PREDICTING FREEZING CURVES IN CODFISH FILLETS USING THE IDEAL BINARY SOLUTION ASSUMPTION

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ABSTRACT

PREDICTING FREEZING CURVES IN CODFISH FILLETS USING THE IDEAL BINARY SOLUTION ASSUMPTION

By

Carlos Eduardo Lescano

A mathematical model to predict freezing curves in food products using the ideal binary solution and the freezing point depression approach was developed. This model considers one-dimensional heat transfer and prediction of thermal properties variation (thermal conductivity and apparent specific heat) at temperatures below the freezing point. The main advantage of the prediction model developed during this investigation is the small amount of experimental information required for the product.

The accuracy of the prediction model was demonstrated by the acceptable agreement between the experimental results and those obtained by the model. Codfish fillets being frozen in an experimental wind tunnel under different conditions provided the experimental data. Experimental results from Long (1955) and Charm et al. (1972) using the same food product, confirmed the reliability of the prediction model.

Freezing rates were more accurately predicted by the model than a modified Plank's equation as used by Eddie and Pearson (1958).

Important influences in the performance of the prediction model were found when experimental errors in freezing point determination, apparent specific heat approximation and density change considerations were analyzed.

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NOMENCLATURE

A_1	Expression defined by equation (3.14A)
A_2	Expression defined by equation (3.14B)
A_3	Expression defined by equation (3.14C)
$\lfloor A \rfloor$	Tridiagonal matrix with variable coefficients, defined by equation (3.15A)
a	Constant used by equation (3.4)
a_1	Expression defined by equation (3.7A)
[B]	Tridiagonal matrix with variable coefficients, defined by equation (3.15B)
b	Constant used by equation (3.4)
b_1	Volume ratio defined by equation (3.7B)
{C}	Column matrix defined by equation (3.15E)
c_p	Specific heat or apparent specific heat, BTU/lb_m-°F
c_{pi}	Specific heat of ice, BTU/lb_m-°F
c_{ps}	Specific heat of solids in food product, BTU/lb_m-°F
c_{pw}	Specific heat of water, BTU/lb_m-°F
c_1	Constant defined by equation (3.6A)
c_2	Constant defined by equation (3.6B)
c_3	Constant defined by equation (3.6C)
c_4	Constant defined by equation (3.6D)
{D}	Column matrix defined by equation (3.16)
d	Total thickness of infinite slab, ft
H	Total enthalpy of food product, referred to -40°F, BTU/lb_m
h	Surface or convective heat transfer coefficient, BTU/hr-ft^2-°F
i	Index

k	Thermal conductivity of food product, BTU/hr-ft-°F
k_c	Thermal conductivity of continuous phase, BTU/hr-ft-°F
k_d	Thermal conductivity of dispersed phase, BTU/hr-ft-°F
k_i	Thermal conductivity of ice, BTU/hr-ft-°F
L	Half of the thickness of infinite slab, ft.
M_s	Molecular weight of solute in binary solution, lb_m/lb - mole
M_w	Molecular weight of water, lb_m/lb - mole
m	Index
m_i	Mass of ice, lb_m
m_s	Mass of solids in food product , lb_m
m'_s	Mass of solute in binary solution, lb_m
m_w	Mass of unfrozen water, lb_m
m_{wT}	Initial moisture content of product lb_m H_2O/lb_m product
m_w'	Mass of unfrozen water at - 40°F, lb_m
m'_{uw}	Unfreezable water fraction, $lb_m H_2O/lb_m$ product
N	Number of nodes in the domain
R	Universal gas constants BTU/lb - mole - °R
T	Temperature in food product, °F
T_i^m	Temperature at any location i at the time m, °F
T_A	Absolute temperature in food product,°R
T_o	Freezing point of pure water, °F
T_{Ao}	Freezing point of pure water expressed in absolute temperature, °R
T_F	Initial freezing point of product,°F
T_{AF}	Initial freezing point of product, expressed in absolute temperature, °R

T_i	Initial temperature of product, °F
T_∞	Temperature of cooling medium, °F
$\{T\}$	Temperature column matrix
V_c	Volume of continuous phase, ft^3
V_d	Volume of dispersed phase, ft^3
X_s	Mole fraction of liquid in binary solution, dimensionless
$X_{s}i$	Initial mole fraction of liquid in binary solution, dimensionless
x	Distance, ft
Δ	Incremental operator
ΔH_s	Heat of fusion of water BTU/lb_m
ΔT_1	Temperature difference defined by equation (2.1A), °F
ΔT_2	Temperature difference defined by equation (2.1B), °F
ΔT_3	Temperature difference defined by equation (2.1C), °F
ρ	Density of product, lb_m/ft^3
ρ_i	Density of ice, lb_m/ft^3
θ	Time, hrs.

I. INTRODUCTION

In freezing preservation of foods, knowledge of temperature-history curves, freezing time and total heat content of the food product being frozen are fundamental information needed to describe the freezing process completely and quantitatively. Such information is invaluable for food scientists and engineers when attempting: a) correlation of the parameters of the freezing process and the quality parameters of the food product; b) prediction of product quality stability during frozen storage and/or c) optimization of the design and use of the freezing equipment.

Prediction of temperature-history curves and freezing times is based on the solution of the particular heat transfer problem involved. Due to inherent non-linearities present in the equations describing the heat transfer case with change of phase, only a limited number of exact solutions are possible.

Two important factors in freezing of foods are: a) free water crystallizes over a range of temperatures and b) thermal and physical properties of the product vary over the same range of temperatures and contribute to the non-linearity of the heat transfer problem. Exact solutions are then no longer possible.

Approximate solutions to this type of heat transfer case are possible through the use of standard numerical techniques coupled with the aid of modern computer technology. All solutions proposed within the last decade rely on experimentally determined thermal properties.

Information on thermal properties at freezing temperatures is limited and of questionable accuracy. In addition, thermal properties seem to be strongly dependent on: a) water content, b) product composition, c) the distribution of product components, d) product temperature, and d) other variables which have not been investigated to date.

At the present stage of the knowledge, the use of mathematical models based on water content, freezing temperature and other easily measurable or predictable variables appears to be justifiable to predict thermal properties. Additional experimental information is still needed however to further refine the models.

Heldman (1972) showed that in order to calculate the unfrozen fraction of water in a vegetable product being frozen, it is a valid assumption to consider the food product as an ideal binary solution. Using the freezing point depression equation (Moore, 1962) and utilizing freezing point of food product and initial moisture content as input data the mass fraction of unfrozen water at any temperature in the freezing range was computed.

If by use of the ideal binary-solution assumption and freezing point depression approach, an acceptable computation of unfrozen water in the product being frozen is obtained, prediction of thermal properties would be possible. With known thermal conductivity and specific heat at temperatures below the initial freezing point, the heat transfer problem can be solved by numerical techniques with the aid of a digital computer.

The specific objectives of this research were as follows:

(1) To derive and solve numerically a mathematical model to predict temperature-history curves for food products

under freezing conditions using the ideal binary-solution assumption and the freezing point depression approach.

(2) To evaluate the proposed mathematical model by comparing theoretical results with experimental freezing curves for codfish fillets.

(3) To compare freezing times obtained by a modified Plank's equation with time obtained by use of the theoretical model.

(4) To use the mathematical model to determine the physical parameters which have significant influence on temperature-history curves.

II. REVIEW OF LITERATURE

2.1 Thermal Properties of Frozen Foods

Bartlett (1944), Ede (1949), Riedel (1949A, 1949B) and Staph and Woolrich (1951) illustrated that water in a food product freezes over a range of temperatures. This phenomenon was attributed to a continuous depression of the freezing point in the unfrozen product fraction as ice formed. The utmost importance of the role of water and ice content in relationship with thermal properties variation during freezing appeared to be evident.

Accurate measurements of thermal properties of foods are not frequently possible due to inherent instrumental errors and the inability to meet, under test conditions, all the assumptions imposed by the heat transfer model being utilized (Reidy and Rippen, 1971). This appears to be one of the reasons why limited information is available for thermal properties, particularly at temperatures below the freezing point.

Reidy (1968) has conducted an extensive review of experimental techniques used to determine thermal properties. He concluded that numerical methods should be used with transient type experiments involving high moisture foods (like meat and fish).

Most of experimental apparent specific heats for foods under freezing have been determined using calorimetric procedures to obtain the total heat content of the sample at different temperatures below the freezing point (Short <u>et al</u>, 1942; Staph, 1949; Staph and Woolrich,1951;

Reidel, 1951, 1955, 1956, 1957A, 1957B; Jason and Long, 1955). By taking the derivative of the total heat content curve, or enthalpy curve, with respect to the temperature, the apparent specific heat values have been obtained. Accuracy of the experimental determinations seemsto be dependent on the number of experimental enthalpies obtained at different temperatures, on the accuracy of the procedure utilized to measure the heat content and finally, on the accuracy of the method utilized to get the derivative of the total heat content curve with respect to the temperature.

Short and Staph (1951), Jason and Long (1955) and Reidel (1956) have provided information on experimental apparent specific heats for codfish under freezing temperatures. In general, apparent specific heats are likely to be constant at temperatures above the freezing point, reach a maximum value at the initial freezing point and continuously decrease when lower temperatures are considered.

Early experimental determination of thermal conductivity for food products under freezing temperatures was obtained using steady state methods. The parallel plate or the concentric cylinder have been the most used techniques. More recently unsteady state methods using the probe method (Sweat et al, 1973) or other models of transient heat transfer cases (Katayama et al, 1973) have been used.

Experimental thermal conductivities for codfish were obtained by Jason and Long (1955), Smith et al (1952), Khatchaturov (1958) and Lentz (1961). All investigations used steady state calorimetric methods. Experimental curves of apparent thermal conductivity values versus temperature showed to be fairly constant at temperatures above the freezing point. An abrupt increase in thermal conductivity values at temperatures just below the freezing point is reported. This is expected since the major part of the free water is transformed into ice in this region and the thermal conductivity of ice is about four times greater than that of water at its freezing point. Because of increases in amount of ice formed are relatively smaller when regions of lower temperatures are considered, the thermal conductivity values are expected to show a rather moderate rate of increase.

From analysis of the experimental evidence reported, it is worth noting that experimental determinations of specific heats and thermal conductivities at temperatures close to the freezing point are not as abundant as they are at lower temperatures. This is probably due to experimental difficulties involved in measuring heat rates or other variables which show abrupt changes in that zone. The relative importance of this fact, in relation with heating or cooling processes remains unknown.

2.1.1 Prediction of thermal properties

The lack of adequate information on thermal properties of food products and the fact that many variables are involved - such as composition, distribution of components, variety and age of biological products - make the quantity of information required for each food product almost infinite. Prediction of thermal properties based on variables easily measurable or predictable has been used to overcome this problem.

Prediction of specific heats based on the components of the food product have been proposed by Siebel (1892), Dickerson (1969), Charm (1971) and others. Long (1955) predicted apparent specific heat of codfish by assuming that product solids were equivalent to a stated concentration of sodium chloride solution.

Theoretical expressions for prediction of thermal conductivities have also been proposed. Eucken (1940) used Maxwell's equation (1904) to compute thermal conductivity of an heterogeneous two-phase system composed of small spheres of one substance dispersed in another substance. Maxwell's equation has also been applied by Long (1955) and Lentz (1961) to products being frozen and values so obtained compared with their experimental results; differences in their findings depend on the type of model they adopted for the food system.

Long (1955) used a mixture of ice, sodium chloride solution of stated concentration and protein as a model for fish muscle, at temperatures below the freezing point. The theoretical curve of thermal conductivity versus temperature showed an excellent agreement when compared with the experimental values.

Lentz (1961) used models of gelatin gel of several concentrations to represent the food system. Thermal conductivities calculated using 20% gels did not provide very good agreement with experimental results for certain non-homogeneous foods.

Expressions claimed to be more adaptable to food systems have been proposed by Kopelman (1966). Isotropic and anisotropic materials - with components distributed in layers or fiber-type orientation - have been modeled. However, equations proposed by Kopelman have not been tested on their accuracy to a great extent (Heldman, 1973).

2.2 Heat Transfer with Liquid-Solid Change of Phase

Many important problems in engineering involve transient heat conduction with freezing or melting. The unique feature of this type of situation is the existence of a boundary, at the frozen-unfrozen interface, whose position is time dependent. This dependence of the free boundary makes the heat transfer problem non-linear and introduces severe mathematical difficulties in its solution (Carslaw and Jager, 1958).

The relatively few exact solutions available correspond to sufficiently simple cases where appropriate equations can be obtained and analytically evaluated. However, most of the situations currently found in engineering practice are solved by applying approximated solutions (Bankoff, 1964).

The earliest and one of the most important exact solutions to the solid-liquid change of phase problem was derived by Neumann (Ingersoll et al, 1948; Carslaw and Jaeger, 1958). Neumann's problem considers one-dimensional heat transfer in a pure substance with a semi-infinite body and a temperature-step input at the boundary. The non-linearity is present only in the free boundary. Since the differential equation and the rest of the boundaries are linear, the solution relies upon the assumption of a mathematical relationship between the position of the free boundary and the time. The distance to the phase change was found to be proportional to the square root of time. Generalizations of Neumann's solution can be found in Carslaw and Jaeger (1958).

Another exact solution was originally presented by Plank (1913) to solve the one-dimensional freezing of an infinite slab, cylinder or sphere under convective boundary conditions. In order to make a solution possible the following assumptions were made: a) the product is a pure substance, i.e. it has a single freezing point, b) the product is initially at liquid state and its constant temperature is the freezing point, c) only steady state heat transfer by conduction is considered in the frozen layer, i.e. no changes in internal energy are considered and d) the frozen layer has a constant thermal conductivity and physical properties, i.e. they are independent of temperature or position. Plank (1941) extended his solution to consider the case of the rectangular parallelepiped. Exact solutions for other particular cases are also available, however, they are not relevant from the standpoint of the present work.

Consideration of more complicated body shapes, boundary conditions and variations of thermal properties during the freezing process introduce additional non-linearities and exact solutions are not possible. Only analytical (or mathematical) and numerical approximations can be used. Bankoff (1964) has compiled the principal contributions to the solution of the heat transfer problem with change of phase. Later contributions have been summarized by Hashemi (1965) and Bakal (1970). Even though analytically approximated solutions encompass a number of important physical problems, they do not include many of the situations frequently found in freezing of foods. In solutions by numerical approximations analog and digital computers have been utilized depending on the type of solution initially applied and preference of the researcher.

Dusinberre (1961) has proposed the use of the apparent specific heat as a way of reducing the moving boundary effect to a property variation. The apparent specific heat takes into account latent heat effects during freezing since by definition it is the derivative of the total enthalpy with respect to the temperature. The important aspect of such a definition is that apparent specific heats are the experimental values normally found in specific heat determinations of frozen foods by calorimetric techniques.

2.3 Freezing Rates in Food Products

Fennema and Powrie (1964) have discussed the various methods that have been used in practice to express freezing rates. All methods used today have some disadvantages and limitations. The manner in which temperature changes during a freezing process negates the existence of a single freezing rate value for proper description of the entire process. The ideal freezing rate criteria will allow description of the entire temperature-history curve at any location point within the product. Because of practical reasons the reference point has been generally considered to be the slowest cooling point.

Prediction of freezing rates based on theoretical solutions of the heat transfer equations have been suggested by several investigators. Empirical modications of the original Plank's equation have been the most widely used in the food industry, due to their simplicity, acceptable accuracy and the unavailability of improved, practical methods. Based on research done by Nagaoka <u>et al</u> (1955), Levy (1958) and Eddie and Pearson (1958) have proposed modified Plank's equations to predict freezing times on elliptical shape whole fish and on fish packs respectively.

The modification of Plank's equation proposed by Eddie and Pearson (1958) for infinite slab shape packs of fish is:

$$\theta = m_{wT} \left[c_{pw} \, \Delta T_1 + \Delta H_s + C_{pi} \, \Delta T_2 \right] \left[1 + .00445 \, \Delta T_1 \right]$$

$$\left(\frac{d}{2h} + \frac{d^2}{8k_i} \right) \frac{\rho_i}{\Delta T_3} \qquad (2.1)$$

where:

$$\Delta T_1 = T_i - T_f \qquad (2.1A)$$

$$\Delta T_2 = T_f - T \qquad (2.1B)$$

$$\Delta T_3 = T_f - T_\infty \qquad (2.1C)$$

Some attempts to handle experimental data on the basis of the theory of similarity have also been reported. Empirical formulas have been proposed by Tchigeov (1956),Khatchaturov (1958) and others, based on relationship of the experimental data with dimensionless numbers used in heat transfer theory.

Considerations of variation of thermal properties of the product during the freezing process led to the use of approximated solutions and computer technology. (Albasiny, 1956; Earle and Earl, 1966; Hohner and Heldman, 1970; Charm, 1971; Charm et al, 1972; Cordell and Webb, 1972; Bonacina and Comini, 1973; Fleming, 1973A; Cullwick and Earle, 1973). Albasiny (1956) using the concept of enthalpy flow and temperature flow proposed by Eyres et al (1947) solved the differential equations which describe the freezing of an infinite slab under convective boundary conditions. Experimental data for thermal conductivity and total heat content at freezing temperatures provided by Long (1955) were utilized. The system of simultaneous first order non-linear ordinary differential equations obtained from the application of the forward finite difference technique, was solved using the Runge-Kutta method and a very early model of a digital computer. Reported results showed good agreement with Long's (1955) experimental temperature distribution and temperature-history curves.

Cordell and Webb (1972) using a basically similar approach, proposed a mathematical model for describing freezing of ice cream brickettes in an air blast tunnel. The basic heat transfer equation for the three-dimensional case, with convective boundary conditions, was transformed using Eyres et al. (1947) and Price and Slack (1954) criteria. The resultant equations were solved using an explicit or forward difference technique. No comparisons with experimental results were reported.

Earle and Earl (1966) using corrected experimental data on thermal conductivity and apparent specific heat of beef (Lentz, 1961) solved the heat transfer problem for cylindrical, spherical and three-dimensional cube shapes of minced beef frozen under convective boundary conditions. The general heat transfer equations which represent the physical problem were solved numerically considering a thermal diffusivity variation with respect to the temperature. A forward finite difference technique was used. Experimental tests were carried out to compare the theoretical model. Minced beef in light gage copper containers was frozen in an air blast tunnel where air velocity and temperature were maintained constant. Earle and Earl (1966) reported good agreement between the mathematical model and experimental temperature-history curves obtained to test the model.

Hohner and Heldman (1970) utilized the ideal binary-solution assumption and the freezing point depression approach as a theoretical model to fit experimental apparent specific heat data for beef and codfish. Based on that information a central-difference (Crank-Nicolson) technique was used to solve the problem in an infinite slab being frozen by convective boundary conditions. Although good agreement with thermal properties prediction was assured, no comparisons of temperature-history results to experimental tests were reported. Predicted freezing points obtained were lower than those reported in the literature. The results for codfish were almost 2°F below experimental value reported by Riedel (1956).

Charm (1971) and Charm et al (1972), used a forward difference technique and a specially derived function to account for variations of thermal conductivity and density during freezing. Prediction of freezing curves for one-dimensional heat transfer in cylinders and slabs with convective boundary conditions was considered. The function defined by Charm (1972) seems to take values from zero to one, being assumed a linear variation of thermal conductivity and specific heat with respect to that function. Charm et al (1972) reported good agreement between the predicted temperature-history curves and freezing curves experimentally obtained for haddock and codfish fillets.

Bonacina and Comini (1973) have also proposed a mathematical model for the solution of the one dimensional freezing case with variable thermal properties. The solution is based upon the approximation of the basic differential heat transfer equation which describes the phenomenon using a method proposed by Lees (1966). Lees' method of approximation for the numerical integration of one-dimensional, quasilinear, parabolic equations is based on the use of three time levels and uses central-difference operators. According to the authors, this method has never been used before in the solution of the heat conduction problems. Bonacina and Comini (1973) used "Tylose" (77% water and 23% methyl cellulose, by weight) to simulate the thermal behavior of meat. They obtained experimental values for thermal conductivity and specific heats at temperatures below the initial freezing point. Experimental freezing curves were reported to show excellent agreement with predicted temperature-history curves.

Fleming (1970; 1973A) has developed a mathematical model to solve the two-dimensional freezing problem in an arbitrary-geometry body with non-linear thermal properties and boundary conditions of first, second and third kind. The alternating direction implicit (ADI) finite difference method was used, requiring discretized values of thermal diffusivities. Experimental and computed freezing curves for stockinette wrapped lamb carcasses have been compared (Fleming, 1970); a good agreement was reported. Fleming (1973B) has used his mathematical model to illustrate theoretical applications on predicting temperature distributions in hind-quarters of beef under freezing and equilibration processes. No comparison with experimental results has been reported in the latter work.

III. THEORY

In order to evaluate the ideal solution assumption and the freezing point depression approach in describing the food behavior under freezing conditions, an adequate correspondence between the selected mathematical model and its physical situation is of critical importance. The mathematical model must represent a simple heat transfer situation without introducing the influences of related phenomena. This situation also helps in making the numerical solution of the mathematical model simpler.

The assumptions considered in the mathematical model, and its finite difference representation are described in the closing section of this chapter. Thermal properties variation involved are computed based on predicted unfrozen water values; the computational procedures and theoretical equations used are illustrated in the earlier sections.

3.1 Unfrozen Water Fraction

Any food can be considered as a complex system made up of a specific arrangement of constituents and phases which provide defined organoleptic, physical and chemical properties.

Staph and Woolrich (1951) explained the freezing of a food product conceiving the food as being composed of a simple mixture of solids and pure water. This mixture was assumed to have some of the properties of a solution or a compound, such as the freezing point depression. Staph and Woolrich (1951) considered that when a food begins to freeze, the concentration of the food solids is increased in the remaining unfrozen water, thereby establishing a lower freezing point for additional change of phase. As additional freezing occurs, there is a gradual depression of the freezing point until all the water is frozen.

Heldman (1972) assumed that water in a food product is responsible for variation of thermal properties in the freezing range and that the food product during freezing is represented by an ideal binary solution with water as a solvent and a chemical compound as a solute. The chemical compound was defined to include the effect of all the food components in the freezing point depression.

Using the freezing point depression equation (Moore, 1962) and utilizing freezing point of product and initial moisture content as input data, Heldman (1972) has proposed an expression which leads to the computation of unfrozen water fraction of the product at any temperature in the freezing range. Acceptable results were reported when compared to experimental values for some foods.

$$\mathrm{Ln}\,(X_s) = \frac{\Delta H_s\, M_s}{R} \left(\frac{1}{T_{AO}} - \frac{1}{T_A}\right) \qquad (3.1)$$

where:

$$X_s = \frac{m_w / M_w}{m_w/M_w + m_s/M_s} \qquad (3.2)$$

With knowledge of the initial molar concentration and the freezing point the first step is to compute the effective molecular weight of solute (M_s). This is possible because at the freezing point ($T_A = T_{AF}$) the left side of equation (3.1) is known ($X_s = X_{si}$).

Sequential use of expressions (3.1) and (3.2) will allow the computation of the unfrozen water content (m_w) at any temperature (T_A) below the initial freezing point.

3.1.1. Correction for unfreezable water content

Unfreezable water is the term applied to the water in the food product that is adsorbed to the surfaces of the skeletal macro-molecular solids by molecular forces, in fine pores by capillary condensation or may be strongly attracted by colloidal hydrophilic substances. This particular water is unavailable as a solvent for other molecules and it is assumed that it cannot crystallize at any temperature (Kuprianoff, 1958). Unfreezable water is expelled by heating at temperatures normally used in standard moisture determinations, therefore, it is included in the initial moisture content value.

Meryman (1960) estimated that 8-10% of the total water in animal tissues is unavailable for ice formation. Daughters and Glenn (1946) found that most fruits and vegetables contain less than 6% of unfreezable water.

Different criteria that have been used to measure unfreezable water include (Duckworth, 1971): a) non-freezability at low temperatures, measuring the unfreezable water either directly or, more commonly, by measuring the amount of ice formed; b) calorimetry; c) nuclear magnetic resonance (N.M.R.); d) differential thermal analysis (D.T.A.) and e) differential scanning calorimetry (D.S.C.) (Parducci and Duckworth, 1972).

Table 3.1 has been taken from Parducci and Duckworth, (1972). It shows unfreezable water content for codfish measured by different methods and researchers. As pointed out by Parducci (1972), the extent of the freezability of water in foods is a subject of considerable controversy among researchers.

TABLE 3.1--Unfreezable water content for codfish

Unfreezable Water* (lb_m water / lb_m product)	Method	Temperature (°F)
10.82 - 10.98	D.T.A.	-292.
11.15 - 11.39	D.T.A.	-76.
13.09	Calorimetry	-76.
12.83	N.M.R.	- 4.

*Corrected values considering 80.3% water content, wet basis (Riedel, 1956).

Under these new considerations, the system representing the food product is assumed to be composed of a known fraction of unfreezable water and an ideal binary solution whose solute is the total solids content. The solvent is the amount of water represented by total moisture content minus the unfreezable water fraction. At any temperature in the freezing range, the total unfrozen water in the product will be the unfreezable water content plus the unfrozen water computed by the use of the ideal binary solution assumption and the freezing point depression approach.

3.2 Prediction of Thermal Properties at Freezing Temperatures

3.2.1 Apparent specific heat

Equation (3.1) is a continuous function which allows the computation, at any temperature below freezing point, of the fractions of unfrozen water and ice.

With knowledge of the amounts of solids, unfrozen water, ice and unfrozen water at -40°F and their correspondent thermal properties, it is possible to compute the total heat content of the product at that particular temperature.

The total heat content based on -40°F can be computed using the expression:

$$H = m_s\ c_{ps}\ (T + 40) + m_w\ [\Delta H_s + c_{pw}\ (T + 40)] + m_i\ c_{pi}(T + 40) - m'_{uw}\ \Delta H_s \qquad (3.3)$$

where:

$$c_{pi} = a + b\ T$$

a = 0.464128 and b = 0.0087111 (from Fennema ,1964) (3.4)

Equation (3.3) is a continuous function that will provide the enthalpy of the food product (H) at any constant temperature (T) below the freezing point.

If a continuous expression is defined to express total heat content of a substance, the apparent specific heat is defined as:

$$c_p = \frac{dH}{dT} \qquad (3.5)$$

which leads to the expression:

$$c_p = c_1 + 2\ m_{wT}\ bT + [\frac{c_2\ m_s\ X_s}{1 - (1 + c_2)\ X_s} + m'_{uw}\ m_{wT}]\ [c_3 - 2\ b\ T] + [c_4 + c_3\ T - b\ T^2]\ \{\frac{c_2\ m_s\ \Delta H_s\ M_w\ X_s}{R(T_A)^2\ [1 - (1 + c_2)\ X_s]^2}\} \qquad (3.6)$$

where:

$$c_1 = m_s\ c_{ps} + m_{wT}\ a + 40\ m_{wT}\ b \qquad (3.6A)$$

$$c_2 = m'_s\ M_w/M_s \qquad (3.6B)$$

$$c_3 = c_{pw} - a - 40\ b \qquad (3.6C)$$

$$c_4 = \Delta H_s + 40\ c_{pw} - 40\ a \qquad (3.6D)$$

Equation (3.6) allows the computation of the apparent specific heat at any temperature in the freezing range. The apparent specific values provided by this equation are approximated by $\Delta H/\Delta T$ in the limit when ΔT tends to zero.

3.2.2 Thermal conductivity

As a consequence of the binary-ideal solution and freezing point depression, the food system in the freezing region is composed of unfrozen water, product solids and ice. The Maxwell (1904) equation, modified by Eucken (1940) can be utilized to predict thermal conductivity of food product in the freezing range.

The Maxwell-Eucken equation is:

$$k = k_c \left[\frac{1 - (1 - a_1\, k_d/k_c)\, b_1}{1 + (a_1 - 1)\, b_1} \right] \tag{3.7}$$

where:

$$a_1 = 3\, k_c \,/\, (2\, k_c + k_d) \tag{3.7A}$$

$$b_1 = V_d \,/\, (V_c + V_d) \tag{3.7B}$$

Since unfrozen water is the continuous phase, the equation is utilized in two steps to consider the two dispersed phases: ice and solids.

The increasing volume fraction of ice and the decreasing volume portion of unfrozen water are calculated at each desired temperature below freezing, using the freezing point depression approach and conservation of mass.

3.3 The Mathematical Model

The mathematical model is based upon the following assumptions:

(1) Energy transport occurs in one dimension through an infinite slab suddenly exposed to constant convective freezing boundary conditions.

(2) The body is a heterogeneous substance with thermal conductivity and apparent specific heat variables at temperatures below the initial freezing point. The substance is composed of an ideal binary solution and unfreezable water at temperatures above freezing. Free water from the solution is transformed to ice, at temperatures in the freezing range, according to its freezing point depression.

(3) Mass transfer from the surfaces to the cooling medium or within the product are neglected. This implies an impervious surface and negligible influence of density differences between the frozen and unfrozen product.

(4) The substance has an initial constant temperature throughout the body.

(5) Specific heat of ice is a decreasing linear function with temperature.

(6) Other physical parameters like specific heat and thermal conductivity of the solid fraction and latent heat of fusion of water are constant with respect to the temperature. Specific heat, thermal conductivity and density of the product are constant at temperatures above freezing.

The transient, one-dimensional heat conduction problem can be described by the following equations:

$$\rho\, c_p\,(T)\,\frac{\partial T}{\partial \theta} = \frac{\partial}{\partial x}\left[k(T)\,\frac{\partial T}{\partial x}\right], \quad 0 < x < L \quad, \theta > 0 \qquad (3.8)$$

$$T\,(x,0) = T_i \quad, \quad 0 \leq x \leq L \quad, \quad \theta = 0 \qquad (3.9)$$

$$\left.\frac{\partial T}{\partial x}\right|_{x=0} = 0 \quad , \quad x = 0 \quad , \quad \theta > 0 \qquad (3.10)$$

$$-k(T) \left.\frac{\partial T}{\partial x}\right|_{x=L} = h\, [\, T(L,\theta\,) - T_{\infty}], \; x = L \quad , \quad \theta > 0 \qquad (3.11)$$

where conditions of symmetry of the problem have been considered and functions k(T) and $c_p(T)$ are known at temperatures below the freezing point.

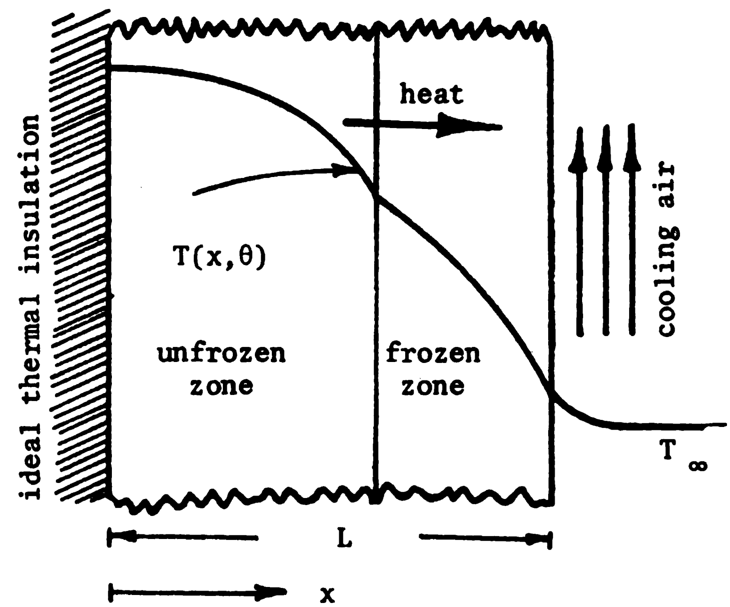
3.3.1 Finite difference model

There are two general approaches to express a complex physical situation and the description of the appropriate differential equations in terms of finite difference equations (Myers, 1971). The first one starts with the differential equations which describe the physical case and then approximate the derivatives using a finite difference criteria (mathematical formulation). The second approach is to derive the difference equations by application of conservation laws to a differential volume increment using the physical case (physical formulation). Heat transfer with change of phase is an example of the usefulness of the latter approach.

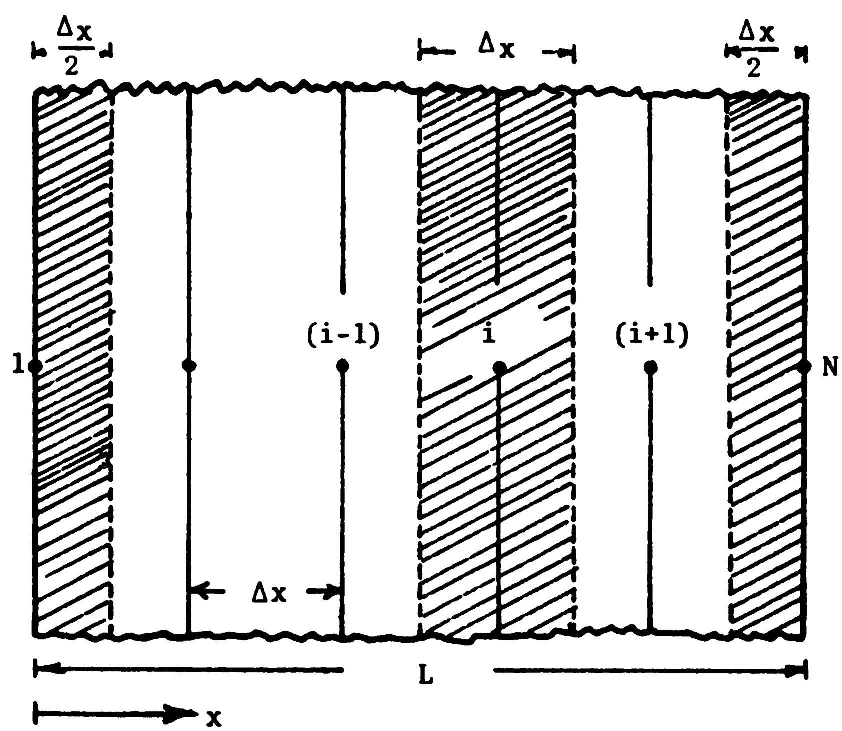
Figure 3.1 shows the schematic representation of the heat transfer case and its corresponding domain division where a typical interior point and the two boundary points have been represented. The energy transfer equation applied to each of the differential volumes shown in Figure 3.1b by dashed lines will provide the finite difference approximation of equations (3.8), (3.10) and (3.11).

The final general finite difference expressions, using the weighting average factor η , are:

Interior point:



a) Schematic diagram of the freezing problem.



b) Representation of typical interior and boundary points.

Figure 3.1. Representation of the freezing problem.

$$- \eta \frac{A_2}{A_1} T_{i-1}^{m+1} + [\eta (\frac{A_2}{A_1} + \frac{A_3}{A_1}) + 1] T_i^{m+1} - \eta \frac{A_3}{A_1} T_i^{m+1}$$

$$= (1- \eta) \frac{A_2}{A_1} T_{i-1}^{m} - [(1 - \eta) (\frac{A_2}{A_1} + \frac{A_3}{A_1}) - 1] T_i^{m}$$

$$+ (1- \eta) \frac{A_3}{A_1} T_{i+1}^{m} \qquad (3.12)$$

Thermal insulation boundary condition point:

$$(2 \eta \frac{A_3}{A_1} + 1) T_1^{m+1} - 2 \eta \frac{A_3}{A_1} T_2^{m+1}$$

$$= - [2 (1- \eta) \frac{A_3}{A_1} - 1] T^m_1 + 2 (1 - \eta) \frac{A_3}{A_1} T_2^m \qquad (3.13)$$

Convective boundary condition point:

$$- 2 \eta \frac{A_2}{A_1} T_{N-1}^{m+1} + [\frac{2\eta}{A_1} (A_2 + \frac{h \Delta x}{c_p (N)}) + 1] T_N^{m+1}$$

$$- \frac{2 h \Delta x}{A_1 c_p(N)} T_\infty = 2 (1-\eta) \frac{A_2}{A_1} T_{N-1}^{m} - [\frac{2(1-\eta)}{A_1} (A_2 + \frac{h \Delta x}{c_p(N)}) - 1)$$

$$(3.14)$$

where:

$$A_1 = \rho (\Delta x)^2 / \wedge \theta \qquad (3.14A)$$

$$A_2 = \frac{k(T^m_i) + k (T_{i-1}^m)}{2 c_p (i)} \qquad (3.14B)$$

$$A_3 = \frac{k(T^m_i) + k (T_{i+1}^m)}{2 c_p(i)} \qquad (3.14C)$$

A_2 and A_3 will be variable when thermal properties are considered at temperatures below the freezing point.

The general finite-difference model can be transformed into the following specific models: Euler, forward difference or explicit ($\eta = 0$); Crank-Nicolson or central difference ($\eta = \frac{1}{2}$) or backward difference or pure implicit ($\eta = 1$).

Because of reasons that will become evident later on, the Crank-Nicolson method was selected for this particular work. The central finite difference representation of the mathematical model can be expressed using matrix notation on the already simplified general finite difference equations. Matrix expressions are:

$$[A]^{(m)}\{T\}^{(m+1)} = [B]^{(m)} \{T\}^{(m)} + \{C\} \tag{3.15}$$

where each of the matrices are defined as shown by expression (3.15A), (3.15B), (3.15C), (3.15D) and (3.15E).

The tridiagonal matrices [A] and [B] are composed of known coefficients at each time step, which vary from one iteration to another. These kinds of equations are similar to the special classes of equations with variable coefficients which have been found to be unconditionally stable, when the use of Crank-Nicolson method was analyzed (Richtmyer and Morton, 1967; Ames, 1969; Mitchell, 1969).

Since at each time step the matrices at the right-hand side are composed by known constant values, we can express (3.15) as:

$$[A]^{(m)} \{T\}^{(m+1)} = \{D\}^{(m)} \tag{3.16}$$

$$[A]^{(m)} = \begin{bmatrix} (1 + \frac{A_3}{A_1}) & -\frac{A_3}{A_1} & & & \\ -\frac{1}{2}\frac{A_2}{A_1} & [1 + \frac{1}{2A_1}(A_2 + A_3)] & -\frac{1}{2}\frac{A_3}{A_1} & & \\ & \cdots & \cdots & \cdots & \\ & & -\frac{1}{2}\frac{A_2}{A_1} & [1 + \frac{1}{2A_1}(A_2 + A_3)] & -\frac{1}{2}\frac{A_3}{A_1} \\ & & & -\frac{A_2}{A_1} & \{1 + \frac{1}{A_1}[A_2 + \frac{h\Delta x}{c_p(N)}]\} \end{bmatrix}^{(m)} \quad (3.15A)$$

$$[B]^{(m)} = \begin{bmatrix} (1 - \frac{A_3}{A_1}) & \frac{A_3}{A_1} & & & \\ \frac{1}{2}\frac{A_2}{A_1} & [1 - \frac{1}{2A_1}(A_2 + A_3)] & \frac{1}{2}\frac{A_3}{A_1} & & \\ & \cdots & \cdots & \cdots & \\ & & \frac{1}{2}\frac{A_2}{A_1} & [1 - \frac{1}{2A_1}(A_2 + A_3)] & \frac{1}{2}\frac{A_3}{A_1} \\ & & & \frac{A_2}{A_1} & \{1 - \frac{1}{A_1}[A_2 + \frac{h\Delta x}{c_p(N)}]\} \end{bmatrix}^{(m)} \quad (3.15B)$$

$$\{T\}^{(m+1)} = \begin{Bmatrix} T_1 \\ T_2 \\ \vdots \\ \vdots \\ T_{N-1} \\ T_N \end{Bmatrix}^{m+1} \quad (3.15C) \qquad \{T\}^{(m)} = \begin{Bmatrix} T_1 \\ T_2 \\ \vdots \\ \vdots \\ T_{N-1} \\ T_N \end{Bmatrix}^{(m)} \quad (3.15D)$$

$$\{C\} = \begin{Bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ \dfrac{2\Delta x h T_\infty}{A_1\ c_p(N)} \end{Bmatrix} \quad (3.15E)$$

which represents a system of simultaneous equations whose solution provides the temperature at any location of the infinite slab under freezing, at a particular time. A simplified technique, which is a special adaptation of the Gauss-Seidel elimination procedure when a tridiagonal matrix is present, can be used to solve the system. (Smith, 1965; Richtmyer <u>et al</u>, 1967).

IV. EXPERIMENTAL DESIGN AND PROCEDURES

4.1 Equipment and Apparatus

The objective of the experimental design was to model an experimental situation capable of meeting the basic assumptions on which the mathematical model is based.

The infinite slab of the food product (codfish in this particular case) was simulated by using a sample holder. The sample holder is shown schematically in Figure 4.1. The sample space was 12 in. by 6 in. with thickness based on the thickness to be used in the particular experimental situation. Styrofoam was used to surround the sample space in order to reduce heat transfer in directions other than normal to the two principal surfaces. Two 1/8 in. thick stainless steel sheets were placed along the bottom of the holding space to contain the sample. A 1/2-in. wide zone at the central part exposed the food product to the air stream.

Convective boundary conditions were provided by a low speed wind tunnel. The wind tunnel had a length of 12.5 ft., a round cross-section of 18 in. diameter and a test section located at about the middle of the length. The blower was driven by a 5 HP, 440/220 volts, three-phase electric motor and was capable of providing mean velocities between 7 to 60 ft/sec. Plastic guides attached longitudinally to the tunnel were located to maintain the central axis of the sample holder in alignment with the central axis of the tunnel. This provided symmetric freezing conditions on both sides of the sample in contact with the air stream.

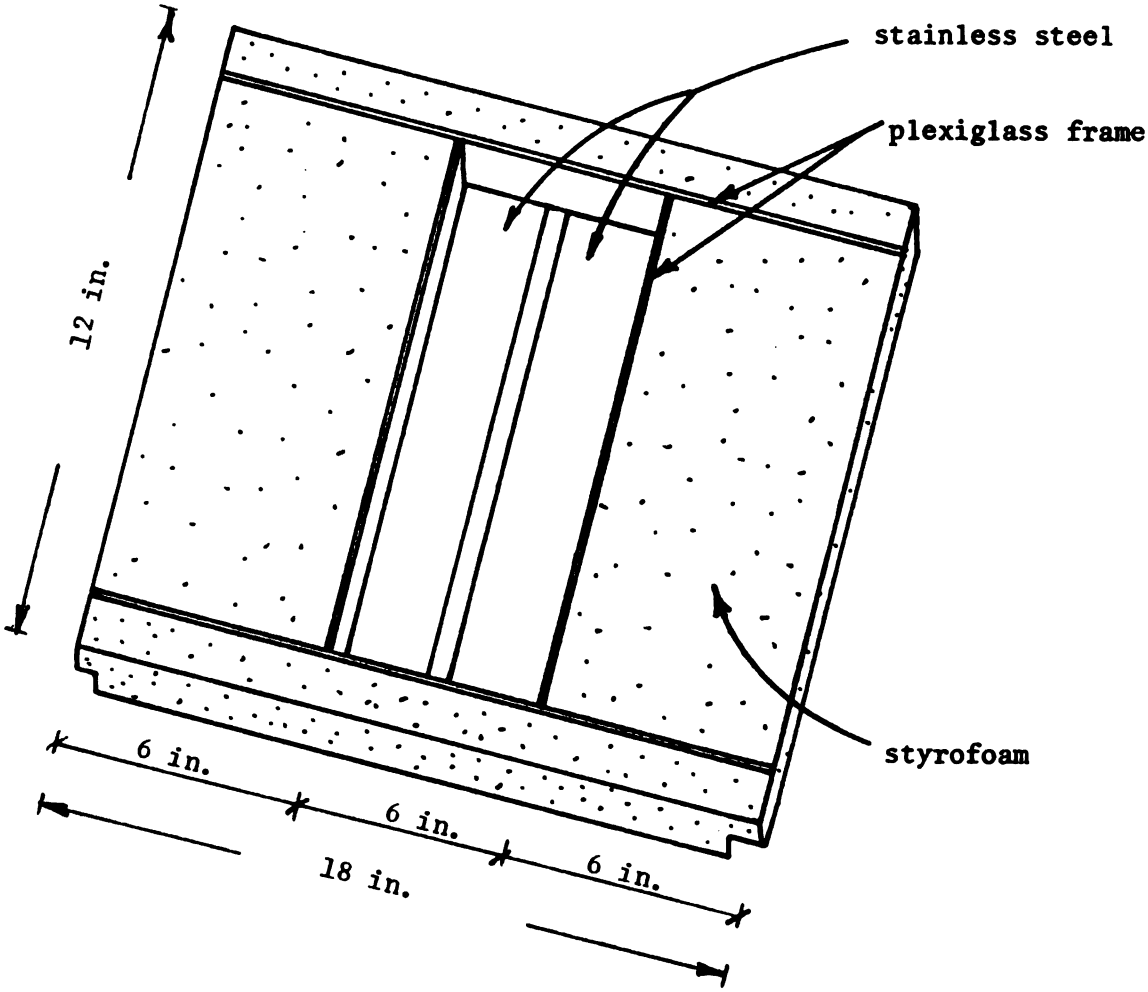


Figure 4.1. Schematic of sample holder.

The experimental tunnel was located in a 22 ft. x 6 ft. x 8 ft. low temperature room with temperatures controlled down to -30°F with an accuracy of ± 1°F. Evaporators of the refrigerating system were located at each end of the longer dimension of the room. The blowers of the evaporators were running continuously during each of the experimental tests.

A temperature recorder with 0.5°F accuracy and 30-gauge copper-constantan thermocouples were utilized to measure temperature of sample and of the cooling medium (air). Mean air velocities over the sample were measured using a Pitot tube and a micromanometer sensitive to 0.001 inch of water. A schematic diagram of the experimental apparatus and equipment used for freezing curve determinations in codfish fillets is shown in Figure 4.2.

4.2 Procedure for Freezing Curve Determination

Samples of fresh codfish fillets, without prior freezing, were shipped from the east coast (Gloucester, Massachusetts) under refrigerated conditions. After a period of more than twelve hours in a temperature controlled room, used to obtain constant temperature throughout the product, the fillets were placed in the sample holder. Thermocouple sensors were located around the geometric center. In order to minimize inaccuracies in getting the geometric center and central axis of sample, five thermocouple locations were used. The sensor showing the slowest cooling temperature-time profile was assumed to be placed at the geometric center.

Starting from the time the sample holder is suddenly located in the test section of the experimental tunnel, the temperature in the

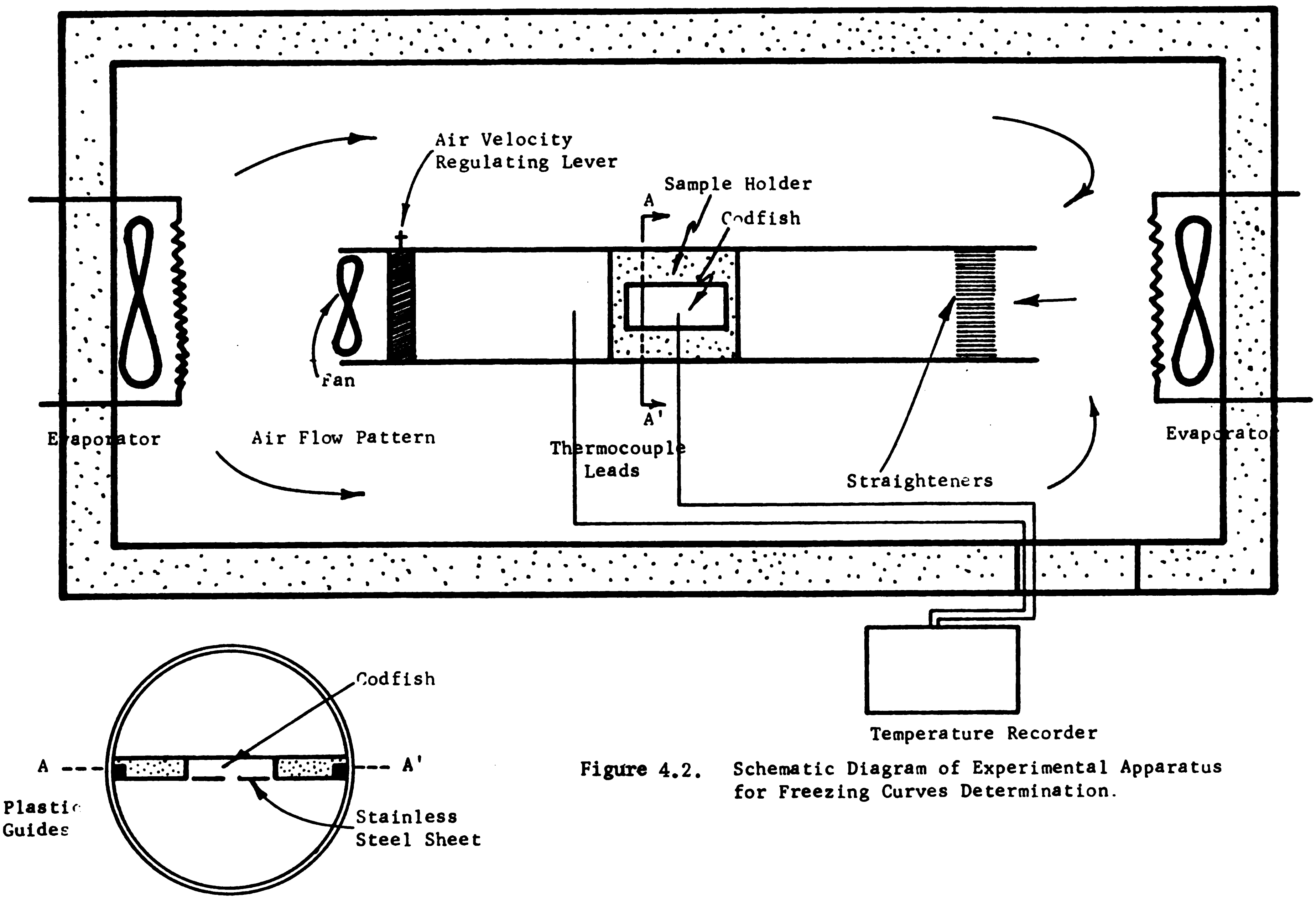


Figure 4.2. Schematic Diagram of Experimental Apparatus for Freezing Curves Determination.

sample and the cooling air were continuously recorded by the temperature recorder located outside the test room.

4.3 Experimental Determination of Convective Heat Transfer Coefficient

The temperature at the surface of the product being frozen under convective boundary conditions decreases with increments of freezing time. This is especially true at the very beginning of the freezing process, when differences between the surface temperature and constant cooling medium temperature are greater. In addition, the particular configuration of the experimental situation does not fit an equation which can be used to calculate the mean convective heat transfer coefficient.

In order to obtain heat transfer coefficients which could adequately describe the convective boundary condition, an experimental determination was attempted. A transient lumped-parameter heat transfer case with temperature independent thermal properties and without change of phase was selected. An aluminum slab located in the same place as the sample was assumed to provide acceptable geometric similitude. Estimation of the mean heat transfer coefficient at each particular mean velocity of cooling medium was obtained based on the characteristic straight line relationship between the logarithm of the dimensionless temperature of the aluminum slab and the cooling time.

The thermocouple point which provided the temperature-history for the cooling process was located 1/4 in. from the surface. A comparison with a location point at 1/2 in. essentially provided the same temperature-history data. This similarity agrees with results from the analysis of sensitivity and optimum experimental design for estimation of convective heat transfer coefficients from experimental temperature-time data (Comini, 1972). For the case of an infinite slab under several experimental tests with different Biot number values, the optimum thermocouple location during the experiment, is the surface of the body. However, if Biot numbers close to zero (like transient lumped-parameter case) are utilized, location of the thermocouple is not a critical factor.

4.4 The Computer Program

A computer program based on the finite-difference model was written in FORTRAN IV in an adequate form to be utilized by a computer CDC 6500. The program was able to handle a maximum of thirty nodes which provided an acceptable amount to choose from when analyzing or simulating the experimental conditions.

The computer program utilized the following as input information:

(a) Cooling medium temperature

(b) Convective heat transfer coefficient

(c) Half of thickness of infinite slab

(d) Time increment value

(e) Number of nodes

(f) Information about the food product:

1) Initial temperature

2) Initial freezing point

3) Initial moisture content

4) Density, apparent specific heat and thermal conductivity above freezing.

5) Density below freezing

6) Unfreezable water content

In order to provide adequate flexibility to the computer program for study of the influence of the approximation of the derivative of the total enthalpy with respect to the temperature (apparent specific heat) the necessary statements were included. Two types of controls were included to stop the program: a) when the temperature at the center of the product is close enough to the cooling medium temperature (within a defined value of 0.001°F) and b) when a defined total freezing process time, previously provided as input data, is reached. A printout of temperature at each of the nodes and their related thermal properties information (apparent specific heat and thermal conductivity) was obtained for every pre-determined time interval. Using the above output information, it was possible to follow the performance of the program very closely.

4.4.1 An optimum operating condition for the computer program

No exact solution is available for a complete accuracy analysis of the heat transfer case under study. For purposes of the present study it is worthwhile to emphasize that, within certain limits, the numerical solution will provide values closer to the true ones, when smaller Δx and $\Delta\theta$ values are utilized. For this situation, the global stability must occur, i.e. the numerical solution should converge to the true values. Since this is the case for the particular numerical solution under consideration, the search for an optimum operating condition was attempted. Considering computer simulations of experimental situations, the operating condition was selected.

In order to set an optimum operating condition for the computer program, a compromise situation between computer time and practical accuracy desired in the results was sought (Myers, 1971).

When thermal properties vary with temperature, as in freezing of foodstuffs, the accuracy of the numerical solution is closely related to the stability of the values of the coefficients which compose the matrices [A] and [D] (Fleming, 1970). These coefficients will depend on the magnitude of temperature variation between neighboring nodes. In other words, the critical situation in testing the accuracy of the model will be the one which provides maximum temperature differences between neighboring nodes. Based on this consideration, the following critical situation was chosen:

- Medium temperature: - 30°F
- Convective heat transfer coefficient: 50 BTU/hr-ft^2-°F
- Thickness of infinite slab: 1 inch
- Initial product temperature: 35°F

Physical and thermal properties for codfish, the food product utilized throughout the present work, were obtained from Riedel (1956) and are presented in Table 4.1.

TABLE 4.1--Numerical values of product physical constants used in the numerical solution

Initial freezing point	30.2°F
Initial moisture content	80.3%
Unfrozen thermal conductivity	0.32 BTU/hr-ft^2-°F
Unfrozen specific heat	0.88 BTU/lb_m-°F
Unfrozen density*	65 lb_m/ft^3
Frozen density*	61 lb_m/ft^3
Unfreezable water content	11%

*From Long (1955)

Tentative trials using Δx · 0.0049 ft (10 nodes) showed a rapid convergence, eliminating local stability problems (or oscillations) at time intervals as high as 0.001 hr. Further decreases in $\Delta\theta$ improved the accuracy of the numerical solution. Larger Δx increments were tried in order to reduce the computer time and obtain acceptable accuracy. The use of $\Delta x = 0.0052$ ft. and $\Delta\theta = 0.0001$ hrs. provided relatively good accuracy in the results (as compared with smaller $\Delta\theta$ values) of the order of 0.01°F. A ratio of 92 sec. computer processing time to 1 hr. of real freezing process time was obtained for that particular situation. Those values were used as a basis of reference when less critical situations - but sometimes more time consuming - were simulated or analyzed.

4.5 Experimental Situations

In order to test the mathematical model, a series of experimental tests were designed. The experimental situations selected, based on the feasibility provided by apparatus and equipment already described, are shown in Table 4.2.

TABLE 4.2-- Experimental tests for freezing curves determination in codfish.

Experimental Parameter	Test Number							
	1	2	3	4	5	6	7	8
A	2.0	2.0	2.0	1.5	1.0	2.0	2.0	2.0
B	-17.5	-17.5	-17.5	-17.5	-20.0	-20.0	-10.5	-10.5
C	40.0	53.0	60.0	40.0	43.0	45.0	41.0	41.0
D	1000	1000	1000	1000	1000	0	1000	3000
E	18.0	18.0	18.0	17.3	16.6	4.57	18.0	33.0

A = Infinite slab thickness, inch
B = Cooling medium temperature, °F
C = Initial product temperature, °F
D = Mean air velocity, ft/min.
E = Mean surface heat transfer coefficient, BTU/hr-ft^2-°F

V. RESULTS AND DISCUSSION

In the following sections, the performance of the mathematical model which considers the binary-solution assumption and freezing point depression approach will be evaluated. Comparison of predicted freezing curves to experimental values, under different conditions, are analyzed. Freezing time values obtained from use of the theoretical model and the modified Plank's equation (1.1) are compared to experimental values.

Influence of some food product parameters on predicted freezing curve shape are also investigated, as well as the usefulness of the mathematical model in description and analysis of the freezing process.

5.1 Thermal Properties Prediction

An adequate prediction of thermal properties in the freezing range is a critical factor in order to obtain an acceptable prediction of temperature-history curves using a computer program based on the mathematical model. Since thermal property values during freezing are different for different products, they will characterize the mathematical model when a particular product is under consideration.

Experimentally determined thermal properties in the freezing range are useful information in order to compare the trends of the theoretically predicted values. For codfish, experimental thermal properties have been presented by Short and Staph (1951), Long (1955), Riedel (1956) and Lentz (1961). As was mentioned in Chapter III, thermal properties prediction (thermal conductivity and apparent specific heat) are dependent upon accurate prediction of unfrozen water. Figure 5.1 shows that predicted unfrozen water are in acceptable agreement with experimental values provided by Riedel (1956). One important aspect to be noted is the accuracy of the prediction at temperatures below 0°F and the fact that at -5°F essentially no additional ice is formed. At temperatures close to the initial freezing point the rate of ice formation increases rapidly. It can be concluded that the major part of ice is formed at temperatures above 20°F, however, rate of formation is still appreciable at temperatures down to 10°F.

The knowledge of unfrozen water content and additional information related to the components allows computation of the total enthalpy by using equation (3.3). Figure 5.2 illustrates the agreement between experimental (Riedel, 1956) and predicted enthalpy values for codfish. At temperatures close to the freezing point, theoretical values are greater than experimental. This situation is a logical consequence of the dramatic increase in ice formation at temperatures closer to freezing point. It should be emphasized that, in general, the theoretical curve follows the same trend as the experimental data. Differences in values near to the freezing point could be explained by probable limitations in experimental determinations.

Figure 5.3 shows predicted and experimental values of apparent specific heat for codfish (Short and Staph, 1951; Long, 1955; Riedel, 1956). Predicted values were calculated using equation (3.6) and the approximation of equation (3.5) when ΔT = 1.0°F. The general trend is followed by the theoretical curves when values closer to the initial freezing point are not considered. Noticeably higher theoretical values are obtained in the region close to the

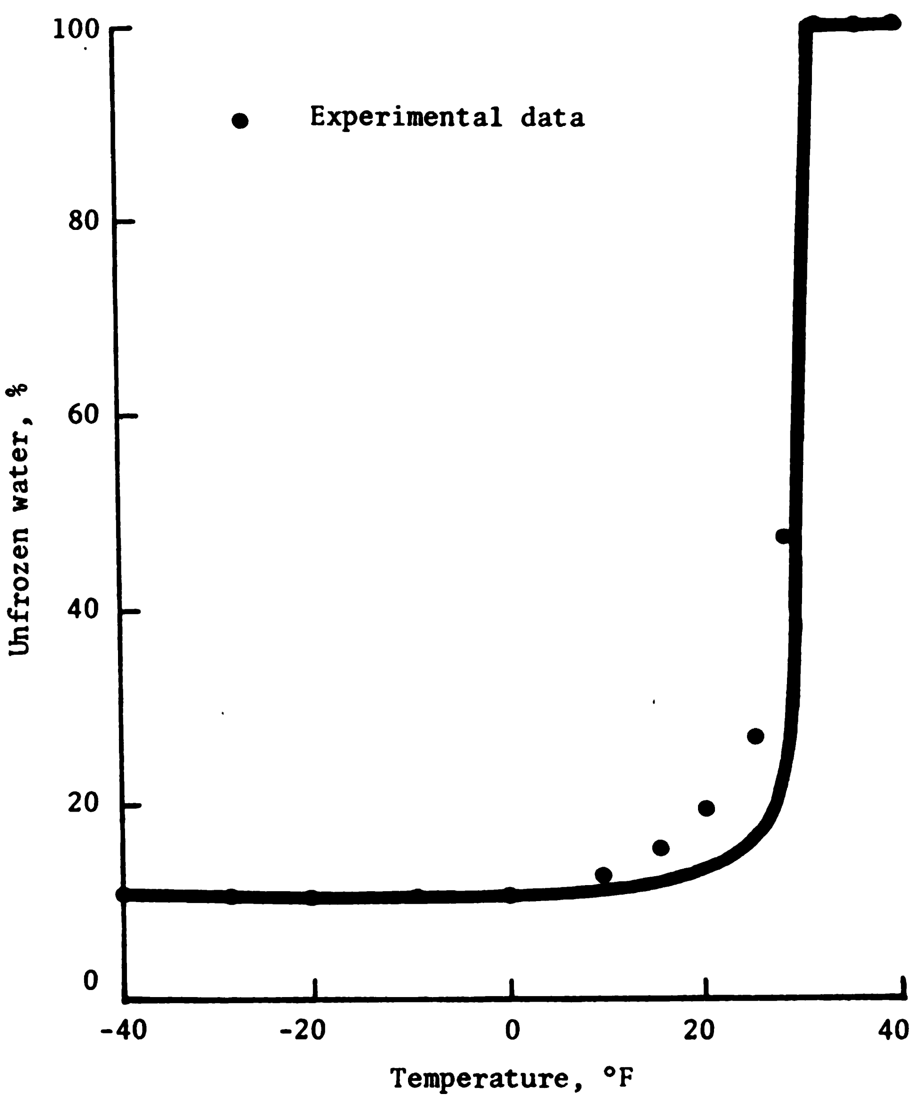


Figure 5.1. Comparison of predicted and experimental unfrozen water percentages as a function of temperature for codfish (from Riedel, 1956).

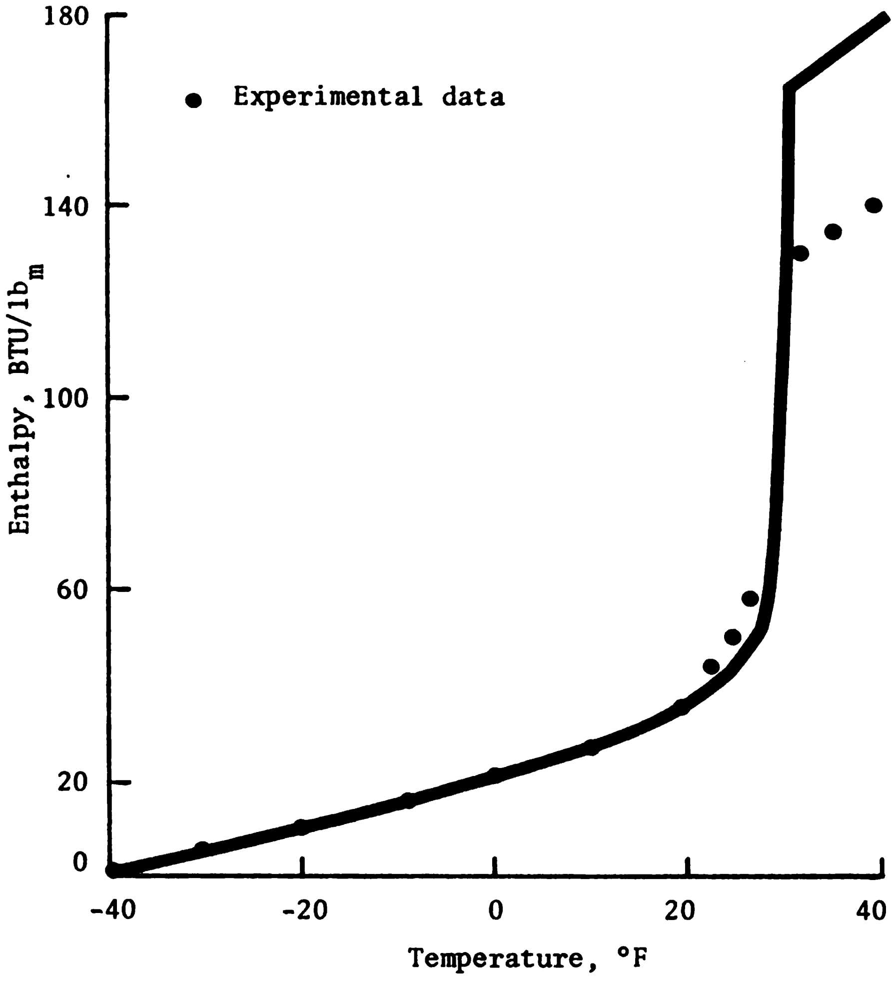


Figure 5.2. Comparison of predicted and experimental enthalpies as a function of temperature for codfish (from Riedel, 1956).

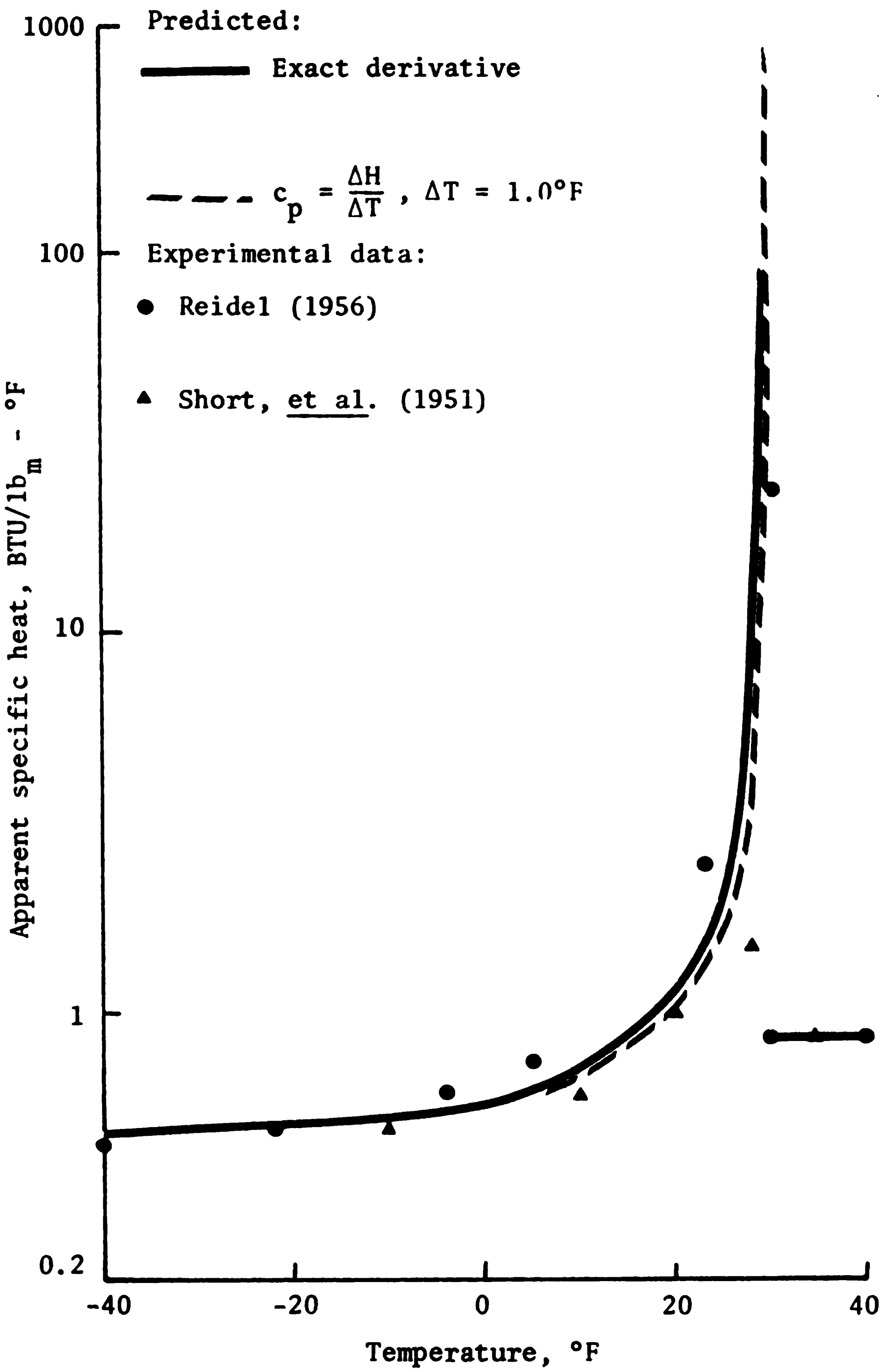


Figure 5.3. Comparison of predicted and experimental apparent specific heats as a function of temperature for codfish (from Riedel, 1956 and Short, et al., 1951).

freezing point as would be expected when considering the enthalpy values from which they are derived. Since apparent specific heat values are going to be used directly in the computer model, any lack of agreement between the theoretical values and the actual values will result in changes in predicted curves.

Figure 5.4 shows the experimental (Long, 1955; Lentz, 1961) and theoretical thermal conductivities for codfish. Appreciable variability in experimental values is obvious. The predicted values fall between the sets of the experimental data and according to the experimental evidence available, the theoretically predicted values can be considered acceptable for our purposes.

Information provided in this section will provide some basis for discussion when experimental and/or theoretical freezing curves are compared or analyzed.

5.2 Predicted Temperature-Time Curves

Theoretical freezing curves at three location points in a codfish fillet being frozen by convective boundary conditions are presented in Figure 5.5. These curves have been obtained using the product thermal properties presented in Table 4.1, with exception of the freezing point. A freezing point of 31°F was used based on experimental freezing curves to be presented later. This particular value characterized the constant temperature section of the experimental freezing curve at the center of the product.

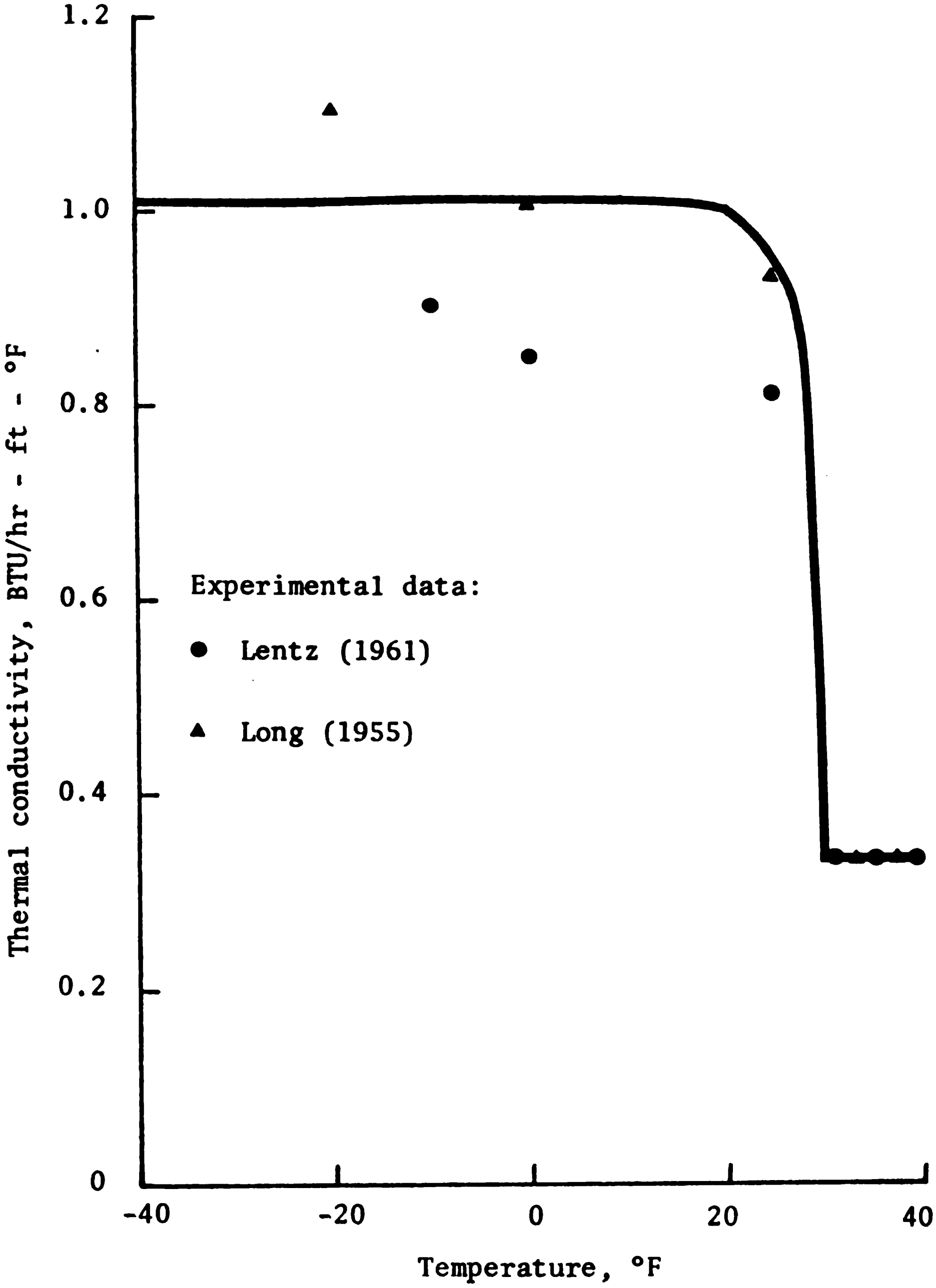


Figure 5.4 Comparison of predicted and experimental thermal conductivities as a function of temperature for codfish (from Long, 1955 and Lentz, 1961).

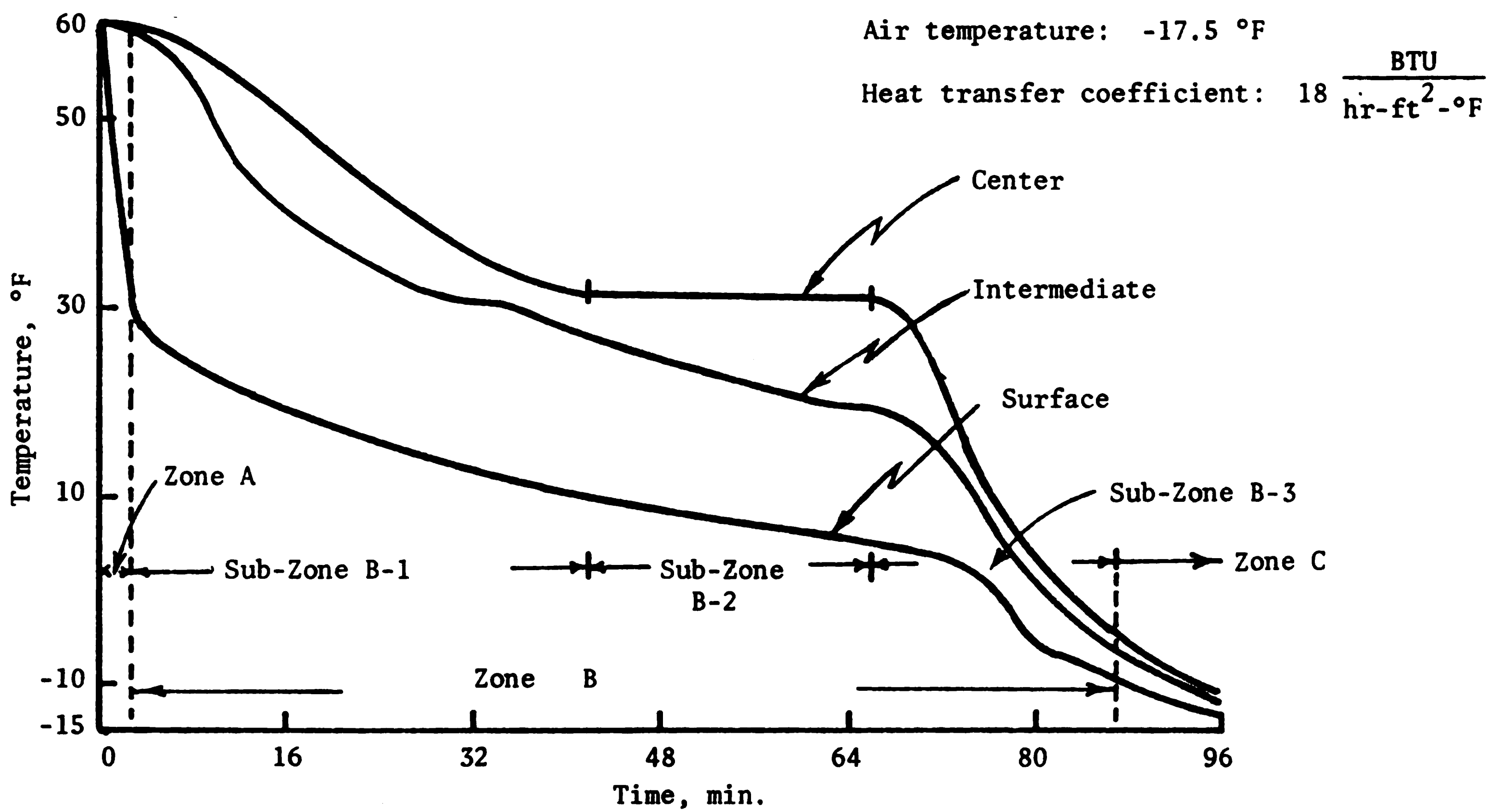


Figure 5.5. Predicted temperature-history curves at three different locations in a 2in.-thick codfish fillet.

5.2.1 Description of predicted freezing curves

The general shape of predicted curves at three different locations within the product presented in Figure 5.5 are similar to those presented by Ede (1955) and Luyet (1966). Ede (1955) obtained experimental freezing curves using a food system composed of water immobilized by the addition of 5% gelatin. Luyet (1966) presented temperature-time recordings at the periphery, in the center and halfway through the radius, in a cylinder of 0.5 M glycerol solution. Both investigators attempted to provide a general explanation for curves of this type to occur. A very complex interdependence of: a) the rate of advancing of the freezing front, b) the rate of heat removal by the refrigerant, and c) the rate of liberation of latent heat removal was emphasized (Luyet, 1966).

The use of a mathematical model to represent the freezing process should provide an additional theoretical basis for a more detailed explanation and interpretation of freezing curve shapes at different locations.

From the standpoint of predominant heat transfer phenomenon present in the freezing curve, the results in Figure 5.5 can be used to define three main zones:

a) A first zone (zone A) starts from the beginning of the freezing process until the surface of the product reaches the initial freezing point. This zone corresponds to a transient heat conduction cooling case with thermal properties assumed independent of temperature. Up to this point, analysis could be made using the characteristic mathematical equations or their representation in Heisler charts.

b) An intermediate zone (zone B) characterized by the change of phase occurring within the product. This zone could be considered limited by the time the surface reaches the freezing point and the time the center reaches -5°F. At -5°F, essentially all the free water of codfish is transformed into ice (Figure 5.1).

The intermediate zone can be divided up into three sections or sub-zones:

(b-1) This region (Zone B-1) is characterized by the displacement of the ice front from the surface to the center of the slab. The temperature gradients within the product will determine the velocity of the freezing front displacement and amount of total heat removal during this period. Temperature gradients during this zone will be dependent on the temperature gradients at the end of the first zone.

(b-2) This region (Zone B-2) is characterized by the constant temperature zone at the center of the product, which indicates latent heat removal. The constant temperature zone may exist at all locations between the center and the surface. Figure 5.5 partially illustrates this. The duration of latent heat removal at the center is greater than at the intermediate point, and the duration at the surface is virtually non-existent. This particular behavior at the surface can be explained by predominant influence of the convective boundary condition. Figure 5.5 shows that removal of latent heat at the center is likely to occur at ever increasing rates. This is expected because as latent heat is removed from locations near the center, temperature gradients are established again.

(b-3) A section (zone B-3) limited by the time most of the latent heat has been removed and the time the center reaches -5°F. This zone is characterized by the increase in temperature at the center. The effect of this new situation at the center is shown by changes on the shape of freezing curves of neighboring points. These changes are manifested in a sequentially delayed manner from center to surface.

c) A third zone (zone C) begins at -5°F and is unbounded at lower temperatures. This zone corresponds to a transient heat conduction cooling case with thermal properties essentially independent of temperature. The initial condition for this situation considers different temperatures from center to surface. During this zone, the freezing curves will converge to the freezing medium temperature with increasing time.

The size of each of the zones described and the magnitude of the temperature gradients in the infinite slab are going to determine the particular shape of the freezing curve. For a given product, zones and temperature gradients will finally depend on the condition of the freezing process.

5.2.2 Process of ice formation and characterization of the freezing process

During the freezing conditions, ice is formed in the food product starting from the time the surface reaches the initial freezing point. According to Luyet (1966) the growth of the ice phase consists of the following consecutive stages: a) nucleation and growth of crystallization units to microscopically visible size, b) invasion by ice into non-occupied territory, c) retardation of the invasion caused by the slow dissipation of latent heat acting as a limiting factor, d) further retardation and cessation of freezing as a result of the action of two other limiting factors, competition for space by neighboring cyrstallization units and depletion of water supply. Any attempt to characterize the freezing process with reference to the process of ice formation in a biological system must consider the four stages cited. In other words, the time interval between the time the surface of the product reaches the freezing point temperature and the time the center of the product reaches a temperature at which essentially no ice is formed is of utmost importance.

5.2.2A Limitations of thermal arrest time definition

The rate of freezing of a food product is often specified as the time required for the product to pass through a prescribed temperature interval.

One of the definitions or methods utilized is the thermal arrest time. Thermal arrest time is defined as the time for the temperature at the center of the product to change from 32°F to 23°F. Based on experimental results, the generality of this criterion has been questioned (Long, 1955) when different initial product temperatures are used. A product with higher initial temperature provides a shorter thermal arrest time and a longer total freezing time than those of another product at lower initial temperature, under the same freezing conditions.

A possible explanation for this behavior can be developed based on the general description of predicted freezing curves presented in a previous section. The surface of a product with lower initial temperature (product A) will reach the initial freezing point in a shorter time than the surface of a product which has a higher initial temperature (product B). In addition, the action of identical convective boundary conditions determines that the surface temperature of product A will always be lower than that of product B. As a consequence, all interior points of product A will also have lower temperatures than those in product B, and the temperature gradient between neighboring points in A will be smaller than that at corresponding points in B.

A combined interaction of comparatively small temperature gradients and total heat content will result in comparatively low rates of latent heat removal at the center of the product with lower initial temperature. The temperature distribution within the product at the beginning of the change of phase zone will be a function of the particular initial condition.

When products A and B - which started the freezing process at the same time - are both considered to have center temperatures of 32°F, two different thermal states at different times of their freezing processes are being considered. Therefore, temperature gradients in product B will be greater than in product A. If the 32°F at the center of the product is assumed to be a new initial condition for products A and B, product B will take a shorter time to reach any temperature below 32°F. This is the explanation for a product with high initial temperature having a short thermal arrest time. As implied in the analysis, the influence of the true initial conditions has been ignored, i.e., any previous history of the ice front advance from surface to center has not been considered.

Since the thermal arrest time criterion is only a fraction of the total ice formation time - which is probably mostly related to stage

c) - it will provide incomplete information about the ice formation process in the whole product and, consequently, an inaccurate indication of freezing rate. The dependence of thermal arrest time on the related temperature gradients and initial conditions does not allow a consistent way of characterizing the freezing process.

5.2.2B Definition of a criterion for freezing time measurements

As discussed in the first part of this section, the ideal criterion to characterize the freezing process, in terms of a freezing rate, should refer to the process of ice formation in a biological product, from its initiation through its completion. According to the evidence presented by Ede (1955), Meryman (1966) and the predicted freezing curves shown in Figure 5.5 a single value for the rate of advance of the freezing front will obviously be an average one. It will be apparent that to obtain such a value will require the use of at least two temperature-sensing elements properly placed: at the surface and at the center of the product. However, there are practical limitations involved in recording those two temperature-history curves. An acceptable description of freezing process can be obtained by recording the temperature-history curve at the center of the product, from the initial condition to a temperature at which no freezable water remains. It should be recognized that the single time-temperature trace does not provide a direct measure of the advance of the freezing front through the sample. A further simplification to be used in practical freezing of foods would be to measure the time for the center of the product to pass from the initial temperature to a defined temperature, at which essentially no more ice crystals are formed.

Figure 5.1 illustrates that essentially no ice is formed in codfish at temperatures below -5°F, therefore, this will be the reference temperature for measuring freezing times in the present study. In other words, for purposes of the present study, freezing time will be defined as the time for the temperature at the center of the product to pass from the initial temperature to -5°F. Consideration of any other lower temperature, as long as the consistency is maintained, will provide an acceptable and practical description of the freezing process.

5.3 Influence of Product Characteristics on Shape of Freezing Curves

The study of sensitivity of predicted freezing curves to changes in some characteristics of the product is attempted in this section. With this in mind, product characteristics considered have been divided according to the nature of their influence:

a) Product characteristic which individually influence the freezing curve, without any indirect action on other properties.

b) Product characteristic which alter the freezing curve shape by indirect action on other properties.

The influence of these product characteristics are shown in Figures 5.6 through 5.10, where the freezing curves - shown by a solid line - are predicted by the mathematical model using prescribed conditions. The prescribed conditions are:

a) Cooling medium temperature: -17.5°F

b) Convective heat transfer coefficient: 18 BTU/hr-ft^2-°F

c) Half of the thickness of infinite slab: 0.08333 ft

d) Time increment value: 0.005 hr

e) Number of nodes in the domain: 12

f) Information about the product:

1) Initial temperature: 53°F

2) Initial freezing point: 31°F

3) Initial moisture content: 0.803 lb_m H_2O / lb_m product

4) Density above freezing: 65 lb_m/ft^3

5) Specific heat above freezing: 0.88 BTU/lb_m-°F

6) Thermal conductivity above freezing: 0.32 BTU/hr-ft-°F

7) Density of product below freezing: 61 lb_m/ft^3

8) Unfreezable water content: 0.11 lb_m H_2O/lb_m product

5.3.1 Independent influence of thermal properties on freezing curve shapes

5.3.1A **Influence of initial thermal conductivity**

Initial thermal conductivity of the product determines the extent of variation on thermal conductivity values at temperatures below the freezing point. Two different initial conductivities will provide different magnitudes of variation of this thermal property during freezing. As a consequence, when these different values were used in the prediction model, which considers all the other conditions as equal, different shapes in the freezing curve will result.

Figure 5.6 illustrates the probable difference obtained if a thermal conductivity of 0.3 BTU/hr-ft-°F is used in place of a value of 0.32. As shown in Figure 5.6, the influence is manifested only in the last part of the freezing curve. As expected, longer freezing times are obtained when using the lower initial thermal conductivity. Discrepancies, as can be observed, are not critically important, even though variation in initial thermal conductivity could be considerable. The longer freezing times obtained indicate that the Maxwell-Eucken equation has provided smaller thermal conductivity values in the region just below the initial freezing point. This logical effect indicates an adequate reaction of the equation used.

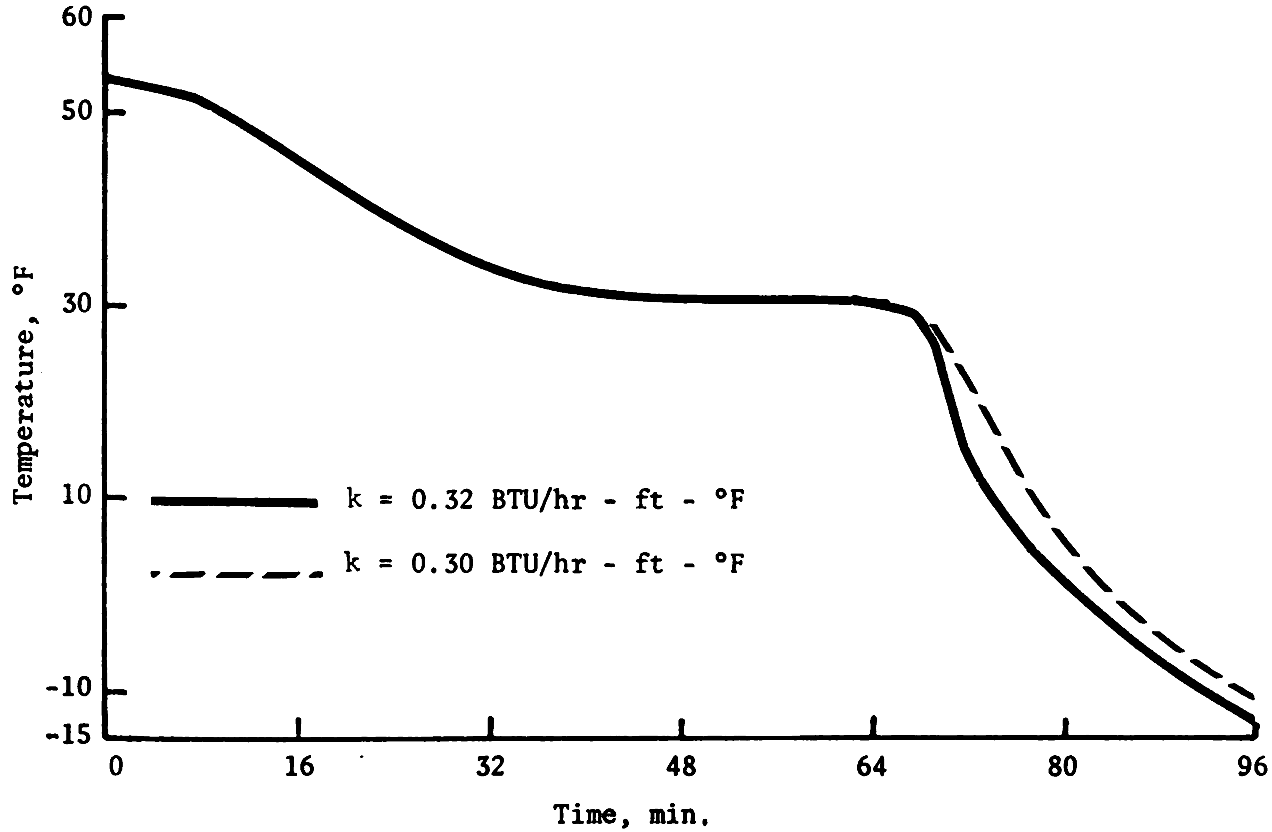


Figure 5.6. Influence of initial thermal conductivity of the product on predicted freezing curve shape.

5.3.1B Influence of apparent specific heat

Apparent specific heat values at temperatures below the freezing point can be obtained using equation (3.6) or an approximation of equation (3.5). As shown in Figure 5.3, approximation $\Delta H/\Delta T$ when $\Delta T = 1.0$ provides smaller values in the region close to the initial freezing point.

Figure 5.7 shows the probable influence of variations in apparent specific heat on the shape of the freezing curve. Higher values provided by the exact derivative of the total enthalpy with respect to the temperature [equation (3.6)] provides longer freezing times. Since the other physical characteristics remain the same, the obtained result was expected. As Figure 5.7 illustrates, the freezing curve corresponding to the exact derivative has a longer temperature constant zone. This increase in time is a result of the abrupt variation in apparent specific heat value at the initial freezing point, when the release of latent heat of fusion of ice is considered.

Apparent specific heats obtained by the approximation of the exact derivative of the enthalpy with respect to the temperature, when $\Delta T = 1.0°F$, were considered in the prediction model. These values provided a better agreement between experimental and theoretical values when freezing curves were compared.

5.3.2 Indirect influence of product physical characteristics on freezing curves

Product characteristics considered under this heading influence the shape of the freezing curve either by an indirect action on the thermal properties (apparent specific heat and thermal conductivity) or by both; indirect and individual action.

The following are considered in this discussion: a) density, b) unfreezable water and c) initial freezing point.

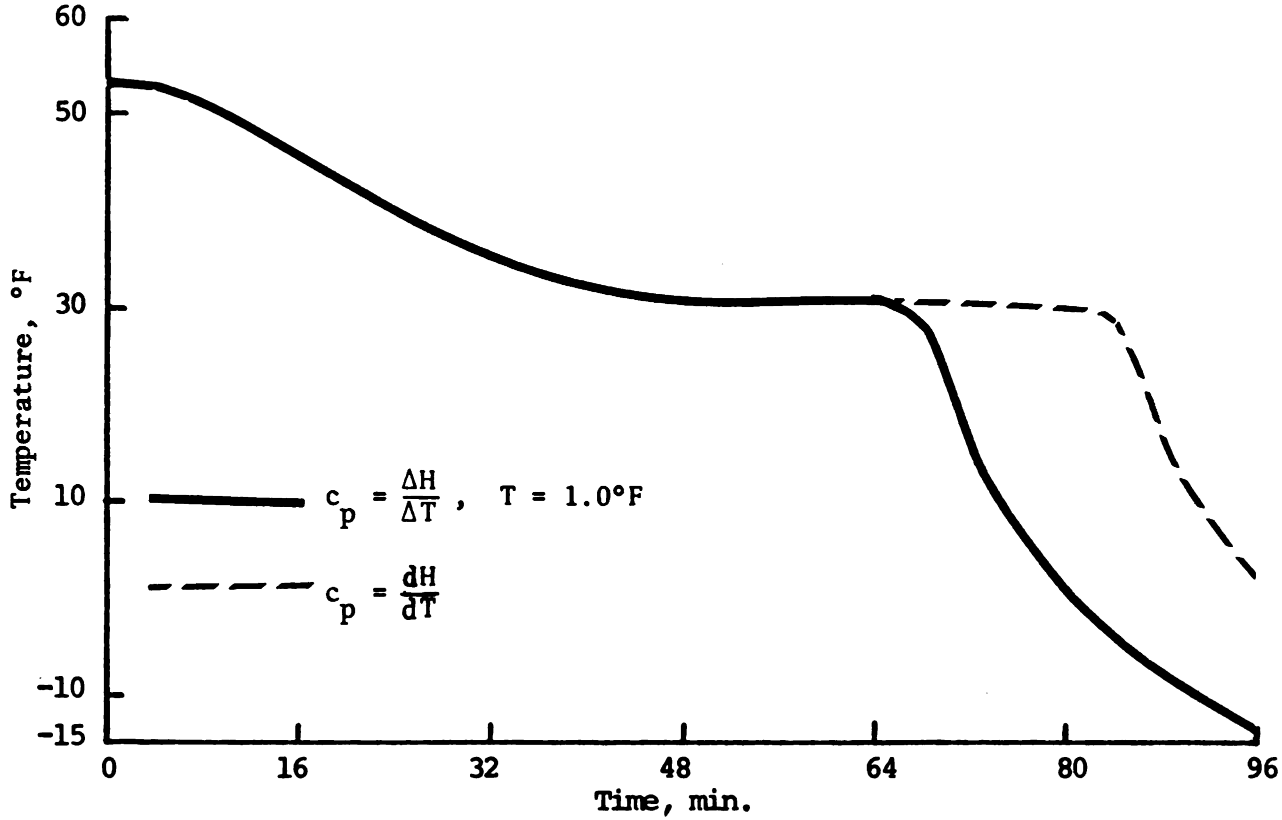


Figure 5.7. Influence of apparent specific heat of the product on predicted freezing curve shape.

5.3.2A Influence of differences in density between frozen and unfrozen product

The density of frozen product is normally utilized in computing thermal conductivity at temperatures in the freezing range. Independent of this utilization, matrices [A] and [D] from the numerical solution have also the possibility of utilizing this value, when temperatures below the initial freezing point are reached. The influence of density changes consideration when matrices [A] and [D] are evaluated, will be analyzed in this section.

Figure 5.8 shows the influence of considering density change for the frozen product when temperatures below the initial freezing point are reached. As was stated before, this value is directly used by the numerical solution through matrices [A] and [D]. Long (1955), theoretically computed fish density variation during freezing in an air-blast tunnel based on volume expansion of constituents of a fish system. Density of fish above freezing was about 65.8 lb_m/ft^3. During the freezing range a continuous decrease in density was reported (Long, 1955) until an essentially constant value of 60.2 lb_m/ft^3 was reached. This change in density was expected to influence the shape of freezing curve if its consideration is taken into account.

The solid line in Figure 5.8 shows the predicted curve which considers 61 lb_m/ft^3 as the codfish density at temperatures below freezing. The dotted line corresponds to the predicted curve which uses 65 lb_m/ft^3 as constant density of the product throughout the freezing process. Discrepancies shown in the last part of freezing curves indicate the importance of considering such a difference in the numerical solution. The shape of curve just below the freezing point is noticeably altered. As observed, shorter freezing times are obtained when differences in density are considered, and a lower value is utilized below the initial freezing point. This effect can be explained if the particular coefficients

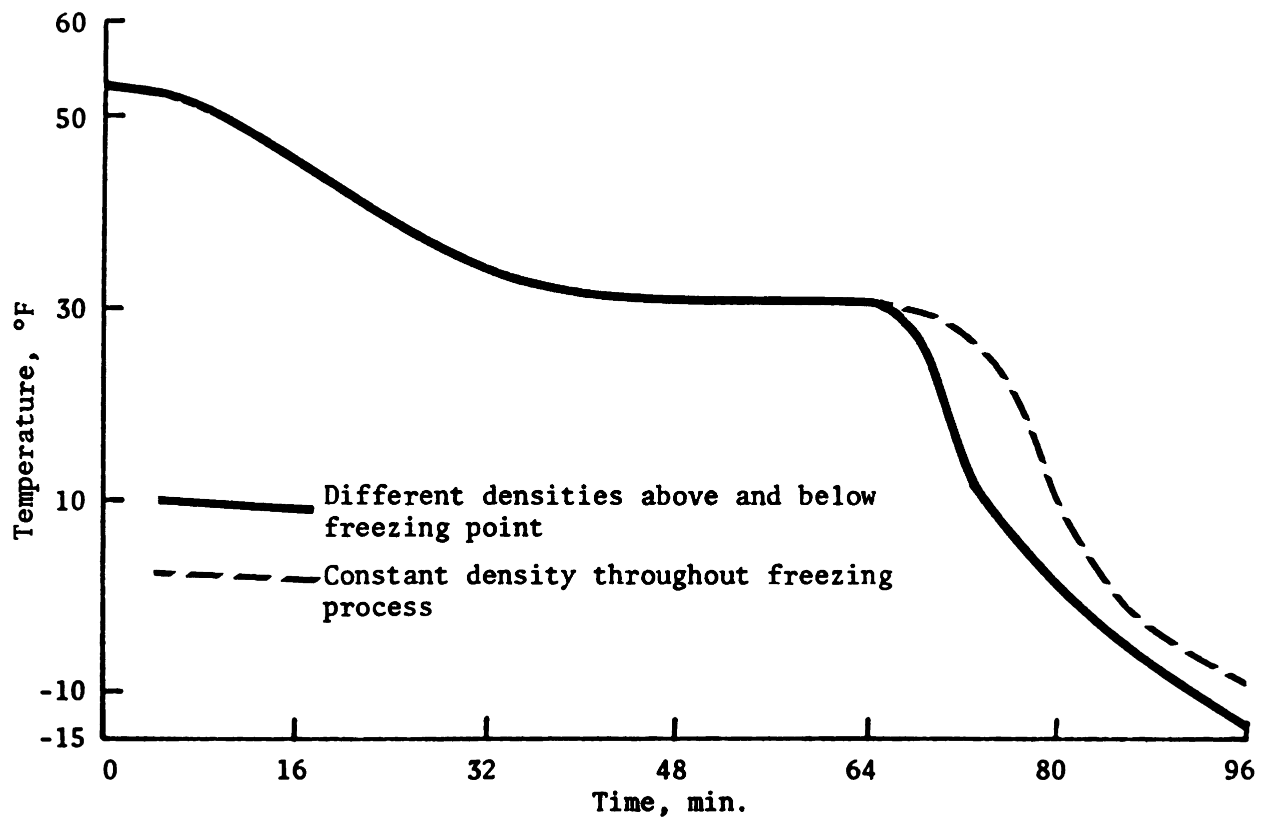


Figure 5.8. Influence of density differences between frozen and unfrozen product on predicted freezing curve shape.

in matrices [A] and [D] are analyzed. Basically, it can be considered that the thermal diffusivity at any point in the freezing range has increased, as a result of the lower density value utilized. As a consequence, rates of heat transfer will increase and lower temperatures will be obtained in a given time interval.

It is worth noting that a constant value for density of frozen product has been considered by the mathematical model. The implementation of a mathematical function to account for the sharp decrease at regions close to the freezing point would probably refine the numerical solution. However, no experimental evidence is available yet to define that function. A theoretical prediction of product density variation in the freezing range, based on information provided by the ideal binary solution and the freezing point depression approach, is also possible. As stated before, density variation in the freezing range was not considered by the mathematical model developed in the present investigation. However, from the results shown in Figure 5.8, influences in the shape of the curve are expected. The importance and extent of this change, as related to the increase in computational time, has to be investigated.

5.3.2B Influence of unfreezable water content

Below the initial freezing point, a food product with some percentage of unfreezable water and the same freezing point, will correspond to a more diluted binary solution. As a result, thermal conductivity and specific heat values will be changed because of differences in rates of ice formation. More diluted solutions will have their thermal properties more influenced by the unfrozen water than the ice, as compared to those of a more concentrated solution. Because of this reason, longer freezing times are expected.

Figure 5.9 illustrates the unfreezable water content influence. When 11% of unfreezable water content is compared to the situation with no unfreezable water, differences at the last part of freezing curve do not seem very important, especially when compared to the relative influence of other parameters.

5.3.2C Influence of initial freezing point

Initial freezing points for codfish have been reported to be 28.4°F (Nagaoka et al, 1955), 30.2°F (Riedel, 1956), or 31°F in the present research. Since a rather wide range of values are available their individual influence in the determination of the freezing curve shapes seems to be important.

Figure 5.10 shows the freezing curves corresponding to each of the initial freezing points considered. When considering that the first part of the freezing process is characterized by a transient heat conduction case with constant thermal properties, the product with higher freezing point will have its center at freezing point temperature in a shorter time. In addition, based on an analysis similar to that used in thermal arrest time, the latent heat removal zone is expected to be of shorter duration. Due to the magnitude of the differences between freezing points considered, this effect might not be noticed. A product with higher freezing point will correspond to a more diluted binary solution, whose rates of ice formation will be lower than those of the comparatively lower freezing point product. As a result, slower freezing rates are expected in the first product.

Comparison of freezing curves presented in Figure 5.10 indicates that results are as expected. Important differences are noted when influence of the initial freezing point variation is analyzed.

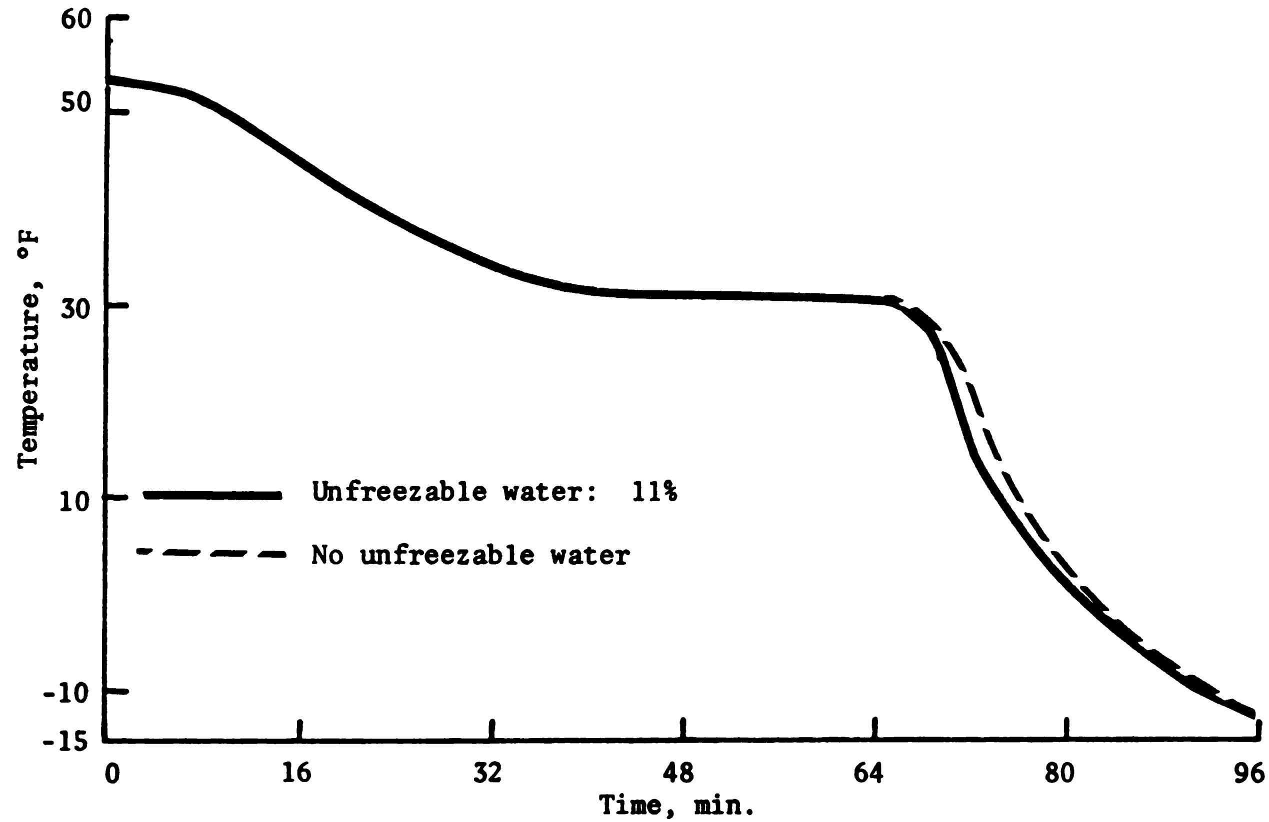


Figure 5.9. Influence of unfreezable water content on predicted freezing curve shape.

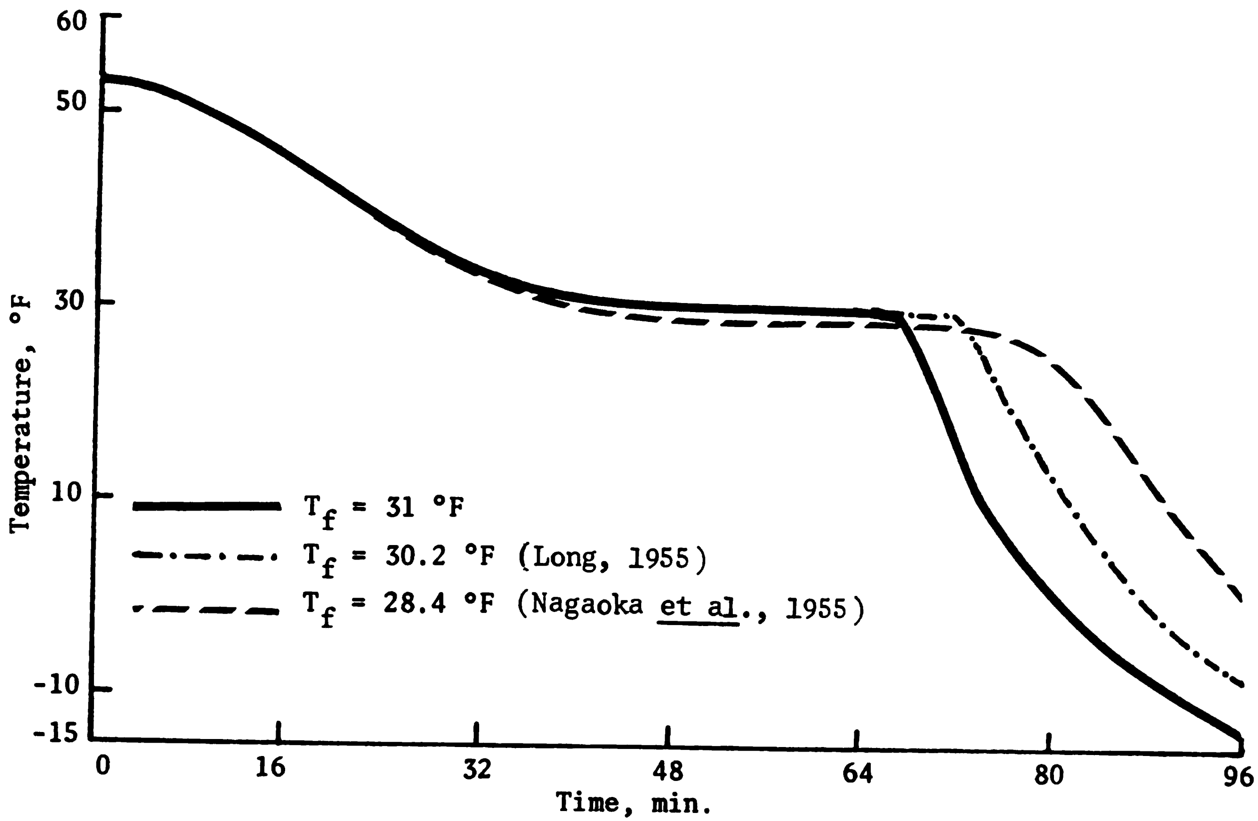


Figure 5.10. Influence of initial freezing point of the product on predicted freezing curve shape.

5.4 Comparison of Theoretical and Experimental Freezing Curves

Experimental values and predicted freezing curves are shown in Figures 5.11 to 5.18. They correspond to the situations presented in Table 4.2.

Figures 5.11, 5.12 and 5.13 differ only in the initial product temperature. Comparison of Figure 5.12 to Figure 5.13 shows that the lower initial temperature product provides longer total freezing times. Since this result is not as it would be expected, experimental errors seems to be related to the situation represented in Figure 5.13.

Figures 5.17 and 5.18 show results obtained under freezing conditions at relatively low cooling medium temperature (-10.5°F) and different intensity of forced convection. Figure 5.16 represents a freezing process obtained under a low value of surface heat transfer coefficient (still air).

Figure 5.16 represents a freezing process obtained under a low value of surface heat transfer coefficient (still air).

Figures 5.11 and 5.15 present a poor agreement between experimental and predicted curves. Experimental errors appear to be influencing the results. Probable sources of error involved in a situation represented by Figure 5.15 will be analyzed in detail later on.

Comparison of curves predicted by the mathematical model to the experimental values demonstrates that, in general, an acceptable agreement is obtained. Discrepancies observed may be explained if the influence of some probable experimental errors is considered.

Experimental errors which might influence the shape of the freezing curve are probably related to: a) the failure to accurately represent the situation considered by the mathematical model in the laboratory, b) errors in experimental determination of some parameters used by the computer model and c) errors involved in the temperature measurement.

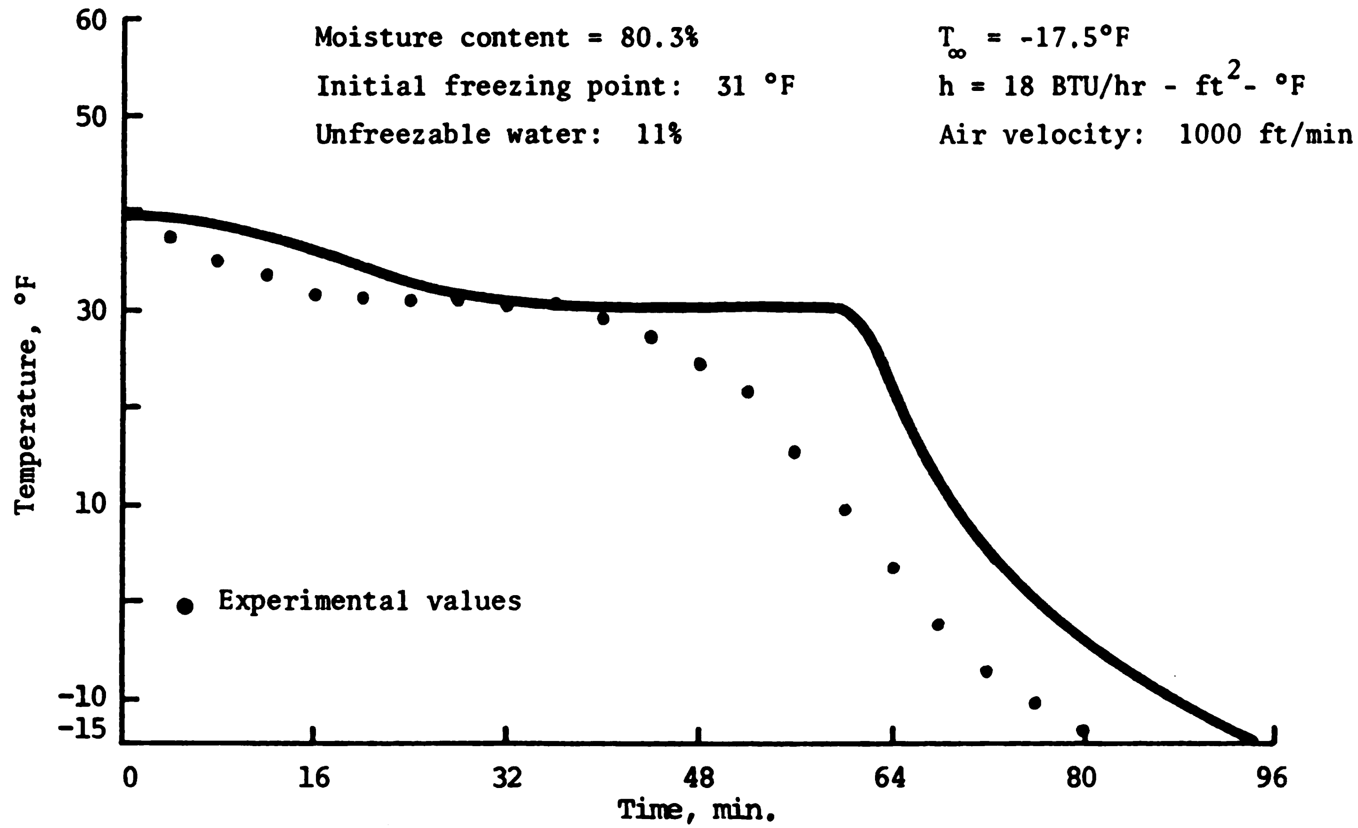


Figure 5.11. Comparison of predicted and experimental freezing curves for a 2 in.-thick infinite slab of codfish. Test number one (Table 4.2).

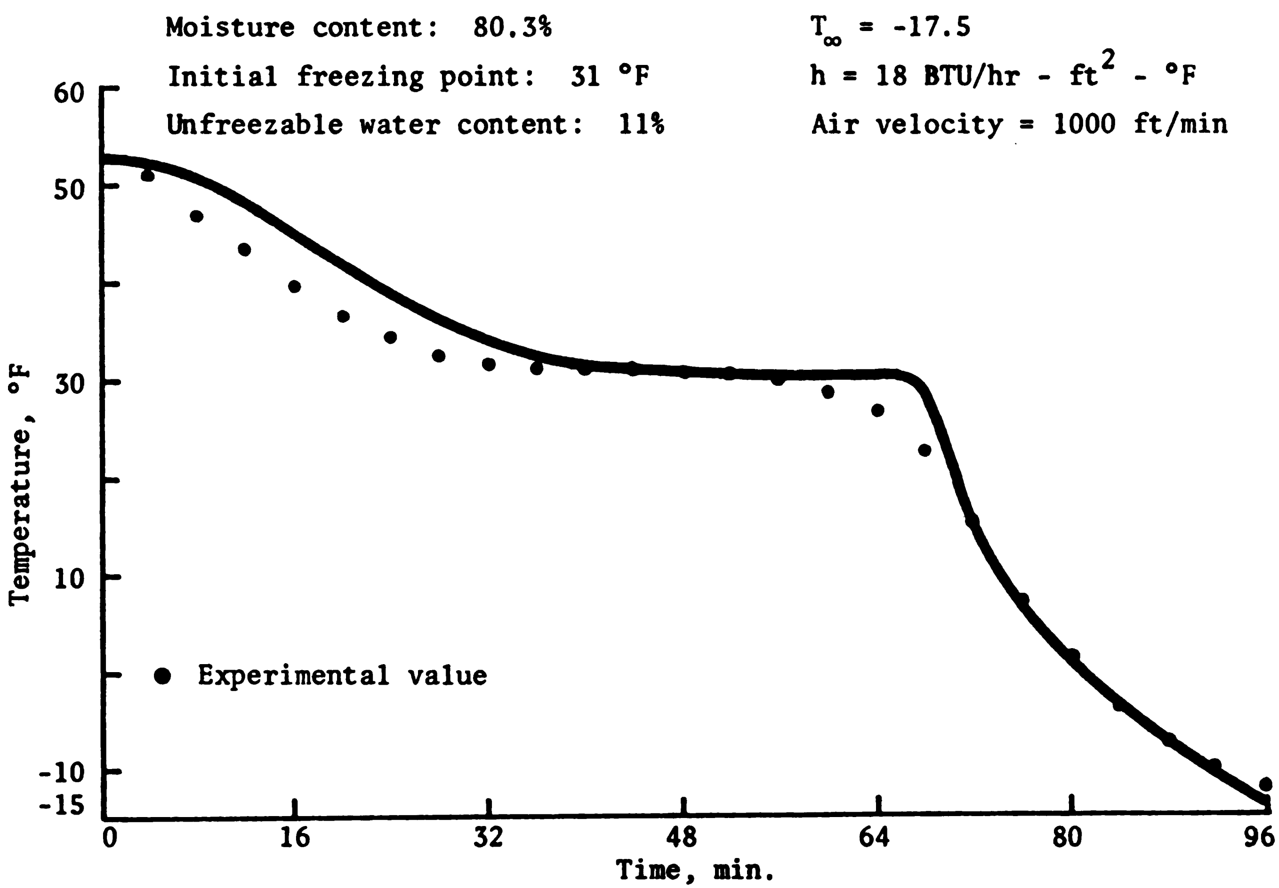


Figure 5.12. Comparison of predicted and experimental freezing curves for a 2 in-thick infinite slab of codfish. Test number two (Table 4.2).

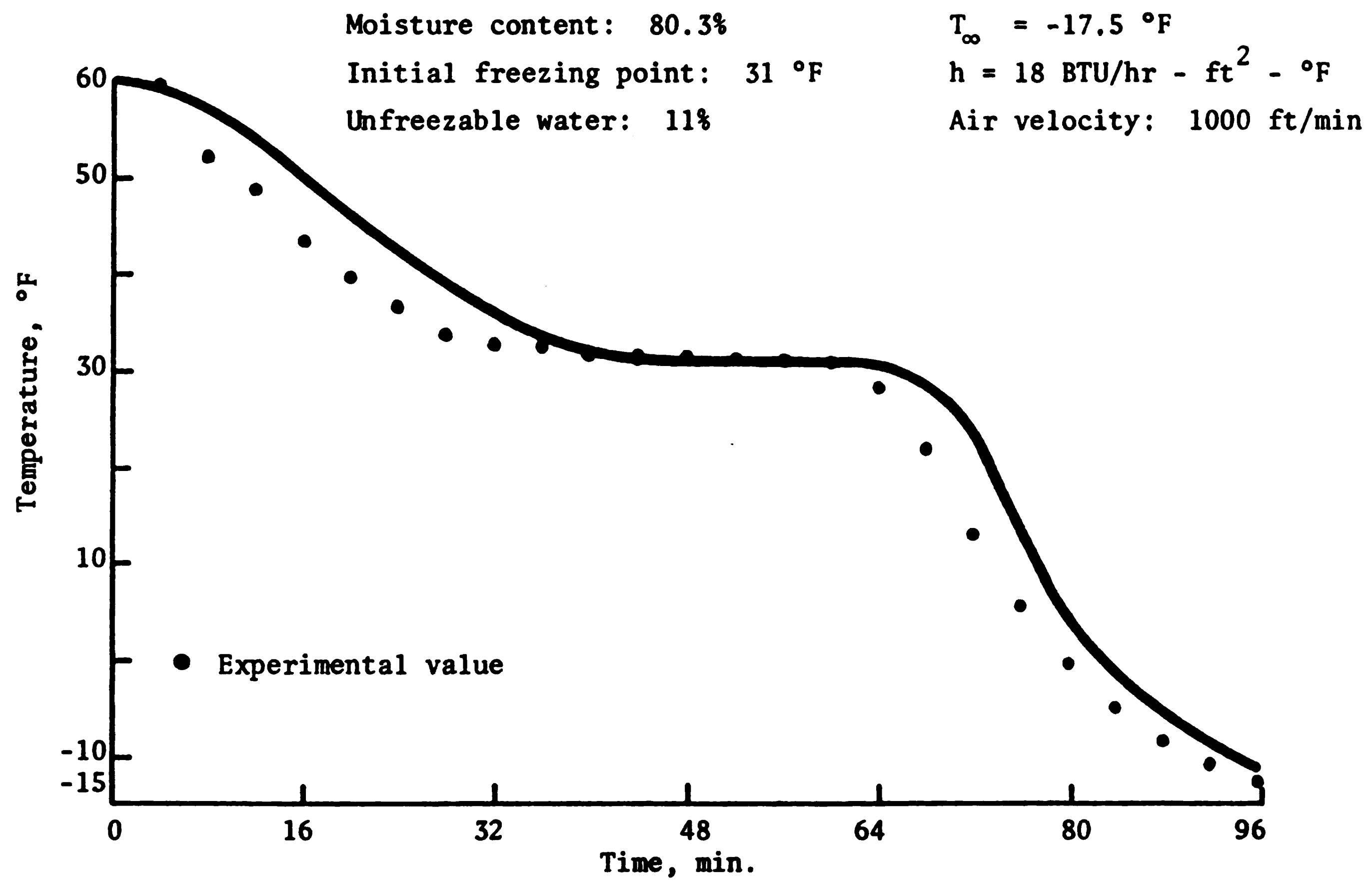


Figure 5.13. Comparison of predicted and experimental freezing curves for a 2 in-thick infinite slab of codfish. Test number three (Table 4.2).

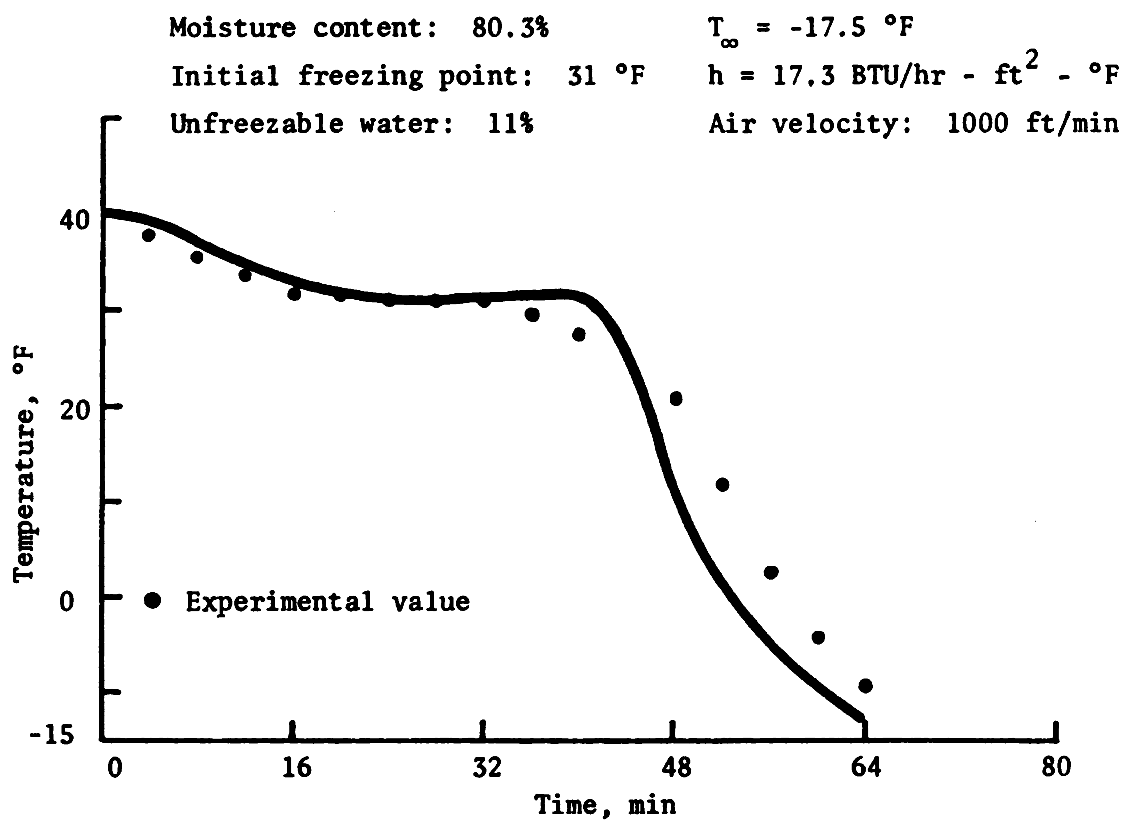


Figure 5.14. Comparison of predicted and experimental freezing curves for a 1.5 in-thick infinite slab of codfish. Test number four (Table 4.2).

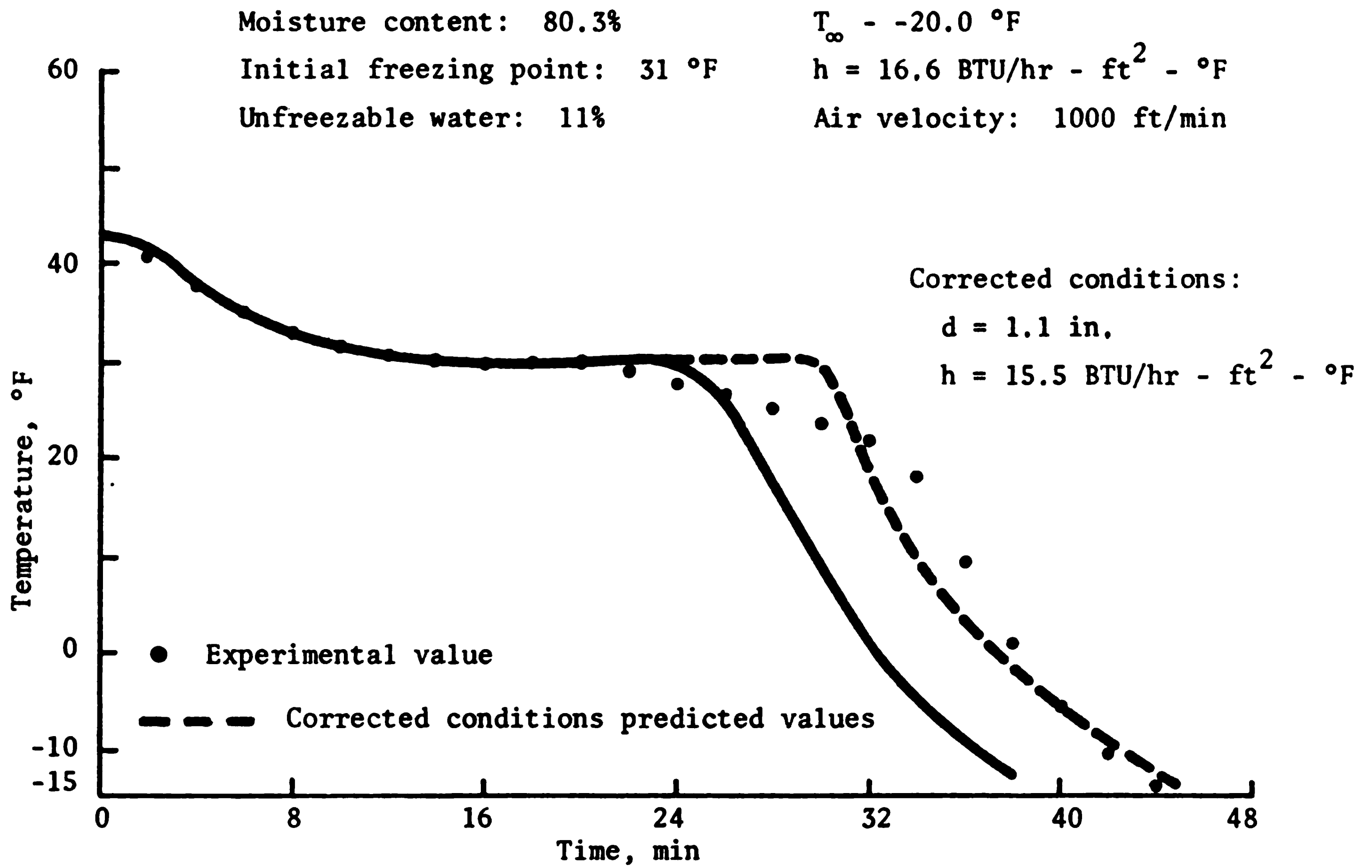


Figure 5.15. Comparison of predicted and experimental freezing curves for a 1 in.-thick infinite slab of codfish. Test number five (Table 4.2).

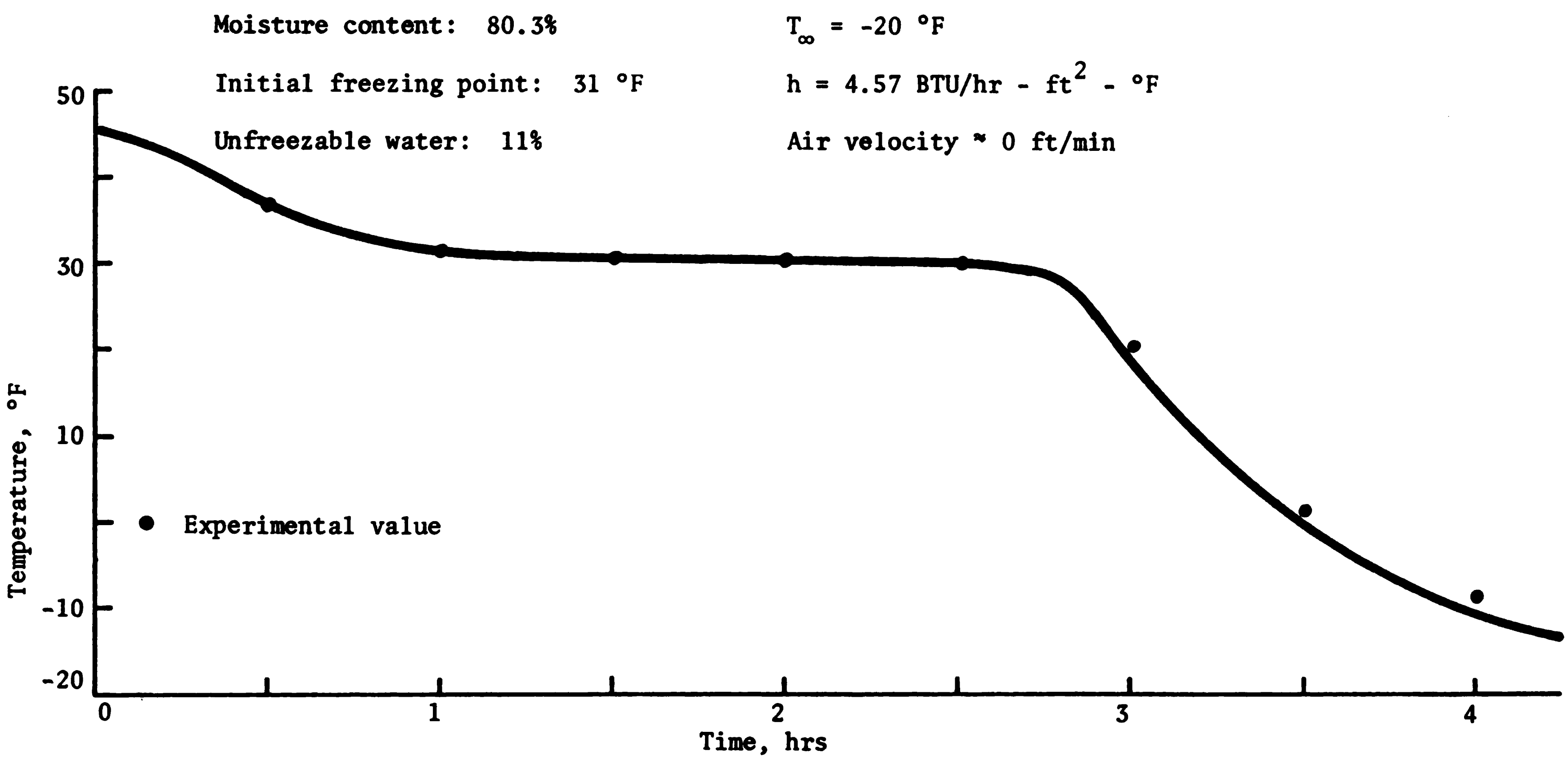


Figure 5.16. Comparison of predicted and experimental freezing curves for a 2 in.-thick infinite slab of codfish. Test number six (Table 4.2).

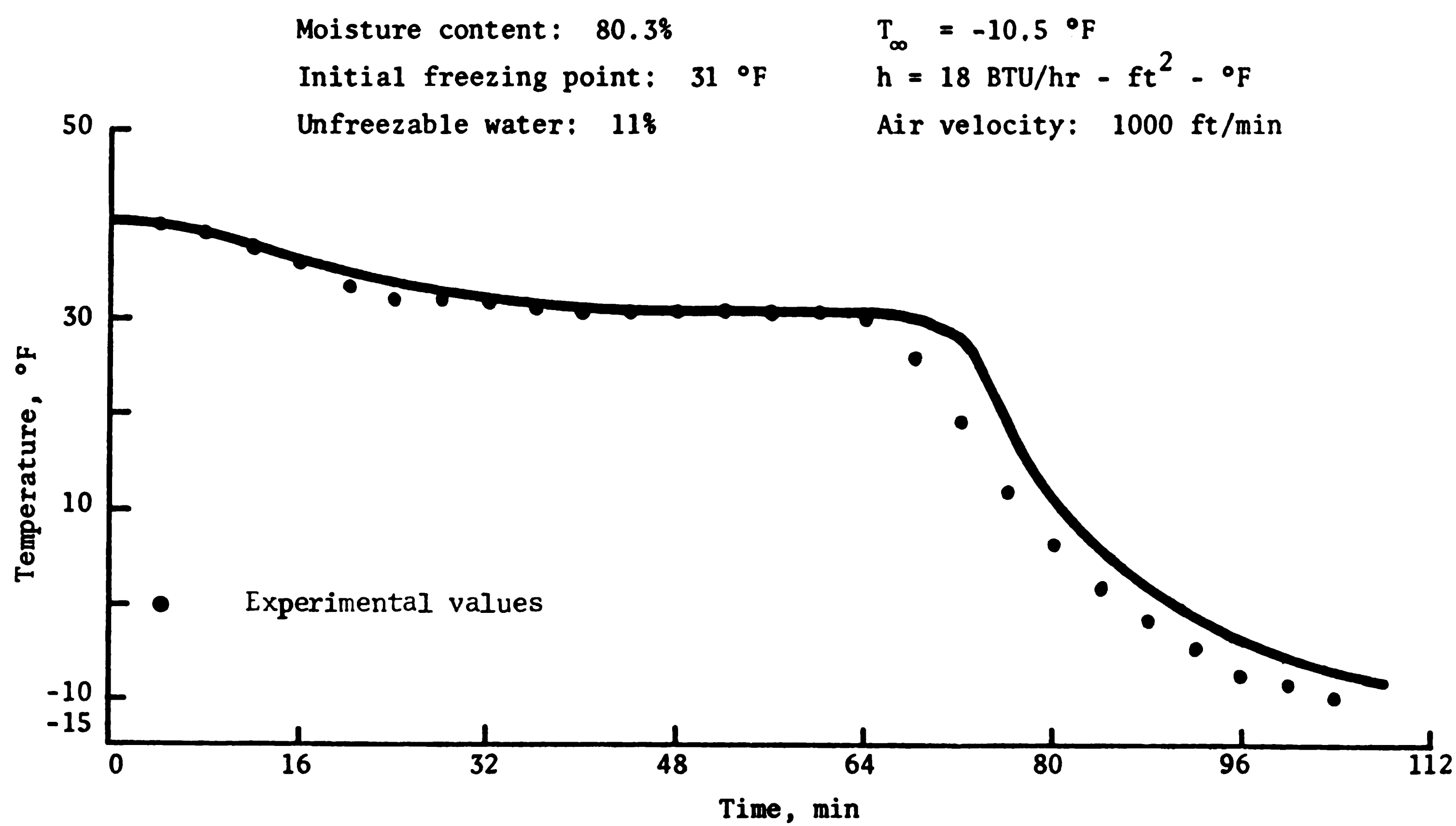


Figure 5.17. Comparison of predicted and experimental freezing curves for a 2 in.-thick infinite slab of codfish. Test number seven (Table 4.2).

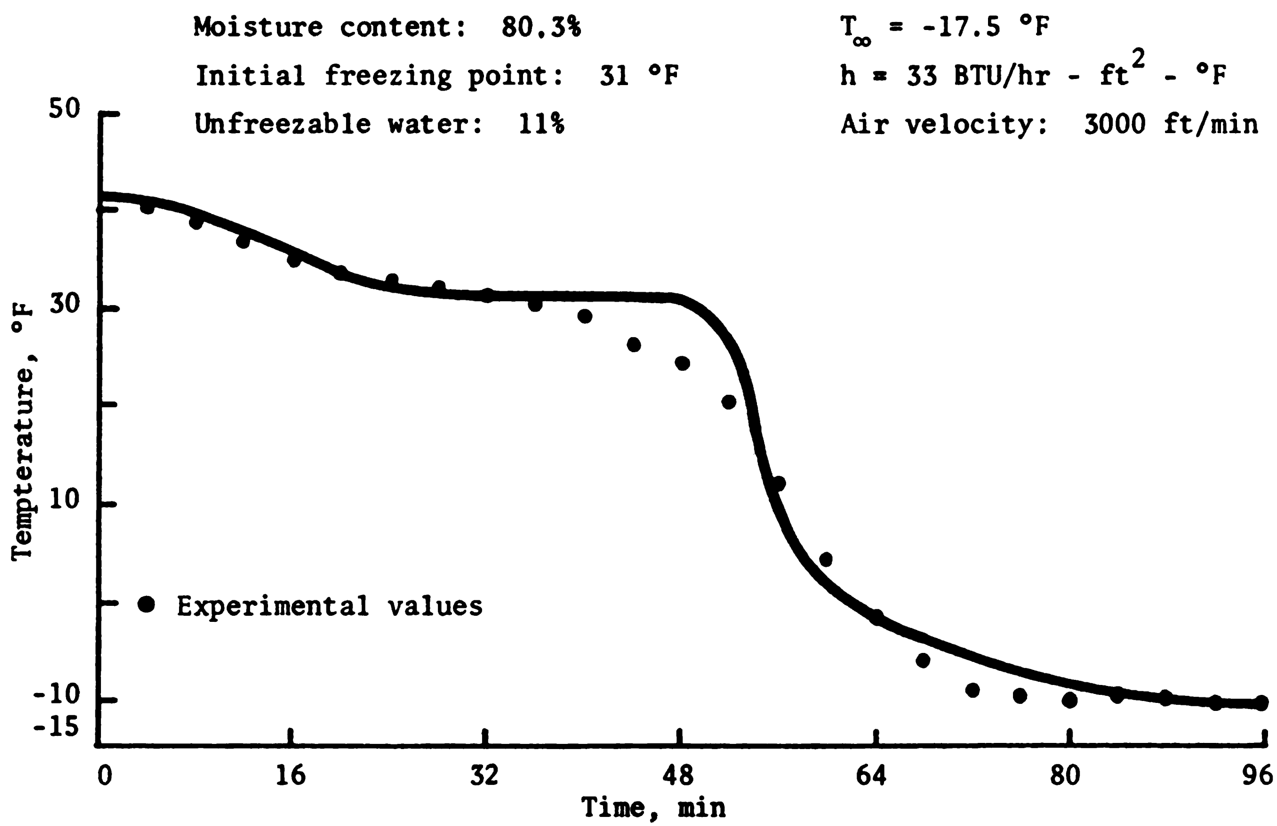


Figure 5.18. Comparison of predicted and experimental freezing curves for a 2 in.-thick infinite slab of codfish. Test number eight (Table 4.2).

Failure to represent the situation that the mathematical model is considering could occur under the following circumstances:

1) Influence of related physical phenomena.

(1a) Mass transfer between the surface of the product and the cooling medium. This related phenomenon is particularly important at the beginning of the freezing process, before the surface temperature reaches the freezing point. Most perishable foods are characterized by a surface easily permeable to water vapor diffusion. Simultaneously with the cooling in air, a diffusion of evaporated water from the surface tissues takes place. The heat of evaporation is absorbed from the product itself and, as a result, increased heat transfer rates are obtained. Changes in temperature profiles at the beginning of the freezing process should influence the general shape of the freezing curve. Since the mathematical model assumes no mass transfer phenomena, the predicted freezing curve should be displaced to the right of the experimental values when moisture losses are of predominant importance. Moisture losses increase with increased air velocity and initial temperature, while other conditions are assumed to remain constant.

Fish frozen in air-blast tunnels, experience between 1 to 2% of weight losses (Long, 1955). A moisture loss of 1% or 0.01 lb. water per lb. fish, under the initial temperatures considered in the present experiments represents about 11 BTU of latent heat of evaporation.

(1b) Volume expansion. Predominant volume increase occurs when water is transformed into ice caused by increases in density of fish during freezing. Because the sample holder design would not allow for volume expansion in codfish sample changes will be manifested by increases in thickness. If total density change in codfish from 65 lb_m/ft^3 to 61 lb_m/ft^3 are considered, an increment in thickness of 0.03175 in. change is expected for the 1 in.-thick sample. The influence of volume expansion on shape of the freezing curve would indicate that longer freezing times would be obtained.

(1c) Contact thermal resistance. When large thicknesses are simulated using codfish fillets, more than one layer is sometimes necessary to achieve the desired dimension. The lack of continuity between codfish layers - in the direction of heat transfer - and the presence of air (thermal conductivity 0.014 BTU/hr-ft-°F) provides a contact resistance not considered by the mathematical model.

If contact resistance has a predominant influence, longer experimental freezing times are expected as compared to those obtained using the mathematical model.

2) Change in surface characteristics. Simulation of a smooth surface is difficult. During freezing, a combined effect of volume expansion, mechanical stresses and manner of placement of codfish fillets in the sample holder change the characteristics of surface The physical situation will be difficult to consider either by the mathematical model or any thermal system designed to provide surface heat transfer coefficient.

If this change is predominant, experimental freezing curves should be displaced to the left of the predicted one. Shorter freezing times will be expected.

3) Influence of sample holder design. The sample holder restricted expansion at part of the bottom and at the lateral surfaces. Influence of temperature gradients along the longitudinal axis could be possible.

Errors involved in experimental determination of parameters used by the mathematical model, such as:

1) Measurement of convective heat transfer coefficient.
2) Measurement of themal properties (initial thermal conductivity and specific heat), unfreezable water, moisture content, initial freezing point, densities of frozen and unfrozen product.

Errors involved in temperature measurement are related to sensing elements, recording equipment, positioning of sensor point in desired place and error in chart reading.

The combined action of the probable experimental errors described and their individual predominance in a given freezing condition will finally determine the type and amount of the discrepancy between theoretical and predicted freezing curves.

5.4.1 Analysis of a typical theoretical and experimental freezing curve.

Experimental points in Figure 5.12 represent the values obtained when a 2-in. thick simulated infinite slab of codfish was frozen in the experimental tunnel at -17.5°F of air temperature. Initial product temperature was 53°F and the experimentally determined mean heat transfer coefficient was 18 BTU/hr-ft^2-°F (1000 ft/min mean air velocity). The predicted freezing curve is represented by the solid curve.

A good description of the experimental freezing curve is achieved by using the prediction model. Differences of agreement are noticed at the sections of the experimental curve between the beginning of the freezing process and the time the center reaches the freezing point temperature. The lower experimental temperatures during this part of the curve may be explained by moisture losses. Moisture losses, as stated before, are not considered by the mathematical model. Therefore, if moisture losses were the predominant factor in discrepancies, the result is as expected. In addition, moisture losses were not considered by the model used to calculate the convective heat transfer coefficient. The small displacement of constant temperature zone to the right seems to indicate a side effect of lower moisture due to losses during the cooling stage. Since the mathematical model does not consider this factor, the theoretical curve tends to remain in the zone of latent heat removal somewhat longer. The last part of the theoretical freezing curve shows an excellent agreement with experimental values.

5.4.2 Freezing Times Comparison

Table 5.1 contains freezing time values corresponding to the experimental situations presented in Table 4.2. The freezing time criterion defined in 5.2 was utilized to obtain these values. Experimental and theoretical freezing times were obtained from Figures 5.11 to 5.18. Equation (1.1) provided values corresponding to the modified Plank's equation.

In general, a small discrepancy is observed between the predicted and the experimental values. The difference is much smaller than that derived when modified Plank's equation is compared to the experimental values. For the situation considered, modified Plank's equation always

TABLE 5.1--Comparison of experimental freezing times to theoretical and modified Plank's equation values

Test Number	Freezing Time, min.		
	Experimental	Theoretical	Modified Plank's Equation
1	69.0	80.0	70.0
2	85.5	85.4	79.3
3	84.0	87.0	84.6
4	60.0	56.0	50.4
5	40.0	34.0	31.0
6	225.0	222.0	208.6
7	93.0	98.0	82.4
8	67.0	70.0	59.5

provides a smaller freezing time than that obtained by the mathematical model.

5.4.3 Freezing curves and small thickness

Figure 5.15 shows the predicted and experimental values corresponding to a 1-in thick codfish fillet. A cooling medium temperature at -20°F and an initial product temperature of 43°F were utilized. The heat transfer coefficient was experimentally determined. A value of 16.6 BTU/hr-ft^2-°F was found when a 1000 ft/min air velocity was used.

A noticeable difference between the theoretical and experimental values is shown. Assuming that the mathematical model provided acceptable results for other curves, a search for probable causes of discrepancy was sought.

The influence of the convective heat transfer coefficient for this particular case was analyzed. Even though improvements were found when small increments of surface coefficient values were considered, the freezing curve was not influenced significantly by this parameter alone.

When possible errors in thickness were analyzed, it was found that, for this particular situation, a more noticeable change of shape in the freezing curve was obtained when thickness was varied. Influences of thickness seem to be more important than influences in convective heat transfer coefficient. Consideration of 10% error in the thickness and in the heat transfer coefficient evaluation caused the theoretical freezing curve to be displaced to the right. The improvement in the agreement between experimental and predicted values was noticeable. This observation seems to indicate that, under certain circumstances, experimental errors have a tremendous importance when small thicknesses are considered in the determination of freezing curves. Errors in thickness seems to be more important than those caused by the heat transfer coefficient.

5.5 Comparison of Mathematical Model with Published Data

Research conducted by Long (1955) and Charm et al (1972) deserves special attention since experimental information which can be used for further comparisons to the mathematical model developed in this investigation can be presented. Throughout this section, thermal properties presented in Table 4.1 will be utilized, unless otherwise stated.

5.5.1 The mathematical model and Long's results

Long (1955) provided an experimental freezing curve for a 6-in. thick block of fish frozen in an air-blast tunnel. Cooling medium temperature was -20°F and initial temperature of the product was 60°F. No information was provided for the surface heat transfer coefficient, however Albasiny (1956) and Eddie and Pearson ((1958) considered 32 BTU/hr-ft^2-°F when they utilized Long's 1955 (data).

Figure 5.19 shows the agreement between data provided by Long (1955) and the corresponding theoretical prediction using the mathematical model. Predicted values at temperatures above the freezing point are in excellent agreement with experimental values. Expected minor discrepancies are shown at temperatures below the freezing point. These differences can be explained by an analysis similar to the one used in previous sections of this chapter. Shorter predicted freezing times can be expected if lower convective heat transfer coefficients are utilized in the model or if the experimental situation fails to adequately represent the situation and the assumptions of theoretical model. Among the causes of error to be considered are: a) larger thickness, b) presence of contact resistances due to air between fish

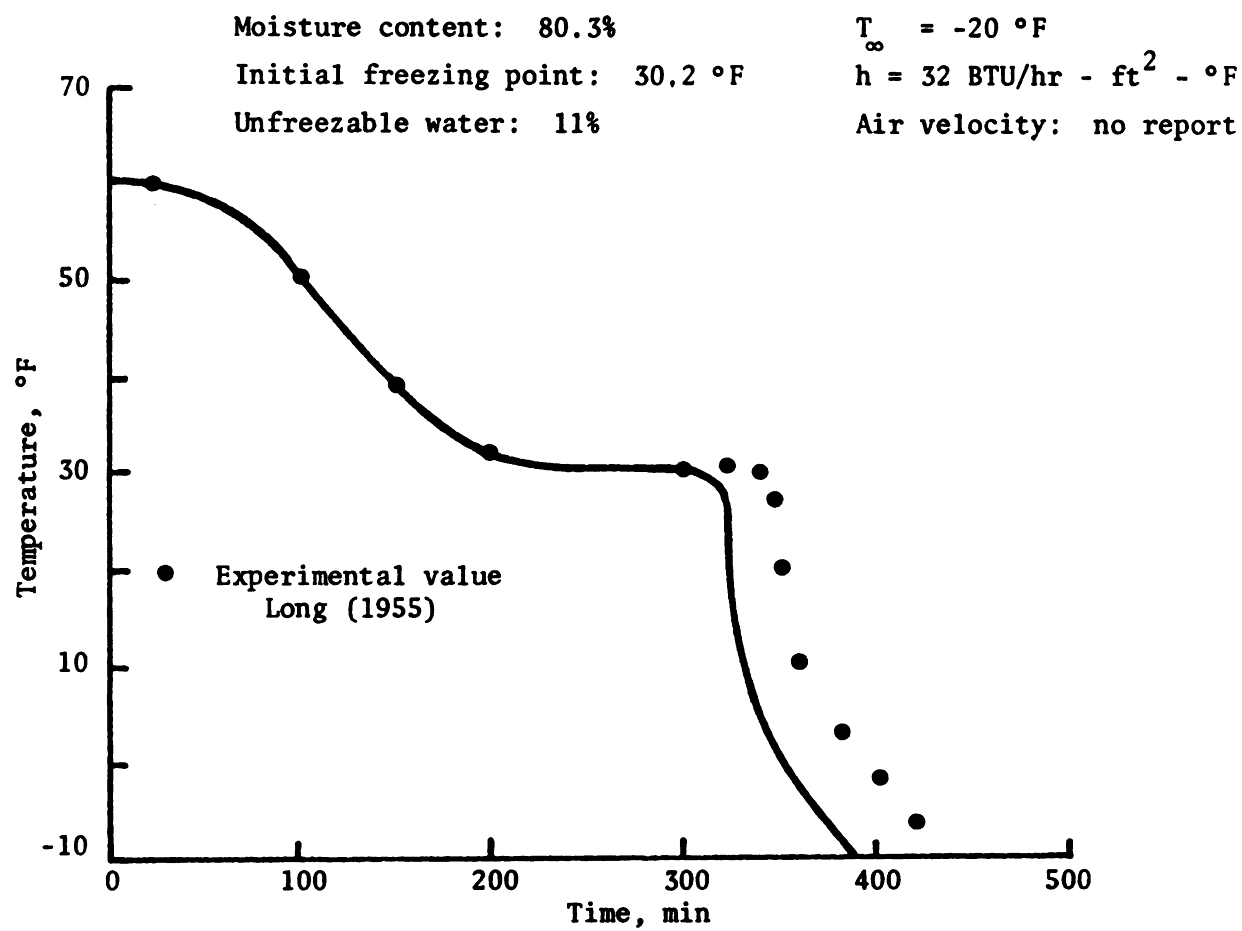


Figure 5.19. Comparison of predicted and experimental freezing curves for a 6 in.-thick infinite slab of codfish (from Long, 1955).

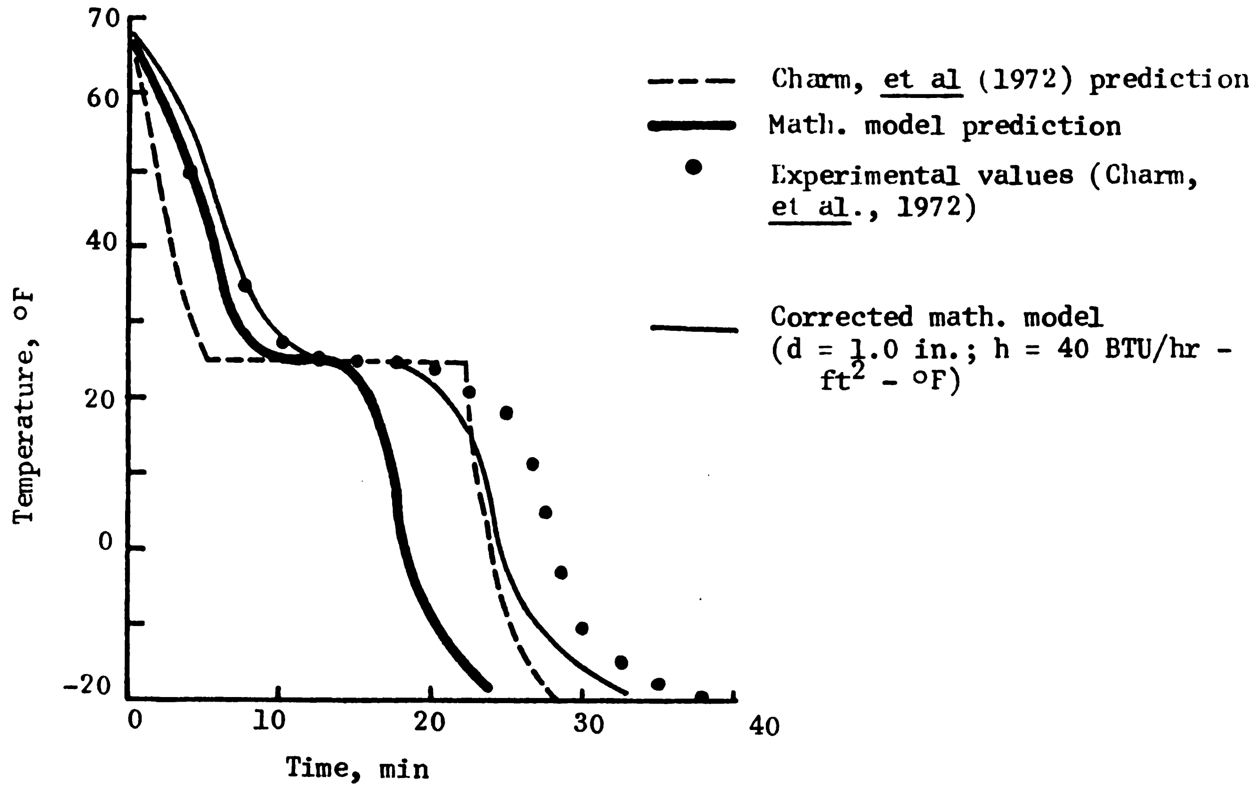
fillets which compose the rather thick slab and c) differences between the true thermal and other physical properties and those described by the model. Other sources of error, discussed in previous sections, seem to have no relevant influence for this particular case.

In spite of the small discrepancies noticed, the mathematical model provides an acceptable agreement when compared to Long's (1955) experimental results. When freezing times were evaluated, using criterion defined in 5.1, the predicted value was 370 min. and the experimental value was 415 min. The use of modified Plank's equation gave a freezing time of 357 min. for this situation. There is a small discrepancy observed in freezing time between the predicted and the experimental values. The difference is smaller than that derived when modified Plank's equation is compared to the experimental value.

5.5.2 The matehmatical model and Charm's results

Charm et al (1972) presented an experimental freezing curve of a codfish fillet, (3 in. x 3 in. x 7/8 in.) simulating an infinite slab by thermal insulation of the lateral surfaces. The freezing process was performed by immersion of the codfish fillet into a Freon 12 and 144 refrigerant mixture (-21.7°F). Initial temperature of the product was 68°F and the experimentally determined convective heat transfer coefficient was 46 BTU/hr-ft^2-°F.

Figure 5.20 shows the experimental points presented by Charm et al (1972) and curves predicted by the mathematical model and by a model proposed by Charm et al (1972). Based on the experimental evidence and the location of the constant temperature zone of Charm's et al (1972) predicted curve, a freezing point of 25°F was used in the mathematical model.



Moisture content: 80.3% | Unfreezable water content: 11%
Initial freezing point: 25°F | T_∞ = -21.7°F

Figure 5.20 Comparison of predicted and experimental freezing curves for a 7/8 in. - thick infinite slab of codfish (from Charm, et al., 1972)

From the two curves predicted by the mathematical model, one of them was obtained by using the same experimental conditions as described by Charm et al (1972). The other one was obtained under the combined influence of two probable sources of experimental errors: failure to represent the thickness of the infinite slab and the surface heat transfer coefficient accurately under an experimental situation.

As Figure 5.20 illustrates, the curves predicted by the mathematical model provide a better description of the general experimental freezing curve as compared to Charm's predicted curve. This is especially true for portions of the curve above the freezing point. If the zone below the freezing point is compared, Charm's predicted freezing time is closer to the experimental values as compared to those predicted by the mathematical model when original freezing conditions are used. If, however, an experimental error of 1/8 in. in thickness (by experimental procedure and/or volume expansion) coupled with an error of about 10% in surface heat transfer coefficient are assumed, (a thickness of 1 in. and a heat transfer coefficient of 40 BTU/hr-ft^2-°F) a curve closer to the experimental values is obtained by the mathematical model. The improvement of the corrected mathematical model curve is more pronounced when the zone below the freezing point is considered. Freezing times predicted by this curve will be closer to the experimental values than those provided by Charm's model.

An additional refinement in predicted values may be obtained if further considerations regarding the characteristics of the product are made. Since 25°F is the initial freezing point for codfish utilized in this particular experiment, considerable changes in other properties which affect the thermal behavior sample are expected. Additional correction of thermal properties andother physical characteristics of the product will definitely change the shape of the predicted freezing curve, as has been shown in Section 5.3, where some of the influences were discussed.

A closer analysis of the freezing curve predicted by Charm's (1972) model demonstrates that the two characteristic inflection points - presented by the experimental curve immediately above and below the constant temperature zone - are not shown. The same situation is noted in another predicted curve presented by Charm et al (1972). The absence of these inflection points influences the ability for the predicted model to simulate the freezing curve. Analysis of the computer program provided by Charm et al (1972) seems to indicate that single values for thermal properties are considered for the zones above and below the freezing point. In other words, these zones are considered to be transient heat conduction cases with constant thermal properties. This consideration is only an approximation of the actual situation, as discussed in Section 5.2. Under the consideration that Charm's model utilizes constant thermal properties in regions above and below the freezing point, the improvement in description of freezing curves obtained by taking into account thermal properties variation in freezing range, is clearly demonstrated by Figure 5.20.

VI. SUMMARY AND CONCLUSIONS

1. A mathematical model to predict freezing curves in food products using the ideal binary solution assumption and the freezing point depression approach was successfully developed and tested by comparison to experimental results. This model considers one-dimensional heat transfer and prediction of thermal properties variation (thermal conductivity and specific heat) during freezing. The prime advantage of this model is the use of a small amount of experimental information about the product. Experimental product characteristics required by the prediction model are:

a. Initial moisture content.

b. Initial freezing point.

c. Thermal conductivity, specific heat and density above freezing.

d. Density below freezing.

e. Unfreezable water content.

2. Accuracy of the prediction model was demonstrated when predicted freezing curves provided acceptable agreement with experimental curves for codfish fillets. Under specified freezing conditions, the inaccuracy of experimental parameters was shown to affect this agreement considerably. Thicknesses of one inch or less, at relatively high surface heat transfer coefficients, provided freezing curves which showed a poor agreement with predicted results. The main source of error was found to be a failure to accurately represent the thickness as well as errors in surface heat transfer coefficient determination.

3. Under the conditions studied, freezing time predicted by the model was closer to the experimental results than that obtained from the modified Plank's equation. The modified Plank's equation always provided a shorter freezing time. In several of the cases studied, differences between the theoretical value and that provided by the modified Plank's equation was not considerable. This fact would indicate that improvements in the theoretical analysis of the freezing process would modify the shape of the freezing curve in the region of maximum latent heat removal.

4. Consideration of possible errors in freezing point determination affected, to a great extent, the shape of the freezing curve. Density changes between the frozen and unfrozen states was important enough to be considered in the model. The inclusion of unfreezable water was shown to affect the freezing curve shape to a lesser extent than the freezing point or density changes.

The importance of the approximation in the apparent specific heat value to the shape of the freezing curve was demonstrated. The approximation of the derivative of the total enthalpy with respect to the temperature, when $\Delta T = 1.0°F$ was found to provide better results than the exact derivative. A variation of 0.002 in the experimental value of initial thermal conductivity of the product had a rather small influence upon the freezing curves.

5. The usefulness of the prediction model in providing information to explain some physical characteristics of the freezing process was demonstrated. The definition of a practical criterion for measuring freezing times was justified. This definition considers the time for the temperature at the center of the product to pass from the initial

temperature to a temperature at which essentially no ice is formed or below. The incorrectness of the thermal arrest time criterion as a means to measure freezing rates was demonstrated.

VII. SUGGESTIONS FOR FURTHER STUDY

1. To investigate the influence of further refinements of the prediction model by: a) inclusion of moisture losses in the boundary condition at the surface of the product, b) consideration of density changes of the product within the freezing range.

2. To study the performance of the prediction model under different directions of heat transfer, geometries of the body and boundary conditions: a) two-dimensional heat transfer and for different shapes, using the Alternating Direction Implicit finite difference method, b) three-dimensional heat transfer and for different shapes, utilizing the finite element method.

3. To evaluate the ability of the ideal binary solution assumption model in predicting thermal properties variation. Comparison to experimental results and parameters estimation using other criteria could be considered.

4. To investigate the generality of the prediction model utilizing food products other than codfish.

5. To apply the prediction model to optimization of the use and design of freezing equipment.

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