equation [Flory (1742) and Huggins (1942)].

$$\ln Aw = \ln\phi_1 + 1 - \frac{V_1}{V_2}\ \phi_1 \quad \chi\phi_2^2 \qquad (13)$$

Busk (1977) has shown that this equation is a good model for the prediction of water activity lowering of food gelling agents.

The concept of additivity of isotherms of mixtures of dehydrated foods, that is, that the amount of water sorbed at a given water activity is derived by the weight percent of each component times the amount it would sorb alone, was used to develop a common sorption isotherm for the mixture [Iglesias et al (1979)]. The water activity of the final product was then found by using the well known BET equation [Brunauer, Emett, and Teller (1938)] as presented below:

$$\frac{Aw}{MC(1-Aw)} = \frac{1}{Wm.Ca} + \frac{(Ca - 1)\ Aw}{Wm\ .\ Ca} \qquad (14)$$

2.2. Methods of Measuring Water Activity

2.2.1. Vapor Pressure Measurement

According to Labuza et al (1984) the measurement of the vapor pressure of foods using the oil manometer is the best available technique and the temperature control seems to be the most critical factor in determining water activity by this method. There are several drawbacks in the manometric method. It is not suitable for biological materials with active respiration or materials containing large amounts of volatile compounds. However, it should be considered as the standard method since vapor pressure is a direct measure of the water activity [Leung (1983)].

Troller (1983) developed a device which consists of a sensitive capacitance sensor for measuring vapor pressure. He describes, as the principal advantage over regular hygrometers, that the contamination of the hygrometer sensors is avoided. The pressure transducer values might be a more accurate estimate of the true water activity, although no significant difference was found between water activity determined by an oil manometer and the pressure transducer [Labuza et al (1984)].

Improvement of accuracy and precision of water activity measurements with a water vapor pressure manometer was accomplished by Nunes et al (1984) using a correction factor for the volume difference between the measurement in the sample and the measurement of the residual pressure. They also had isothermal conditions for the whole system during each experiment.

2.2.2. Hygrometers

The dew point hygrometers is based on the condensation of water by a mirror at the dew point. The mirror can be cooled by Peltier effect and the dew formation is detected photoelectrically [Leinstner and Rodel (1975)]. According to Prior (1979) this method can be used over a wide range of temperatures and is accurate to 0.003 water activity units. Problems with electric hygrometers have been reported in the literature related to loss of precision due to aging and contamination of sensors [Leung (1983)].

2.2.3. Isopiestic Methods

Felt (1973) developed this technique for measuring water activity in the range of 0.80 to 0.99. The sample is equilibrated with a reference protein in an evacuated desiccator for 24 hours at 25^{o}C. As soon as equilibration is reached the moisture content of the reference protein was determined. As shown by Hagenmaier (1972) some oilseed proteins absorb a given amount of water at a specific water activity and temperature. The value of the water activity of the sample was determined by the moisture absorbed by the protein.

Vos and Labuza (1974) introduced a modification in this method by replacing the protein with microcrystalline cellulose. The water activity of the sample is proportional to the amount of water absorbed and read off a standard sorption isotherm curve of microcrystalline cellulose. The accuracy is claimed to be of 0.005 water activity units. A similar method was developed [McCune et al (1981)] using the proximity equilibration cell with filter paper as reference. Spiess and Wolf (1983) recommended microcrystalline cellulose as a reference material; however, there is a need for the standardization of this technique.

In the graphical interpolation method [Landrock and Proctor (1951)], the sample is equilibrated with sulphuric acid solutions of different water activity values. The weight loss or gain of the sample are plotted as a function of water activity and the determination of the water activity of the sample is made at the point where no weight changes occur. A modification of this method [Multon et al (1980)] by using a dynamic stream of conditioned air for humidity control had a standard error of 0.02 water activity units.

2.2.4. The Salt Liquifaction Test

This method is based on the property of salt crystals to attract water vapor and to liquify if the water vapor pressure of the surrounding air exceeds the water vapor pressure of a saturated solution of the salt [Northolt and Heuvelman (1982)]. The method consists in placing a 50 g sample in a jar of 500 ml with a transparent lid until equilibrium temperature is reached. Vaseline is then spread on the inside of the lid and salt crystals are placed over the thin layer of Vaseline. Observation of the liquifaction of the salt crystals are made each hour or so. In this procedure, using salts of different water activities, one can estimate the water activity of the sample.

2.2.5. Using the Thermocouple Psychrometer

This method measures water activity based on wet bulb depression [Campbell et al (1966 and 1979)]. To measure the water activity a sample is placed in a chamber containing the thermocouple and sealed to reach equilibrium. After equilibrium, the thermocouple can be cooled by Peltier effect [Peck (1968)] and the water condenses on the thermocouple. However, for water activities below 0.95 the Peltier effect is insufficient to condense water on the thermocouple [Weibe et al (1981)]. It can also be wetted with distilled water [Richards (1958)]. The rate of evaporation of the water from the thermocouple is dependent upon the water activity of the test sample and is proportional to the instrument reading in microvolts.

Accuracy of 0.0023 water activity units in the range of water activity of 0.935 to 1.000 have been reported [Prior (1979)] and accuracy of 0.0005 and 0.00001 water activity units have also been cited by Leung (1983) and the Decagon Instrument Manual (1984).

The thermocouple psychrometer is a fast and reliable method to measure water activity. However, the apparatus requires frequent recalibration and the calibration varies from one psychrometer to another [Ehling (1962) and Rawlins (1977)].

2.3. Freezing Point Depression

Initial freezing temperature is the temperature at which solid and liquid phases can exist at one atmosphere of pressure. Freezing point data can be used for a variety of purposes such as calculating refrigeration requirements [Heldman (1982)] ascertaining chemical purity and detecting adulteration of products [Fennema (1973)].

The most common methods used to determine initial freezing temperatures are time vs. temperature data, enthalpy vs. temperature [Levy (1970)] or cryoscopic osmometry for liquid systems [Fennema (1977)]. The time vs. temperature approach is the most commonly used method. The problem with this method is the supercooling, the temperature at which nucleation takes place and can be responsible for errors in the determination of the initial freezing temperature because of the tendency of giving lower results for the measurement when higher degrees of undercooling occur, mainly in liquid systems [Hoare (1960)].

Corrections can be made by extrapolations of the freezing curves [Saylor (1957)]. For nonliquid foods, additional problems result from nonuniform composition and temperature distribution in the product and the determination of the initial freezing temperature is more difficult.

Taking into consideration these complications in the determination of the initial freezing temperatures of foods, Heldman and Lai (1982) developed a method that consists of measuring the vapor pressure of the unfrozen product and the vapor pressure of the frozen product. The linear regression of Ln pressure vs. temperature is made for each set of data separately. The point where the two straight lines intersect is considered the initial freezing temperature. Time requirements are a major disadvantage of this method.

Supercooling is necessary to determine initial freezing temperature. It is a nonequilibrium condition and is very difficult to reproduce [Knight (1967)]. In water-ice systems, a complete investigation on supercooling was made by Dorsey (1948). In his results, he found that the purest available water had a nucleation temperature between -20 and -25^oC while tap water had a nucleation temperature between -5 and -10^oC. Even using the same specimen Dorsey found a range of temperature much larger than any possible experimental error.

Composition plays a major role on the nucleation temperature (supercooling). Cordiez et al (1982) have shown when working with stearic acid-water emulsions that different emulsifiers resulted in different ranges of supercooling for the emulsions studied. Biological materials such as foods can produce different nucleation temperatures depending on composition, and it is found that the nucleation rate increases as the supercooling is increased [Reid (1983)]. The extent of supercooling also affects the texture of frozen solutions [Mezits and Puente (1979)].

3. THEORETICAL CONSIDERATIONS

3.1. Derivation of Equations Used for the Prediction of Water Activity and Initial Freezing Temperatures

For an aqueous system the initial freezing temperature can be described as the temperature at which the first ice crystal exists in equilibrium with the solution. When this equilibrium occurs, the vapor pressure of the aqueous solution should be the same as that of ice at the same temperature [Denbigh (1981)]. As a result,

$$\mu_1 = \mu_2 \tag{15}$$

or expressed in the differential form

$$d\mu_1 = d\mu_2 \tag{16}$$

or

$$\frac{d\mu_1}{T} = \frac{d\mu_2}{T} \tag{17}$$

By the definition of ideal solution,

$$\mu_2 = \mu_1 + RT\ln X_i \tag{18}$$

Rearranging the above expression we get

$$\ln X_w = \frac{-\mu_1}{RT} + \frac{\mu_2}{RT} \tag{19}$$

$$\frac{\partial \ln X_w}{\partial T} = \frac{-1}{R}\,\frac{\partial(\mu_1/T)}{\partial T} + \frac{1}{R}\,\frac{\partial(\mu_2/T)}{\partial T} \tag{20}$$

$$= \frac{h_1 - h_2}{RT^2} \tag{21}$$

Note. 1 refers to pure liquid and 2 refers to ice.

Therefore,

$$\frac{\partial \ln X_w}{\partial T} = \frac{L}{RT^2} \tag{22}$$

The temperature coefficient of L is given by:

$$\left(\frac{\partial L}{\partial T}\right) = \left(\frac{\partial h_1}{\partial T}\right) - \left(\frac{\partial h_2}{\partial T}\right) \tag{23}$$

$$= C_{p1} - C_{p2}$$

$$= \Delta C_p$$

By integration, considering ΔC_p constant,

$$L_w - L = \Delta C_p\ (T_w - T) \tag{24}$$

substitution in equation (22) results in,

$$\frac{\partial \ln X_w}{\partial T} = \frac{L_w - \Delta C_p\ (T_w - T)}{RT^2} \tag{25}$$

by integration between x = 1 and x = x and T = Tf we have the following equation (assuming Aw = Xw),

$$-\ln Aw = \frac{(L_w - \Delta C_p . T_w).}{R}\left(\frac{1}{T_f} - \frac{1}{T_w}\right) + \frac{\Delta C_p}{R} \cdot \ln \frac{T_w}{T_f} \tag{26}$$

Equation (26) can be simplified by the assumption that $C_p = 0$, and written in the following manner [Lerici et al (1983)];

$$-\ln Aw = \frac{Lw}{R} \left(\frac{1}{T_f} - \frac{1}{T_w}\right) \tag{27}$$

or

$$-\ln Aw = 722.37 / T_f - 2.644 \tag{28}$$

Equation (25) can be expanded in order to include the activity coefficient as following:

$$-\ln Xw \,.\gamma = \frac{(L_w - \Delta C_p.T_w).}{R} \left(\frac{1}{T_f} - \frac{1}{T_w}\right) + \frac{\Delta C_p.}{R} \ln \frac{T_w}{T_f} \tag{29}$$

Considering $\Delta C_p = 0.0381$ KJ/^oC mole, R = 0.00832 KJ/^oC . mole and Lw = 6.010 KJ/mole equation (29) may be written as [Chirife and Fontan (1981)];

$$-\ln X_w \,.\gamma = 27.622 - \frac{528.373}{T_f} - 4.579 \ln T_f \tag{30}$$

The application of equation (30) to predict water activity at 25^oC has been accomplished in liquid foods [Lerici et al (1983)]. The difference between the predicted and experimental value was less than 0.01 water activity units; the same result as obtained by Chirife and Fontan (1981) for binary solutions of sugars. For most practical applications in food studies the accuracy of 0.02 water activity units is considered sufficient [Troller and Christian (1978)]. However, to predict initial freezing temperature from a given water activity the deviation of 0.02 water activity units can lead to an error in the determination of ±2^oC.

Rey and Labuza (1981) used cryoscopic osmometry to determine water activity of carrageenan gels. The cryoscopic osmometry method does not measure water activity directly, but measures the colligative property of initial freezing temperature that can be used in the equations described. For all the solutes studied, osmometric results predicted the water activity to within 0.0005 water activity units of the reported literature value.

3.2. Development of a Method to Predict Percent Unfrozen Water at Subfreezing Temperatures

A method to determine the percent unfrozen water at subfreezing temperatures can be proposed as explained below:

(a) Inputs

initial freezing temperature
water activity at 20^oC
moisture content
% unfrozen water at -40^oC

(b) Calculate the equivalent molecular weight [Heldman (1974)] assuming that Aw provided in part (a) is equal to Xw. Use the following equation,

$$Me = \frac{m_s \cdot X_w}{m_w/18 - (m_w/18) \cdot X_w} \quad (31)$$

(c) Water activity at subfreezing temperatures is known to be equal to the vapor pressure of ice divided by the vapor pressure of supercooled water at the same temperature [Fennema (1981) and Storey and Staimby (1970)]. Therefore, Aw can be determined at any desired temperature.

(d) The mole fraction of unfrozen water can be calculated by

$$X_u = \frac{m_u/18}{m_u/18 + m_s/Me} \qquad (32)$$

(e) then the activity coefficient at -40^oC is

$$\gamma = Aw / X_u \qquad (33)$$

(f) The activity coefficient at the second temperature, close to the initial freezing temperature, can be calculated using the known value of the mass fraction of unfrozen water in equation (32) and (33).

(g) The relationship of the activity coefficient as a function of temperature is assumed to be linear. Therefore, straight line between the value of the activity coefficient at -40^oC and its value at the second temperature makes possible to have the activity coefficient at any temperature for any product. As an example when calculating the percent unfrozen water at -20^oC, the following procedure should be followed:

  (1) from the plot the activity coefficient versus temperature determine the value of the activity coefficient at -20^oC

  (2) calculate the mole fraction of unfrozen water at -20^oC by rearranging equation (33) for X_u. Calculate also the value of the water activity at -20^oC.

$$x_u = Aw/\gamma$$

(3) Calculate the percent unfrozen water at $-20^{o}C$ by

$$\% \, m_u = \frac{18. \, (m_s/Me).X_u}{(1 - X_u)} \cdot \frac{100}{MC} \qquad (34)$$

The only disadvantage of the method is the assumption of linearity of the activity coefficient as a function of temperature and there are only two points to draw the straight line.

4. MATERIALS AND METHODS

For the extraction of the liquid fraction from the food products, the use of a manual press was necessary. The food products were obtained from a supermarket with the special attention to selection of the same varieties of fruits and vegetables and the same type of beef and cod.

4.1. Determination of Moisture Content

Moisture content of all products were measured by standard methods. Two to five grams of each sample were placed in an aluminum dish previously weighed on a Mettler balance precise to 0.0001 grams. The sample was then put in a vacuum drier at $95^{o}C$ (29.5 in Hg) until reaching constant weight and transferred to a desiccator to cool. The moisture content was calculated from the difference between the initial and final weight of the sample [AOAC (1965)].

4.2. Determination of Soluble Solids

4.2.1. Fruits and Vegetables

A whole fruit or vegetable was washed, cut in small pieces and blended in a Waring blender at high speed until a homogeneous liquid system was obtained. The liquid mixture was divided into five portions and centrifuged at 5000 rpm for 10 minutes in a refrigerated centrifuge at 15°C.

After centrifugation, the samples were filtered under vacuum through a Whatman no. 1 filter paper and the percent soluble solids was determined using a refractometer [AOAC (1965)].

4.2.2. Beef Samples

Samples of bottom round steak wrapped in aluminum foil were pressed manually in a vise having facing plates measuring 10x2.5 cm. Maximum pressure reached during the pressing operation was not measured. Immediately after maximum pressure was obtained the vise was opened and the liquid fraction removed. Before pressing, visible fat and connective tissue were removed. The procedure to determine percent of soluble solids was the same as described for fruits and vegetables [AOAC (1965)].

4.3. Determination of Water Activity

4.3.1. Experimental Determination at 20°C

The water activity for each product was determined in triplicate using a Decagon SC-10 Thermocouple Psychrometer (Pullman, WA). The measurement system was previously calibrated with saturated salt solutions of known water activities [Greenspan (1977) and Resnik et al (1984)]. The data for microvolt reading of various salt solutions in the range of interest was used to develop a regression equation [Gill (1978)] that was applied to determine the unknown water activities of the samples.

regression equation - $A_w = 1.0000 - 0.0013\ mV$

mV = microvolt reading

$r^2 = .997$

A solid cylindrical sample measuring 1x1 cm or 1 ml of the liquid fraction was placed in the instrument chamber where equilibrium conditions were achieved in approximately one hour, depending upon the product. When there was no change in the microvolt reading in the sample for a period of 10 minutes equilibrium was assumed and the thermocouple junction was wetted with distilled water and the microvolt output was measured. The output is proportional to the equilibrium relative humidity of the sample chamber.

4.3.2. Theoretical Value of Water Activity Calculated from Initial Freezing Temperature

4.3.2.1. Description of the System Used to Determine Initial Freezing Temperature for the Food Products

The system (Figure 1) consisted of a Neslab RTE-9 cooling unit (A) with automatic temperature control, Hewlett-Packard 85 microcomputer (B), 3479A Hewlett-Packard data acquisition system, vacuum insulated double wall glass bottle (7 cm inside diameter x 34.5 cm height), pyrex glass tube (1.6 cm inside diameter x 15 cm height) and 22 gauge copper-constantan thermocouples. Ethanol (200 proof) was used as cooling medium circulating in a copper coil (0.3 cm inside diameter, 2 mm thick and 14 turns of 4 cm inside diameter). The copper coil was inside the vacuum insulated double wall glass bottle which was full of

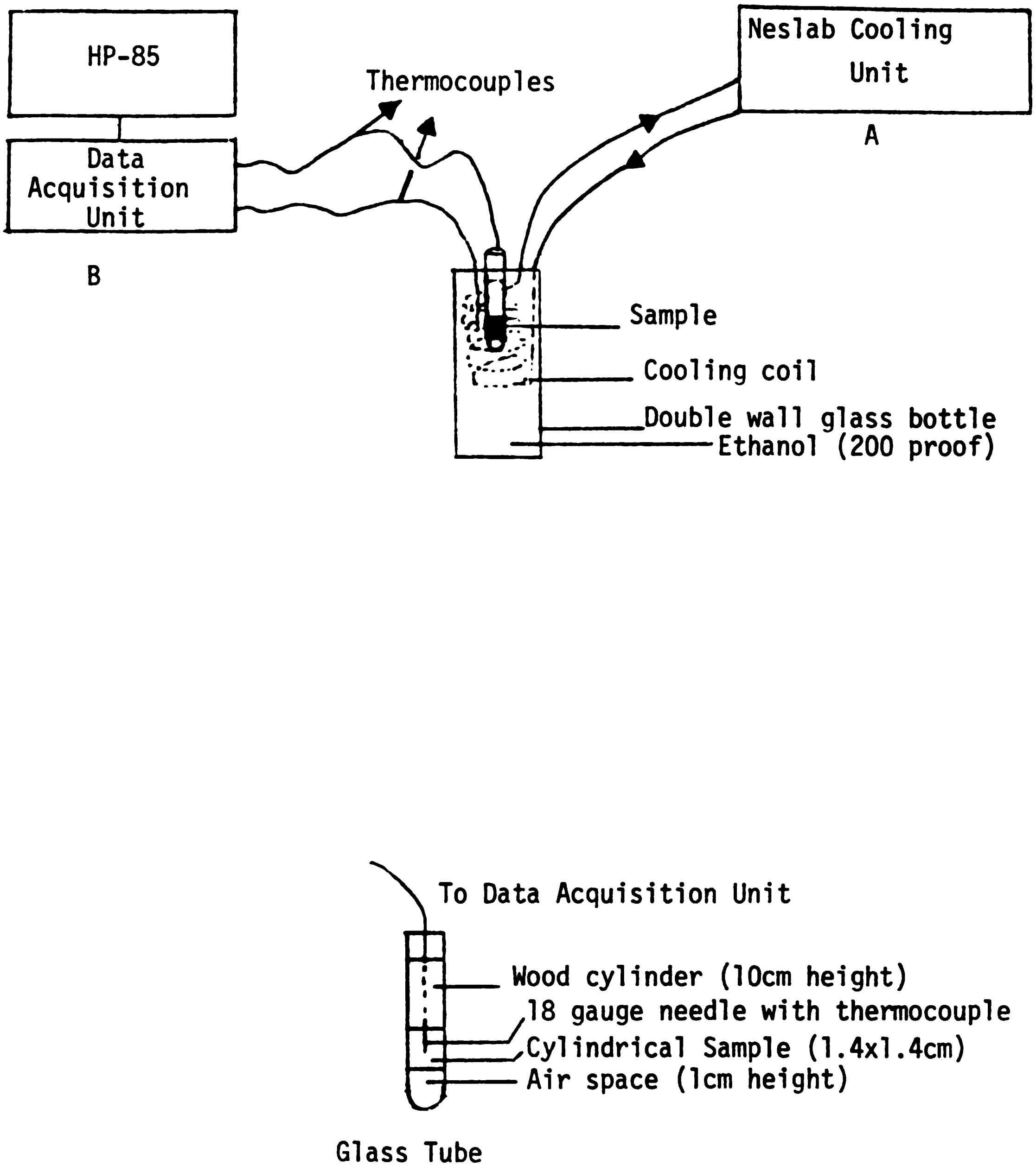

Figure 1. Equipment Used to Determine Initial Freezing Temperature of Foods.

ethanol. Two thermocouples were used. One thermocouple was placed in the center of the sample and the other in the vacuum insulated double wall glass bottle approximately 1 cm from the glass tube which contained the sample and on the same horizontal plane at the approximate midpoint of the sample.

The thermocouple for the sample was welded at the end and placed inside a 18 gauge needle. The needle with the thermocouple was placed in the center of a round piece of wood (10 cm of height) that fitted the inside wall of the glass tube tightly. This procedure assured a constant location of the thermocouple in the center of the samples.

The initial freezing temperature of each sample, liquid fraction and whole product, was determined from a freezing curve (temperature vs. time) temperature. A thermocouple (copper - constantan) was inserted at the center of a 1.4x1.4 cm cylindrical sample or 1 ml liquid fraction and placed in a test tube. The product, thermocouple and test tube were placed in an alcohol cooling bath (Neslab, Portsmouth, NH) at $-13^{o}C$. The temperature vs. time data was collected at 3 and 6 seconds time intervals for the liquid fraction and the whole product, respectively. These time intervals were chosen in order to be able to describe the supercooling. The initial freezing temperature was determined from the computer output (temperature vs. time). Table 1 presents the data obtained for pear juice from an HP-85 computer. It is observed that as soon as the maximum supercooling temperature was reached the product temperature returned to the initial freezing temperature. At the initial freezing temperature a plateau with approximately constant temperature ($\pm 0.02^{o}C$) was formed. From the

Table 1. Data obtained from an HP-85 computer during the determination of initial freezing temperature of pear juice at -13°C.

Time (s)	Temperature of product (°C)
51	-0.0688
54	-0.4528
57	-0.81249
60	-1.1723
63	-1.5093
66	-1.8206
69	-2.1571
72	-2.4436
75	-2.7291
78	-2.9876
81	-3.2755
84	-3.5097
87	-3.7689
90	-4.0027
93	-4.2376
96	-4.4704
99	-4.6519
102	-4.8860
105	-5.0687
108	-5.2766
111	-5.4573
114	-5.6402
117	-5.8210
120	-6.1339
123	-6.2901
126	-6.2901
129	-6.4448
132	-6.6017
135	-6.7586
138	-4.2312
141	-2.0312
144	-1.8200
147	-1.7395
150	-1.6862
153	-1.6840
156	-1.7080
159	-1.7069
162	-1.7037
165	-1.7087

computer data presented in Table 1 the highest temperature on this plateau was taken as the initial freezing temperature of the product.

4.3.2.2. Calculations of Water Activity Using Thermodynamic Relationships

The water activity was calculated by using the value of the measured initial freezing temperature determined as described in the previous section in the equations (28) and (30).

4.4. Supercooling and Initial Freezing Temperature Experiments

To obtain a more consistent supercooling in the samples, the same procedure as previously described was used for the determination of the initial freezing temperature. Instead of maintaining the cooling medium at constant temperature, the cooling bath temperature was decreased at the same time as the sample temperature was decreased while maintaining a 2 to 3^oC difference between sample and cooling bath.

The initial freezing temperature of the samples was measured from the plateau formed during latent heat removal using the same procedure described in Section 4.3.2.2.

4.5. Calculation of the Activity Coefficient for Frozen Products

4.5.1. Percent Unfrozen Water at Subfreezing Temperatures

The data for the percent unfrozen water at subfreezing temperatures was obtained from Riedel (1949a, 1949b, 1951, 1955, 1956, 1957a, 1957b) who used calorimetry to determine enthalpy of the food products. The data from Riedel was adapted by Dickerson (1968) for tables of percent unfrozen water.

4.5.2. Determination of Equivalent Molecular Weight

The equivalent molecular weight for each food was calculated using equation (31) [Heldman (1974)]. Considering the mole fraction of water (X_w), the water activity of the product measured at 20°C or calculating it from the freezing point depression equation, and by previous knowledge of the mass fraction of water, the equivalent molecular weight can be calculated using the equation (31). An example of the calculation is presented for pear:

Aw at 20°C = .9833

moisture content 84.87%

solid content 15.13%

using equation (30)

$$Me = \frac{15.13 \cdot 0.9833}{(84.87/18) - (84.87/18) \cdot 0.9833}$$

$$Me = 189$$

4.5.3. Calculation of the Mole Fraction of Unfrozen Water

The mole fraction of unfrozen water at subfreezing temperatures was calculated using equation (32). The values for the mass fraction of unfrozen water (M_u) were obtained from Riedel (1957) and the equivalent molecular weight of the solids was determined as previously described in section 4.5.2.

4.5.4. Calculation of the Activity Coefficient of the Frozen Product

The correction for ΔC_p as a function of temperature was necessary in order to calculate the activity coefficient at subfreezing temperatures. Expressions for the specific heat of supercooled water and ice for temperatures up to 233°K were obtained from Leyendekkers and Hunter (1985). Equation (35) was obtained by incorporating the correction for ΔC in equation (25). A detailed derivation is presented in Appendix B.

$$-\ln\gamma = \frac{-3190.929}{T_f} + 0.0358\,T_f - 24.117\ln T_f + 137.200 + \ln X_u \qquad (35)$$

The values of the activity coefficient calculated by equation (35) were used to develop regression equations of activity coefficient as a function of temperature for each product.

4.5.5. Determination of the Theoretical Value of the Water Activity at Subfreezing Temperatures

Experimental data from Fennema (1981) and Storey and Stainsby (1970) demonstrated that the equilibrium vapor pressure for frozen products is equal to the vapor pressure of ice at the same temperature. Therefore, the definition of water activity at subfreezing temperature is the vapor pressure of ice divided by the vapor pressure of supercooled water at the same temperature for any product.

4.6. Statistical Analysis

Statistical analysis of the data was performed by applying a two tail student's 't' test to verify if there was difference between the means of two samples. In situations where there were more than two sets of samples analysis of variance was applied in order to detect any significant difference among samples [Gill (1978)].

5. RESULTS AND DISCUSSION

The results obtained in this research deal with the prediction of the initial freezing temperature and water activity of complex food systems using thermodynamic relationships. The method proposed to experimentally determine the initial freezing temperature was applied to several types of food products. A procedure to predict the percent of unfrozen water at subfreezing temperature has been developed.

5.1. Determination of Initial Freezing Temperature of Complex Foods

5.1.1. The Use of Constant Medium Temperature

Figures 3 to 12 are freezing curves obtained by plotting temperature vs. time for the product. The phenomenon of supercooling takes place in all the determinations of the initial freezing temperature as observed from the freezing curve of the product.

According to Fennema (1973), the supercooling in excess of 2^oC is generally undesirable since it will result in a lower estimation of the initial freezing temperature and corrections by extrapolation of the freezing curves [Hoare (1960)] can not be estimated accurately. His discussions deal primarily with liquid systems (Figure 2) and additional problems such as temperature distribution and nonuniform composition throughout the product occur in nonfluid systems [Heldman and Lai (1982)].

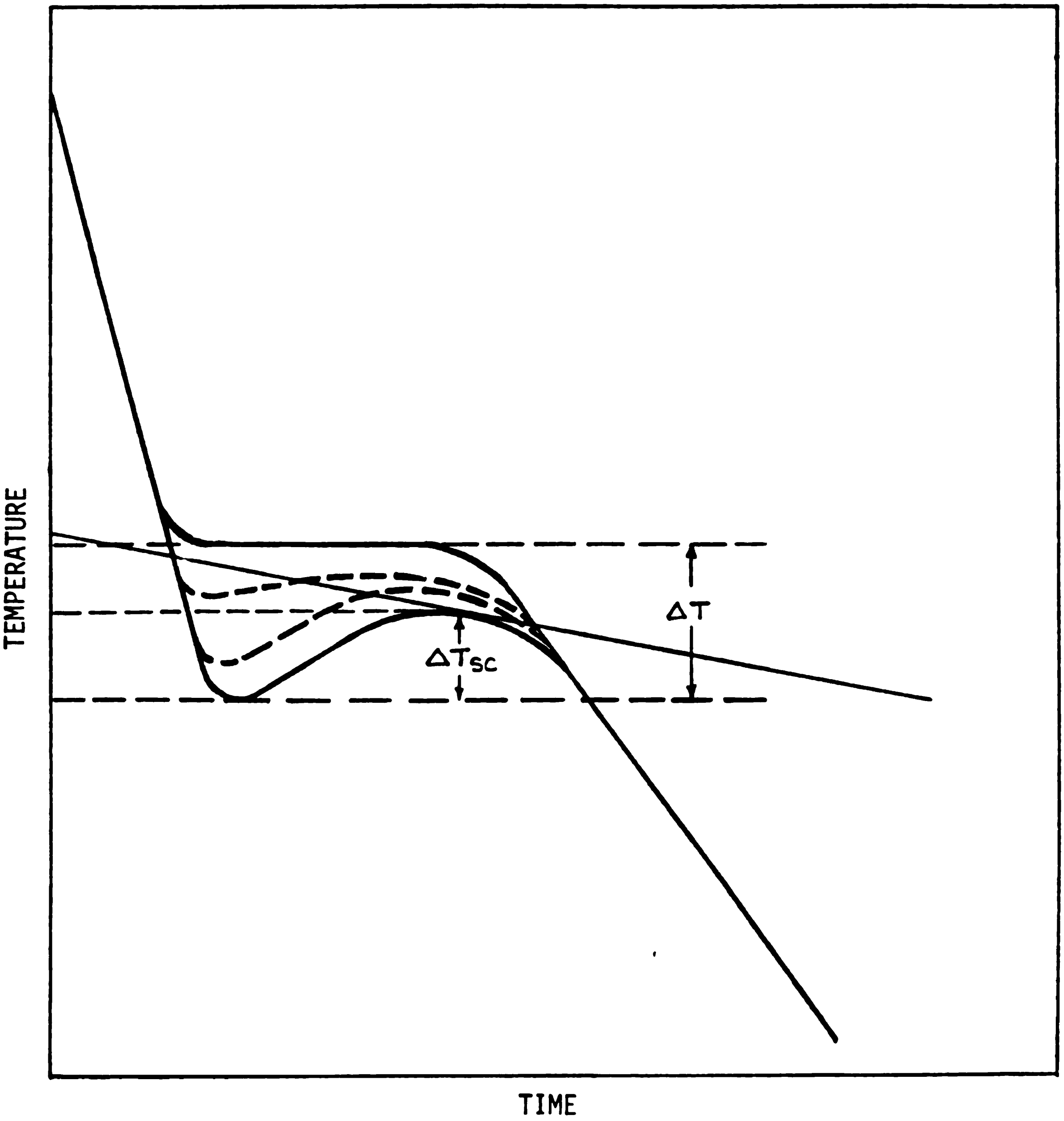

Figure 2. Freezing curves from Hoare (1960).

The results of this investigation for cod and liquid fraction from beef (Figure 3 and 4) show that the conditions found in Figure 2 may take place when the product is exposed to a constant medium temperature and the curve shapes found in this illustration are more commonly found in fluid systems such as the liquid fractions of the foods studied in this research.

With a constant cooling medium temperature the product may not freeze because the cooling medium temperature may not be low enough for the product to reach the temperature of nucleation. This fact can be observed in Figure 5 where a cooling medium temperature of $-8^{\circ}C$ was used to determine initial freezing temperature of pear. The product reached the cooling medium temperature and did not freeze until the medium temperature was lowered to its temperature of nucleation. As soon as the medium temperature was lowered, ice crystal formation was initiated. Without supercooling, nucleation will not initiate and as a result the water will not freeze. Knight (1967) observed that a product can be left indefinitely without freezing, assuming there is no vibrations or any other disturbance in the product, only by increasing the product temperature one degree above of its temperature of nucleation. This fact was observed in Figure 5 in this investigation. The use of constant temperature in the determination of initial freezing temperature of food products (Table 2) is not recommended due to the fact that each product has a different range of nucleation temperatures and the range of medium temperatures where the supercooling takes place is also variable for different products.

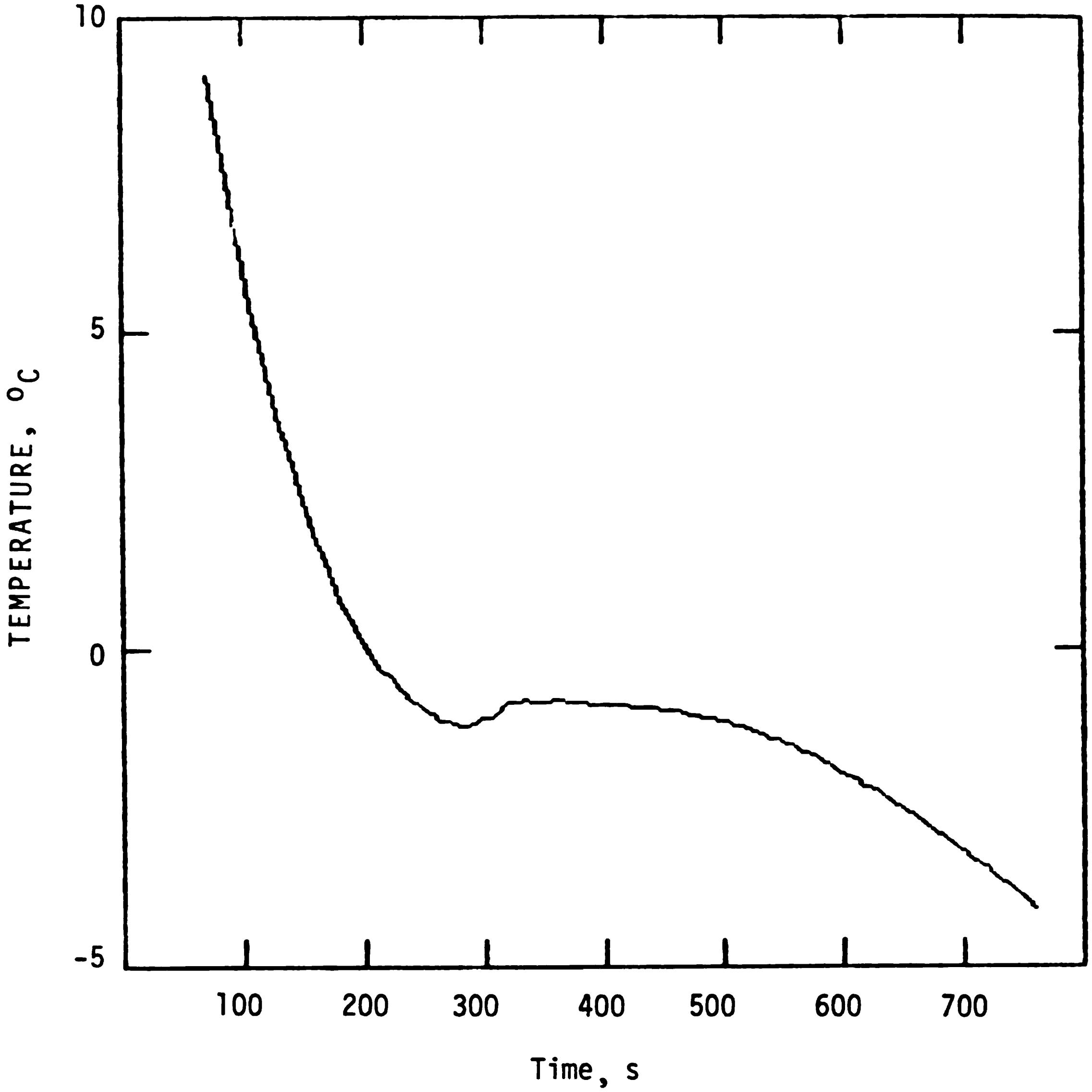

Figure 3. Freezing curve for cod at -13 °C.

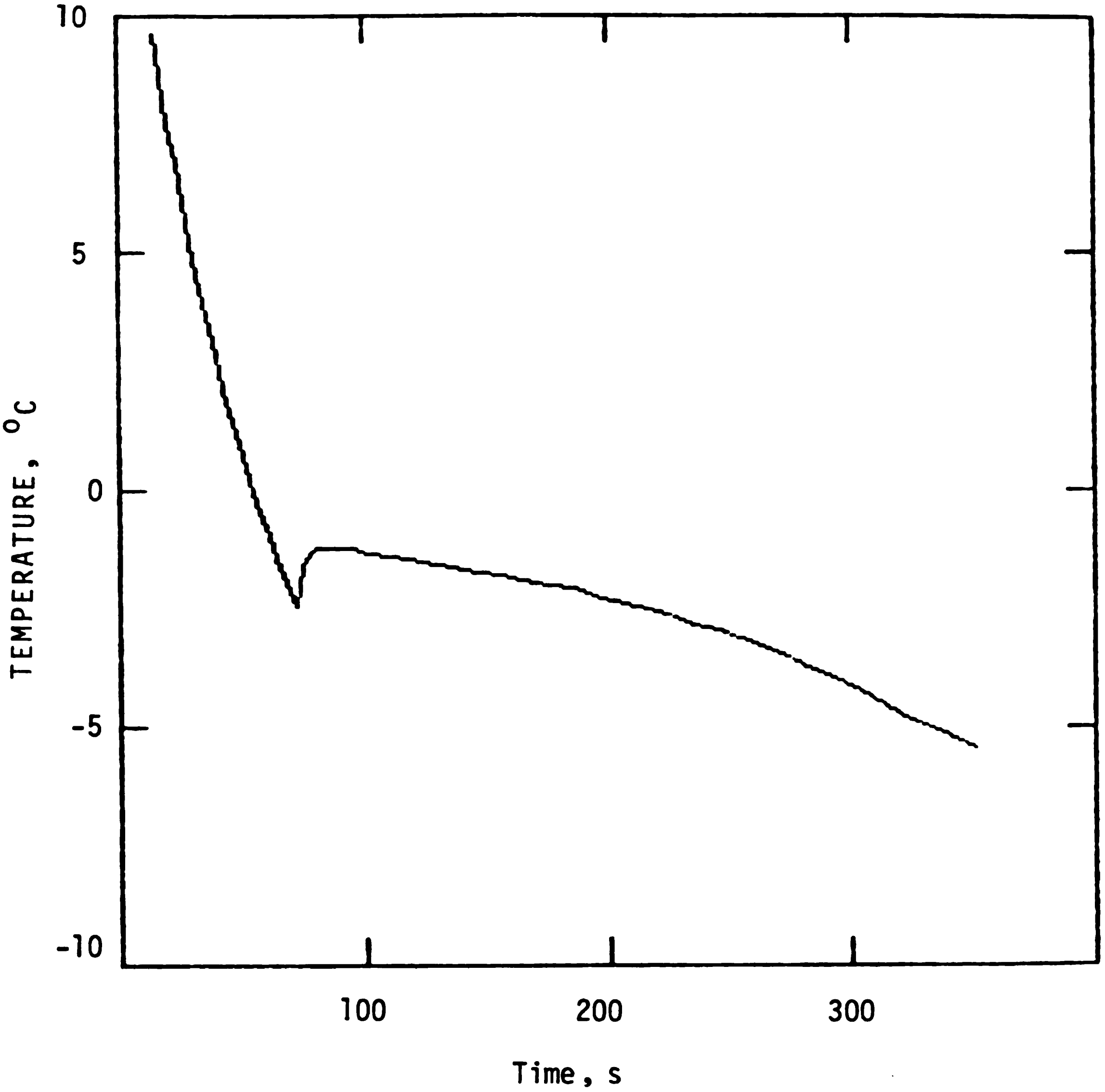

Figure 4. Freezing curve for liquid fraction from beef at -13 °C.

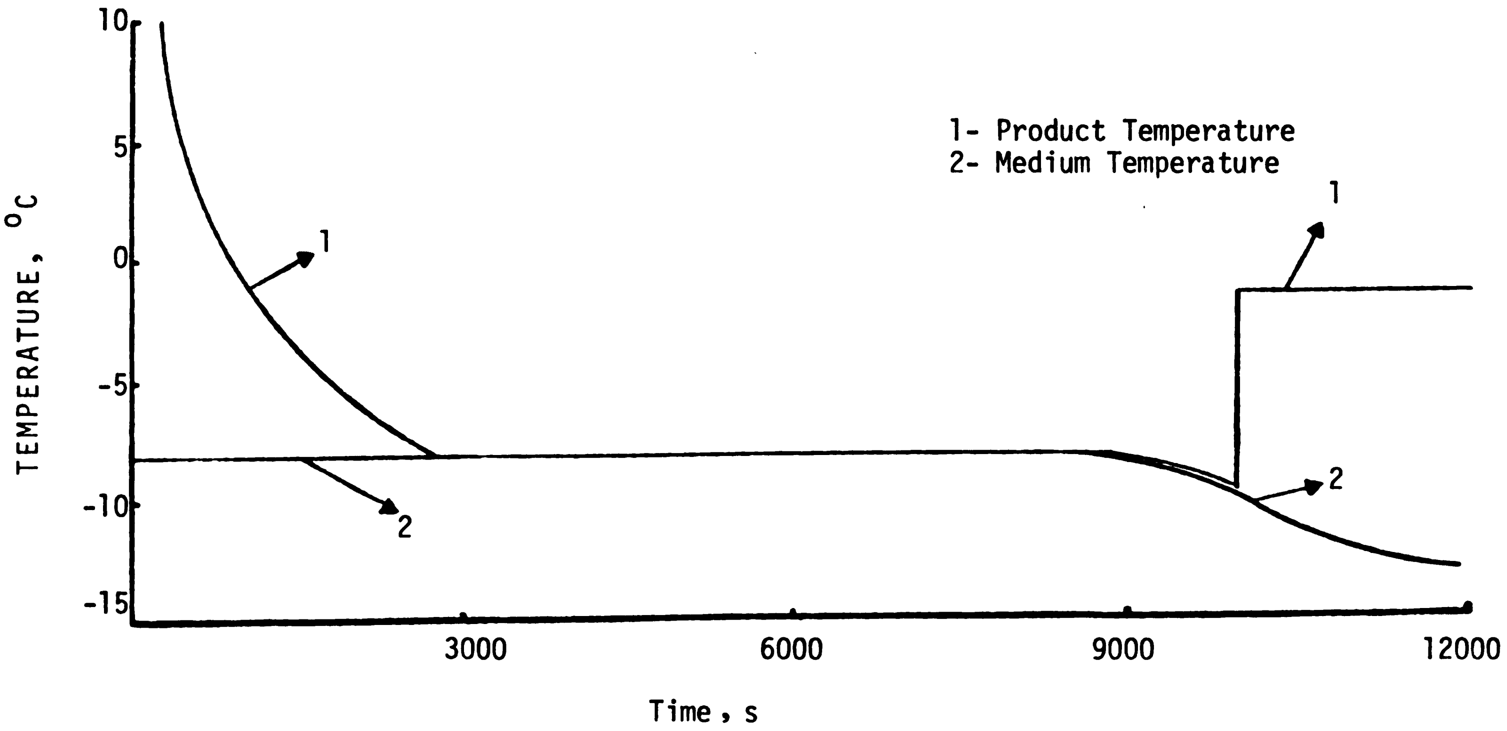

Figure 5. Effect of the temperature on the determination of the initial freezing temperature for pear.

Table 2. Determination of Initial Freezing Temperature Using Constant Medium Temperature of -13°C.

Product	Fraction	T_f (°C)	Literature (references)
Pear	whole	-1.69 ± 0.12	-1.61 (Heldman 1982)
	liquid	-1.65 ± 0.14	
Tomato	whole	-0.64 ± 0.08	-0.72 (Heldman 1982)
	liquid	-0.64 ± 0.08	
Beef	whole	-1.16 ± 0.03	-1.67 (Lai 1982)
	liquid	-1.15 ± 0.06	
Cod	whole	-0.96 ± 0.05	-1.00 (Riedel 1956)
chicken	whole	-0.81 ± 0.05	-1.00 (Dickerson 1968)

results are mean of 10 determinations

The medium temperature has influence on the degree of supercooling as observed for the data on beef and pear (Table 3). The degree of supercooling decreased for lower medium temperatures as observed in Table 3. When lower medium temperatures were used to determine the initial freezing temperature of pears and beef, the temperature of maximum supercooling was lowered considerably. This observation was caused by the water near the surface of the product freezing rapidly. The ice front moves rapidly and reaches the center resulting in promotion of the nucleation of water. Therefore, the temperature of maximum supercooling in the center is increased. This effect is similar to seeding; the addition of ice crystals in order to decrease the supercooling as used in the determination of the initial freezing temperature of milk [Radewonuk et al (1983)].

Low medium temperatures tend to result in freezing curves without a well defined plateau and make the accurate determination of the initial freezing temperature even more difficult. This situation was found for products such as chicken, cod, liquid fraction from beef and pear. It is evident that the shape of the freezing curve for cod and liquid fraction from beef (Figure 3 to 4) do not represent equilibrium conditions as observed for the freezing curve of water (Figure 6) where the perfect horizontal plateau was obtained after the supercooling was reached and the latent heat of fusion was being liberated during phase change. The determination of the initial freezing temperature using this curve (Figure 3) as reference could cause error in the calculation of the initial freezing temperature for cod due to nonequilibrium condition during phase change as described by Hoare (1960) and Fennema

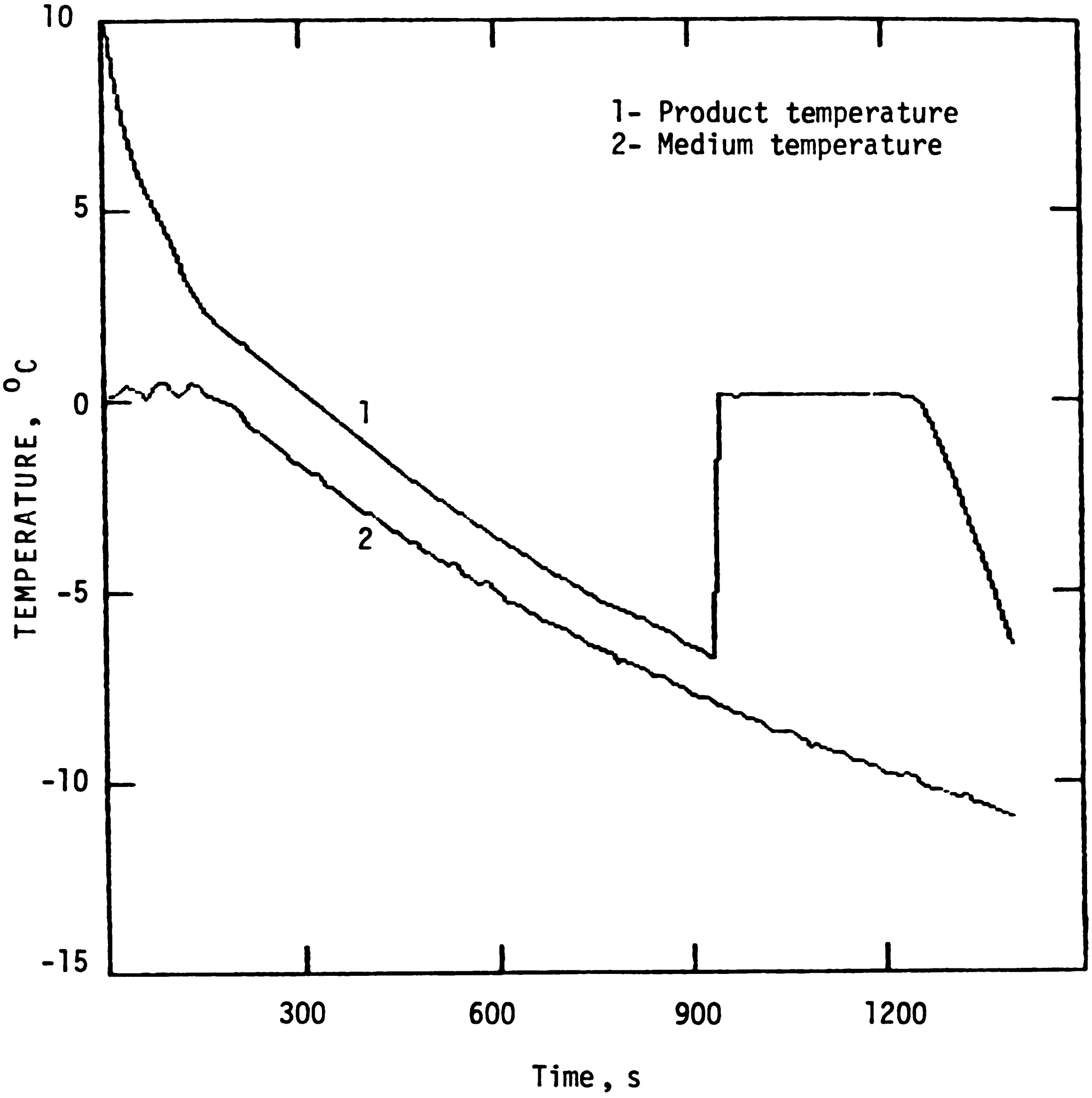

Figure 6. Freezing curve for water at (T - Tm = 2 to 3 ^{o}C).

Table 3 . Variation of Supercooling with Temperature.

T_m (°C)	Pear		Beef	
	T_f (°C)	T_{sc} (°C)	T_f (°C)	T_{sc} (°C)
-5	-	-	-1.00 ±	-4.88 ±
-8	-	-	-1.08 ± .06	-1.66 ± .44
-13	-1.76 ± .10	-10.6 ± 1.4	-1.21 ± .08	-1.59 ± .18
-15	-1.49 ± .05	-3.1 ± .4	-	-
-18	-2.04 ± .09	-2.5 ± .5	-	-

T_m = constant cooling bath temperature

T_{sc} = Supercooling temperature.

T_f = initial freezing temperature.

(1973).

5.1.2. The Use of Constant Temperature Difference Between the Sample and the Cooling Bath

Temperature vs. time freezing curves for food products obtained by maintaining a difference of 2 to 3°C between the medium temperature and the sample throughout the phase change are presented in Figure 7 to 12. As is evident from these results, the shapes of the freezing curves are different from those measured by Hoare (1960) and Fennema (1973). These curves have significant supercooling and have horizontal lines during latent heat removal with variations in the plateau ranging from 0.01 to 0.03°C as illustrated in Figure 7. This situation represents a true equilibrium and the highest point on this plateau is taken as the initial freezing temperature of the product. The return from the temperature of nucleaton (supercooling) to the initial freezing temperature is rapid in all freezing curves having an angle of approximately "90°" with the plateau formed when the samples start to generate the latent heat of fusion during phase change. The main reason for this type of freezing curve include the fact that temperature gradients in the sample were minimized when compared to condition with constant medium temperature. It is observed that the freezing curves for beef (Figure 8), apple (Figure 9), tomato (Figure 10), potato (Figure 11) and pear (Figure 12) permit easy determination of the initial freezing temperature as compared to Figures 3 and 4. In the previous examples, the plateau formed during freezing does not approximate a horizontal line at constant medium temperature.

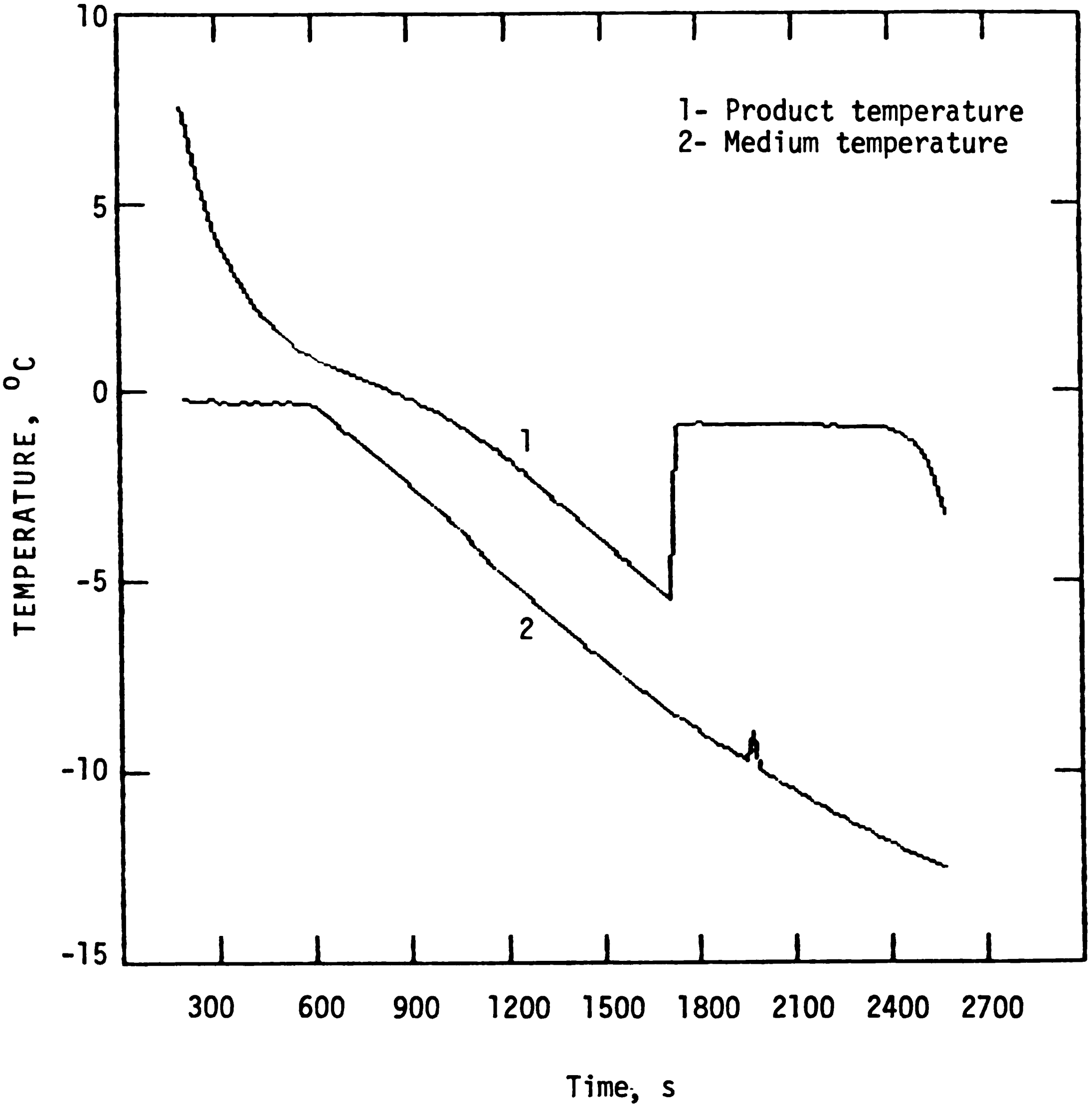

Figure 7. Freezing curve for cod at (T - Tm = 2 to 3 °C).

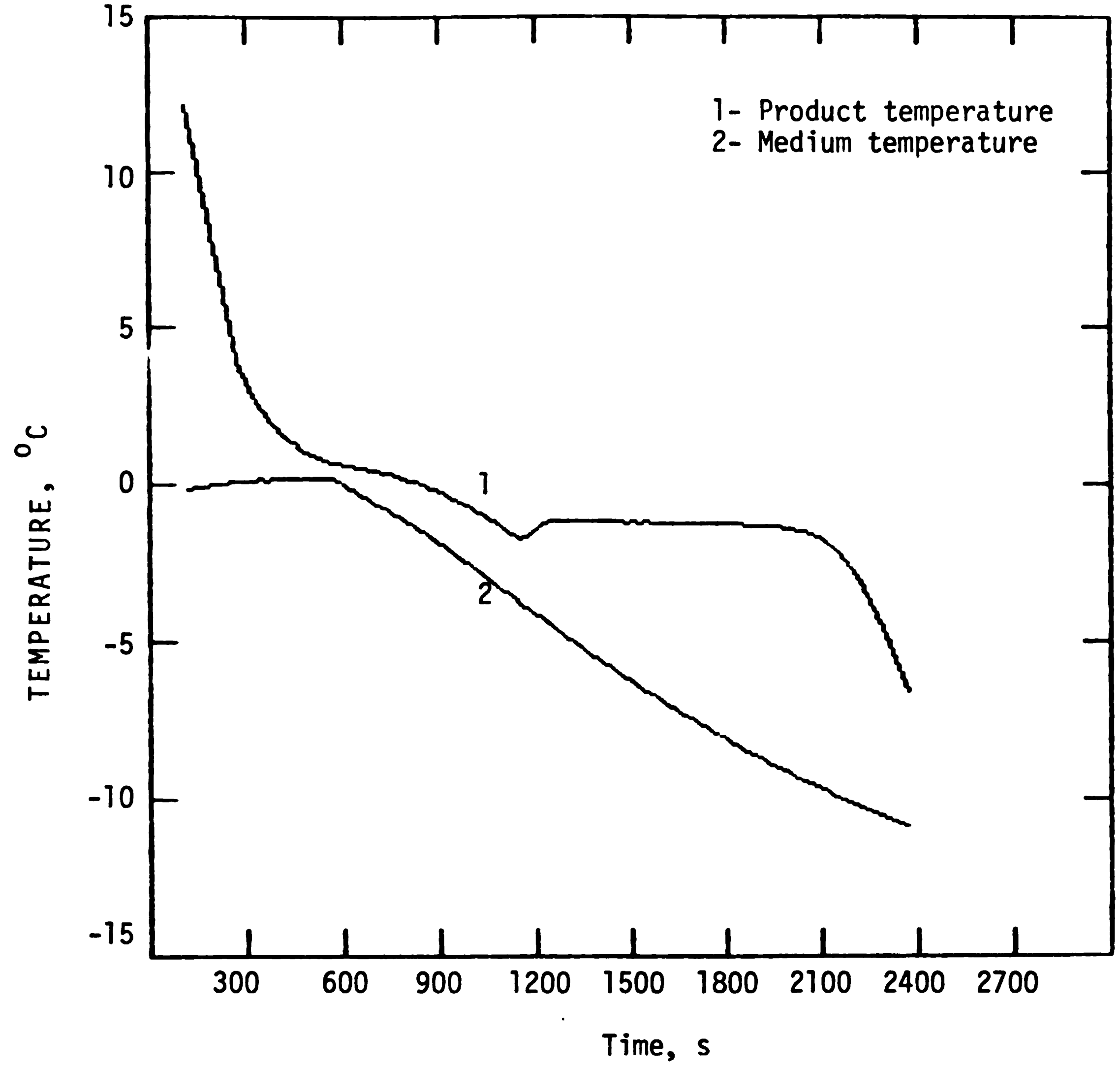

Figure 8. Freezing curve for beef at (T - Tm = 2 to 3 °C).

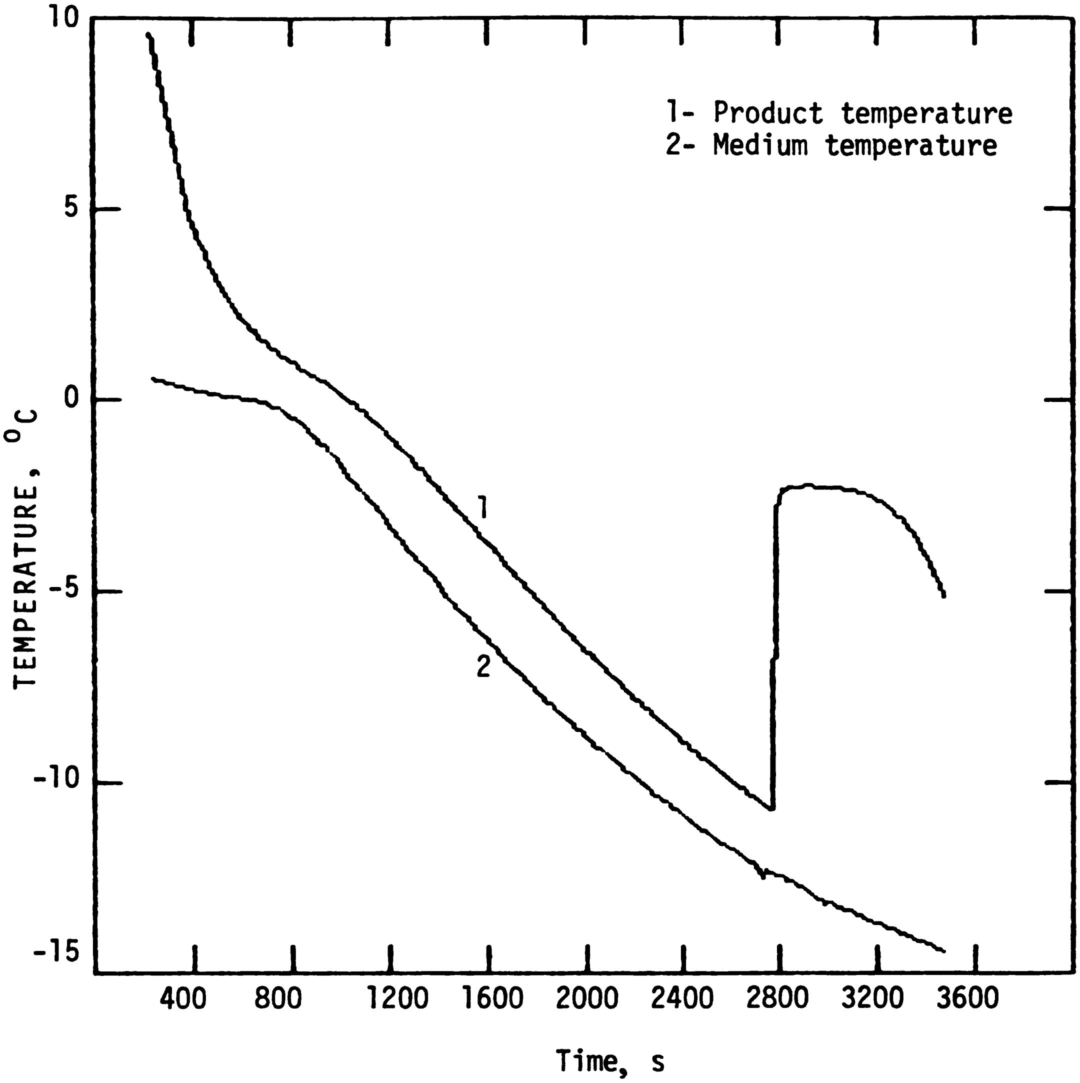

Figure 9. Freezing curve for apple at (T - Tm = 2 to 3 °C).

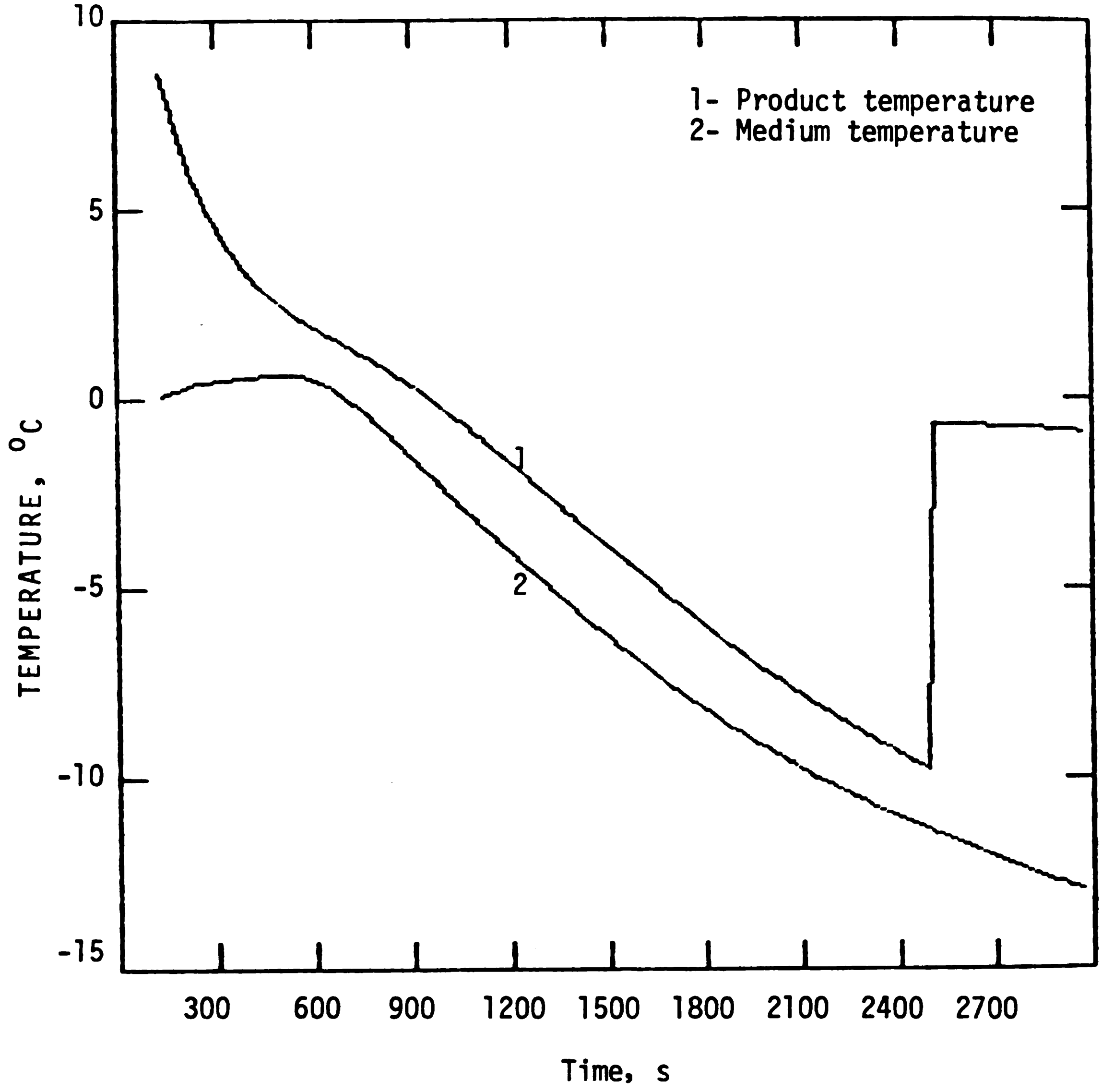

Figure 10. Freezing curve for tomato at (T - Tm = 2 to 3 °C).

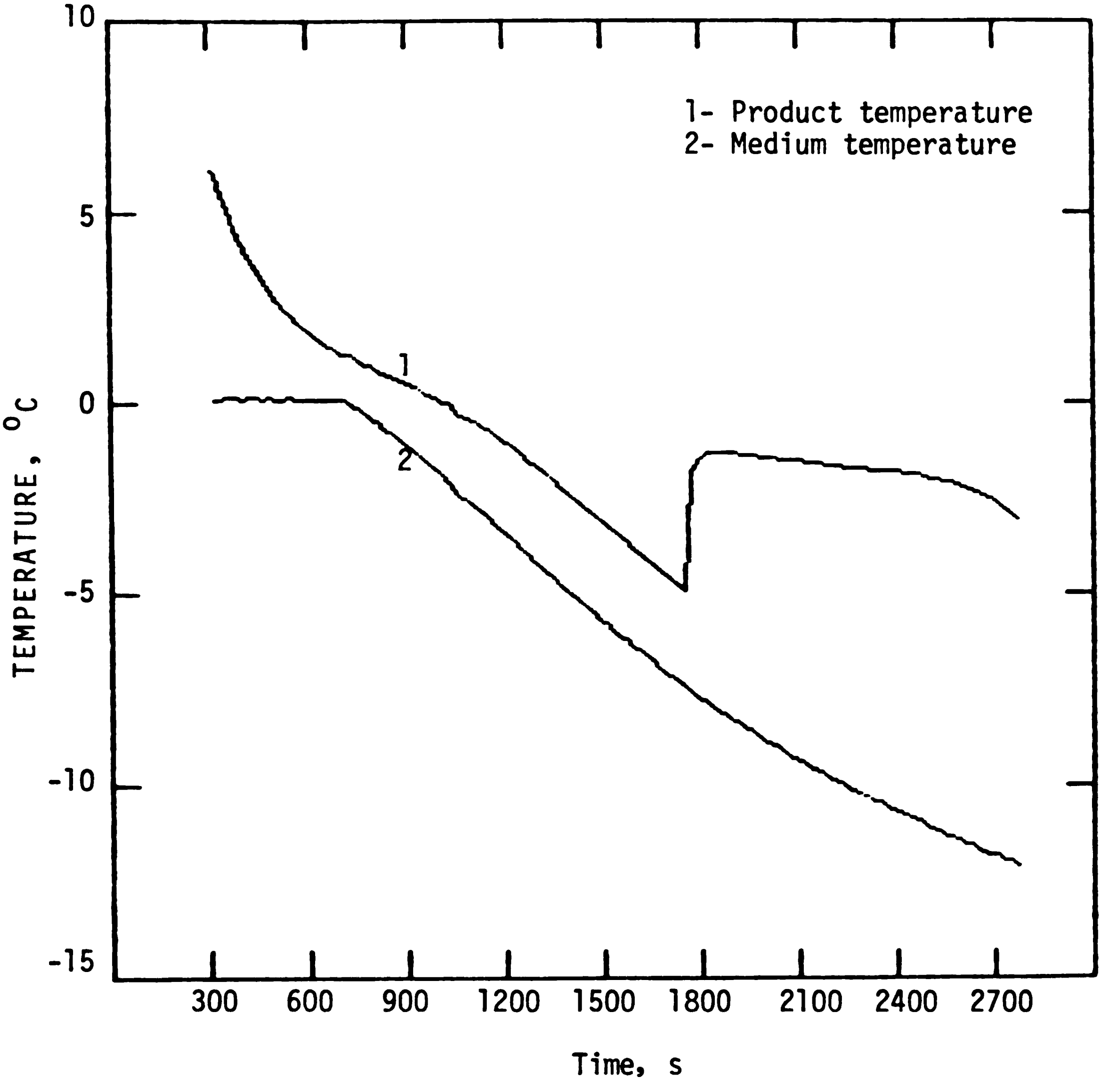

Figure 11. Freezing curve for potato at (T - Tm = 2 to 3 ^{o}C).

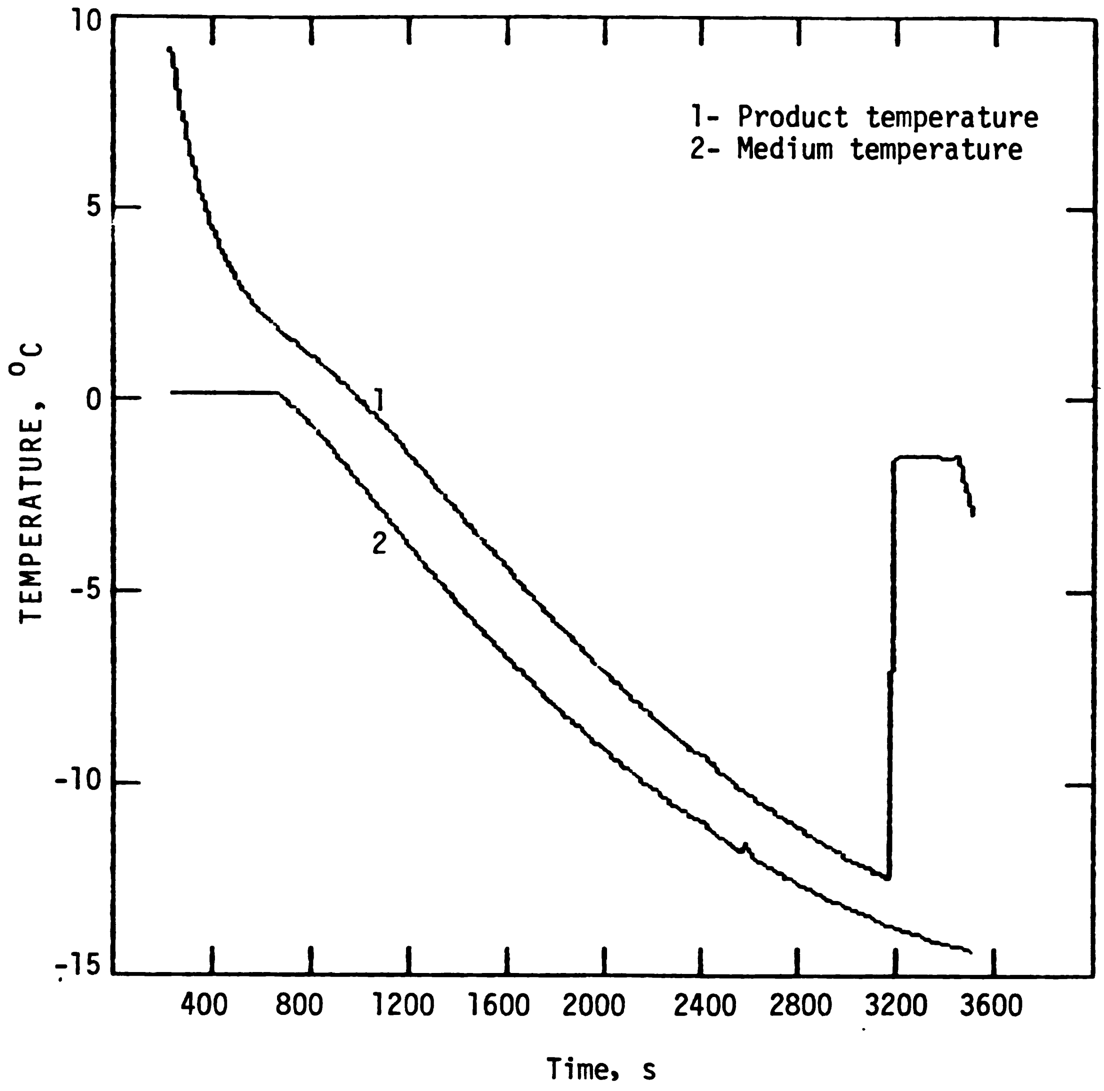

Figure 12. Freezing curve for pear at (T - Tm = 2 to 3 ^{o}C).

The temperature at which maximum supercooling takes place is extremely variable for the same product. Dorsey (1948) determined that the temperature of nucleation for water can vary up to 10°C. For the food products studied in this research when using a constant temperature difference of 2 to 3°C between the sample and the cooling bath the highest range of variation was for pear (±1.94°C) as shown in Table 4. Considering the greater complexity of composition of samples used in this research, the above variation is not unexpected.

The difference in initial freezing temperature for the products in Table 2 (cod, beef and pear) when compared to Table 4 could be in part the result of the use of samples from different origins although the products were always obtained from the same source and the same variety of food product was used to perform the experiments.

The method developed based on the results of this research is appropriate to determine initial freezing temperature of complex food systems because for all the products studied, the equilibrium as represented by the horizontal plateau at the initial freezing temperature was reached at the initial freezing temperature as observed for cod and the other food products (Figure 7 to 12). Another reason may be related to the maximum supercooling temperature that is variable for each product. The proposed method ensures that the nucleation temperature for the product is achieved due to the constant decrease of the cooling bath temperature.

Table 4. Freezing Constants Using Tm - Ts = 2 to 3 °C.

Product	T_f (°C)	T_{sc} (°C)	T_{m*} (°C)
Pear	-1.69 ± 0.15	-9.78 ± 1.94	-12.39 ± 0.90
Beef	-0.97 ± 0.13	-3.83 ± 1.49	-5.95 ± 1.46
Cod	-0.94 ± 0.03	-4.75 ± 1.10	-7.28 ± 0.95
Potato	-1.42 ± 0.09	-4.83 ± 0.52	-7.82 ± 0.25
Tomato	-0.72 ± 0.05	-8.16 ± 1.77	-10.13 ± 1.29
Apple	-2.06 ± 0.19	-9.28 ± 1.02	-11.08 ± 0.91

T_m = cooling medium temperature

T_{sc} = temperature of maximum supercooling

T_{m*} = medium temperature at which maximum supercooling occured.

5.1.3. Effect of Geometry and Sample Size on the Cooling Curve of Products

The solution for the heat transfer problem of constant decreasing in cooling medium temperature is given by Ozisik (1980) with the assumption that the product is initially at 0°C. To solve this problem the variation in cooling medium temperature with respect to time must be known in order to calculate the temperature in the center of the sample at desired time intervals according to the equations:

Slab

$$T(o,t) = 1.297 - 0.007t - \frac{4}{\ell}\sum\frac{\sin(m\,\pi/2)}{\beta}\left\{\exp(-0.00131\beta^2 t)\left[\frac{5.331}{\beta^2} - 1.297\right] - \frac{5.331}{\beta^2}\right\} \quad (36)$$

Cylinder

$$T(0,t) = 1.297 - 0.007t - \frac{2}{r}\sum\frac{1}{\beta J(\beta r)}\left\{\exp(-0.00131\beta^2 t)\left[\frac{5.331}{\beta^2} - 1.297\right] - \frac{5.331}{\beta^2}\right\} \quad (37)$$

The example presented in this section was calculated for the temperature in the center of a sample of beef (α = 1.313 x 10 cm/s) and the cooling medium temperature varied according to the relation:

$$T = -1.297 - 0.007\ t \quad (38)$$

determined by performing a linear regression of temperature as a function of time [Gill (1978)] using the data obtained from the freezing curve of the product as explained in section 4.3.2.2. It was also assumed that the medium temperature was equal to the temperature at the wall of the glass tube used to determine initial freezing temperature of food products.

The results for a cylinder and a slab sample of beef are presented in Table 5. It can be observed that for the same time interval lower

Table 5. Effect of sample size and geometry on the temperature in the center of a sample of beef with the cooling medium decreasing in temperature as a function of time.

	Slab (half thickness, cm)			Cylinder (radius, cm)		
Time (s)	0.7	2.0	3.0	0.7	2.0	3.0
0	0	0	0	0	0	0
200	-1.31	-0.017	-0.002	-1.97	-0.07	-0.028
300	-2.09	-0.085	-0.003	-2.73	-0.27	-0.039
400	-2.76	-0.206	-0.012	-3.44	-0.58	-0.070
500	-3.48	-0.377	-0.034	-4.14	-0.96	-0.150
600	-4.18	-0.589	-0.073	-4.84	-1.40	-0.270
700	-4.89	-0.841	-0.129	-5.55	-1.89	-0.450
800	-5.59	-1.127	-0.205	-6.24	-2.41	-0.640
900	-6.29	-1.446	-0.300	-6.94	-2.97	-0.880
1000	-6.99	-1.795	-0.415	-7.64	-3.55	-1.160

Temperature is ^{o}C.

temperatures in the center will be reached for smaller samples as expected. The geometry is also important. It is evident in Table 5 that for the same magnitude of half thickness (slab) and radius (cylinder) higher cooling rates will be achieved by the cylindrical shape.

Sample size and geometry are important when determining initial freezing temperature of food products due to the fact that smaller samples may freeze too fast. In this situation (rapid freezing) the equilibrium at the initial freezing temperature may not be observed. Larger samples would require longer times to reach the initial freezing temperature; however, the rate of cooling of the cooling medium can be increased to achieve faster determinations.

For the products analyzed and the equipment available in this research, the radius of 0.7 cm and the cooling medium decreasing in temperature according to equation (38) provided the conditions required to achieve the equilibrium at the initial freezing temperatures.

5.2. Effect of the Liquid Fraction on the Water Activity and Initial Freezing Temperature

The results in Tables 2 and 6 indicate that there is no significant difference ($p<0.01$) between the initial freezing temperatures for the liquid fraction and the whole product as measured in this research using the horizontal plateau during latent heat removal from freezing curves. This observation seems reasonable because the liquid fractions contain the soluble solids responsible for the water activity lowering and freezing point depression of foods. Some literature values [Dyer

Table 6. Determination of Water Activity

Product		Predicted A	 B	Experimental SC-10
Pear	1	.9831 ± .002	.9837 ± .002	.9833 ± .0013
	2	.9834 ± .001	.9840 ± .001	.9836 ± .0013
Tomato	1	.9938 ± .001	.9938 ± .001	.9948 ± .0002
	2	.9936 ± .001	.9938 ± .001	.9945 ± .0003
Beef	1	.9889 ± .001	.9885 ± .001	.9904 ± .0008
	2	.9888 ± .000	.9890 ± .001	.9899 ± .0051
Cod	1	. 9904 ± .001	.9907 ± .001	.9924 ± .0040
Chicken	1	.9922 ± .001	.9922 ± .001	.9930 ± .0003

1= whole product 2= liquid fraction

A = calculated from initial freezing temperature by equation (28)

B = calculated from initial freezing temperature by equation (30).

SC 10 = determined experimentally at 20 °C using a thermocouple psychrometer et al (1967), Hill and Sunderland (1966)] indicate that the vapor pressure of the liquid phase is higher (10%) than the vapor pressure of the whole product, suggesting that the product structure has an influence on the water activity. This difference was not observed in current investigation. Labuza (1975) concluded that the effect of capillaries on water activity is very small in food systems. The pore size in foods varies from 10 to 100 μ and in this range, the effect on water activity lowering would be from 0.000001 to 0.00001 water activity units. This magnitude would be considered negligible for most food applications. Another explanation for the observations that water activities and initial freezing temperatures are equal for the liquid fraction and the whole product, is that only the soluble solids are responsible for the depression of the water activity and the initial freezing temperature of food systems [Chen and Karmas (1980) and Miraco et al (1981)].

Tables 2 and 6 suggest that a determination of the initial freezing temperature of the liquid fraction in a food product could be used to evaluate that of the whole product because significant differences between initial freezing temperature of the liquid fraction and the whole product for the foods analyzed in this research could not be detected. Based on this observation, any method described in the literature for the determination of the initial freezing temperature in liquid systems, such as osmometry [APHA (1967) and AOAC (1965)], can be used to determine the initial freezing temperature of the whole product. The advantage of this technique is that it is rapid (3 minutes for each determination) and the results are reliable [Fennema et al (1973)].

5.3. The Use of Thermodynamic Expressions in the Prediction of Initial Freezing Temperature and Water Activity of Foods

According to Lerici (1983), equations (28) and (30) are recommended only for the determination of water activity in liquid food systems. However, the results presented (Table 2 and 6) indicate that the values of water activity calculated using these equations are in close agreement with the values determined experimentally by an SC-10 thermocouple psychrometer. This may be due to the fact that in this research, only products with high water activities ($Aw > 0.98$) were measured. According to Labuza (1975), these equations should only be applied in situations where the products have very low solid content. Nevertheless, Lerici (1983) used these equations at higher concentrations (>20%) for electrolytes and nonelectrolyte solutions as well as some liquid foods and found negligible differences between the values of water activity determined experimentally and calculated by the thermodynamic equations.

Differences between the results for water activity determined using the two equations could not be detected for the products analyzed. The complete equation (30) is recommended to be used for all situations since the difference in heat capacity of ice and water is not assumed to be equal to zero.

The results for the evaluation of the initial freezing temperature using the value of the water activity determined by a thermocouple psychrometer at $20^{o}C$ as calculated from equations (28) and (30) are presented in Table 7. Although a student's 't' (test statistic) between the results of the two equations showed that significant difference

Table 7. Values of initial freezing temperature found experimentally and predicted using the water activity obtained with a SC-10 Thermocouple Psychrometer.

Product		T_f measured, ^oC	T_f predicted, ^oC	
			A	B
Pear	1	-1.69 ± 0.14	-1.69 ± 0.13	-1.82 ± 0.13
	2	-1.65 ± 0.12	-1.65 ± 0.13	-1.78 ± 0.18
Tomato	1	-0.64 ± 0.07	-0.50 ± 0.02	-0.63 ± 0.03
	2	-0.64 ± 0.08	-0.52 ± 0.03	-0.65 ± 0.03
Beef	1	-1.16 ± 0.03	-0.96 ± 0.08	-1.08 ± 0.08
	2	-1.16 ± 0.01	-0.99 ± 0.05	-1.12 ± 0.06
Cod	1	-0.96 ± 0.10	-0.74 ± 0.02	-0.87 ± 0.02
Chicken	1	-0.81 ± 0.05	-0.68 ± 0.05	-0.80 ± 0.04

1 = whole product 2 = liquid fraction

A = T_f calculated by equation (28)

B = T_f calculated by equation (30)

T_f Predicted = used values of Aw determined by a SC-10 at 20^oC.

($p<0.01$) does not exist, the use of the complete expression (equation 30) is recommended for the reasons previously presented.

The reason for the differences in results using equation (30) as compared to equation (28) is that the calculation of the initial freezing temperature is accomplished by trial and error using an HP-41cx pocket calculator. Softwear from Hewlett Packard (Math Application Pac) to solve equation (30) was used to determine the initial freezing temperature when the water activity of the product is known. It is possible that better results could be obtained using a high speed computer. For the products analyzed, the approach using water activity determined at room temperature (20^{o}C) predicted initial freezing temperature to within 0.1^{o}C of experimental value in most situations.

5.4. Effect of Product Composition on Water Activity and Initial Freezing Temperature

The data presented in Tables 8 and 9 illustrate the variation in water activity as a function of the soluble solids and total solids. It is observed in that the higher solid concentration had a noticable effect on the depression of water activity and initial freezing temperature for food products. The value of the water activity determined experimentally (Aw_e) did not differ significantly ($p<0.01$) from the values calculated using equation (28) or equation (30) by performing an analysis of variance [Gill (1978)] and considering each column as a treatment group. Based on the results of statistical analysis, regression equations of the experimentally determined water activity (Aw_e) as a function of the

Table 8. Initial Freezing Temperature and Water Activity of Some Food Products (Lerici et al 1983).

Product	TS	T_f	Aw_i	Aw_r	Aw_e	Aw_{ss}
Freeze-	10	-0.6	.994	.994	.997	.998
dried	20	-1.6	.985	.985	.990	.989
Skim Milk	30	-2.3	.978	.978	.982	.981
	40	-4.1	.961	.961	.971	.972
Regression equation		Aw = 1.007 - 0.001 TS		$r^2 = 0.99$		
Dried	5	-0.5	.995	.995	.998	.997
Tomato	10	-0.9	.991	.991	.989	.991
Juice	15	-1.6	.985	.985	.985	.985
	40	-2.0	.981	.981	.980	.979
Regression equation		Aw = 1.002 - 0.001 TS		$r^2 = 0.97$		

TS = Total solids

Aw_i = calculated by equation (28)

Aw_r = calculated by equation (30)

Aw_e = determined experimentally at 25°C

Aw_{ss} = calculated by regression equation (Aw_c x TS)

Table 9. Initial Freezing Temperature and Water Activity of Some Binary Solutions (Lerici et al 1983).

Solution	SS	T_f	Aw_i	Aw_r	Aw_e	Aw_{ss}
Sucrose	5	-0.3	.997	.997	.996	.998
	10	-0.6	.994	.994	.992	.992
	15	-1.0	.990	.990	.988	.987
	20	-1.4	.987	.987	.983	.981
	30	-2.8	.973	.973	.971	.969
	40	-4.7	.955	.955	.955	.958
Regression equation		Aw = 1.004 - 0.0012 SS			r^2 = .982	
Lactose	1	-0.1	.999	.999	.999	.999
	3	-0.3	.997	.997	.997	.997
	5	-0.4	.996	.996	.995	.997
	8	-0.6	.994	.994	.995	.992
Regression equation		Aw = 1.000 - 0.003 SS			r^2= 1.00	
Glycerol	5	-1.1	.990	.990	.991	.996
	10	-2.3	.976	.976	.981	.981
	20	-5.5	.948	.949	.958	.952
	30	-9.7	.906	.909	.927	.922
	40	-15.0	.853	.859	.887	.893
Regression equation		Aw = 1.010 - 0.003 SS			r^2=.980	

SS = percent soluble solids

soluble solids or total solids were determined for each product.

The general trend is that the regression equations have an intercept very close to one (one is ideal) in all of the results (Table 8 and 9) for pure binary solutions and food systems. All of the regression equations have very high correlation coefficients and the differences between the predicted and the experimental values of the water activity were not significant ($p<0.01$). Frenzi et al (1974) proposed a relationship for binary solutions in which the water activity was a function of the molality of the solution. For some products this relationship is not linear [Miraco et al (1981) and Chirife and Fontan (1980)] and a quadratic coefficient must be determined. However, the results (Table 8 and 9) presented a linear relationship of water activity as a function of the solid content.

It is possible, based on these observations, that a simple measurement of the percent soluble solids in the product by a refractometer could be used to determine the freezing point depression and the water activity of the product, if the water activity is known as a function of the soluble solids. For this situation, equation (30) could be modified and presented in the following form:

$$-\ln Aw\ (SS) = 27.622 - \frac{528.373}{Tf} - 4.579 \ln T_f \qquad (39)$$

SS = soluble solids.

This procedure requires that an empirical relationship between water activity and soluble solids must be determined for each product in question.

In situations where it is difficult to extract the liquid fraction of the product such as beef, chicken, cod etc., it would be necessary to determine the water activity as a function of the total solids. This would allow prediction of water activity by a simple measurement of the moisture content using any method available.

Bakshi and Johnson (1983) determined initial freezing temperature as a function of the percent total solid for whey at various concentrations and found the relationship to be linear (Table 10). These results are consistent with the results of this investigation. An increase in the total solid of a product lowered the water activity and the initial freezing temperature of the product as is evident in Tables 8 and 9. However, products with the same amount of soluble solids can not have the same water activity and initial freezing temperature due to different components have different activity coefficients as determined by Chen and Karmas (1980) for many food components.

5.5. Percent Unfrozen Water at Subfreezing Temperatures

Percent unfrozen water at subfreezing temperatures for several food products are presented in Tables 11 and 12 and A.1 to A.14. From these data, the mole fraction of unfrozen water, activity coefficient and water activity were calculated by the method described in part five of the Materials and Methods Section.

The activity coefficient varies as expected for most of the products analyzed. Apparently the relationship of the activity coefficient and temperature is linear according to the regression

Table 10. Initial Freezing Temperature of Whey as a Funciton of Solid Content (Bakshi and Johnson; 1983).

T_f, ^oC	Solid Content (%)
-0.23	2.80
-0.39	4.72
-0.84	9.67
-1.37	14.93
-1.93	19.76

Regression equation $T_f = 0.0825 - 0.0997$ Solids $r = 0.998$

Table 11. Freezing Characteristics of Beef.

T^oC	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-1.1	92	68.54	.9905	.9989	.9894	.9894
-2.2	48	35.76	.9820	.9968	.9788	.9789
-3.3	37	27.56	.9768	.9914	.9684	.9693
-4.4	28	20.86	.9695	.9882	.9581	.9583
-5.6	24	17.88	.9647	.9834	.9487	.9470
-6.7	22	16.39	.9616	.9742	.9368	.9370
-7.8	20	14.90	.9579	.9675	.9256	.9271
-9.4	18	13.41	.9534	.9570	.9124	.9126
-12.2	15	11.18	.9446	.9399	.8878	.8880
-15.0	13	9.69	.9367	.9223	.8639	.8635
-17.8	12	8.94	.9317	.9023	.8407	.8401
-20.5	12	8.94	.9317	.8790	.8189	.8220
-23.3	11	8.19	.9259	.8609	.7971	.8119
-28.9	10	7.45	.9190	.8223	.7557	.7528
-40.0	10	7.45	.9190	.7424	.6822	.6812

$\% m_u$ = % unfrozen water (Riedel) m_u = mass of unfrozen water

X_u= mole fraction of unfrozen water

γ = activity coefficient

Aw_c = Water activity calculated by $X_u \times \gamma$

Aw_e = Experimental value of water activity

Me = 700.14

Table 12. Freezing characteristics of Cod.

T^oC	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-1.1	88	70.66	.9914	.9980	.9894	.9894
-2.2	45	36.14	.9833	.9955	.9788	.9789
-3.3	32	25.96	.9768	.9914	.9684	.9693
-4.4	26	20.88	.9714	.9863	.9581	.9583
-5.6	22	17.67	.9663	.9799	.9469	.9470
-6.7	20	16.60	.9642	.9734	.9385	.9370
-7.8	18	14.45	.9591	.9663	.9268	.9271
-9.4	16	12.85	.9543	.9561	.9124	.9126
-12.2	14	11.24	.9481	.9364	.8878	.8880
-15.0	13	10.44	.9443	.9149	.8639	.8635
-17.8	12	9.64	.9440	.8905	.8407	.8401
-20.5	11	8.83	.9348	.8761	.8190	.8220
-23.3	10	8.03	.9288	.8583	.7971	.8119
-28.9	10	8.03	.9288	.8137	.7557	.7528
-40.0	10	8.03	.9288	.7345	.6822	.6812

Me = 576.63   all the symbols as in table 11 equations presented in Table 13. Based on these results, it is evident that the calculated values of the activity coefficient and mole fraction of unfrozen water are accurate. By multiplication of the mole fraction of unfrozen water by the activity coefficient, a value equal to the experimental water activity is obtained. In addition, no significant differences could be detected between the calculated value of water activity and experimental value of the water activity at subfreezing temperatures (Table 11 and 12).

As is evident for the specific cases of beef and cod (Table 10 and 11), the assumption that the activity coefficient is one during the freezing process results in a prediction of low values for the percent of unfrozen water at each subfreezing temperature, as shown by Heldman (1974). The results for beef illustrate a range of the activity coefficients from 0.9989 close to the initial freezing temperature to 0.742 at -40°C. This can be explained by the fact that these products (beef and cod) contain high amounts of solids (Table 14) and the concentration effect during freezing causes a significant deviation from Raoult's Law. The water activity of these products can not be assumed equal to the mole fraction of unfrozen water. For these products, equation (35) can only be applied to determine the percent unfrozen water at subfreezing temperatures if the activity coefficient is known as a function of temperature for the product in question.

In fruits and vegetables, the assumption that the water activity at subfreezing temperatures is equal to the mole fraction of unfrozen water seems to be a reasonable approach. The range of activity coefficients calculated in this investigation is from 0.940 to 1.003.

Table 13. Regression equations of the activity coefficient as a function of Temperature.

Product	Equation	r^2
Apple juice	$\gamma = 1.005 + 0.003\ T$	.992
Asparargus	$= 1.005 + 0.003\ T$	.973
Bilberries	$= 1.003 + 0.003\ T$	.974
Bilberry Juice	$= 1.003 + 0.002\ T$	.963
Carrot	$= 1.002 + 0.002\ T$	.943
Orange Juice	$= 1.006 + 0.003\ T$	.990
Peach	$= 1.001 + 0.002\ T$	.911
Raspberry	$= 1.004 + 0.003\ T$	.990
Raspberry Juice	$= 1.004 + 0.003\ T$	.993
Spinach	$= 1.002 + 0.003\ T$	.941
Strawberry	$= 1.005 + 0.003\ T$	.981
Strawberry Juice	$= 1.005 + 0.003\ T$	.980
Tomato Pulp	$= 1.001 + 0.002\ T$	.965
Pear	$= 1.008 + 0.002\ T$	.965
Beef	$= 1.017 + 0.007\ T$	.996
Cod	$= 1.016 + 0.007\ T$	.997

T in ^{o}C.

Table 14. Moisture and Soluble Solids Content.

Product	%moisture	%soluble solids	Total Solids
Pear	84.87±0.80	12.47	15.13
Tomato	94.11±0.44	4.45	5.89
Beef	72.62±0.53	15.90	27.38
Cod	80.27±0.18	-	19.63
Chicken	76.56±1.00	-	23.44

The low variation can be explained by the low soluble solid content in these products as well as the simple composition when compared to beef and cod. The concentration effect and the deviation from Raoult's Law seems to be negligible and in this situation, the method developed by Heldman (1974) to predict percent unfrozen water can be applied with small differences from the experimental values of percent unfrozen water at subfreezing temperatures.

5.6. A Method to Predict Percent of Unfrozen Water at Subfreezing Temperatures

Tables 15, 16 and 17 present the predicted values of percent unfrozen water at subfreezing temperatures for cod, beef and pear calculated by the procedure described in this research (Part 3.2.). Comparison of this data to the experimental values obtained by Reidel (1957) shows that the prediction was accomplished to within 5% of the experimental value in all cases. When compared to values calculated by the method developed by Heldman (1974), it can be observed that the prediction of unfrozen water are in close agreement for the two methods in the specific case of pear (Figure 13). This agreement should be associated with the fact that the variation in activity coefficient for pear at subfreezing temperatures is small (from 1.002 to 0.96). The assumption that the activity coefficient is one at these temperatures does not significantly influence the prediction of percent unfrozen water for pear. For cod (Figure 14) and beef (Table 17), the variation of activity coefficient as a function of temperature is from

Table 15. Percent unfrozen water calculated by the method developed in this research compared to Riedel's vaules for cod.

T ^{o}C	γ_1	X_{u1}	$\%m_{u1}$	γ_2	X_{u2}	$\%m_{u2}$
-1.1	.9980	.9914	88	.998	.991	88
-2.2	.9955	.9833	45	.995	.984	47
-3.3	.9914	.9768	32	.990	.976	34
-4.4	.9863	.9714	26	.982	.975	30
-5.6	.9799	.9663	22	.974	.972	26
-6.7	.9734	.9642	20	.966	.969	24
-7.8	.9663	.9591	18	.958	.967	22
-9.4	.9561	.9543	16	.946	.964	20
-12.2	.9364	.9481	14	.926	.958	17
-15.0	.9149	.9443	13	.908	.951	15
-17.8	.8905	.9440	12	.888	.946	13
-20.5	.8761	.9348	11	.870	.941	12
-23.3	.8583	.9288	10	.852	.935	11
-28.9	.8137	.9288	10	.812	.930	10
-40.0	.7345	.9288	10	.734	.929	10

1 = values from Riedel

2 = values calculated by the method developed in this research

γ = activity coefficient

Table 16. Percent unfrozen water calculated by the method developed in this research compared to Riedel's value for pear.

T ^{o}C	γ_1	X_{u1}	$\%m_{u1}$	γ_2	X_{u2}	$\%m_{u2}$
-2.2	1.0020	.9769	72	1.002	.976	72
-3.3	1.0019	.9664	49	1.001	.967	51
-4.4	1.0010	.9571	38	.999	.959	39
-5.6	.9988	.9480	31	.997	.949	35
-6.7	.9958	.9407	27	.995	.941	28
-7.8	.9954	.9311	23	.991	.933	25
-9.4	.9941	.9178	19	.991	.920	20
-12.2	.9886	.8981	15	.988	.898	15
-15.0	.9863	.8759	12	.983	.878	12
-17.8	.9837	.8546	10	.979	.858	10
-20.5	.9738	.8410	9	.976	.839	9
-23.3	.9668	.8246	8	.971	.821	8
-28.9	.9651	.7788	6	.965	.778	6

1 = values from Riedels

2 = values calculated by the method developed in this research

Table 17. Percent unfrozen calculated by the method developed in this research compared to the Riedel's values for beef.

T°C	γ_1	X_{u1}	$\%m_{u1}$	γ_2	X_{u2}	$\%m_{u2}$
-1.1	.9989	.9905	92	.999	.991	92
-2.2	.9968	.9820	48	.997	.982	48
-3.3	.9914	.9768	37	.990	.978	39
-4.4	.9882	.9695	28	.982	.975	34
-5.6	.9834	.9647	24	.974	.972	30
-6.7	.9742	.9616	22	.966	.969	27
-7.8	.9675	.9579	20	.958	.967	25
-9.4	.9570	.9534	18	.948	.962	22
-12.2	.9399	.9446	15	.929	.955	19
-15.0	.9223	.9367	13	.910	.949	16
-17.8	.9023	.9317	12	.892	.942	14
-20.5	.8790	.9317	12	.874	.937	13
-23.3	.8609	.9259	11	.854	.933	12
-28.9	.8223	.9190	10	.818	.923	10
-40.0	.7424	.9190	10	.742	.919	10

1 = data from Riedel

2= data calculated by the method developed in this research

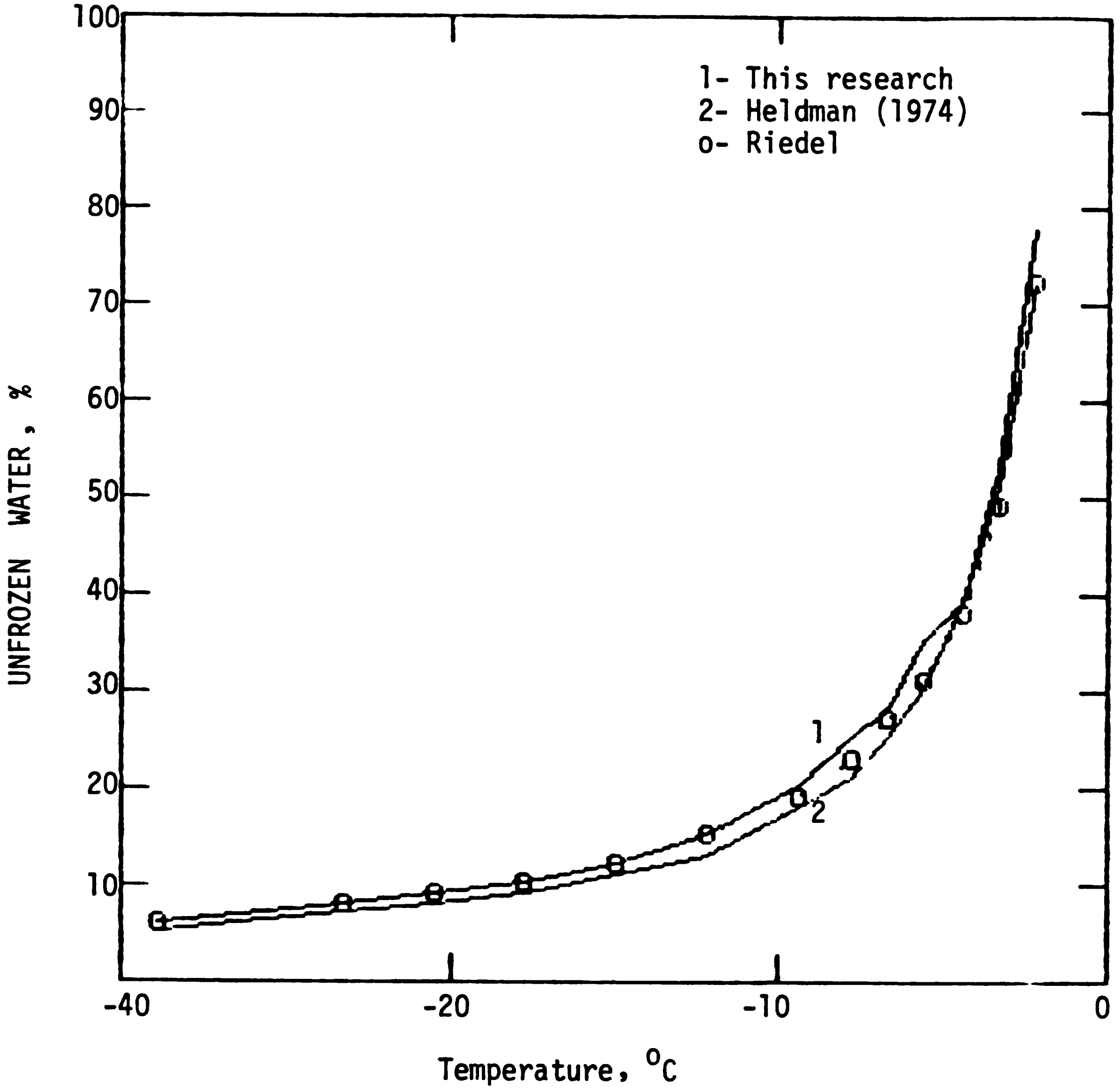

Figure 13. Percent unfrozen water for pear.

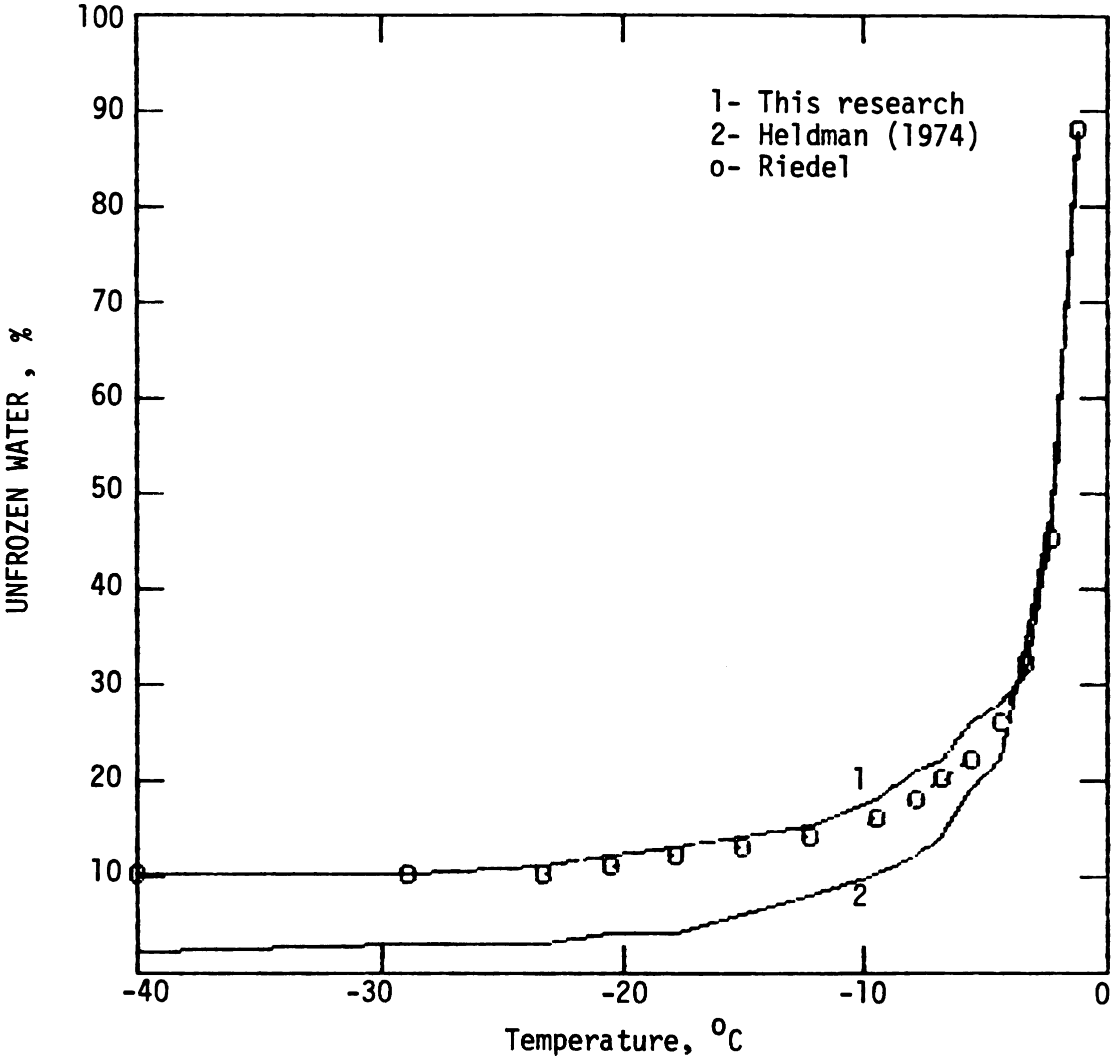

Figure 14. Percent unfrozen water for cod.

0.999 to 0.73. Therefore, the assumption that the activity coefficient is one [Heldman (1974)] causes prediction of lower values for the percent of unfrozen water at subfreezing temperatures. The activity coefficient tends to be constant at temperature near the initial freezing temperature. As a result, the selection of the temperature, close to the initial freezing temperature, in order to calculate the activity coefficient should be at least one degree below the initial freezing temperature of the product. This procedure ensured a linear relationship between activity coefficient and temperature for the products studied in this research.

The limitations of this procedure to determine percent unfrozen water at subfreezing temperature are: a) the assumption of linear relationship between the activity coefficient and temperature; b) the percent unfrozen water at a subfreezing temperature (-40°C) must be previously known in order to predict the percent unfrozen water for the product.

Based on these results, the activity coefficient as a function of temperature can be calculated and the percent of unfrozen water at one temperature must be known in order to predict percent unfrozen water at subfreezing temperatures using the procedure presented in this research.

6. CONCLUSIONS

1. The initial freezing temperature and the water activity of the liquid fraction from a food product are the same as for the whole product indicating that only the soluble solids are responsible for the depression of the activity and initial freezing temperature for the food products studied in this research.

2. Thermodynamic expressions used to predict the water activity of liquid foods can also be applied in complex food systems for the reason explained above.

3. Thermodynamic equations can be used to predict initial freezing temperature of a complex food system using water activity data obtained at room temperature.

4. The measurement of initial freezing temperature for food products using constant temperature difference between the cooling medium and sample produces freezing curves with a well defined horizontal plateau indicating the equilibrium condition during the latent heat removal.

5. Activity coefficients calculated for complex food systems using thermodynamic relationships can be used to explain the freezing characteristics of water in food products.

6. Prediction of unfrozen water at subfreezing temperatures in complex food systems, can be accomplished by the procedure developed in this research by assuming linear relationship between activity

coefficient and temperature resulting in predicted values of percent unfrozen water within 5% of the experimentally determined value.

APPENDIX A

Table A.1. Freezing Characteristics of Pears

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-2.2	72	60.34	.9769	1.0020	.9788	.9789
-3.3	49	41.06	.9664	1.0019	.9684	.9693
-4.4	38	31.84	.9571	1.0010	.9581	.9583
-5.6	31	25.98	.9480	.9988	.9469	.9470
-6.7	27	22.63	.9407	.9958	.9385	.9370
-7.8	23	19.27	.9311	.9954	.9268	.9271
-9.4	19	15.92	.9178	.9941	.9124	.9126
-12.2	15	12.57	.8981	.9886	.8878	.8880
-15.0	12	10.06	.8759	.9863	.8639	.8635
-17.8	10	8.38	.8546	.9837	.8407	.8401
-20.5	9	7.54	.8410	.9738	.8190	.8220
-23.3	8	6.70	.8246	.9668	.7971	.8119
-28.9	6	5.02	.7788	.9651	.7539	.7528

Me = 189 all the symbols equal to table 11

Table A.2. Freezing Characteristics of Apple Juice

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-2.2	63	54.94	.9794	.9994	.9788	.9789
-3.3	44	38.37	.9707	.9976	.9684	.9693
-4.4	34	29.64	.9624	.9955	.9581	.9583
-5.6	28	24.46	.9548	.9917	.9469	.9470
-6.7	24	20.93	.9476	.9886	.9368	.9370
-7.8	20	17.44	.9378	.9882	.9268	.9271
-9.4	17	14.82	.9276	.9836	.9124	.9126
-12.2	14	12.21	.9134	.9720	.8878	.8880
-15.0	11	9.59	.8923	.9681	.8639	.8642
-17.8	9	7.84	.8714	.9647	.8407	.8401
-20.5	8	6.97	.8576	.9549	.8190	.8220
-23.3	7	6.10	.8405	.9484	.7971	.8119

Me = 199.05 87.20 % moisture T_f = -1.44 °C

Table A.3. Freezing Characteristics of Asparargus.

T °C	%m_u	m_u	X_u	γ	Aw_c	Aw_e
-1.1	55	50.93	.9899	.9995	.9894	.9894
-2.2	28	25.92	.9803	.9985	.9788	.9789
-3.3	20	18.52	.9726	.9957	.9684	.9693
-4.4	16	14.82	.9660	.9918	.9581	.9583
-5.6	12	11.11	.9551	.9914	.9469	.9470
-6.7	10	9.26	.9466	.9896	.9368	.9370
-7.8	9	8.33	.9410	.9849	.9268	.9271
-9.4	7	6.48	.9254	.9830	.9124	.9126
-12.2	6	5.56	.9142	.9712	.8878	.8880
-15.0	5	4.63	.8987	.9613	.8639	.8635
-17.8	4	3.70	.8764	.9593	.8407	.8401

Me = 255.43 92.60 % moisture T_f = -0.66 °C

Table A.4. Freezing Characteristics of Bilberries.

T ^oC	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-2.2	50	42.55	.9802	.9986	.9789	.9789
-3.3	35	29.79	.9720	.9963	.9684	.9693
-4.4	27	22.97	.9640	.9939	.9581	.9583
-5.6	22	18.72	.9561	.9904	.9469	.9470
-6.7	19	16.17	.9496	.9865	.9368	.9370
-7.8	17	14.47	.9440	.9818	.9268	.9271
-9.4	14	11.91	.9328	.9781	.9124	.9126
-12.2	11	9.36	.9160	.9692	.8878	.8880
-15.0	9	7.66	.8992	.9607	.8639	.8635
-17.8	7	5.96	.8741	.9618	.8407	.8401
-20.5	6	5.10	.8559	.9568	.8190	.8220
-23.3	5	4.26	.8323	.9534	.7968	.8119

Me = 312.07 85.10 % moisture T_f = -1.11 ^oC

Table A.5. Freezing Characteristics of Bilberry Juice.

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-2.2	50	44.75	.9812	.9976	.9788	.9789
-3.3	35	31.33	.9733	.9950	.9684	.9673
-4.4	27	24.17	.9657	.9921	.9581	.9583
-5.6	22	19.69	.9582	.9883	.9469	.9470
-6.7	19	17.01	.9519	.9842	.9368	.9370
-7.8	17	15.22	.9466	.9791	.9268	.9271
-9.4	14	12.53	.9359	.9749	.9124	.9126
-12.2	11	9.85	.9198	.9652	.8878	.8880
-15.0	9	8.05	.9036	.9560	.8639	.8635
-17.8	7	6.27	.8796	.9557	.8407	.8401
-20.5	6	5.37	.8622	.9499	.8190	.8220
-23.3	5	4.48	.8392	.9495	.7557	.8119

Me = 220.95 89.5 % moisture T_f =-1.11 °C

Table A.6. Freezing Characteristics of Carrots.

T °C	%m_u	m_u	X_u	γ	Aw_c	Aw_e
-2.2	50	43.75	.9802	.9986	.9788	.9789
-3.3	35	30.61	.9719	.9964	.9684	.9693
-4.4	27	23.63	.9639	.9939	.9581	.9583
-5.6	22	19.25	.9561	.9904	.9469	.9470
-6.7	19	16.63	.9495	.9866	.9368	.9370
-7.8	17	14.88	.9439	.9819	.9268	.9271
-9.4	14	12.25	.9327	.9782	.9124	.9126
-12.2	11	9.63	.9159	.9693	.8878	.8880
-15.0	9	7.88	.8992	.9607	.8639	.8635
-17.8	7	6.12	.8738	.9621	.8407	.8401
-20.5	6	5.25	.8559	.9568	.8190	.8220
-23.3	5	4.38	.8321	.9570	.7971	.8119

Me = 254.57 87.5 % moisture T_f = -1.11 °C

Table A.7. Freezing Characteristics of Orange Juice.

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-2.2	53	41.17	.9776	1.0013	.9788	.9789
-3.3	37	32.93	.9721	.9962	.9684	.9693
-4.4	29	25.81	.9647	.9931	.9581	.9583
-5.6	23	20.47	.9559	.9906	.9469	.9470
-6.7	20	17.80	.9496	.9865	.9368	.9370
-7.8	17	15.13	.9412	.9847	.9268	.9271
-9.4	15	13.35	.9339	.9770	.9124	.9126
-12.2	12	10.68	.9187	.9664	.8878	.8880
-15.0	9	8.01	.8945	.9658	.8639	.8635
-17.8	8	7.12	.8828	.9523	.8407	.8401
-20.5	7	6.23	.8623	.9497	.8190	.8220
-23.3	6	5.34	.8496	.9382	.7971	.8119

Me = 209.65 89 % moisture T_f = -1.17 °C

Table A.8. Freezing Characteristics of Peaches.

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-2.2	69	58.71	.9794	.9995	.9788	.9789
-3.3	48	40.85	.9707	.9976	.9684	.9693
-4.4	37	31.49	.9623	.9956	.9581	.9583
-5.6	30	25.53	.9539	.9927	.9469	.9470
-6.7	26	22.13	.9472	.9890	.9368	.9370
-7.8	22	18.72	.9381	.9879	.9268	.9271
-9.4	18	15.32	.9254	.9860	.9124	.9126
-12.2	15	12.77	.9118	.9737	.8878	.8880
-15.0	12	10.21	.8921	.9684	.8639	.8635
-17.8	10	8.51	.8733	.9627	.8407	.8401
-20.5	8	6.81	.8465	.9675	.8190	.8220
-23.3	7	5.96	.8284	.9623	.7671	.8119

Me = 217.24 85.1 % moisture T_f = -1.56 °C

Table A.9. Freezing Characteristics of Raspberries.

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-2.2	56	46.31	.9805	.9984	.9788	.9789
-3.3	39	32.25	.9723	.9960	.9684	.9693
-4.4	30	24.81	.9643	.9936	.9581	.9583
-5.6	24	19.85	.9557	.9908	.9469	.9470
-6.7	21	17.37	.9497	.9865	.9368	.9370
-7.8	18	14.89	.9418	.9841	.9268	.9271
-9.4	15	12.41	.9310	.9801	.9124	.9126
-12.2	12	9.92	.9151	.9702	.8878	.8880
-15.0	9	7.44	.8900	.9707	.8639	.8635
-17.8	8	6.62	.8780	.9575	.8407	.8401
-20.5	7	5.79	.8629	.9491	.8190	.8220
-23.3	6	4.96	.8436	.9449	.7971	.8119

Me = 338.54 82.7 % moisture T_f = -1 .22 °C

Table A.10. Freezing Characteristics of Raspberry Juice.

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-2.2	56	49.56	.9818	.9970	.9788	.9789
-3.3	39	34.52	.9740	.9943	.9684	.9693
-4.4	30	26.55	.9665	.9913	.9581	.9583
-5.6	24	21.24	.9585	.9879	.9469	.9470
-6.7	21	18.59	.9529	.9831	.9368	.9370
-7.8	18	15.93	.9454	.9803	.9268	.9270
-9.4	15	13.28	.9352	.9756	.9124	.9126
-12.2	12	10.62	.9203	.9647	.8878	.8880
-15.0	9	7.97	.8965	.9637	.8639	.8635
-17.8	8	7.08	.8850	.9499	.8407	.8401
-20.5	7	6.20	.8708	.9405	.8190	.8220
-23.3	6	5.31	.8524	.9352	.7971	.8119

Me = 338.54 88.5 % moisture $T_f = -1.22$ °C

Table A.11. Freezing Characteristics of Spinach.

T °C	%m_u	m_u	X_u	γ	Aw_c	Aw_e
-1.1	50	45.10	.9906	.9988	.9984	.9894
-2.2	25	22.55	.9814	.9974	.9788	.9789
-3.3	18	16.24	.9744	.9938	.9684	.9693
-4.4	14	12.63	.9673	.9904	.9581	.9583
-5.6	11	9.92	.9588	.9876	.9469	.9470
-6.7	10	9.02	.9548	.9811	.9369	.9370
-7.8	9	8.12	.9501	.9754	.9268	.9271
-9.4	7	6.31	.9367	.9741	.9124	.9126
-12.2	5	4.51	.9136	.9718	.8878	.8880

Me = 414.14 90.2 % moisture T_f = -0.56 °C

Table A.12. Freezing Characteristics of Strawberry.

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-1.1	79	70.54	.9901	.9993	.9984	.9894
-2.2	40	35.72	.9807	.9981	.9788	.9789
-3.3	28	25.00	.9727	.9956	.9684	.9693
-4.4	21	18.75	.9639	.9939	.9581	.9583
-5.6	18	16.07	.9502	.9866	.9369	.9370
-7.8	13	11.61	.9430	.9828	.9268	.9271
-9.4	10	8.93	.9271	.9841	.9124	.9126
-12.2	8	7.14	.9105	.9751	.8878	.8880
-15.0	7	6.25	.8990	.9609	.8639	.8635
-17.8	6	5.36	.8842	.9508	.8407	.8401
-20.5	5	4.47	.8643	.9475	.8190	.8220

Me = 274.35 89.3 % moisture T_f = -0.88 °C

Table A.13. Freezing Characteristics of Strawberry Juice.

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-1.1	79	72.44	.9904	.9990	.9984	.9894
-2.2	40	36.68	.9812	.9976	.9788	.9789
-3.3	28	25.68	.9734	.9949	.9684	.9693
-4.4	21	19.26	.9648	.9931	.9581	.9583
-5.6	18	16.51	.9592	.9872	.9469	.9470
-6.7	15	13.76	.9515	.9845	.9368	.9370
-7.8	13	11.92	.9444	.9814	.9268	.9271
-9.4	10	9.17	.9289	.9822	.9124	.9126
-12.2	8	7.34	.9127	.9727	.8878	.8880
-15.0	7	6.42	.9014	.9584	.8639	.8635
-17.8	6	5.50	.8868	.9484	.8407	.8401
-20.5	5	4.59	.8673	.9443	.8190	.8220

Me = 274.35 91.7 % moisture T_f = -0.88 °C

Table A.14. Freezing Charcteristics of Tomato Pulp.

T °C	$\%m_u$	m_u	X_u	γ	Aw_c	Aw_e
-1.1	62	57.60	.9900	.9994	.9894	.9894
-2.2	31	28.80	.9803	.9985	.9788	.9789
-3.3	22	20.44	.9724	.9959	.9684	.9693
-4.4	18	16.72	.9665	.9913	.9581	.9583
-5.6	14	13.01	.9573	.9891	.9469	.9470
-6.7	12	11.15	.9506	.9855	.9368	.9370
-7.8	10	9.29	.9413	.9846	.9268	.9270
-9.4	8	7.43	.9276	.9836	.9124	.9126
-12.2	6	5.57	.9057	.9803	.8878	.8880
-15.0	5	4.65	.8892	.9716	.8639	.8635

Me = 220.5   92.9 % moisture T_f = -0.72 °C

APPENDIX B

Derivation of Equation for Correction of ΔC_p for Temperature

According to Leyendekkers and Hunter (1985) the specific heat of supercooled water and ice vary as in the following equations (for temperatures up to 233 K):

$$\text{Ice} \quad C_p = 2.369 + 0.130\,T \quad \text{J mol}^{-1}\text{K}^{-1} \tag{B.1}$$

$$\text{Supercooled water} \quad C_p = 121.480 - 0.168\,T \quad \text{J mol}^{-1}\text{K}^{-1} \tag{B.2}$$

The difference in specific heat between supercooled water and ice is obtained by subtracting equation (B.1) from (B.2) resulting in,

$$\Delta C_p = 119.111 - 0.298\,T \tag{B.3}$$

substituting equation (B.3) in equation (25) the following expression is obtained:

$$-\ln X_w \gamma = \frac{1}{R}\int \frac{L_w - (119.111 - 0.298\,T)\,(T_w - T)\,dT}{T^2} \tag{B.4}$$

Integrating between T_f and T_w results in the final expression after proper mathematical operations and assuming $R = 8.314$ J mol^{-1}K^{-1}, $L_w = 6010$ J mol^{-1} K^{-1} and $T_w = 273.15$ K,

$$-\ln X_w \gamma = \frac{-3190.929}{T_f} + 0.0358\,T_f - 24.117 \ln T_f + 137.200 \tag{B.5}$$

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