SIMULATION OF TEMPERATURE HISTORY AND
ESTIMATION OF THERMAL PROPERTIES OF FOOD
MATERIALS DURING FREEZING

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(ABSTRACT)

Freezing is a very common method of food preservation around the world. Accurate simulation of the freezing process in food materials is very important for the design of superior freezing processes and more efficient refrigeration equipment.

The accuracy of numerical methods is very significant for reliable prediction of temperature history in food materials during freezing. However, accurate simulation of the freezing process in foods is difficult due to its inherent nonlinearity. In this study, a technique was presented and used to assess the accuracy of the Crank-Nicolson and the Two-Step methods in solving this nonlinear problem. Overall, the accuracy of the Two-Step method was higher than that of the Crank-Nicolson method. These numerical methods were also implemented to simulate one-dimensional freezing experiments. Again, the results of the Two-Step method exhibited better agreement with the experimental data than the Crank-Nicolson results.

The thermal properties of food materials change substantially with temperature
during freezing. The estimation of these properties is very important in simulating freezing and determining the freezing time of foods. Mathematical modeling of the thermal properties of foods has been an appealing alternative to experimental methods. These models are generally based on the assumption that food materials are ideal binary solutions. One of the goals of this research study is to estimate thermal properties of aqueous solutions of basic food substances (sucrose, methyl-cellulose, and wheat gluten) during freezing. Temperature data from one-dimensional freezing experiments were used to estimate the temperature dependent thermal properties of these materials during freezing using the Modified Box-Kanemasa estimation method. The estimated thermal properties were then compared with models from the literature. Generally, the estimated thermal properties did not agree well with the predicted properties using the models from the literature, especially in the case of methyl-cellulose and wheat gluten. Hence, the models examined in this research study need to be modified to account for the chemical and the physical processes that occur during freezing.
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NOMENCLATURE

A: Constant (m\(^{-1}\))

\(b\): Estimated parameter vector which contains the thermal conductivity (W/m K) and volumetric specific heat (J/m\(^3\)K) values

\(c_a\): Apparent Specific Heat (J/kg K)

\(c_p\): Specific Heat (J/kg K)

F: Non-homogeneous function (W/m\(^3\))

G: Gibbs Energy (J)

h: Heat Transfer Coefficient (W/m\(^2\)K)

\(h_a\): Enthalpy per unit mass (J/kg) of air

\(h_i\): Enthalpy per unit mass (J/kg) of ice

\(h_s\): Enthalpy per unit mass (J/kg) of solutes

\(h_w\): Enthalpy per unit mass (J/kg) of water

H: Enthalpy (J)

i: Grid number

k: Thermal Conductivity (W/m K)

L: Thickness (m)

m: Mass fraction

M: Molecular weight
n: Time Step
p: Exact Solution for the Non-homogeneous Heat Equation (°C)
q: Heat Flux (W/m²)
R: Universal Gas Constant
S: Entropy (J/K)
t: Time (sec)
T: Temperature (°C)
Tₐ: Ambient Temperature (°C)
Tₖ: Final Temperature (°C)
Tᵢ: Initial Temperature (°C)
X: Molar Fraction
x: Location (m)
X: Sensitivity coefficient matrix
Y: Measured temperature vector
β: Parameter vector which contains the thermal conductivity (W/m K) and volumetric specific heat (J/m³ K) values
ΔH: Latent heat of fusion (J)
Δh: Latent heat of fusion per unit mass (J/kg)
Δt: Time Step (s)
Δx: Grid Size (m)
Δt*: Dimensionless Time Step (Δt* = α Δt/L²)

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\( \Delta x^+ \): Dimensionless Grid Size \((\Delta x^+ = \Delta x/L)\)

\( \rho \): Density \( (\text{kg/m}^3) \)

\( \tau \): Time Constant \((\text{s})\)

\( \mu \): Chemical Potential

\( \nabla \): Matrix derivative operator

**Subscripts:**

0: Location \( x=0 \)

a: Apparent

i: Ice

\( W_u \): Water mass in unfrozen food material

if: Initial freezing

L: Location \( x=L \)

f: Freezing temperature

fw: Freezing temperature of pure water

s: Product solutes

t: Total

w: Water

**Superscripts:**

k: Iteration number

n: Time step

T: Transpose
Chapter 1

INTRODUCTION

Freezing is one of the most commonly used methods around the world to preserve foods and biological substances. It is generally used in the food industry to maintain the quality of products during transportation and storage. Inherent changes occur in food products during the different levels of their production. These changes can be classified into three main categories: 1. physical, 2. chemical, and 3. microbial changes. Physical transmutations, which are classified as the first type of changes in food materials, are mostly associated with crystallization and desiccation during freezing. However, chemical changes of food products during frozen storage generally include lipid oxidation, protein insolubilization, and loss of vitamins. Microbial changes consist of proliferation of microbes in foods. Generally, physical and chemical changes continue to occur even in very low temperature environments; however, these phenomena are dramatically slowed when food materials are frozen. Furthermore, microbial activities are halted at temperatures below -12°C. Consequently, the freezing process is an effective method to protect the quality of food products from these various detrimental changes.

Physical changes in food products are closely influenced by the temperature behavior in the food matter during and after freezing. For instance, "freezer burn", which
is the dehydration and discoloration of the surface of food during frozen storage, is usually accelerated by temperature fluctuations during storage. Also, the retardation of freezing causes several detriments, such as enzyme activity and microbial formations. In addition, some techniques of processing high moisture foodstuffs are influenced by the size of ice crystals in the food which is directly influenced by the freezing rate of the aqueous medium. The accurate prediction of temperature and thermal properties during freezing is of great importance in the conception of freezing processes, the estimation of freezing durations, and the design of refrigeration equipment. Hence, superior knowledge of the freezing process in foods is very critical in maintaining high quality food products and in improving process efficiency which results in reducing energy costs.

The process of freezing varies in many aspects from one food material to another. The physical properties of a food material throughout the freezing process are dependent on various physical and chemical characteristics of that particular food material. Most foods have a high moisture content, and consequently, water serves as a means of dispersing the constituents of food materials. The molecular configuration of each of the components in a food material and their interaction with water molecules as well as other substances in the material has a significant role in defining the microscopic transformation of the food during the freezing process. For instance, the initial freezing temperature of a food material is mainly dependent on the nature and concentration of the solutes in the water phase of the food.

Water begins to transform to ice as soon as the food product reaches its initial freezing temperature. As ice crystals continue to form, the liquid water content of the
food gradually decreases causing a continuous depression of the freezing point of the medium to a lower temperature. The process progresses over a temperature range until all the water is frozen. This gradual transformation of water into ice crystals causes the physical properties of the food to change as functions of the temperature. Rapid variation of the properties has a direct effect on the heat transfer throughout the food material, and hence, it alters the dynamics of the freezing process. The continuous and simultaneous change of the thermal properties and the freezing temperature of the food originate a complex heat transfer process that translates into a highly nonlinear mathematical problem.

Determining the thermal properties of food materials is very important for the simulation of the freezing process and the estimation of the freezing time of different foods. Various experimental techniques have been used to determine properties of a wide variety of food products. The thermal properties of diverse unfrozen as well as frozen food materials have been introduced in the literature. However, due to inherent instrumental inaccuracies, reliable evaluation of the thermal properties of foods is very hard to obtain. Also, the thermal properties of the same food product can vary significantly due to slight differences in composition or water content. Consequently, mathematical modeling of thermal properties of foods as a function of their basic chemical composition and water content has been a very appealing alternative to experimentation. However, these mathematical models generally have many restrictions and are also built on basic concepts that reduce their applicability on certain foods or freezing procedures. Generally, foods are assumed to be ideal solutions. An ideal
solution is defined as a solution where all molecules (solvent and solutes) are of the same size and all forces between molecules are equal (Smith and Van Ness, 1987). Consequently, the predictive models might not applicable to foods that are non-homogeneous or contain non-soluble substances such as fats; hence, experimental verification of these models is necessary to determine their accuracy in predicting the thermal properties of food materials.

1.1 Goals and Objectives

The main goal of this research study is to conduct a comprehensive analysis of the freezing process by examining it from assorted facets namely analytical, numerical, as well as experimental considerations. To achieve this goal, three primary objectives have been established:

1. Develop an analytical accuracy technique for testing numerical methods and select an effective scheme to simulate temperature in food materials during onedimensional freezing processes.

2. Construct an experimental apparatus and design an experimental procedure to conduct temperature measurements in aqueous solutions of basic food materials.

3. Estimate the thermal properties of these food solutions during freezing using the experimental temperature measurements and compare the estimates with values obtained from existing mathematical models from the literature.

The accuracy analysis was performed using an analytical problem which is a non-
homogeneous modification of the one-dimensional freezing problem with an exact solution. Two finite difference methods, the Crank-Nicolson and the Two-Step method, were implemented to solve this problem. The accuracy of the Crank-Nicolson method and the Two-Step method were evaluated and a comparison of the two methods was performed. An experimental apparatus was designed and built to contain food solutions and record temperature measurements during freezing. Aqueous solutions of different basic food materials were used in these experiments. Temperature measurements, obtained from the experimental setup, were then used to estimate the thermal properties of the food solutions during freezing using a statistically based minimization method which is the Modified Box-Kanemasu Method. Finally, the estimated thermal properties were compared with thermal properties calculated using mathematical models from the literature.

The results of this research study are of great importance for the improvement of the freezing techniques used in the food industry and the design of refrigeration equipment. In fact, accurate estimation of thermal properties of food materials during freezing would result in greater accuracy in the simulation of the temperature behavior of food products and the evaluation of their freezing time. These improvements in the numerical simulation of the freezing process translates into better freezing processes, and hence, results in greater food quality and increased processing efficiency.
Chapter 2

LITERATURE REVIEW

Freezing is the most widely used method of preserving food products around the world. It is generally employed to protect foods from various detrimental changes such as lipid oxidation, loss of vitamins, and microbial proliferations. Inherent detrimental transmutations of foods, which occur during different levels of processing, storage, and transportation, are substantially slowed, and halted in some cases, at very low temperatures. The effectiveness of the preservation of food materials using freezing is mainly dependent on the temperature behavior of the frozen product, the freezing rate, and also the composition and properties of the food material. Consequently, investigation of the various aspects of the freezing process, primarily temperature variations, thermal properties, and water content of food materials, is very significant for the design of more proficient freezing techniques which could result in longer shelf-lives for food products and lower energy costs.

Quality deterioration of food products has been studied for the last five decades. Many researchers related the acceleration of the quality deterioration of foods to poor regulation of food temperature during freezing and storage. Singh and Wang (1977), for instance, indicated that temperature fluctuations during frozen storage cause the
desiccation of food products. Fennema et al. (1973) studied chemical changes in food materials during storage (e.g., lipid oxidation, enzymatic browning). They deduced that these chemical reactions are highly influenced by the rate of freezing and the temperature changes during storage. Various other research studies have confirmed that better designed freezing processes and accurate control of the temperature during frozen storage considerably reduces the deterioration rate of foods. Subsequently, various aspects of the freezing process, as well as frozen storage, of food products have been investigated in many research studies. In fact, diverse analytical, experimental, and numerical studies have been presented in the literature over the last few decades.

In this chapter, a review of the literature will be presented to describe the various research studies conducted on the freezing process of food materials. Analytical research studies will be first addressed. The mathematical models, introduced in the literature to describe the thermal properties of food materials during freezing, will be then discussed. Then, the numerical methods that have been used for the simulation of the freezing process will be examined. Finally, a review of the various experimental methods introduced in the literature to investigate the different aspects of the freezing process, including the thermal properties of food materials during freezing, will then be presented.

2.1 Analytical Solutions of Freezing in Food Materials

Analytical solutions of the freezing problem have been considered by several studies in the literature. Carslaw and Jaeger (1959) presented an analytical solution for

An approximate analytical solution was suggested by Grange et al. (1976). In their analysis, they assumed that the latent heat is released at a constant temperature and they employed an integral method to solve the problem. De Michellis and Calvelo (1982) used three distinct phases (precooling, freezing, and tempering) to solve for the temperature within food materials during freezing. They used the heat conduction equation with constant coefficients to obtain analytical solutions for the precooling and tempering phases. Zaritzky (1982) developed an analytical solution for temperature in meats during storage and distribution using average values for the thermal properties and convective boundary conditions. The same type of boundary conditions were imposed by Zuritz et al. (1986) to determine temperature in cylindrical shaped food materials during storage. Sastry and Kilara (1983) simulated temperature in frozen peas during fluctuating temperature storage. They assumed sinusoidal temperature boundary conditions. Here, an analytical solution of the one-dimensional heat equation was obtained using constant thermal properties over small temperature ranges.

Several other analytical studies have been performed to solve the freezing problem. Generally, analytical studies of the freezing of food materials have been restricted to simple geometric shapes, uncomplicated boundary conditions, and non-varying thermal properties. Consequently, researchers have sought other means of analysis, namely
experimental investigations and numerical simulations, to explore the freezing process of food materials.

2.2 Numerical Simulations of the Freezing in Food Materials

Numerical simulations are essential to predict the freezing process of food materials. Numerical methods have been developed and extensively evolved through the years due to the increasing availability of mathematical models in the literature and high speed digital computers in the last few decades. Numerous forms of finite difference and finite element methods have been developed and employed to solve non-linear problems, such as the freezing of food materials.

2.2.1 The Crank-Nicolson finite difference method

The Crank-Nicolson finite difference method is an implicit numerical scheme which incorporates a central difference in the discretization of the heat conduction equation. This numerical method has been employed in various types of heat transfer problems due to its second order accuracy in time and location. The Crank-Nicolson numerical scheme is usually based on an iterative process. The iterative scheme is generally not necessary for constant coefficient linear problems, however, it is essential for solving non-linear problems such as the freezing process of food materials.

The Crank-Nicolson finite difference method has been widely employed for the simulation of the temperature in food materials during freezing and also during frozen
storage. Hohner and Heldman (1970) employed this finite difference scheme to simulate freezing in an infinite slab of beef and codfish with convective boundary conditions. They utilized the ideal binary solution assumption in their freezing model to fit experimental apparent specific heat data for beef and codfish. Lescano (1973) simulated temperature in codfish during one-dimensional freezing using the Crank-Nicolson method. Heldman (1974b) employed this numerical scheme to simulate freezing within spherical food products. Heldman and Gorby (1975b) estimated freezing times of various food materials using the Crank-Nicolson method. Scott and Heldman (1990) used the same method to simulate temperature of food materials in frozen storage.

2.2.2 Review of Other Numerical Methods

Charm (1971) and Charm et al. (1972) employed a forward finite difference scheme to simulate one-dimensional freezing processes with slab and cylindrical shapes and convective boundary conditions. Lescano (1973) used the Crank-Nicolson finite difference method to simulate freezing of codfish and compared numerical results with experimental measurements. Mannapperuma and Singh (1989) used an explicit finite difference method with an enthalpy formulation to predict temperature during freezing and thawing in foods.

Other researchers used the three time level finite difference method developed by Lees (1966). This method is a second order accurate scheme that can be solved by means of standard elimination procedure without any iterations. Bonacina and Comini (1971) are the first to use Lees's finite difference method to solve the freezing problem. They
simulated freezing in a slab of tylose under fixed temperature boundary conditions. Bonacina et al. (1973) extended the use of this method by including the latent heat term into the specific heat. Cleland and Earle (1977) also used the three time level scheme with convective boundary conditions. They modified the nodal configuration to reduce oscillations in the numerical process. The same formulation was implemented by Rebellato et al. (1978) in a finite element scheme to simulate two dimensional freezing with fixed temperature, fixed heat flux, and convective boundary conditions. Wilson and Singh (1987) used Lees' method to simulate freezing in spherical shaped foods and they reported good agreement with experimental results.

The accuracy of numerical simulations have been discussed by many researchers in the literature. In order to evaluate numerical methods, numerical results have been generally compared to experimental data. Discrepancies between numerical and experimental results have usually been reported in research studies. Cleland and Earle (1982) and Cleland et al. (1982) reported discrepancies between experimental data and numerical simulations. They asserted that the freezing rate had a large effect on the magnitude of the discrepancies. Cleland and Earle (1984) explained that in the case of a high Biot number, the finite difference method usually underpredicted freezing times, and gave temperature profiles which deviated from experimental profiles. Pham and Willix (1990) also examined the effect of Biot number on the accuracy of finite difference solutions. They improved their numerical results by using new thermal property data. Various other studies employed finite element methods to simulate the freezing process. However, it has been reported that even though the finite element method is more
complex than the finite difference method, it does not present better accuracy, especially for simple geometries (Cleland and Earle, 1984).

2.2.3 The Two-Step method

An alternative for the Crank-Nicolson numerical method, which has been widely used for the simulation of the freezing process, is the Two-Step finite difference method. This numerical scheme is a central finite difference scheme introduced first by Douglas (1958). This method is a newly employed for the simulation of the freezing process. Douglas used this method to demonstrate the convergence of the iterative scheme of the Crank-Nicolson to solve non-linear parabolic differential equations (Sod, 1985). The Two-Step method is based on a Taylor expansion of the present temperature to evaluate an intermediate temperature value. The intermediate temperature values are used to evaluate the thermal properties of the material to solve for the temperature at the next time step. Consequently, the Two-Step method does not require iterations for the simulation of the temperature history of food materials during freezing.

2.3 Mathematical Models for Thermal Properties

The evaluation of thermal properties of food materials is essential for the numerical simulation of the freezing process. Due to the complications encountered in the evaluation of thermal properties experimentally, efforts have been made to build mathematical models based on thermodynamic and chemical properties of aqueous media.
Heldman (1974a) developed a thermodynamic approach to predict the ice and the water content of foods during freezing. He used a dilute binary solution assumption to formulate the freezing process into a mathematical model. Dickerson (1981) reported good agreement between the temperature predicted using Heldman's model and experimental measurements performed by Riedel (1969) for fruits and vegetable juices. However, he observed larger discrepancies between the predicted results using Heldman's model and experimental data from Riedel (1969) for meat and fish. Dickerson (1981) illustrated that the discrepancies between the model and experimental data were caused by the water deficiency in meat and fish. Heldman and Singh (1981) and Heldman (1982) assumed the availability of water unfreezable at -40°C to improve the mathematical model formulated by Heldman (1974a). Once modifications were enforced in the model, they reported better agreement between mathematical predictions and experimental measurements. Choi and Okos (1985) developed constitutive equations to determine thermal properties of foods. They included regression equations for the properties of proteins, carbohydrates, fats, fibers, and ash, as temperature dependent quantities. Their model is based on the projected freezing point depression using the molar fraction of the water in the dilute solution. They also assumed that mass and volume of basic elements are conserved during mixing.

Various basic assumptions have been established in the literature to initiate relationships between the basic molar compositions of food materials and their thermal properties. Choi and Okos (1985) assumed in their study that the thermal properties of foods are linearly related to the molar fraction of five basic components (water,
carbohydrates, proteins, fats, and ash). Miles et al. (1983) also assumed that the thermal conductivity of a food product is linear with basic compositions. Models proposed by Schwartzberg (1976) and Heldman and Singh (1981) used similar assumptions for the evaluation of specific heats. They also determined the enthalpy and the apparent specific heat by combining the effects of sensible and latent heat. Keey (1972) assumed a combination of parallel and series thermal conductivities using distribution factors to formulate thermal conductivity of porous materials. He used the porosity and moisture content of the food material to calculate the distribution factors. After evaluating nine models, Murakani and Okos (1989) selected Keey's model to evaluate the thermal conductivity of different porous foods. Mannapperuma and Singh (1989) indicated that the depression of the freezing point is directly related to the change in the vapor pressure induced by the solutes in the solution. They derived a model for the thermal properties of foods during freezing using basic thermodynamic laws and models from the literature.

Various studies have focused on the thermal properties of certain foods above their initial freezing temperature. Most of these studies assumed that thermal properties of unfrozen food materials are polynomial functions of temperature. Fernandez-Martin et al. (1972) developed a quadratic function of temperature to predict the thermal conductivity of skim milk for a temperature range of 5 to 75°C. Lamb (1976) suggested a model to approximate specific heats of food materials above freezing from fractional water content. Martens (1980) concluded that temperature and water content are the majors factors that effect the thermal diffusivity of foods. He suggested a regression equation for thermal diffusivity of various foods as a function of water fraction and
temperature. In another analysis, Choi and Okos (1983) presented a model for the specific heat of tomato juice as a function of temperature and total solid content.

2.4 Experimental Analyses of Freezing in Food Materials

Experimental analyses have been performed for years to investigate the freezing process of various food products. The temperature, thermal properties, and water content of foods before, during, and after freezing have been examined by many researchers using diverse experimental methods. Bartlett (1944), Ede (1949), and Riedel (1949a, 1949b) conducted different types of freezing experiments and demonstrated that water in food products freezes over a range of temperature, and hence, the thermal properties of the food matter change substantially with temperature throughout the freezing process. Staph and Woolrich (1951) published a 20 year review for calorimetric analyses on fruits, vegetables, and fish. They indicated that as ice formation occurs, the concentration of solutes increases, causing a depression of the freezing point of the food medium. They also introduced the concept of apparent specific heat to account for the enthalpy of phase change over an extended temperature range.

Many measurement techniques have been developed and employed to evaluate different features of the freezing process in food products. Dickerson (1968) and Rahman (1991) discussed different experimental methods that they utilized to measure thermal properties of various frozen and unfrozen food products. Mohsenin (1980) also presented an extensive description of various methods used for the measurement of thermal
properties of food materials.

Lind (1991) discussed many experimental techniques, steady and transient, that have been utilized to examine different aspects of the freezing process. She indicated that the enthalpy of fusion, or latent heat, of food materials is often measured using either the mixing method, the adiabatic calorimeter, or the differential scanning calorimeter. The mixing method consists of placing the food sample in a water bath at a known temperature and allowing it to reach steady-state. The enthalpy of fusion is then calculated using the heat balance equation. The adiabatic calorimeter, developed by Riedel (1955), is based on the minimization of the temperature difference between the sample and the water bath in which the sample is immersed. The Differential Scanning Calorimeter, or DSC, monitors the energy flow into or from the sample holder used to maintain its temperature identical to the temperature of a reference holder. The DSC method has been employed to examine various aspects of the freezing process in food materials. Duckworth (1971), Ross (1978), and Roos (1986) used the DSC technique to evaluate the unfreezable water in foods. Wang and Kolbe (1991) also reported the use of DSC to determine the initial freezing point, unfreezable water content, apparent specific heat, and enthalpy of surimi during freezing. Lind (1991) reported that Differential Thermal Analysis or DTA has also been used to determine the heat of fusion of food materials. In the DTA method, the sample and the reference holders are subjected to the same energy input while their temperatures are being measured.

The Nuclear Magnetic Resonance Spectroscopy, or NMR, is another experimental technique that also has been employed by different researchers to examine water in food
materials during freezing. Weisser (1980) indicated that the NMR method is useful in determining the amount of the liquid phase and the solid phase, especially crystallized water, in food materials (Lind, 1991). Steinberg and Leung (1975) reported the use of this method to measure unfrozen water content and bound water content in foods. Weisser and Harz (1984) also employed a pulsed NMR method to examine the freezing process in sucrose solutions. Various other researchers reported the use of other experimental techniques for the measurement of thermal properties of food materials.

2.4.1 Estimation of Thermal Properties of Food Materials

The knowledge of thermal properties of food products is essential for the simulation of temperature within foods during freezing and frozen storage and also important for the estimation of freezing time. The simulation of the freezing process is the most important phase of the design process for superior freezing techniques and more efficient refrigeration equipment. Consequently, the thermal properties of food materials have been addressed by many researchers and evaluated using various methods. Generally, the thermal properties of foods have been determined only for unfrozen or completely frozen foods due to the inherent temperature dependency and large variation of food properties during freezing. In addition, the thermal properties of food materials are usually determined independent one from another due to the simplicity of the experimental methods pursued. These properties include thermal conductivity, specific heat, density, and thermal diffusivity.

The thermal conductivity of food materials has been determined using various
experimental methods with minimal mathematical operations. Methods of measuring thermal conductivities of food materials can be classified into two classes: 1. steady-state methods, and 2. transient methods. In both categories, a steady heat flux is applied to the specimen and the resulting temperature rise is measured in one point of the specimen (Choi and Okos, 1985).

The Guarded Hot Plate technique, which is a steady-state method, has been widely used to measure thermal conductivity of foods. In this method, a heat flux is applied to the specimen and the steady-state temperature change across the slab specimen is measured and used to calculate the thermal conductivity of the material. Lentz (1961) evaluated thermal conductivities of different kinds of meats, fats, and gelatin gels using this method. Buma and Meerstra (1969) also used the Guarded Hot Plate method to measure thermal conductivities of dairy products. Carslaw and Jaeger (1959) employed this steady-state technique to measure thermal conductivities of various solid foods. A study by Mohsenin (1980) used this method with different food and agricultural materials.

The Fitch (1935) Method is a common transient method to measure the thermal conductivity of food materials. In this method, the specimen is placed between two copper blocks. The top copper block is maintained at a constant temperature by adding heat. The added heat is measured by the temperature rise with time of the lower copper block. The main disadvantage of this method is the poor insulation of the system. Mohsenin (1980) also used the Fitch method to evaluate thermal conductivities of food and agricultural materials.

The Probe Method is another transient method to measure thermal conductivity
of food. This method was introduced by Schleirmacker (1888) and modified by Nix et al. (1967) (Choi and Okos, 1985). This method consists of a constant heat source, imbedded in the food material, transmitted to an infinite solid along a thin resistance wire. The thermal conductivity of the food material is determined using the temperature rise as a result of a known energy pulse of the source. Sweat et al. (1973), Baghe-Khandan (1978), and Hough and Calvelo (1978) have applied this transient method to measure thermal conductivities of frozen meats. The Probe Method has also been employed by Ramswamy and Tung (1981) to measure the thermal conductivity of frozen apples. Renaud et al. (1992) employed a hot wire probe method to determine thermal properties (i.e., thermal conductivity and diffusivity) of aqueous solutions of sucrose, starch, gelatin, and ovalbumin. The experimental results were then compared to models from the literature, and they concluded that an experimental validation of the ice fraction and the unfreezable water is necessary to improve the models.

Specific heats of food materials have been measured using various methods. The general scheme of these methods consists of non-varying specific heats. The Differential Scanning Calorimetry, or DSC, is the most widely used method for the measurement of specific heat of food materials (Heldman and Singh, 1981). Riedel (1951, 1955, 1957a, 1957b) used this calorimetric method to evaluate enthalpy and heat content of various foods. Riedel (1969) also employed this method to determine the specific heat of foods rich in water. Ramaswamy and Tung (1981) used the DSC method to determine apparent specific heat of apples. Note that the apparent specific heat incorporates the sensible heat with the latent heat of fusion. Wang and Kolbe (1991) also reported the use of DSC to
determine the apparent specific heat and enthalpy of surimi during freezing.

The Guarded Hot Plate Method was also developed and used for the measurement of specific heats of foods. In this method, the specimen is surrounded by electrically-heated thermal guards. These thermal guards are maintained at the same temperature as the specimen, which is also being heated electrically. The electric energy supplied to the specimen is set equal to the heat gained by the specimen and used to solve for the specific heat of the specimen. This method was used by Fenandez-Martin (1972) to determine the specific heat of milk products. Mohsenin (1980) also employed this technique for the evaluation of specific heats of different food and agricultural products.

Various other methods were employed for the evaluation of thermal properties of foods including the density and the thermal diffusivity. The general scheme of these techniques is to evaluate the thermal properties independently of one another and without considering the effect of temperature variations. Therefore, these methods can not be employed for the evaluation of thermal properties in the phase transition region due to the large variations of the properties with temperature (Lind, 1991). The main advantage of these techniques is the uncomplicated experimental procedures and the simplicity of the mathematical manipulations used to calculate the thermal properties. Albin et al. (1979) reported estimation of thermal diffusivity of food materials using a least squares method from temperature measurements. He used a minimization scheme to evaluate thermal diffusivity of unfrozen and completely frozen food products.

In conclusion, due to the simplicity of the experimental methods used to determine thermal properties of food materials, simultaneous estimation of temperature dependent
thermal properties of food materials has been very scarce in the literature. In this study, a least squares minimization method, known as the Modified Box-Kanemasu Method, was employed to estimate the thermal conductivity and volumetric heat capacity during freezing (as functions of temperature) using transient temperature measurements.

2.4.2 Modified Box-Kanemasu minimization method

The Modified Box-Kanemasu estimation method is a direct modification of the Gauss method which consists of the minimization of an objective function, namely the least squares function containing measured and calculated temperatures. This method was proposed to improve the convergence of the Gauss method by suggesting small corrections in the direction of the parameter variations. Consequently, it ensures the continuous decrease of the least squares function to minimize the number of iterations and also eliminate oscillations that could occur from one iteration to another which usually leads to instabilities in the estimation process. The Modified Box-Kanemasu minimization process requires an analytical or numerical temperature solution and experimental measurements of the temperature. The process is primarily based on an iterative process to minimize the difference between the analytical solution and the experimental data by updating the thermal properties of the materials. This estimation process was first introduced by Box and Kanemasu (1972). They stated that the Gauss method does not always lead to convergence in the case of poor initial guesses for the parameters or severe non-linearity in the model. In order to improve the Gauss method, Box and Kanemasu suggested a small correction in the direction proposed by Gauss.
The Box-Kanemasu estimation method was thoroughly discussed by Beck and Arnold (1977). Various aspects of this estimation method and similar iterative least squares schemes were discussed by Beck (1988). He presented a detailed analysis of the different characteristics of parameters and function estimations using these minimization methods. Jurkowsky et al. (1992) examined an iterative least squares scheme by simultaneously estimating thermal conductivity and thermal contact resistance without any internal temperature measurements. They concluded that the non-convergence of the estimation procedure is primarily due to small sensitivity coefficients and the unbalance of the sensitivity matrix. Scott and Saad (1993) employed the Box-Kanemasu method for the estimation of kinetic parameters associated with the curing of epoxy resin. They concluded that near linear dependency between the sensitivity coefficients results in inaccurate parameter estimations and in some cases induces non-convergence of the estimation process. Scott and Scott (1993) also employed the Box-Kanemasu method to determine optimal time for cryogenic tumor treatment to achieve a desired minimum temperature at specified locations in the tumor. They deduced that the use of information from previous procedures with different tumor dimensions significantly improved the accuracy of the estimation process.

In conclusion, the Modified Box-Kanemasu estimation method has been employed in many engineering areas over the years. It has also been proven to be an effective method for the simultaneous estimation of temperature dependent thermal properties. Consequently, in this research study, the Modified Box-Kanemasu was selected for the estimation of temperature dependent thermal properties of food materials during freezing.
Chapter 3

THEORETICAL INVESTIGATION

The design of more proficient freezing processes is very important in reducing refrigeration costs and prolonging the shelf-lives of food materials. Over the years, researchers have studied various aspects of the freezing process in diverse food materials to diagnose, and hence, accurately predict properties of the food, the freezing time, and other variables. Analytical and experimental analyses have been performed to investigate temperature, thermal properties, freezing time, and other parameters of the freezing process of food materials. Furthermore, various studies have been focused on the formulation of mathematical models to predict thermal properties of food products. Consequently, various concepts have been employed to establish relationships between the physical and chemical behaviors of the various ingredients during freezing in the food mixture and the effective thermal properties of the food material. As a result of the phase change process, food materials undergo very sudden structural changes, and consequently, thermal properties of foods are temperature dependent during freezing. Due to the inherent temperature dependency of the thermal properties, freezing within food materials is a very non-linear mathematical problem, and hence, it is generally solved numerically using various finite difference and finite element methods.
In this section, a detailed analysis will be presented to describe the various aspects of the freezing problem and the analytical concepts employed in the research procedure. The one-dimensional freezing process and the mathematical formulation of the thermal properties of foods during freezing will be addressed first. The various analytical methods and numerical techniques that were employed in the research process will then be thoroughly discussed.

3.1 One-Dimensional Freezing Process

Due to the high water concentration, food materials undergo a phase change process over a temperature range. The freezing temperature of the food matter is continuously depressed during freezing causing very strong correlations between the thermal properties and the temperature. Generally, phase change problems of pure substances are formulated into two governing equations for the two phases, an equation for the position of the moving phase boundary, and the initial and boundary conditions. In order to reduce the number of the equations involved, researchers have combined the two governing equations and the moving phase boundary location into one heat conduction equation by introducing the apparent specific heat \( c_a \) formulation. The apparent specific heat incorporates the heat of fusion (or latent heat) released during freezing with the heat capacity of the food material. During freezing, the thermal conductivity, \( k \), and the density, \( \rho \), of the food material are also functions of temperature due to the inherent transformation of the water to ice crystals. The strong correlation
between the thermal properties of the food and the temperature induces strong
mathematical nonlinearity in the freezing problem.

Considering one-dimensional freezing of an infinite slab of a food material (Fig. 3.1), a mathematical description of the problem can be formulated using the one-
dimensional transient heat conduction equation with variable coefficients and heat flux
and/or convective boundary conditions, as shown below:

\[
\frac{\partial}{\partial x} \left( k(T) \frac{\partial T}{\partial x} \right) = \rho(T) c_a(T) \frac{\partial T}{\partial t} \quad 0 < x < L \quad t > 0 \tag{3.1}
\]

\[T(x,0) = T_i \quad 0 \leq x \leq L \quad t = 0 \tag{3.2}\]

\[-k(T) \frac{\partial T}{\partial x} \bigg|_{x=0} = q_0 + h \left( T_a - T(0,t) \right) \quad x = 0 \quad t > 0 \tag{3.3}\]

\[k(T) \frac{\partial T}{\partial x} \bigg|_{x=L} = q_L + h \left( T_a - T(L,t) \right) \quad x = L \quad t > 0 \tag{3.4}\]

Where \( T \) is temperature, \( x \) is the location in the slab, \( t \) is time, \( k \) is thermal
conductivity, \( \rho \) is density, \( c_a \) is apparent specific heat, \( h \) is the heat transfer coefficient
of the boundary surface, \( q \) is the heat flux into the slab, and \( L \) is the thickness of the slab. \( T_i \) and \( T_a \) are the initial temperature of the slab and the ambiant temperature,
respectively. The subscripts 0 and L respectively indicate the heat flux at \( x=0 \) and the
heat flux at \( x=L \). The thermal properties, \( \rho, k, \) and \( c_a \), are all functions of temperature,
\( T \), which is a function of time, \( t \), and the location, \( x \).
Figure 3.1 The one-dimensional freezing process in a slab

- $T_s$: Ambient Temperature
- $q_0$: Heat Flux at $x=0$
- $q_L$: Heat Flux at $x=L$
3.2 Thermal Properties of Foods During Freezing

3.2.1 Water Fraction

The freezing process varies in many aspects from one food material to another depending on the basic compositions, the distinct physical properties of each of the ingredients in the food mixture, and their chemical interactions. One of the most important similar characteristics of food materials is the high concentration of water which serves as a disperse milieu for mineral and organic substances in the food matter. Furthermore, high water concentration institutes the phase change phenomenon which prompts the sudden changes of the food properties during the freezing process. Actually, water molecules start to align in an organized lattice to form ice crystals as soon as the food material reaches its initial freezing temperature. As the freezing process begins, the water concentration in the food mixture starts to decrease, inducing an imbalance between the chemical potential of the solutes and the solvent (water), and consequently, the freezing point of the solution is slightly depressed to a lower temperature. Since water transformation to ice crystals is a continuous process, the freezing temperature of the food material is continuously depressed throughout the freezing process until all the water is transformed to ice. The dependency of the water concentration on the temperature of the food material results in a strong correlation between the thermal properties and temperature of the food material.

Mathematical models for the thermal properties of food materials undergoing freezing are essentially based on the assumption that food materials are ideal binary
solutions. Subsequently, the unfrozen water fraction in food mixtures is related to the temperature of the food medium by the equality of the chemical potentials of the different fundamentals of the system, namely solutes and solvent. The chemical potential of a certain compound $i$ is defined as the free energy change of the solution due to a small change in the concentration of that element with the temperature, the pressure, and the molar fraction of each of the other elements, $j$, in the solution held constant:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j}$$  \hspace{1cm} (3.5)

where $n_i$ and $n_j$ are the number of moles of, respectively, the element $i$ and the element $j$ in the solution, $T$ is temperature, and $p$ is pressure. The Gibbs energy of the solution, $G$, is defined as follows for a closed system:

$$G = H - TS$$  \hspace{1cm} (3.6)

where $H$ is the enthalpy, $T$ is the temperature, and $S$ is the entropy of the system.

The freezing point depression of a solution can be derived from the equilibrium between the chemical potential of the solutes and the solvent and using an ideal binary solution assumption. The relationship between the water molar fraction and the freezing temperature of the solution was derived by Moore (1962). Detailed description of the formulation of this relationship, expressed in Eq. 3.7, was presented by Leung (1986).

$$\ln(X_w) = \frac{\Delta H_f}{R} \left( \frac{1}{T_{f_c}} - \frac{1}{T_f} \right)$$  \hspace{1cm} (3.7)
where $X_w$ is the molar fraction of the solvent which is water in this case, $T_f$ is the freezing point of the solution, $T_{fw}$ is the freezing point of the pure solvent which is 273.15 K ($0^\circ$C) for water, $\Delta H_f$ is the heat of fusion, or latent heat, of the solvent, and $R$ is the universal gas constant. The relationship in Eq. (3.7) was employed by many researchers to build mathematical models to predict the thermal properties of food materials during freezing. Heldman (1974a), for instance, used the freezing point depression concept to predict the relationship between the unfrozen water fraction and temperature of foods during freezing. He asserted that the accuracy of Eq. (3.7) in predicting the freezing point depression of food materials is directly related to how close the food medium is to an ideal binary solution. Schwartzberg (1976), Hsieh et al. (1977), Larkin et al. (1982), and others also employed the same concept in their analysis of freezing in food materials.

The water molar fraction can be related to the water mass fraction using the expression presented by Heldman (1974a):

\[
X_w = \frac{m_w/M_w}{m_w/M_w + m_s/M_s}
\]  

(3.8)

here, $m_w$ and $m_s$ are the mass fractions of the water and the solutes, respectively, and $M_w$ and $M_s$ are the molecular weights of water and the effective molecular weight of the product solutes, respectively. The solid particles dispersed in the aqueous food mixture are combined with the solutes, and therefore, variables with the subscript $s$ are effective quantities for the solutes-solids system.
The initial freezing temperature of the product, \( T_{ip} \), and the mass fractions of the water and solutes above freezing can all be determined experimentally, and hence, are assumed to be known. The molecular weight of the solute-solid system in the food material, \( M_r \), can then be established from Eqs. (3.7) and (3.8). These equations can be combined as follows (Heldman, 1974a):

\[
\ln \left( \frac{m_w/M_w}{m_w/M_w + m_s/M_s} \right) = \frac{\Delta H_f}{R} \left( \frac{1}{T_{fw}} - \frac{1}{T_f} \right)
\]  

(3.9)

All of the quantities in this equation are previously defined from Eqs. (3.7) and (3.8). The molar fraction of unfrozen water can be determined for temperatures below the initial freezing temperature using Eq. (3.9) by substituting the temperature of the food for \( T_r \). The mathematical formulation presented by Eq. (3.9) demonstrates that the unfrozen water mass fraction \( (m_w) \) continuously decreases as the temperature of the food material decreases. Actually, the water mass fraction converges to zero as the temperature decreases towards 0 K (-273.15°C).

The thermal properties are directly related to the relative concentration of each of the components in the food matter. Consequently, the calculation of the unfrozen water fraction and the ice fraction is necessary for the evaluation of thermal properties of the food material at temperatures below the initial freezing point.
3.2.2 Density of Foods During Freezing

The density of food materials is directly dependent on the mass fraction of water, the different solutes, the solid ingredients, and sometimes air, existing in the food matter. Generally, mathematical models predicting food density are based on the assumption that mass and volume are conserved during mixing of food materials (Mannapperuma and Singh, 1989).

Hsieh et al. (1977) and Heldman and Singh (1981) introduced a model to predict the density of food products during freezing. This model is primarily based on the mass fraction of water, ice, air, and the solutes-solids system, along with the appropriate density for each of the components, as follows:

\[
\frac{1}{\rho(T)} = \frac{m_w(T)/\rho_w + m_i(T)/\rho_i + m_s/\rho_s + m_a/\rho_a}{m_t}
\]  

(3.10)

such that \( T, m, \) and \( \rho \) denote, respectively, temperature, mass fraction, and density. The subscripts \( w, i, s, a, \) and \( t \) indicate unfrozen water, ice, solute-solid content, air, and total, respectively. The density of water, ice, solute-solid system, and air are all assumed to be independent of temperature.

The density of the solute-solid phase of the food product can be determined using Eq. (3.10) along with the density and the mass fraction of the food material above freezing:
\[ \frac{1}{\rho_s} = \frac{m_i/\rho_u - m_{wu}/\rho_w - m_a/\rho_a}{m_s} \]  

(3.11)

such that \( \rho_u \) and \( m_{wu} \) are, respectively, the density and water content of the food product above freezing. The mass fractions of the different ingredients in the food above freezing are all assumed to known.

The ice mass fraction \( (m_i) \) of the food product can be written as a function of the water fraction during freezing \( (m_{wu}) \) and the water mass fraction of the food above freezing \( (m_{wu}) \):

\[ m_i(T) = m_{wu} - m_w(T) \]  

(3.12)

The density of the food product is considered to be constant throughout the temperature domain above the initial freezing temperature. Below the initial freezing temperature of the food, the food density is a continuous and smooth function throughout the temperature domain (Fig. 3.2). The difference between the density of water and the density of ice is small (about 8\%) relative to the changes in the apparent specific heat; consequently, the change of food density is not expected to be substantial during the freezing process. In fact, this density model exhibits no significant or abrupt variations (compared to the thermal conductivity and the apparent specific heat) even in the initial freezing temperature of the food product, and consequently, the density function is not anticipated to play a pivotal role in the nonlinearity of the freezing problem.
Figure 3.2 Predicted Density, $\rho$, of a Food Material during Freezing Using Model Introduced by Hsieh et al. (1977).
3.2.3 Thermal Conductivity of Foods During Freezing

Unlike the density and apparent specific heat, thermal conductivity is dependent on the structural arrangement of the food mixture and the orientation of the temperature gradient. In addition to the large difference between the thermal conductivity of water and ice, thermal conductivity of food materials undergo sharp changes during the freezing process, and consequently, researchers encounter various difficulties in the estimation of thermal conductivities of food materials (Heldman, 1982).

Kopelman (1966) was the first to develop a mathematical model to predict the thermal conductivity of two-phase systems. He based his model on the analysis of two-component dispersed, fibrous, and layered materials and assumed the presence of a continuous and discontinuous phases. Heldman and Gorby (1975) argued that the model proposed by Kopelman (1966) fails to describe the thermal conductivity of food materials during freezing due to the multiple phases that constitute the food structure (water, ice, solid components, etc.). They suggested a two step modification for the Kopelman model to incorporate three phases for the prediction of thermal conductivity of food materials. The model was further altered to account for air in food materials, and consequently, the mathematical formulation was modified to include three steps (Scott, 1987). In the first step, two phases were considered: 1. continuous water phase, and 2. discontinuous ice phase. The formulation of this step is represented as follows:

\[ V_i = \frac{m_i(T) / \rho_i}{m_w(T) / \rho_w + m_i(T) / \rho_i} \]
\[ Q_1 = V_i^{2\beta} \left( 1 - \frac{k_i(T)}{k_w} \right) \]

\[ k_{wi} = k_w \left( \frac{1 - Q_1}{1 - Q_1(1 - V_i^{1/\beta})} \right) \quad (3.13) \]

In the second step, two phases were also considered: 1. continuous water-ice phase, and 2. discontinuous solid phase. This step is formulated as follows:

\[ V_s = \frac{m_s/\rho_s}{m_w(T)/\rho_w + m_i(T)/\rho_i + m_s/\rho_s} \]

\[ Q_2 = V_s^{2\beta} \left( 1 - \frac{k_s}{k_{wi}} \right) \]

\[ k_{wis} = k_{wi} \left( \frac{1 - Q_2}{1 - Q_2(1 - V_s^{1/\beta})} \right) \quad (3.14) \]

In the third step, two phases were again considered: 1. continuous water-ice-solid phase, and 2. discontinuous air phase. This step is formulated as follows:

\[ V_a = \frac{m_a/\rho_a}{m_w(T)/\rho_w + m_i(T)/\rho_i + m_s/\rho_s + m_a/\rho_a} \]
\[ Q_3 = V_a^{2/3} \left( 1 - \frac{k_a}{k_{wss}} \right) \]

\[ k(T) = k_{wss} = k_{wis} \left( \frac{1 - Q_3}{1 - Q_3 \left( 1 - V_a^{1/3} \right)} \right) \]  \hspace{1cm} (3.15)

In this model, the thermal conductivity of water and the solid elements dispersed in the food matter were assumed to be constant. The thermal conductivity of the solute-solid system, \( k_s \), was determined using the Kopelman model. However, the thermal conductivity of ice, \( k_i \), was assumed to be a second order polynomial function of the temperature, as presented by Scott (1987), due to its significant variation with temperature compared to that for the thermal conductivity of water, \( k_w \).

The thermal conductivity of food materials are assumed to be independent of the temperature above freezing. Below the initial freezing temperature, the thermal conductivity is described by Eqs (3.13), (3.14), and (3.15). The variation of the thermal conductivity of foods during freezing is expected to be greater than the variation of the density due the large difference between the thermal conductivity of water and ice. However, due to the small changes in the function \( k(T) \) (Fig. 3.3) compared to the changes of the apparent specific heat (Section 3.2.4), the thermal conductivity function is expected to have a minimal effect on the nonlinear behavior of the freezing process.
Figure 3.3 Predicted Thermal Conductivity, $k$, of a Food Material during Freezing Using Model from Heldman and Gorby (1975).
3.2.4 *Apparent Specific Heat of Foods During Freezing*

The apparent specific heat of a food material incorporates the sensible heat with the latent heat of fusion. This formulation was employed by many researchers, such as Lescano (1973), Heldman and Gorby (1975), and Schwartzberg (1976), to describe the freezing process. The apparent specific heat is generally determined by differentiating the enthalpy of the food mixture with respect to the temperature at constant pressure. The formulation of the enthalpy is based on the assumption that the enthalpies of the different components in the food material are additive (Schwartzberg, 1976):

\[
h(T) = h_w(T)m_w(T) + h_i(T)m_i(T) + h_a(T)m_a + h_s(T)m_s
\]

(3.16)

where \( h \) is enthalpy per unit mass, \( m \) is the mass fraction, and \( T \) is temperature. The subscripts \( w, i, a, \) and \( s \) indicate, respectively, water, ice, air, and solute-solid system, in the food mixture.

The apparent specific heat of the food material can then be obtained by differentiating the enthalpy formulation in Eq. (3.16):

\[
\frac{\partial h}{\partial T} = c_a = c_w m_w(T) + c_i m_i(T) + c_{air} m_a + c_s m_s + h_w(T) \frac{\partial m_w}{\partial T} + h_i(T) \frac{\partial m_i}{\partial T}
\]

(3.17)

where \( c_a \) is the apparent specific heat of the food mixture. According to Eq. (3.12), the increase of the ice mass fraction is exactly equal to the decrease of the water fraction in the food mixture (\( dm_i = -dm_w \)). Also, the difference between the water enthalpy and the ice enthalpy is the latent heat of fusion (\( \Delta h_i = h_w - h_i \)). Consequently,
the apparent specific heat of a food mixture can be described as follows:

\[ c_a = c_w m_w(T) + c_i m_i(T) + c_{air} m_a + c_s m_s + \Delta h_f \frac{dm_w}{dT} \]  

(3.18)

Since the specific heat and the water content of the food product above freezing are assumed to be known, the specific heat of the solute-solid system can be calculated as follows:

\[ c_s = \frac{m_i c_u - m_{uw} c_w - m_a c_{air}}{m_s} \]  

(3.19)

where all parameters are already defined in previous equations. As shown in Fig. 3.4, the apparent specific heat presents very large and abrupt variations at the initial freezing temperature due to the sudden release of latent heat of fusion. The effect of this sudden and large change establishes very strong nonlinearity in the freezing problem.

### 3.3 Numerical Methods

During the freezing process, various structural transformations occur within the food material. These inherent physical transmutations result in the continuous depression of the freezing temperature of the food product, and consequently, the phase change process extends over a wide temperature range. The complexity of the freezing process
Figure 3.4 Predicted Apparent Specific Heat, $c_a$, of a Food Material during Freezing Using Model from Heldman and Gorby (1975).
as a physical and chemical transformation of the food matter translates into a highly nonlinear mathematical problem. In fact, the strong correlation between the temperature of the food and its thermal properties results in the formulation of the freezing process as a parabolic partial differential equation with highly temperature dependent coefficients. Exact analytical solutions for these types of problems are not attainable. However, an estimate for the solution can be obtained numerically. In this research study, two finite difference methods were employed to solve the freezing problem: 1. the Crank-Nicolson implicit method, which has been previously used by many researchers, as described in Chapter 2; and, 2. the Two-Step explicit method, which is newly applied to the analysis of foods during freezing.

3.3.1 The Crank-Nicolson Finite Difference Method

The Crank-Nicolson finite difference scheme is an implicit method which incorporates a central difference in the discretization of the heat conduction equation. In this numerical method, thermal properties are usually computed by averaging thermal properties from the current time step and the future time step. The process generally requires iteration procedures especially for nonlinear problems due to the presence of thermal properties from the future time steps. This method has been widely employed for the simulation of the freezing process within food materials and various other types of engineering problems due to its second order accuracy.

The heat conduction equation could be discretized either by approximating the derivatives from the differential equation using finite differences (mathematical
formulation) or by applying conservation of energy on a control volume which is characterized by a differential volume increment, as shown in Fig. 3.5 (control volume formulation). The control volume approach was selected to formulate the one-dimensional freezing problem due to its energy conservation advantage over the finite difference approach. Thus, the discretized conservation of energy equation can be written as follows:

\[
\frac{k_-^{n+1/2}}{2 \Delta x} T_{i-1}^{n+1} = \left( \frac{k_-^{n+1/2} + k_+^{n+1/2}}{2 \Delta x} + \left( (\rho c_a)^{n+1/2}_- + (\rho c_a)^{n+1/2}_+ \right) \frac{\Delta x}{2 \Delta t} \right) T_i^{n+1} + \frac{k_+^{n+1/2}}{2 \Delta x} T_{i+1}^{n+1} - \left( \frac{k_-^{n+1/2} + k_+^{n+1/2}}{2 \Delta x} - \left( (\rho c_a)^{n+1/2}_- + (\rho c_a)^{n+1/2}_+ \right) \frac{\Delta x}{2 \Delta t} \right) T_i^n - \frac{k_-^{n+1/2}}{2 \Delta x} T_{i-1}^n \tag{3.20}
\]

Here, the superscript and subscript, respectively, indicate the time step and the location. The subscripts \(i, i+1, i-1, +, \) and \(-\) signify the different locations in the control volume shown in Fig. 3.5. The superscript \(n+\frac{1}{2}\) used with the thermal properties indicates the average of the thermal properties (i.e. thermal conductivity, \(k\), and volumetric apparent specific heat, \(\rho c_a\)) from time step \(n\) and time step \(n+1\), as presented by Eqs. (3.21) and (3.22):

\[
(\rho c_a)^{n+1/2} = \frac{(\rho c_a)^n + (\rho c_a)^{n+1}}{2} \tag{3.21}
\]
Figure 3.5  Thermal Properties in a Differential Volume Increment
\[ k^{n+1/2} = \frac{k^n + k^{n+1}}{2} \]  \hspace{1cm} (3.22)

Note that the presence of temperature dependent thermal properties from the future time step, \( n+1 \), necessitates an iterative process.

### 3.3.2 The Two-Step Finite Difference Method

The Two-Step finite difference method was first introduced by Douglas (1958). This numerical scheme is a modification of the Crank-Nicolson method. It was actually used by Douglas (1958) to prove the convergence of the iterative scheme of the Crank-Nicolson numerical scheme (Sod, 1985). The Two-Step formulation of an interior point is also presented by Eq. (3.20); however, the temperature at the intermediate time step, \( n+1/2 \), is obtained by a Taylor expansion about the temperature at the time step \( n \):

\[ T_i^{n+1/2} = T_i^n + \frac{\Delta t}{2} \left. \frac{\partial T_i^n}{\partial t} \right|_{i} + ... \]  \hspace{1cm} (3.23)

The second order and higher terms are then truncated and the heat conduction equation is used to transform the time derivative to a second order space derivative. Thus, the temperature at \( n+1/2 \) is computed as follows:

\[ T_i^{n+1/2} = T_i^n + \frac{\Delta t}{2(\rho c_p)} \left. \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) \right|_{i} + ... \]
\[ T_i^n = T_i^n + \frac{\Delta t}{((\rho c_p)_i^n+(\rho c_p)_i^m)} \left( \frac{k^i T_i^n-(k^i T_i^{n-1}+k^m T_i^m)}{((\rho c_p)_i^n+(\rho c_p)_i^m)} \frac{T_i^n+k^i T_i^{n+1}}{(\Delta x)^2} \right) \] (3.24)

The intermediate temperature is then used to compute the thermal properties at the time step \( n+\frac{1}{2} \) instead of averaging the properties from time step \( n \) and properties from time step \( n+1 \). The computation of the intermediate temperature requires only temperatures and thermal properties from time step \( n \), and therefore, no iterations are required for the Two-Step scheme.

3.5 Computer Program

The computer program "FREEZE", described in Appendix A, was written to simulate the temperature history of food materials during freezing. This program has two versions which use different finite difference methods to solve for the temperature: 1. the Crank-Nicolson method, and 2. the Two-Step Method. The flowcharts of each of the two programs are shown in Figs. 3.6 and 3.7. Although these computer programs employ separate numerical methods, they utilize the same input and output algorithms, as shown in Figs. 3.6 and 3.7.

Two groups of inputs are needed for the execution of the computer programs: 1. thermal properties of the food material above freezing and its initial freezing point, and 2. dimensions of the slab, boundary conditions (which include constant temperature,
Figure 3.6 Flowchart for the Freezing Program Using the Crank-Nicolson Method.
Figure 3.7 Flowchart for the Freezing Program Using the Two-Step Method.
convective, and heat flux boundary conditions), grid size, time step, and the total time of the simulation.

The computer program prompts the user to enter these inputs and also save them into two separate files. Samples of these input files are shown in Section A.2. To rerun the program with information from a previous simulation, the user can use the input files instead of reentering the information. In addition, the two versions of the freezing program (i.e. the Crank-Nicolson version and the Two-Step version) provide the same type of output file where all the temperature outputs and the input information are listed. A sample output file is described in Section A.3.

3.6 The Modified Box-Kanemasu Estimation Method

The Box-Kanemasu estimation method was used to estimate the thermal properties of food materials undergoing freezing. This method is a direct modification of the Gauss minimization method described by Beck and Arnold (1977). It is based on the minimization of an objective function, namely the least squares function $S$:

$$S = (Y - T(\beta))^T(Y - T(\beta))$$

(3.25)

where $Y$ is the measured temperature vector, $T$ is the calculated temperature vector, and $\beta$ is the exact parameter vector which consists of the thermal conductivity, $k$, and the apparent volumetric specific heat ($C$) which is defined as the apparent specific heat multiplied by the density ($\rho C_p$), for this research study. The calculated temperatures

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are determined by directly solving the freezing problem (direct problem) using a finite difference procedure.

The least squares function, $S$, is differentiated with respect to the parameters which, in this case, are the thermal properties of the food product. To minimize the least squares function, the resulting quantity is then set equal to zero;

$$\nabla_{\beta} S = 2 \left[-X(\beta)^{T}(Y - T(\beta))\right] = 0 \quad (3.26)$$

where $X$ is the sensitivity matrix defined as $\left[\nabla_{\beta} T(\beta)^{T}\right]^{T}$. Since the freezing process is a nonlinear problem, it is not possible to solve explicitly for the parameter vector $\beta$. Consequently, two approximations must be used to transform Eq. (3.26) into an iterative form: 1. $X(b)$ must be used as an approximation to $X(\beta)$, where $b$ is an estimate of $\beta$, and, 2. $T(\beta)$ is approximated using the first two terms of a Taylor expansion of $T(\beta)$ around $b$. Using these estimations Eq. (3.26) can then be rewritten as follows:

$$[X(b)]^{T}[Y - T(\beta) - X(b)(\beta - b)] \approx 0 \quad (3.27)$$

The parameter vector can then be computed as

$$\beta = b + P(b) [(X(b))^{T}(Y - T(b))] \quad (3.28)$$

where $P(b)$ is a vector defined by

$$P(b) = [(X(b))^{T}X(b)]^{-1} \quad (3.29)$$

An iterative format for Eq. (3.28) can be introduced, as presented by Beck and Arnold (1977):
\[ b^{(k+1)} = b^{(k)} + h^{(k+1)} \nabla_g b^{(k)} \]  

\[ \nabla_g b^{(k)} = F^{(k)} [f^{(k)}]^T (Y - T^{(k)}) \]  

where the superscript \( k \) is the iteration number, and \( h^{(k+1)} \) is a scalar interpolation factor that changes from one iteration to another. In each iteration, the least squares function, \( S \), is estimated as a second order polynomial function of the scalar \( h \). The value of \( h^{(k+1)} \) is then calculated by minimizing the estimated function (Beck and Arnold, 1977);

\[ h^{(k+1)} = G^{(k)} [S^{(k)} + S_0^{(k)} + 2G^{(k)}]^{-1} \]  

where \( G^{(k)} \) is defined as \( [\Delta_g b^{(k)}]^T (F^{(k)})^{-1} \Delta_g b^{(k)} \), and \( S_0 \) and \( S_I \) are, respectively, the values of \( S \) for \( h \) equal to 0 and 1. The scalar \( h^{(k+1)} \) is then used to calculate the estimates for the parameters at the \((k+1)\)st iteration. A modification of the flowchart presented by Beck and Arnold (1977) is presented in Fig. 3.8 to illustrate the Box-Kanemasu estimation procedure.

The Box-Kanemasu minimization method was proposed by Box and Kanemasu (1972) to improve the convergence of the Gauss method. They suggested, as discussed above, small corrections in the direction of the parameters variations to ensure a continuous decrease of the least squares function \( S \), and consequently, reduce the number of the iterations and diminish instable behavior in the estimation process. However, the
Calculate $\Delta_b^{(k)}$ and $G^{(k)}$

$G^{(k)} \geq 0$

Yes

Set $\alpha = 1.0$ and $A = 1.1$

No

Print: $G$ is negative

Calculate $S^{(k)}_s$ at $b^{(k)} + \alpha \Delta_b^{(k)}$

$S^{(k)}_s < S^{(k)}_0$

Yes

$S^{(k)}_s \geq S^{(k)}_0 - \alpha G^{(k)}(2-A^{-1})$

No

Replace $\alpha$ by $\alpha/2$

$\alpha < 0.01$

Yes

Print: $\alpha$ less than 0.01

No

Terminate calculation

Proceed to next iteration

$h^{(k+1)} = (\alpha^2 G^{(k)})/(S^{(k)}_s - S^{(k)}_0 + 2\alpha G^{(k)})$

$h^{(k+1)} = \alpha A$

Figure 3.8 Flowchart of the Modified Box-Kanemasu Estimation Procedure
Box-Kanemasu minimization method can endure various critical problems that lead to nonconvergence of the estimation procedure. For instance, correlation (or linear dependency) of the sensitivity coefficients usually results in the nonconvergence of the minimization process. In fact, correlation of the sensitivity coefficient signifies that the least squares function $S$ has more than one minimum. Even in the case of near linear dependency of the sensitivity coefficients difficulties in the convergence could be encountered (Beck and Arnold, 1977). Consequently, the analysis of the sensitivity coefficients of the parameters is necessary prior to the estimation procedure.

The Box-Kanemasu method was used for the estimation of the transient thermal properties of food materials during freezing. In this case, the estimation process is referred to as a "function estimation process", as described by Beck (1988). The thermal properties, namely the thermal conductivity and apparent volumetric specific heat, are assumed to be piecewise linear functions of the temperature of the food material:

$$k = k_i + \frac{k_{i-1} - k_i}{T_{i-1} - T_i} (T - T_i)$$

(3.33)

$$C = C_i + \frac{C_{i-1} - C_i}{T_{i-1} - T_i} (T - T_i)$$

(3.34)

for the temperature interval $T_i < T < T_{i+1}$. The values $k_1$, $k_2$, ... and $C_1$, $C_2$, ... are the parameters to be determined. The number of the parameters is dependent on the number of temperature intervals which are determined according to the behavior of the thermal properties. Actually, the temperature intervals are expected to be smaller.
around the freezing point of the food due to the larger thermal property variations, as shown in Figs. (3.9) and (3.10). Above the initial freezing point and at very low temperature (30°C below the initial freezing temperature) the thermal properties were assumed to be constants. Temperature dependent thermal properties of basic food materials were estimated using temperature measurements during freezing experiments.

The estimation process is based on the comparison of the measured temperature at the heat flux boundary and the temperature simulated using the Two-Step finite difference method. The simulated temperatures are calculated based on the measured initial temperature, $T_i$, of the sample and the experimental values of the temperature boundary condition, $T_b$, and heat boundary condition, $q_b$. The temperature simulation consists of numerically solving a direct one-dimensional heat conduction problem, formulated as

$$\frac{\partial}{\partial x}\left(k(T)\frac{\partial T}{\partial x}\right) = C(T) \frac{\partial T}{\partial t} \quad 0 < x < L \quad t > 0 \quad (3.35)$$

$$T(x,0) = T_i \quad 0 \leq x \leq L \quad t = 0 \quad (3.36)$$

$$-k(T) \left. \frac{\partial T}{\partial x} \right|_{x=0} = q_b(t) \quad x = 0 \quad t > 0 \quad (3.37)$$

$$T(L,t) = T_b(t) \quad x = L \quad t > 0 \quad (3.38)$$

Where $T$ is temperature, $x$ is the location in the slab, $L$ is the thickness of the sample, $t$ is time, $k$ is thermal conductivity, $C$ is apparent volumetric specific heat, $T_i$ is the
Figure 3.9 Thermal Conductivity, $k$, as a Piecewise Function of Temperature.

Figure 3.10 Apparent Volumetric Specific Heat, $C$, as a Piecewise Function of Temperature.
measured initial temperature of the experimental sample, $q_b$ is the heat flux imposed on one the inner boundary of the experiment, and $T_b$ is the measured temperature on the outer boundary of the experiment, respectively.

The computer program "NLINA" (Beck, 1993) used to estimate the thermal properties of food materials is included in Appendix B. The estimated piecewise linear functions of temperature were then compared to thermal properties calculated using models presented by Eqs. (3.7) through (3.19), which will be presented in Chapter 6.
Chapter 4

ACCURACY ANALYSIS

The availability of high speed digital computers has prompted the development and use of various numerical schemes to simulate the freezing process in food materials. Finite element and finite difference methods are the most popular techniques used, and numerous forms of these methods have been used over the years. Even though the finite element methods are generally more complex, they do not present any advantage over the finite difference methods for freezing problems with simple geometries (Cleland and Earle, 1984). Hence, most researchers have used finite difference methods for the simulation of the one-dimensional freezing problem. These methods were also employed in this research study.

The accuracy of numerical simulations of the freezing process has been discussed by many researchers. Numerical results are usually analyzed through comparison with experimental data. Disagreements between experimental results and numerical simulations are generally attributed to experimental errors, numerical inaccuracies, and analytical biases. Numerical inaccuracies are due to inherent characteristics of the numerical solution technique, while analytical biases are associated with the formulation of the mathematical model. However, relatively little has been done to differentiate between
these different types of errors, and therefore, there is no conclusive explanation for the primary cause of the disagreements.

The overall goal of this chapter is to analyze the accuracy of the numerical simulation of one-dimensional freezing process in food materials. The main objectives of this analysis are:

1. to analyze the accuracy of the Crank-Nicolson finite difference method and to compare that with the Two-Step finite difference method (both numerical methods were discussed in earlier chapters).

2. to analyze the effect of the time step and grid size on the accuracy of each of the finite difference schemes employed in this research study (i.e. the Crank-Nicolson and the Two-Step method).

3. to compare numerical simulations of the freezing process with actual experimental data.

An analysis was conducted to investigate the two numerical methods and determine how the nonlinearity of the freezing problem effects the accuracies of the respective solutions. In this analysis, a non-homogeneous one-dimensional heat equation with an exact analytical solution was first presented and numerically solved using the two numerical schemes. The significance of this technique rests on the distinction of the numerical errors from any experimental errors or other analytical biases. In addition, this procedure is a very useful tool which could be applied to various types of nonlinear problems. Finally, simulations resulting from the two numerical methods were compared with experimental temperature measurements presented by Lescano (1973).
4.1 Accuracy Analysis

The analysis of the numerical methods is very important for the simulation of the freezing process or other highly nonlinear processes. In optimal conditions, a problem with an exact solution should be selected for the analysis to exactly quantify the numerical errors. However, an analytical solution for the freezing problem presented in Chapter 3 (Eqs. (3.1-4)) is not attainable, and thus, the approach here is to use a comparable problem for which an analytical solution can be obtained. For instance, the same partial differential equation of the freezing problem with a non-homogeneous term, \( F(x,t) \), could have an exact solution:

\[
\frac{\partial}{\partial x} \left( k(T) \frac{\partial T}{\partial x} \right) = \rho(T) c_a(T) \frac{\partial T}{\partial t} + F(x,t)
\]  

(4.1)

such that the thermal properties \((k, \rho, c_a)\) are the same functions of temperature, presented in Chapter 3 and used in the freezing problem, and \( F \) is a function of time \( t \) and location \( x \). The non-homogeneous function \( F \) was suitably determined after a function was selected as an exact solution. An exact analytical solution, \( p(x,t) \), was selected as an exponentially decaying function of time \( t \) multiplied by a symmetric cosine function of the location \( x \):

\[
p(x,t) = (T_i - T_f) \cos(A(x - L/2) + \pi/2) \exp(-t/\tau) + T_f
\]

(4.2)
such that $T_s, T_p, A,$ and $\tau$ are constants, $x$ is the location, $t$ is time, and $L$ is the thickness of the slab. It is also important to note that other functions could have been selected. However, in this case, the exponentially decaying function was selected because it mimics the general behavior of the temperature within a food material in a one-dimensional heat conduction process. The non-homogeneous function was then calculated:

$$F(x,t) = \frac{\partial}{\partial x} \left( k(p) \frac{\partial p}{\partial x} \right) - \rho(p)c_a(p) \frac{\partial p}{\partial t}$$  \hspace{1cm} (4.3)

where $F$ is clearly a known function of $x$ and $t$ and can be exactly determined. The function $F$ is then substituted into the differential equation presented by Eq. (4.1) as a non-homogeneous term. Consequently, the function $p$ is an exact analytical solution for the following governing equation and initial and boundary conditions:

$$\frac{\partial}{\partial x} \left( k(T) \frac{\partial T}{\partial x} \right) = \rho(T)c_a(T) \frac{\partial T}{\partial t} + \frac{\partial}{\partial t} \left( k(p) \frac{\partial p}{\partial x} \right) - \rho(p)c_a(p) \frac{\partial p}{\partial t}$$ \hspace{1cm} (4.4)

$$T(x,0) = p(x,0), \hspace{1cm} 0 \leq x \leq L, \hspace{1cm} t = 0$$ \hspace{1cm} (4.5)

$$T(x,0) = p(x,0), \hspace{1cm} x = 0, \hspace{1cm} t > 0$$ \hspace{1cm} (4.6)

$$T(x,0) = p(x,0), \hspace{1cm} x = L, \hspace{1cm} t > 0$$ \hspace{1cm} (4.7)

This problem is a non-homogeneous modification of the freezing problem. This modification was performed to create a problem with an exact analytical solution and a
degree of non-linearity similar to that of the freezing problem. It is important to note that this procedure also can be applied to various other nonlinear problems. Two different finite difference schemes were then used to solve the problem numerically, and the resulting numerical estimates were compared to the exact solution $p(x,t)$. This procedure was repeated using a variety of time steps and grid sizes, and a comparison between the accuracies of the two methods was performed.

### 4.2 Results of Accuracy Analysis

The accuracy analysis was performed to evaluate the two finite difference methods, namely the Crank-Nicolson and the Two-Step methods, by comparing the numerical solutions with the exact solution of the analytical problem described previously. This accuracy appraisal of the two numerical methods is very important in quantifying the effects of the time step and the grid size on the accuracy of the numerical solutions.

Both methods were implemented using a Fortran program (Appendix C) to solve the analytical problem described by Eqs. (4.4) through (4.7). The computer program prompts the user to set the time step and the grid size as well as other parameters of the problem (e.g., the thermal properties and the moisture content of unfrozen food, the initial freezing temperature, and the thickness of the slab). The exact analytical solution, described by Eq. (4.2), is then computed and a comparison is performed between the numerical solutions and the analytical solution. The comparison, which was performed for a variety of time steps and grid sizes, consists of the computation of the mean and
the maximum nodal errors for each of the numerical schemes. The mean error is defined as the average of all nodal errors throughout the entire time domain, and the maximum error is the largest of all these errors. All calculated errors are then nondimensionalized by dividing them by $T_f/T_i$ from Eq. (4.2). The dimensionless time step, $\Delta t^*$, as defined in the Nomenclature, was selected to vary from 0.0015 to 1.0, and dimensionless grid sizes, $\Delta x^*$, also defined in the Nomenclature, ranging from 0.005 to 0.1 were used with each of the dimensionless time steps.

4.2.1 Stability

Both numerical methods exhibited very unstable behavior, characterized by very large errors or total divergence of the process, as the dimensionless time step was increased greater than 0.5 or the dimensionless grid size was decreased less than 0.01. This observation affirms the recommendation proposed by Segerlind and Scott (1988) which suggests that in order to avoid oscillations in a finite difference or finite element scheme, the quantity $\Delta t/\Delta x^2$ must be smaller than an upper bound which is directly dependent on the properties of the material. Due to the non-linearity of the problem and the continuous and large variations of the properties of food materials throughout the process, this upper bound can not be determined analytically. In this case, the accuracy analysis approach can be employed to determine the limiting values for the time step and grid size for maximum stability. Based on the observations from this analysis, the range of the dimensionless time step and dimensionless grid size were respectively reduced to $0.015 \leq \Delta t^* \leq 0.5$ and $0.01 \leq \Delta x^* \leq 0.1$. 

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4.2.2 **Accuracy**

The Two-Step numerical schemes showed a very substantial improvement in the accuracy as the dimensionless time step decreased from 0.5 to 0.015, as shown in Figs. 4.1 and 4.2 for the mean error and the maximum error, respectively. In fact, both the mean error and the maximum error of the Two-Step scheme dropped by more than 97% as $\Delta t^+$ decreased for a dimensionless grid size of 0.05 and 0.1. In addition, the accuracy of the Two-Step method also improved as the dimensionless grid size increased from 0.01 to 0.1, as shown in Fig. 4.3 for $\Delta t^+$ equal to 0.05. The mean and the maximum error of the numerical solution decreased with the increase in grid size by approximately 82.5% and 70%, respectively.

The accuracy of the Crank-Nicolson method was not as responsive as the Two-Step method to variations in the time step and grid size. In this case, the mean and maximum errors exhibit in Figs. 4.1 and 4.2, respectively, a decrease of less than 26.8% and 28.7% as the dimensionless time step decreased from 0.5 to 0.015. Furthermore, as the dimensionless grid size was increased from 0.01 to 0.1, the mean and the maximum error showed reductions of 66.4% and 8.5%, respectively, as shown in Fig. 4.3.

Overall, the accuracy of the Two-Step method showed significant improvement as the time step decreased and the grid size increased. As shown in Table 4.1, the mean and the maximum Two-Step errors exhibited a decrease of more than 97% and 70%, respectively, as the dimensionless time step decreased from 0.5 to 0.015 and the dimensionless grid size increased from 0.01 to 0.1. This result can be verified by Eq. (3.24) which indicates that the difference between the temperature of the previous time
Figure 4.1 Mean Numerical Error vs Dimensionless Time Step, $\Delta t^+$, for Dimensionless Grid Size, $\Delta x^+$, of 0.05 and 0.1 Using the Crank-Nicolson (C.N.) and the Two-Step (T.S.) Methods.
Figure 4.2 Maximum Numerical Error vs Dimensionless Time Step, $\Delta t^+$, for Dimensionless Grid Size, $\Delta x^+$, of 0.05 and 0.1 Using the Crank-Nicolson (C.N.) and the Two-Step (T.S.) Methods.
Figure 4.3 Maximum and Mean Numerical Errors vs Dimensionless Grid Size, $\Delta x^+$, for a Dimensionless Time Step, $\Delta t^+$, of 0.05 Using the Crank-Nicolson (C.N.) and the Two-Step (T.S.) Methods.
Table 4.1 Overall Change and Percent Decrease* of Dimensionless Number Errors

<table>
<thead>
<tr>
<th>Variation</th>
<th>Dimensionless Time Step</th>
<th>Dimensionless Grid Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>from 0.5 to 0.015</td>
<td>from 0.01 to 0.1</td>
</tr>
<tr>
<td>Error Type</td>
<td>Mean</td>
<td>Maximum</td>
</tr>
<tr>
<td>Two-Step Error Change</td>
<td>0.05 to $10^{-3}$</td>
<td>0.45 to 0.01</td>
</tr>
<tr>
<td>% Decrease</td>
<td>0.978</td>
<td>0.971</td>
</tr>
<tr>
<td>Crank-Nicolson Error Change</td>
<td>0.1 to 0.07</td>
<td>0.76 to 0.54</td>
</tr>
<tr>
<td>% Decrease</td>
<td>0.268</td>
<td>0.287</td>
</tr>
</tbody>
</table>

* Percent decrease is defined as the difference between the initial and the final dimensionless error divided by the initial dimensionless error.

Step, $T^n$, and the intermediate temperature, $T^{n+
u}$, decreases as the time step decreases and/or the grid size increases. On the other hand, the Crank-Nicolson method presented higher errors than the Two-Step method. These errors did not feature much improvement as the time step and grid size were varied. In fact, the Crank-Nicolson method improvements were much smaller than that of the Two-Step method, as shown in Table 4.1. In this case, the persistent larger errors are mainly due to the non-convergence of the iterative process inherent to the Crank-Nicolson scheme.

Finally, a subsequent recommendation can be concluded from this error analysis. In this case, it is recommended to use a dimensionless time step and grid size, respectively, smaller than 0.2 and larger than 0.05 for good accuracy for both numerical methods. Furthermore, based on this accuracy analysis, it is anticipated that the Two-Step
method will provide more accurate solutions for the freezing problem than the Crank-Nicolson method. These insightful tips are very useful for the selection of a numerical method as well as improving its accuracy to solve the freezing problem. Furthermore, this accuracy analysis process can be easily applied on various kinds of nonlinear problems, such as melting, sublimation, curing processes, and various other heat transfer problems with changing thermal properties.

4.3 Numerical Simulation of the Freezing of Codfish

The two numerical methods were also employed to simulate actual freezing experiments. Numerical results from the simulations were compared with data from freezing experiments conducted by Lescano (1973). The experimental data consist of temperature measurements at the center of a one-dimensional slab-shaped codfish during freezing. The two finite difference schemes were implemented in a Fortran program with a user driven menu to set all the boundary and initial conditions, the thickness of the slab, the unfrozen properties (thermal properties, moisture content, and the initial temperature), and also the time step and the grid size of the computational procedure. The thermal properties, the initial freezing temperature, and the moisture content of unfrozen codfish used and shown in Table 4.2 were obtained from Lescano (1973). The time step and the grid size were selected in order to achieve the best accuracy possible for each of the numerical methods, according to the recommendations concluded from the analytical analysis of the methods discussed previously.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Freezing Temperature</td>
<td>-1°C</td>
</tr>
<tr>
<td>Initial Moisture Content</td>
<td>0.803</td>
</tr>
<tr>
<td>Unfrozen Thermal Conductivity</td>
<td>0.5538 W/m K</td>
</tr>
<tr>
<td>Unfrozen Specific Heat</td>
<td>3.6842 kJ/kg K</td>
</tr>
<tr>
<td>Unfrozen Density</td>
<td>1041.2 kg/m³</td>
</tr>
</tbody>
</table>

The experimental study conducted by Lescano (1973) consisted of eight experiments using infinite slab shaped samples with a thickness of 5.08 cm (2 inches). The temperature was measured at the center of the slab during freezing. The freezing rate of the experiments varied from one experiment to another according to the initial temperature of the slab, the temperature of the air, and the heat transfer coefficient. Five representative experiments, described in Table 4.3, were selected out of the total eight experiments and simulated using both of the numerical methods.

### 4.4 Results of the Numerical Simulation of Freezing of Codfish

The selected experiments from Lescano (1973) present diverse initial temperatures, ambient temperatures, and air velocities. The numerical simulations of these experiments were performed using the two numerical methods following the guidelines concluded from the accuracy analysis. Typically, the dimensionless time step was kept smaller than 0.2 and the dimensionless grid size larger than 0.05 to ensure the best accuracy possible.
Table 4.3 Experimental Tests for Freezing of Codfish (Lescano, 1973)

<table>
<thead>
<tr>
<th>Experimental Parameters</th>
<th>2</th>
<th>3</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slab Thickness (cm)</td>
<td>5.08</td>
<td>5.08</td>
<td>5.08</td>
<td>5.08</td>
<td>5.08</td>
</tr>
<tr>
<td>Ambient Temperature (°C)</td>
<td>-27.5</td>
<td>-27.5</td>
<td>-28.89</td>
<td>-23.61</td>
<td>-23.61</td>
</tr>
<tr>
<td>Initial Temperature (°C)</td>
<td>11.67</td>
<td>15.56</td>
<td>7.22</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Mean Air Velocity (m/s)</td>
<td>5.08</td>
<td>5.08</td>
<td>0</td>
<td>5.08</td>
<td>15.24</td>
</tr>
<tr>
<td>Heat Transfer Coef. (W/m²K)</td>
<td>102.2</td>
<td>102.2</td>
<td>25.95</td>
<td>102.2</td>
<td>187.37</td>
</tr>
</tbody>
</table>

for both numerical schemes.

As shown in Table 4.3, Exp. 2 and Exp. 3 have similar ambient temperatures and air velocities, however, the initial temperature of Exp. 2 (11.67°C) is lower than the initial temperature of Exp. 3 (15.56°C). The results of the simulations of these two experiments shown in Fig. 4.4 indicate that the Two-Step solutions exhibited much better agreement with experimental data than the Crank-Nicolson solutions. The maximum and the mean discrepancy of the simulated temperature with the measured temperature are defined, respectively, as the maximum and the average difference between the numerical and experimental temperatures. These values were then calculated as percentages of the total experimental temperature range. The maximum and mean errors of the Two-Step method were respectively, 14.0% and 5.9%, lower than the Crank-Nicolson errors for Exp. 2 and,
Figure 4.4: The comparison of the Two-Step (T.S.) and Crank-Nicolson (C.N.) results with experimental data for Exp. 2 and Exp. 3 from Lescano (1973).
Table 4.4 Maximum and Mean Percent Errors* of each of the Numerical Methods for Simulations of Experiments from Lescano (1973)

<table>
<thead>
<tr>
<th>Numerical Method</th>
<th>Error</th>
<th>Test Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Two-Step (T.S.) Method</td>
<td>Maximum</td>
<td>7.2%</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>2.1%</td>
</tr>
<tr>
<td>Crank-Nicolson (C.N.) Method</td>
<td>Maximum</td>
<td>21.2%</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>8.0%</td>
</tr>
<tr>
<td>% Difference Between T.S. and C.N.</td>
<td>Maximum</td>
<td>14.0%</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>5.9%</td>
</tr>
</tbody>
</table>

* Percent error is defined as the difference between the experimental temperature and the numerical temperature solution divided by the maximum temperature change, which is the difference between the initial and the ambient temperature, and then multiplied by 100.

18.4% and 6.4%, lower for Exp. 3, as shown in Table 4.4.

As shown in Fig. 4.4, the Two-Step method solutions were very close to the experimental data from Exp. 2 and 3 at and below the initial freezing temperature. However, the largest Two-Step discrepancy for both experiments occurred above the freezing temperature. In this case, the large error above freezing is primarily due to rapid change of the temperature on the surface of the slab which freezes prior to the center core. The mathematical model employed is essentially based on the equilibrium of the chemical potential of the liquid phase and the solid phase of the food medium to calculate the molar fraction of the unfrozen water within the food material, as described in Chapter 3. Subsequently, due to the rapid temperature variation on the boundaries during the
early stages of the experiments, the equilibrium hypothesis fails to duplicate the actual process. Thus the error can be mainly attributed to the model rather than the numerical method. On the other hand, the temperature simulated using the Crank-Nicolson method showed relatively large discrepancies above as well below the freezing temperature (Fig. 4.4). This result was anticipated from the accuracy analysis. As mentioned earlier, the large error of the Crank-Nicolson method is primarily due to the non-convergence of its inherent iterative scheme.

The freezing rate in Exp. 6 was much slower than those in Exp. 2 and Exp. 3 due to the zero mean air velocity and consequently lower heat transfer coefficient (Table 4.3). As shown in Fig. 4.5, the Two-Step method results again were much closer to the experimental data than the Crank-Nicolson results. From Table 4.4, the mean and maximum errors of the Two-Step method (respectively 4.2% and 14.1%) were smaller than those of the Crank-Nicolson method (respectively 7.8% and 16.5%). For both numerical methods, the maximum discrepancies were recorded below the initial freezing temperature. The larger discrepancies below freezing could be caused by the inaccuracy of the models used to predict the thermal properties of codfish during freezing. Above the freezing temperature, the numerical simulations showed better agreement with experimental data than simulations of Exp. 2 and Exp. 3. This was due to the smaller heat transfer rate and consequent slower freezing rate. Although Exp. 6 has a slower freezing rate, the Two-Step solutions exhibited larger discrepancies with the measurements from Exp. 6 than Exp. 2 and Exp. 3, shown in Table 4.4. The larger discrepancies could be due to inaccuracy in the models used to simulate the thermal properties. However,
Figure 4.5 The Comparison of the Two-Step and Crank-Nicolson Results with Experimental Data from Exp. 6 from Lescano (1973).
since the same food material (codfish) was used in all the experiments, the larger discrepancies observed between the experimental data from Exp. 6 and the numerical solutions could be caused by inaccurate heat transfer coefficients.

Exp. 7 and Exp. 8 had similar initial and ambient air temperatures. However, Exp. 8 had a larger mean air velocity and consequently a larger heat transfer coefficient than Exp. 7 (Table 4.3). Again, the Two-Step temperature solutions were much closer than the Crank-Nicolson solutions for both experiments throughout the entire temperature range, -23.61 to 5°C, as shown in Fig. 4.6. The mean and maximum discrepancies of the Two-Step method were much smaller than those of the Crank-Nicolson scheme, as shown in Table 4.4. For both experiments, the numerical errors were primarily higher below the freezing temperature. The larger discrepancies below freezing could be caused by inherent inaccuracy in the experimental measurement of the heat transfer coefficients or the mathematical models used to predict the thermal properties of codfish.

Furthermore, both numerical methods (i.e. the Crank-Nicolson and the Two-Step method) exhibited better agreement with the experimental data for Exp. 8 than Exp. 7 (Table 4.4), although Exp. 7 has a slower freezing rate than Exp. 8. The larger discrepancies with Exp. 7 could be caused by inaccurate experimental measurements of the codfish temperature or the heat transfer coefficients of the experiments.

Finally, it is very evident that the Two-Step method exhibited more accurate results than the Crank-Nicolson method in simulating all five experiments from Lescano (1973). All of the Two-Step solutions showed better agreement with the experimental data than the Crank-Nicolson solutions, as indicated in Table 4.4. Concurrently, the
Figure 4.6 The Comparison of the Two-Step (T.S.) and Crank-Nicolson (C.N.) Results with Experimental Data for Exp. 7 and Exp. 8 form Lescano (1973).
accuracy analysis also introduced strong evidence that the Two-Step method is more reliable for the simulation of the freezing process than the Crank-Nicolson method.

4.5 Accuracy Analysis Summary and Conclusions

The Crank-Nicolson and the Two-Step finite difference methods were analytically evaluated using an accuracy analysis. The accuracy evaluation of the numerical methods was conducted using an analytical problem with an exact solution. The numerical solutions of the problem were compared with the exact solution for a variety of time steps and grid sizes. Then, both finite difference methods were applied to simulate temperature in codfish during one-dimensional freezing experiments. The numerical solutions were then compared with actual experimental measurements acquired by Lescano (1973).

In conclusion, the Two-Step method produced better results than the Crank-Nicolson method in the accuracy analysis. Based on this analysis, it is suggested to keep dimensionless time step and grid size respectively smaller than 0.2 and larger than 0.05 for both numerical methods. The numerical simulations of the temperature in codfish during freezing exhibited results that concurred with the conclusions obtained from the accuracy analysis. In each case, the Two-Step solutions showed better agreement with the experimental data than the solutions of the Crank-Nicolson method. Consequently, for the simulation of the temperature in food materials during one-dimensional freezing process, it is recommended to employ the Two-Step finite difference method with small time step and large grid sizes. Remarkably, the accuracy analysis was very useful in
developing a clear insight on the accuracy and the stability of each of the numerical methods. It allowed for the distinction between numerical errors and analytical biases in the mathematical model. Furthermore, this analysis technique could be applied to various types of nonlinear heat transfer problems, such as melting, sublimation, and curing processes. It is a very useful tool to compare numerical methods and distinguish between different types of errors in simulating actual processes.

Although, the Two-Step method exhibited more accurate results than the Crank-Nicolson in this study case, it is possible to improve the accuracy of the Crank-Nicolson method and find it to be closer to that of the Two-Step method by further manipulating the time step and the grid size. In fact, larger time step and grid size ranges are needed for the evaluation of optimal time step and grid size to maximize the accuracy of the Crank-Nicolson method. In fact, in order to improve the accuracy of the Crank-Nicolson method much smaller time steps are needed which significantly increases the computation time. Hence, the time step and the grid size ranges were selected for practical reasons such as reducing the computation time and efficient numerical simulations.
Chapter 5

EXPERIMENTAL PROCEDURES

Experimental data are essential for the evaluation of the thermal properties of food materials during freezing. In this research study, the Modified Box-Kanemasu estimation method was employed to estimate the thermal properties of basic aqueous food mixtures as functions of the temperature. This method compares experimental temperature measurements with numerically simulated temperatures of food materials during freezing. The focus of this chapter is on the development and the utilization of the experimental design for the measurement of the required temperature data.

The experimental design was planned on the requirements of the estimation procedure. According to these requirements, temperature measurements during the freezing process are needed; therefore, a device is needed to measure and record temperature with time within a food sample during freezing. The mathematical model used to describe the freezing process is based on the one-dimensional heat transfer process; therefore, the dimensions of the sample holder used should be chosen to ensure one-dimensional heat transfer. Also, for the simultaneous estimation of the thermal conductivity and apparent volumetric specific heat, the heat flux must be measured or known at one boundary.
In the following sections, the experimental apparatus used will first be described, followed by a discussion of the measurement techniques used. The different types of the sample materials are then analyzed. Finally, the experimental procedures used are presented.

5.1 Experimental Apparatus

An experimental apparatus was designed to measure the temperature of aqueous food materials during freezing. This setup was conceived to retain solutions as well as solid products in a geometry which limits the freezing experiment to a one-dimensional heat transfer process. All the boundaries parallel to the direction of the heat transfer are designed to be insulated, while one of the remaining two boundaries (perpendicular to the direction of the heat transfer) are used to impose a heat flux and the other is assumed to be a time varying known temperature. Thus, the experimental procedures included the implementation, measurement, and control of a heat flux boundary condition and measurement of temperature at both boundaries.

A Lexan container with outer dimensions of 19 cm x 19 cm x 4 cm and inner dimensions of 14 cm x 14 cm x 4 cm was built. The container consists of two symmetric parts, each with a thickness of 2 cm (Fig. 5.1). A 0.04 cm thick heater-thermistor assembly (Fig. 5.2) was placed at the horizontal plane of the Lexan container to form two distinct chambers which hold similar quantities of test solutions (Fig. 5.3). The heater in the heater-thermistor assembly was employed to provide a heat flux boundary condition
Figure 5.2 Heater-Thermistor Assembly
Figure 5.3 Schematic of the Experimental Apparatus
for each of the two sample chambers, while the thermistors on either side of the heater were to measure temperature at the heat flux boundary in each cavity.

On each side of the sample holder, two aluminum plates were firmly positioned to contain food samples in the experimental cavities as shown in Fig. 5.3. On the inner side of each aluminum plate, a temperature sensor (i.e. thermistor) was placed to measure the outer boundary temperature of the sample. A spring-screw system was designed to apply pressure on each of the aluminum plates against the container to retain the test material (Fig. 5.3) in the sample chambers. This system also allows the aluminum plates to move due to any expansion of the sample during freezing. Rubber O-rings were positioned between the aluminum plates and the sample holder and on either side of the heater-thermistor assembly to prevent leakage.

The heater-thermistor assembly depicted in Fig. 5.2 is a Kapton enclosed resistance heater sandwiched between two thermistors. The heater element is a 10 Ω resistance made of 70% copper-30% nickel alloy which is very temperature stable with a temperature coefficient of resistance (or TCR) of 0.0017Ω/°C. The temperature sensors (i.e. thermistors) are 100 Ω platinum resistances with a TCR of 0.385Ω/°C. Each of the temperature sensors was attached to a circuit bridge of three 100 Ω resistances powered by a 3 volt DC power source, as shown in Fig. 5.4. The resistances of the temperature sensors vary linearly with temperature (due to its high TCR of 0.385Ω/°C) inducing voltage variations with temperature across the circuit bridges. The bridge-thermistor systems were calibrated for a -40 to 25°C temperature range using thermocouple
Figure 5.4 Schematic of the Electric Bridge
temperature measurements. Simultaneous measurements of the voltage across the bridges and the temperature of each thermistor were performed in a steady-state heat transfer experimental procedure. A linear relationship between the temperature and the voltage for each of the bridge-thermistor assemblies was then derived from the experimental measurements.

The circuit bridges were connected to a data acquisition system (National Instruments SCXI1000) which is controlled through a 486 IBM compatible computer. The voltage measurements across each of the circuit bridges were collected by the data acquisition unit and then transferred to a data file in the computer. A schematic of the data acquisition system and connection between the various experimental units are shown in Fig. 5.5. The heater, positioned in the center of the experimental apparatus (Fig. 5.3), was connected to a DC power supply (HP 6024A) which was also connected to the data acquisition board. The various experimental parameters, such as the data transfer frequency, the power supply output to the heater, and the number of measurements, are all digitally controlled through the data acquisition from the computer. A computer program was written using Lab Windows, a data acquisition software from National Instruments, to control all necessary data transfer and the various experimental parameters; this program is listed in Appendix D.
Figure 5.5 Schematic of Experimental Measurements and Data Collection
5.2 One-Dimensional Heat Conduction Process in the Apparatus

A one-dimensional conduction process was assumed in the experimental apparatus throughout this research study. Using this assumption, the heat conduction within the test materials in the direction parallel to the heater was neglected and also the temperature across the aluminum plates on the outer boundaries was assumed to be uniform on the entire plate surface.

The assumption of one-dimensional heat conduction within the test sample was reinforced by calculating and comparing the thermal resistances in the direction normal to the heater and the direction parallel to the heater. The thermal resistance normal to the heater was computed based on the heat conduction through the food material and it is formulated as:

\[ R_N = \frac{L_N}{k_mA_N} \]  \hspace{1cm} (5.1)

where \( R_N \) is the thermal resistance normal to the heater, \( L_N \) is the thickness of the food sample, \( k_m \) is the thermal conductivity of the food material, and \( A_N \) is the cross sectional area of the test cavity. The thermal resistance parallel to the heater was calculated based on the heat conduction through the insulation around the experimental apparatus (Fig. 5.3). The thermal resistance parallel to the heater was formulated as

\[ R_p = \frac{L_i}{k_iA_p} \]  \hspace{1cm} (5.2)
where \( R_p \) is the thermal resistance parallel to the heater, \( L_i \) is the thickness of the insulation, \( k_i \) is the thermal conductivity of the insulation, and \( A_p \) is the area of the total area around the food sample.

The calculations were performed for values of \( k_m \) and \( k_i \) of 0.5 and 0.03 W/m K, respectively. The calculated thermal resistance of the food material was found to be 0.02 K/W. However, the thermal resistance of the insulation was found to be 61.5 K/W. Since the thermal resistance of the food material is much smaller than that of the insulation, it was concluded that the one-dimensional heat transfer process assumption is valid.

The temperature of the aluminum plates were assumed to be uniform across the entire area. The validity of this assumption was verified by comparing the thermal resistance of the aluminum plate and the convective thermal resistance at its surface. The thermal resistance of the aluminum plate in the direction parallel to the heater was determined using

\[
R_A = \frac{L_A}{k_A A_A}
\]  

(5.3)

where \( R_A \) is the thermal resistance of the aluminum plate in the direction parallel to the heater, \( L_A \) is the length of the aluminum plate, \( k_A \) is the thermal conductivity of aluminum, and \( A_A \) is the cross-sectional area of the aluminum plate. The convective thermal resistance at the surface of the plate was computed using
\[ R_c = \frac{1}{hA} \quad (5.4) \]

where \( h \) is the heat transfer coefficient which was estimated to be 10 W/m\(^2\)K (assuming free convection only) and \( A \) is the surface area of the aluminum plate.

The thermal resistance of the aluminum plate in the direction parallel to the heater was found to be 0.13 K/W. However, the convective thermal resistance was determined to be 3.7 K/W. The uniform temperature across the aluminum surface assumption was then concluded to be valid since the convective thermal resistance is large compared to the conductive thermal resistance within the aluminum plate.

### 5.3 Calibration of Temperature Sensors

The temperature sensors employed in the experimental apparatus consist of temperature varying platinum resistances enclosed in a thin Kapton envelope (Minco Corp.). The calibration of the thermistor/bridge assemblies was essential in determining the transfer function between the measured voltages across the bridges and the corresponding temperatures of the thermistors. Since the resistances of the thermistors are linear functions of temperature (with a slope of 0.385 \( \Omega^\circ C \)), voltages across the circuit bridges were expected to behave nearly linear with temperature.

During the calibration process, temperature and voltage measurements were collected simultaneously. Type E thermocouples (chromel-constantan) were selected for temperature measurements due to their small size (=1.3 mm in diameter) and high
temperature sensitivity. In addition, E type thermocouples are known to be very effective and accurate over a wide temperature range (-100°C to 1000°C). Two thermocouples were made and each was attached to a 10 cm x 10 cm x 0.16 cm copper plate. Each thermocouple was placed in a groove placed across the center of a copper plate, as shown in Fig. 5.6, and glued. Good contact was assured between the copper plate and the thermocouple. Each of the thermocouple-plate assemblies was then covered with a uniform thin layer of silicone grease (Silicone heat sink compound; Dow Corning Corp.).

A temperature sensor was then positioned on top of the silicon layer. Another uniform layer of silicone grease, with a similar thickness as previous silicone layers, was then spread on each of the temperature sensors. The heater-thermistors setup was then sandwiched between the two identical assemblies (copper plate-thermocouple, temperature sensor, and the silicone grease layers) and the resulting system was placed between two aluminum plates. Pressure was then applied on both sides of the aluminum plates in order to assure equal thicknesses for all silicone layers. After removing the aluminum plates, the thickness of the apparatus was measured and recorded. The heater was connected to the DC power supply (HP9024A) which was controlled by the data acquisition system. All the thermistors and the thermocouples were also connected to the data acquisition system (National Instruments SCXI 1000) for data collection.

The calibration apparatus was positioned in a low temperature freezer (Model PR73-65H; Environment Equipment Co.) and the output of the DC power supply to the heater was set to high (~50 Watts) in order to obtain temperature readings greater than 25°C from the thermocouples. The system was allowed to reach steady state.
Copper Plate and Thermocouple Assembly (10.15 cm x 10.15 cm)

Figure 5.6 Calibration Apparatus for the Temperature Sensors
Temperature and voltage readings were then recorded and saved in a data file. The power output to the heater was then slightly decreased, and the system was allowed to reach its new steady-state condition, and then the temperature and voltage readings were again recorded and saved in the data file. The same procedure was performed numerous times until the temperatures recorded by the thermocouples were well below -30°C.

The temperature readings recorded in this calibration procedure are all results of a one-dimensional steady-state heat transfer process. All of the thermal conductivities of the materials (i.e. Kapton, silicone grease, and copper) involved in the calibration process are known. The total thickness of the apparatus as well as the thickness of each of the elements (i.e. heater and thermistors) in the apparatus are also known through measurements. Consequently, the thickness of each of the silicone grease layers can be calculated assuming equal thicknesses for all layers. Given the steady-state boundary temperatures of the apparatus, the thickness and the thermal conductivity of each of the material layers within the system, temperatures of the platinum resistance thermistors were calculated using steady-state one-dimensional heat conduction equation:

\[ q'' = -k_i \frac{\Delta T_i}{\Delta x_i} = -k_i \frac{(T_{i_1} - T_{i_2})}{e_i} \] \hspace{1cm} (5.5)

where \( q'' \) is the heat flux per unit area which is half of the power delivered to the heater divided by the area. The subscript \( i \) indicates the layer in the calibration setup. The value \( k_i \) is the thermal conductivity, \( T_{i_1} \) and \( T_{i_2} \) are boundary temperatures, and \( e_i \) is thickness, of the layer \( i \). Once the temperatures of the sensors were calculated, a linear
relationship was then determined between the voltages of the circuit bridges and the temperatures using linear regression.

5.4 Experimental Parameters

The experimental procedure includes the measurement of the temperatures at the two boundaries and controlling the pulsing heat flux on one boundary. Various parameters (i.e. the temperature measurement frequency, the heat flux pulse magnitude, rate and duration) must be set in the data acquisition program to perform this experimental procedure. This part of the experimental design was done prior to implementing any experiments. The temperature measurement frequency was first selected according to the expected response time of the temperature variations of the experiment. As shown in Table 5.1, a time of 5 seconds was allowed between two consecutive temperature scans. This time lag was chosen because it allowed for

<table>
<thead>
<tr>
<th>Table 5.1 Experimental Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. measurement frequency</td>
</tr>
<tr>
<td>Rate of heat Pulse</td>
</tr>
<tr>
<td>Heat pulse magnitude</td>
</tr>
<tr>
<td>Heat pulse duration</td>
</tr>
</tbody>
</table>
temperature variations greater than the resolution of the data acquisition system and also small enough to monitor all temperature variations of the sample material.

To optimize a suitable heat flux procedure for the experimental process, the convergence of the estimation process, which is characterized by the number of iterations, and the magnitude of the sensitivity coefficients (see Chapter 3) were considered. The optimization procedure was necessary to avoid any convergence problems in the estimation process with the actual experimental measurements. Thermal properties were estimated using numerically simulated temperature values. The heat flux magnitude, duration and frequency were varied and the convergence rate of the estimation process as well as the magnitude of the sensitivity coefficients were monitored. The convergence rate was examined using the number of iterations needed for the estimation process to converge; fewer iterations indicate faster convergence. The sensitivity coefficients, which are defined in Section 3.6 as the sensitivity of the temperature of the food material to changes in the thermal properties, have a significant effect on the stability and the convergence of the estimation process; larger sensitivity coefficients result in a more stable process and a faster convergence rate. The optimization procedure was repeated for various sets of heat flux pulses. A power pulse of 15 Watts with 3 minute duration and a total cycle of 9 minutes was selected. These values were selected because they provided faster convergence and higher sensitivity coefficients in the estimation process.
5.5 Test Materials

Food products are generally made up of water and three major groups, namely carbohydrates, proteins, and fats. The concentration and types of these basic ingredients vary substantially from one food material to another. The freezing process in food products differs according to the basic compositions of the food material and the thermal and physical properties of each of the ingredients. This research study is mainly focused on the analysis of food materials rich in carbohydrates and proteins. The standard test materials were chosen from these two basic groups. Sucrose and methyl-cellulose were selected to represent the carbohydrates group. However, the basic structure of these two materials are quite different; sucrose is a simple carbohydrate with a small molecular structure and the methyl-cellulose is a complex carbohydrate which is formed by very large molecules. The wheat gluten was selected as a vegetable protein. The test materials are solutions of each of these basic food materials prepared with different water concentrations. Freezing experiments were performed on the prepared mixtures. Experimental temperature measurements were then employed to estimate the transient thermal properties of these test materials during the freezing process.

5.5.1 Sucrose

Sucrose is the regular household sugar from which various food products, such as candies and other confections, are made. Sucrose belongs to a simple group of carbohydrates referred to as "disaccharide" because it contains 12 carbon atoms and has
the general formula \(C_{12}H_{22}O_{11}\), as shown in Fig. 5.7. Sucrose is produced in plants by combining two of the simplest carbohydrates or monosaccharides, namely glucose and fructose. Actually, sucrose is formed by a condensation reaction where glucose and fructose are combined with the elimination of a water molecule. Sucrose is found in many fruits and vegetables, such as sugar cane and sugar beets, from which it is generally commercially extracted due to its relatively large quantities in these plants (around 15%). This compound is a crystalline compound and very soluble in water (203.9 grams of sucrose per 100 grams of water at 20ºC). The solubility of the sucrose increases as the temperature of the water increases. Due to its small molecules, sucrose has strong affinity for water molecules, and hence, it forms a homogeneous solution.

5.5.2 Methyl-cellulose

Methyl-cellulose or Methocel, a trademark of the Dow Chemical Company, is a water soluble carbohydrate polymer derived from cellulose. Methocel is used in various kinds of food products due to its unique physical and chemical characteristics. It is made by the reaction of wood or cotton cellulose fibers with chemical reactants in the presence of caustic soda. The resulting fibrous product is then treated with methyl-chloride and then purified and ground to a fine, uniform white powder. Methocel is a cellulose ether product which has a polymeric backbone of basic repeating structure of anhydroglucose \((C_8H_{14}O_5)\), as shown in Fig. 5.8. This product has been used for over 50 years in foods, pharmaceuticals, cosmetics, paints, ceramics, and other applications.

For this research study, a premium grade, obtained from Dow Chemical Company,
Figure 5.7  Sucrose Molecule (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11})
Anhydroglucose Unit (C$_7$H$_{14}$O$_5$)

n is the number of anhydroglucose Units in a methyl-cellulose molecule.

Figure 5.8 Methyl-cellulose Molecule
was employed as a basic food component for freezing experiments. Methocel premium
products have been mainly used as additives in the manufacturing of food products and
drugs. Methocel is usually used in baked products to aid gas retention by thermal
gelation during baking. It also provides more moist texture in baked foods, improves
emulsification of butters, and increases the shelf-life of food products. Furthermore,
Methocel is used in salad dressing and sauces to improve the stability of oil-in-water
emulsions and retain suspension of solid particles in the liquid. It is also used in frozen
desserts to modify ice crystal size to give a smoother texture and improve emulsion
stability (Table 5.2). The standard grade of Methocel has the same chemical formation,
but can have a slightly higher level of impurities. This grade is used in various industrial
applications such as cosmetics, paints, ceramics, and other products.

5.5.3 Wheat Gluten

Wheat gluten is a very rich source of protein for many kinds of food products due
to its high protein content. This food ingredient is mainly used in bread making and
pastry. Due to their large size, protein molecules are more attracted to each other than
to water to water molecules causing colloidal dispersions in water. A protein molecule
consists generally of a large chain of amino acid molecules bonded by peptide links. A
peptidelink is formed between the amino (-NH2) group of an amino acid molecule with
acidic (-COOH) group of another amino acid molecule, as shown in Fig. 5.9. A typical
protein molecule consists of about 500 amino acid molecules joined together. Protein
molecules can contain various kinds of amino acids, each of these can have several
Peptide Linkage between Two Acid Molecules

Figure 5.9 A Fragment of a Protein Molecule
Table 5.2 General properties of Methocel (Dow Chemical Corporation)

**Water solubility**: Methocel dissolves in water with no sharp solubility limit. Methocel powders must first be thoroughly dispersed in the water to prevent lumping.

**No ionic charge**: Methocel is a non-ionic and will not complex with metallic salts or ionic species to form insoluble precipitates.

**Thermal gelation**: Aqueous solutions of Methocel gel when heated above a particular temperature, providing controllable quick-set properties. The gels go back into solution upon cooling.

**Low taste and odor**: Important in food and pharmaceutical applications.

**Water retention**: Methocel is a highly efficient water retention agent. This is valuable in food products, ceramics, and many other applications.

**Thickening**: Methocel thickens both aqueous and non-aqueous systems. The viscosity is relative to the concentration and temperature.

**Suspension**: Methocel is used to control settling of solid particles (e.g. herbs and spices in salad dressing and antacid suspension).

**Emulsification**: Methocel stabilizes emulsions by reducing surface and interfacial tension and by thickening the aqueous phase.

different configurations; thus, protein molecules have very complex structures. However, protein molecules can be classified into two main groups: 1. globular proteins which have rounded molecules, and 2. fibrous proteins which have straight or spiral molecules.

Wheat gluten protein is an example of a fibrous protein. Molecules of wheat gluten protein are coiled and behave like a spring. Consequently, when pulled, gluten
would stretch and return to its original shape when released. Due to the size involved, unstable colloidal dispersions are formed when wheat gluten is mixed in water. However, when slowly hydrated, wheat gluten forms a dough. Protein molecules start to interact with water molecules as soon as they come in contact and bond together to form a network.

5.6 Test Substance Preparation

Freezing experiments were performed on aqueous solutions of each of the three substances discussed earlier. Various concentrations of each test material were employed: 4.8, 9.1, 16.7, 28.6, 37.5, 44.5, and 50 percent of the total mass. The preparation of the test solutions was performed in the following careful and organized procedure:

1. One 1000 ml beaker is first cleaned and wiped dry. Then, it is placed on a digital scale and tarred.

2. An appropriate amount of water (i.e. 800 grams which is enough to fill the experimental apparatus) is poured in the beaker and then placed on the scale and the exact water mass is recorded.

3. A second beaker is cleaned, wiped dry, and the required amount of the test substance (sucrose, methyl-cellulose, or wheat gluten) is calculated using the desired concentration and the recorded mass of the water in the first beaker.

4. The second beaker is then placed on the scale, tarred, and the required amount of test substance, calculated earlier, is poured.

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6. The test substance in the second beaker is then mixed with the water in the first beaker using the appropriate mixing technique.

Due to the difference between the properties of the basic ingredients used in this research study, different techniques were employed for the mixing process of the test materials. In the case of sucrose, the mixing process was straightforward for all concentrations due to the high solubility of sucrose in water. A stirring hot plate (Fisher Scientific Corp.) was employed in this case. For higher concentrations (44.45 and 50 percent), higher temperatures were used to accelerate the solubility of the sucrose. The stirring hot plate apparatus was also used to form a colloidal dispersion of low concentration (less than 28.57 percent) of wheat gluten. However, for higher concentrations, the wheat gluten was placed in a sizable container and water is blended in very slowly as the mixture is being mixed by hand to form a homogeneous "dough". This technique is also used in the case of high concentrations (37.5 percent or more) of methyl-cellulose. In the case of lower concentrations of methyl-cellulose, a high shear mixing technique, using a food blender, was employed.

5.7 Experimental Procedure

Once the test substance was ready, the experimental process was started immediately to avoid any dehydration of the test sample. The experimental procedure progresses as follows:

1. The test substance was placed in the experimental apparatus described earlier and
the aluminum plates were fitted on both sides of the Lexan container with pressure applied using the springs-bolts system. In the case of solid samples, the test material was first carefully packed in the container (to avoid any air gaps) and then the aluminum plates were fitted firmly on the container. However, in the case of liquid samples, the aluminum plates were first fitted on the container, then the liquid sample was poured using funnels through 0.62 cm holes into each of the two cavities of the apparatus, as shown in Fig 5.10. In this case, the same amounts of the sample liquid was poured simultaneously on each side in order to assure a pressure balance between the two experimental cavities.

2. One inch styrofoam insulation layer (thermal conductivity of 0.03 W/m K) was then placed on the peripheric area of the experimental apparatus, as shown in Fig. 5.3, to assure a one-dimensional heat transfer process.

3. The computer, the data acquisition system, and the DC power supply were then activated, and the various experimental parameters were set in the Lab Windows (National Instruments) program; see Appendix D for listing of the data acquisition program.

4. The experimental apparatus was then connected to the data acquisition system and the power supply.

5. The data acquisition program was initiated and the experimental apparatus was placed in the low temperature freezer.

6. Once the temperatures recorded by the thermistors decreased below -25°C the data acquisition program was terminated and the voltage measurements were saved in
Figure 5.10 Liquid Sample Placement Inside the Experimental Cavity.
a file. The recorded voltages for a typical experiment are shown in Figs. 5.11a and 5.11b. The voltage data was then transformed to temperature using the calibration of the thermistors.
Figure 5.11a Voltage Measurements Across Circuit Bridges during a Freezing Experiment.

Figure 5.11b Temperature measurements during a freezing Experiment.
Chapter 6

RESULTS AND DISCUSSION

The prediction of the thermal properties of food materials is essential for the simulation of freezing and the estimation of the freezing time. The accurate evaluation of these parameters is of great importance for the design of freezing processes and refrigeration equipment. Hence, various mathematical models have been introduced by researchers to predict the thermal properties of foods from their basic compositions and unfrozen properties. However, these models are generally formulated on the assumption that food materials are ideal binary solutions. This suggests that the applicability of these models is then reduced to food products with high water content and properties imminent to those of an ideal solution, even though they are used for a variety of food products. However, due to the lack of experimental data for temperature dependent thermal properties of food materials during freezing, the accuracy of these predictive models is still unknown.

One of the main objectives of this research study is to determine the thermal properties of basic food materials and compare them to thermal properties predicted using mathematical models from the literature. As presented in Chapter 5, experimental temperature measurements were performed using transient one-dimensional freezing
experiments. The thermal properties of the food materials were then estimated using the Modified Box-Kanemasu minimization method with the experimental data. In this chapter, the estimated thermal properties will be presented and compared with predicted thermal properties using mathematical models from the literature (Chapter 3).

6.1 Estimation Procedure for the Thermal Properties

The estimation procedure used consisted of the minimization of an objective function, namely the least squares of an objective function containing measured and simulated temperatures. The simulated temperatures were calculated by directly solving the one-dimensional freezing problem using finite differences. In the estimation process, the thermal properties of the food material, namely thermal conductivity and apparent volumetric specific heat, were assumed to be piecewise linear functions of temperature during the freezing process, as discussed in Chapter 3. However, above freezing as well as at very low temperatures (30°C below the initial freezing temperature), the thermal properties were assumed to be constant due to their expected insignificant variation with temperature. The temperature intervals were selected according to the rate of the variation of each of the thermal properties with temperature. Due to the expected abrupt variation at the initial freezing temperature, very small intervals were selected near the initial freezing point. The temperature intervals increased as the temperature further decreased.

Initial estimates for the thermal properties are essential to begin the estimation
process. Furthermore, the convergence and stability of the estimation procedure is greatly affected by the accuracy of the initial guesses of the thermal properties. The use of accurate initial estimates will exhibit a stable estimation process and faster convergence rate (less iterations), and hence, they must be carefully selected. In this research study, the initial estimates for the thermal properties were determined using the mathematical models presented in Chapter 3. For the evaluation of the initial estimates, the unfrozen properties and initial freezing temperature of the food materials must be provided. Therefore, thermal properties of pure food components published by Choi and Okos (1985) and properties of pure water were used to evaluate the unfrozen properties of each of the test materials (solutions of sucrose, methyl-cellulose, and wheat gluten). The initial freezing temperatures of each of the test substances were determined using Differential Scanning Calorimetry (DSC) data.

6.2 Discussion of Estimated Thermal Properties

6.2.1 Estimated Thermal Properties of Sucrose Solutions

Sucrose solutions with concentrations varying from 4.8 to 50% by weight were used in this research study. The temperature dependent thermal properties (thermal conductivity and apparent volumetric specific heat) were estimated using the Modified Box-Kanemasu estimation method, discussed in Chapter 3, for all of the concentrations.

In this section, two sub-sections will be presented; the first sub-section will include a description of the general characteristics of the estimated thermal properties of sucrose
solutions. These characteristics were also found to be applicable to the thermal properties of methyl-cellulose and wheat gluten solutions. The second sub-section will include characteristics distinctive to the sucrose solutions.

6.2.1.1 General Characteristics of the Thermal Properties

The estimated thermal conductivities of sucrose solutions increased steadily throughout the freezing process, as shown in Fig. 6.1. Due to water solidification, the mass fraction of water and ice in the food material decreased and increased, respectively. Hence, the overall thermal conductivity of the solution steadily increased as the freezing process continued due to the higher thermal conductivity of ice compared to that of pure water.

The thermal conductivities of sucrose solutions exhibited significant changes as the concentration of the sucrose increased from 4.8 to 50% of the total weight. In fact, the thermal conductivity of the unfrozen sucrose solution decreased as the mass fraction of the sucrose increased, as shown in Fig. 6.2. The thermal conductivity of pure sucrose is smaller than that of pure water; therefore, as the concentration of sucrose increased, the effective thermal conductivity of the aqueous sucrose mixture decreased and approached the thermal conductivity of pure sucrose. Furthermore, the overall change of the thermal conductivity, $\Delta k$, of sucrose solutions with temperature (from 0°C to -40°C) decreased as the concentration of sucrose increased, as shown in Fig. 6.3, due to the decrease of the water mass fraction in the sucrose mixture. In this case, $\Delta k$ is defined as the difference between the thermal conductivity of the completely frozen material and that of the

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Figure 6.1 Estimated Thermal Conductivity, $k$, of Sucrose Solutions vs Temperature for Various Sucrose Concentrations.
Figure 6.2 Thermal Conductivity of Unfrozen Solutions, $k_u$, of sucrose, Methyl-cellulose and Wheat Gluten vs Concentration.

Figure 6.3 Overall Change of Thermal Conductivities, $\Delta k$, during Freezing vs Concentration.
unfrozen material.

The apparent volumetric specific heats of the sucrose solutions showed large increases at the initial freezing temperature, and then, steadily decreased during the remainder of the freezing process, as shown in Fig. 6.4. Note that the latent heat of fusion is included in the apparent specific heat. These large increases at the beginning of freezing were due to the release of the latent heat as a significant portion of the water transformed to ice. The mass fraction of unfrozen water decreases as the freezing process progresses, and hence, less and less water solidification occurs as the temperature of the solution further decreases from the initial freezing point. The decline of the apparent volumetric specific heat was also assisted by the smaller specific heat and density of ice compared to those of pure water.

The volumetric specific heat of unfrozen sucrose solutions significantly decreased as the mass fraction of sucrose increased from 4.8 to 50%, as shown in Fig. 6.5. Since the volumetric specific heat of pure sucrose is smaller than that of pure water and the mass fraction of sucrose increased in the solution, the effective volumetric specific heat of the mixture decreased.

6.2.1.2 Distinctive Characteristics of the Thermal Properties

The estimated thermal properties of sucrose solutions also exhibited different characteristics which are not common with the other food materials (i.e. methyl-cellulose and wheat gluten) used in this research; in this section, these characteristics will be presented.
Figure 6.4 Estimated Apparent Volumetric Specific Heat, $C$, of Sucrose Solutions vs Temperature for Various Sucrose Concentrations.
Figure 6.5 Apparent Volumetric Specific Heat of Unfrozen Solutions, $C_u$, of Sucrose, Methyl-cellulose and Wheat Gluten vs Concentration.
The thermal conductivities of low concentration sucrose solutions exhibited sudden and large increases at the beginning of the freezing process, and then, approached constant values shortly below the initial freezing temperature (within 5°C below the initial freezing point), as shown in Fig. 6.1. Actually, at low sucrose concentrations, the freezing process of sucrose solutions is similar to freezing of pure water. Thus, the thermal conductivity of the low concentration sucrose solutions exhibited sudden increases similar to the step change of the thermal conductivity during the freezing of pure water.

At higher concentrations, the thermal conductivities of sucrose solutions gradually increased below the freezing temperature (Fig. 6.1). The gradual increase in the thermal conductivities of high concentration sucrose solutions extend over a larger temperature range than at lower concentrations. This indicates that the freezing process of sucrose solutions deviates further from the freezing of pure water as the concentration of sucrose increases.

The apparent volumetric specific heats, $C$, of low concentration sucrose solutions exhibited sudden and large increases at the initial freezing temperature, and then, rapidly decreased for the remainder of the freezing process, as shown in Fig. 6.4. This is mainly due to the release of the latent heat of fusion as a significant amount of the water freezes at the initial freezing point. Again, this demonstrates that the freezing process of low concentration sucrose solutions is very similar to the freezing of pure water where the latent heat of fusion is released at a single temperature (0°C).

At higher concentrations, the apparent volumetric specific heats ($C$) gradually increased below the initial freezing point (Fig. 6.4). After reaching a peak, the apparent
volumetric specific heats slowly decreased for the remainder of the freezing process. The overall behavior of $C$ was more uniform than at lower sucrose concentrations. This is mainly due to the release of latent heat of fusion over a larger temperature range as the concentration increases. As the concentration of sucrose increases, the sucrose molecules interfere between the water molecules and prevented them from forming ice crystals. In this case, the diffusion process becomes more important in the freezing process because water molecules must first migrate between sucrose molecules before they join to form ice.

Furthermore, at very low temperatures, the apparent volumetric specific heats of high concentration sucrose solutions are larger than those of low concentrations sucrose solutions. The freezing of high concentration sucrose solutions extends over a larger temperature range. Thus, the solutions of high sucrose concentrations release more latent heat than those of low sucrose concentrations at low temperatures.

6.2.2 Estimated Thermal Properties of Methyl-Cellulose Solutions

The general behavior of the estimated thermal properties of methyl-cellulose solutions, as shown in Figs. 6.6 and 6.7, was overall similar to that associated with the sucrose solutions, as discussed in Section 6.2.1.1. In this section, distinctive characteristics of the estimated thermal properties of methyl-cellulose solutions will be presented and compared to those of the sucrose solutions.

Generally, the thermal conductivities of methyl-cellulose solutions increased steadily as the temperature decreased from the initial freezing point and approached
Figure 6.6 Estimated Thermal Conductivity, $k$, of Methyl-cellulose Solutions vs Temperature for Various Methyl-cellulose Concentrations.
Figure 6.7 Estimated Apparent Volumetric Specific Heat, $C$, of Methylcellulose Solutions vs Temperature for Various Concentrations.
constant values as the freezing process proceeded, as shown in Fig. 6.6. The thermal conductivity of methyl-cellulose solutions at low concentrations exhibited more steady increase at the initial freezing point compared to those of the sucrose solutions. Furthermore, the changes in the thermal conductivities of low concentration methyl-cellulose solutions extended for larger temperature ranges than those of sucrose. This indicates that the freezing of low concentration methyl-cellulose solutions deviates more from the freezing of pure water than freezing of low concentration sucrose solutions due to the more complex molecular structure of methyl-cellulose.

At high concentrations, the thermal conductivities of methyl-cellulose solutions exhibited increased at the early stages of the freezing and approached constant values thereafter. The increase of the thermal conductivities of the methyl-cellulose solutions decreased significantly after the earlier stages of freezing as opposed to the thermal conductivities of high concentration sucrose solutions which increased throughout the entire freezing process. This difference is mainly due to the inherent structural differences between the methyl-cellulose and sucrose solutions. In fact, the sucrose solution allows diffusion to occur even in advanced stages of the freezing due to the small size of sucrose molecules, and hence, freezing continues to progress and the thermal conductivity of the solution continues to increase even at lower temperatures. However, due to the large size of the methyl-cellulose molecules, the diffusion process in the high concentration solutions is impeded after the early stages of the freezing; hence, the freezing process is significantly slowed and the thermal conductivity of the methyl-cellulose solution approached constant after the early stages of the freezing process.
Furthermore, the change in the thermal conductivities of unfrozen methyl-cellulose solutions with concentration, as shown Fig. 6.2, was more significant than in the case of sucrose solutions for the same concentration change (4.8 to 50%). This larger change with methyl-cellulose is mainly due to the complex molecular structure of methyl-cellulose and its consequent greater effect on the properties of the aqueous solution compared to sucrose.

The apparent volumetric specific heats of methyl-cellulose in aqueous mixtures, shown in Fig 6.7, varied significantly with temperature and also with concentration. The overall characteristics of the apparent volumetric specific heats of methyl-cellulose are similar to those of sucrose described in Section 6.2.1.1. However, less abrupt increases at the initial freezing point were observed compared with the those associated with the sucrose solutions. This is mainly due to the difference in the molecular behavior of sucrose and methyl-cellulose and their interactions with water molecules during the freezing process. Due to the larger methyl-cellulose molecular structure compared to that of sucrose, the freezing process is delayed by a slower diffusion process of water molecules, and consequently, the release of the latent heat was not instantaneous as with the freezing of sucrose solutions.

6.2.3 Estimated Thermal Properties of Wheat Gluten Solutions

The estimated thermal properties of the wheat gluten solutions are shown in Figs. 6.8 and 6.9. These results exhibit characteristics similar to those observed in the cases of sucrose and methyl-cellulose, as mentioned in Section 6.2.1.1.
Figure 6.8 Estimated Thermal Conductivity, $k$, of Wheat Gluten Solutions vs Temperature for Various Concentrations.
Figure 6.9  Estimated Apparent Volumetric Specific Heat, $C$, of Wheat Gluten Solutions vs Temperature for Various Concentrations.
The thermal properties of sucrose solutions also presented distinctive features which are not common with the sucrose or methyl-cellulose solutions. For instance, the initial freezing temperature of wheat gluten did not vary significantly compared to the initial freezing temperature of sucrose and methyl-cellulose (Fig. 6.8). This is due to the difference between the chemical structure of wheat gluten, which is mainly protein, and sucrose and methyl-cellulose which are carbohydrates, as described in Chapter 5.

The thermal conductivity of the high concentration wheat gluten exhibited increases smaller and larger than the increases of the thermal conductivities of sucrose and methyl-cellulose solutions, respectively. Furthermore, the change of the thermal conductivity of unfrozen wheat gluten solutions was larger than the change of the thermal conductivity of sucrose and smaller than that of methyl-cellulose.

The apparent volumetric specific heats of wheat gluten solutions exhibited the same overall characteristics as sucrose and methyl-cellulose solutions, as described in Section 6.2.1.1. However, similar to the methyl-cellulose solutions, the large increases in C of low concentration wheat gluten solutions were more gradual than those of low concentration sucrose solutions, as shown in Fig. 6.9. This is mainly due to the complex molecular configuration of wheat gluten and the consequent obstruction of the freezing process. Thus, the release of the latent heat was delayed further from the initial freezing temperature.
6.3 Comparison of Estimated and Predicted Thermal Properties

Predictive models have been developed and utilized by many researchers to determine the thermal properties of food materials. These models present an attractive alternative to experimental methods due to their low cost and time efficiency. As discussed in Chapter 3, mathematical models proposed in the literature are generally based on the assumption that food materials are ideal binary solutions. Henry K. Leung (1985) mentioned in his analysis of the mathematical models that in the formulation of these models, food materials are assumed to have colligative properties. Colligative properties, as discussed by Adamson (1973), are properties that depend solely on the quantity of the materials in the mixture but do not account for the chemical nature of these substances. The mathematical models used to predict thermal properties of food materials are based on the assumption of an ideal binary solution and on the basic compositions and the unfrozen properties of the food material without accounting for the chemical and structural properties of each of the substances and the potential chemical reactions which could occur between the ingredients upon mixing. In addition, in order to formulate the freezing point depression process, researchers assumed chemical equilibrium between the solvent and the solutes of the food mixture.

One of the main objectives of this research study is to compare the thermal properties predicted using mathematical models with estimated thermal properties, discussed earlier in this chapter. The thermal conductivities, \( k \), of the test food materials were predicted using the model introduced by Kopelman (1966) and then modified by
Heldman and Gorby (1975); the mathematical formulation of this model is presented in Section 3.2.3 by Eqs. 3.13, 3.14, and 3.15. The prediction of the apparent volumetric specific heat, \( C \), includes the prediction of the density, \( \rho \), and apparent specific heat, \( C_a \), of the food material. The density was determined using the model, introduced by Hsieh et al. (1977), described in Section 3.2.2 by Eq. 3.10, and the apparent specific heat was predicted using the model presented by Schwartzberg (1976) and described in Section 3.2.4 by Eq. 3.18.

The comparison between the predicted and estimated thermal properties is essential to establish insights on the accuracy of the mathematical models with different kinds of food ingredients. The three basic food substances analyzed previously (sucrose, methylcellulose, and wheat gluten) were employed in this analysis. In each case, selected concentrations (4.8, 28.6, and 50%) were used in the comparisons. The results for the remaining concentrations (9.1, 16.7, 37.5, and 44.5%) will be included in Appendix E.

6.3.1 Estimated and Predicted Thermal Properties of Sucrose Solutions

The estimated thermal properties of sucrose solutions during freezing, described in Section 6.2, were compared with predicted values using mathematical models from the literature. The estimated and predicted thermal properties exhibited similar overall behavior (Section 6.2); however, discrepancies between the estimated and the predicted quantities were generally observed with the thermal conductivities as well as the apparent volumetric specific heats of sucrose solutions. These discrepancies varied in magnitude with concentration and temperature.
In order to quantify the difference between the predicted and estimated thermal properties, 95% confidence regions were calculated for the estimated thermal properties at selected temperatures. The confidence region for each estimated parameter, $b_i$, were evaluated as

$$b_i \pm \left[ \frac{S}{P_{ii}} \right]^{1/2} t_{1-\alpha/2}(N-p)$$

(6.1)

where $p$ is the number of parameters estimated, $N$ is the number of temperature measurements, $P_{ii}$ is the $i$th diagonal term of the $P$ matrix (Eq. (3.29)) which represents the variance of the parameter, $S$ is the sum of the squared residuals, and $t_{1-\alpha/2}(N-p)$ is the value of the $t$ distribution for $(1-\alpha/2)$ confidence region and $(N-p)$ degrees of freedom (Beck and Arnold, 1977).

The predicted thermal conductivities of sucrose solutions exhibited good agreement with the estimated thermal conductivities in the case of low sucrose concentration. As shown in Fig. 6.10, the predicted thermal conductivities of 4.8 and 28.6% sucrose solutions were overall within the 95% confidence region of the estimated thermal conductivities for the same concentration. However, in the case of the 50% sucrose concentration, the predicted thermal conductivity deviated further from the estimated thermal conductivity of the solution (outside the 95% confidence region). As the freezing process progressed, the mathematical model overestimated the thermal conductivity of the sucrose solution. In this case, the higher number of the sucrose molecules resulted in less intimate contact between the water molecules, and hence, the rate of freezing dropped.
Figure 6.10 Comparison of Estimated Thermal Conductivities, $k$, and Predicted Thermal Conductivities using the Model for Sucrose Solutions.
The predicted volumetric specific heats of sucrose were generally outside the 95% confidence regions of the estimated volumetric specific heats for all concentrations (Fig 6.11). The mathematical models predicted higher apparent volumetric specific heats in the early stages of the freezing process. In the remainder of the freezing process, the predicted values were higher than the estimated values. In all cases, both the predicted and estimated apparent volumetric specific heats exhibited sharp increases at the initial freezing temperature and steadily decreased thereafter (Fig. 6.11). At the lower concentrations (4.8% and 28.6%), although the estimated apparent volumetric specific heat of sucrose solutions were smaller than the predicted values, they exhibited sharp and sudden increases, similar to those increases in the predicted values, at the initial freezing temperature. In the case of 50% sucrose concentration, the estimated apparent volumetric specific heat gradually increased at the initial freezing temperature, as shown in Fig 6.11; however, the predicted apparent volumetric specific heat presented sharp and sudden increase.

The mathematical models, presented in Chapter 3, are established on the assumption that food materials are binary ideal solutions. However, aqueous sucrose solutions are not ideal although sucrose is very soluble in water. The validity of the ideal solution assumption depends on the microscopic characteristic of the solution. The properties of a solution are mainly a result of the various characteristics of the elements in the mixture including their sizes, ionic behavior, chemical properties and the interaction of each of the molecules with another.

In the case of sucrose, as the concentration increases, the aqueous solution
Figure 6.11 Comparison of Estimated Apparent Volumetric Specific Heat, $C$, and Predicted Volumetric Specific Heat for Sucrose Solutions.
properties further deviated from being ideal. One obvious sign of the non-ideality of a solution is the high viscosity of the mixture. Thus, as the concentration of the sucrose increased, the predicted thermal conductivity deviated more from the estimated thermal conductivity of the sucrose solution. In addition, a step increase was exhibited in the predicted apparent volumetric specific heats at the initial freezing point due to the release of the latent heat of fusion. This behavior was also observed with the estimated apparent volumetric specific heat with the 4.8% and 28.6% sucrose concentrations. However, in the case of the 50% concentration, a gradual increase was observed below the freezing point instead of the expected step increase.

Although some of the predicted thermal conductivities of sucrose solutions were within the confidence regions of the estimated values (concentrations 4.8 and 28.6%), the predicted thermal conductivities were generally higher than the estimated values during the freezing process, as shown in Fig. 6.10. The predicted apparent volumetric specific heat of sucrose solutions were larger than the estimated values in the first part of the freezing process (with all concentrations), as shown in Fig. 6.11. However, in the later stages of the freezing process, the predicted values were smaller than the estimated quantities.

The main reason for the discrepancies between the estimated and the predicted thermal properties is that the mathematical models are built on the assumption that the freezing process occurs instantaneously as the molecules reach the freezing temperature. Due to the ideal solution assumption and the continuous equilibrium between the chemical potential of the solvent and the solutes, the models do not account for various other
processes in the solution during the freezing process, such as the diffusion of water molecules to form ice crystals, discussed by Hobbs (1974), and the sweeping of sucrose molecules by the ice front, which was discussed by Franks (1989). First, the diffusion of water molecules through sucrose molecules to align and form ice crystals is a very important process (especially in cases of high concentrations). This process occurs throughout the freezing process and causes the retardation of the solidification process. Thus, the thermal conductivity of the solution was generally lower than the predicted thermal conductivity and the release of the latent heat was retarded to later stages of the freezing process (Hobbs, 1974). Also, increasing in the sucrose concentration augments the effect of diffusion in the freezing process. Actually, as the number of sucrose molecules increases, the water molecules are more restricted from aligning and forming ice crystals, and hence, the freezing process is delayed (Hobbs, 1974).

Furthermore, the propagation of the phase front inside the sucrose solution sweeps the sucrose molecules closer together and makes the sucrose distribution nonhomogeneous throughout the medium. As a result of this process, at very low temperatures, pockets of very high concentrated sucrose solutions are formed. Due to the high viscosity of these solutions, the diffusion rate of the water molecules is near zero, and hence, the water content of these pockets is called the unfreezable water of the system.

6.3.2 Estimated and Predicted Thermal Properties of Methyl-Cellulose Solutions

The thermal properties of methyl-cellulose were also predicted using mathematical models and compared with the values found using the Modified Box-Kanemasu estimation
method, as discussed in Section 6.2. The overall behavior of the estimated thermal properties was generally consistent with the overall behavior of the predicted thermal properties. As discussed in Section 6.2, the thermal conductivities of the methyl-cellulose generally increased throughout the freezing process and the volumetric specific heats increased in the beginning of the freezing process and then decreased during the remainder of the process.

The predicted thermal conductivities of methyl-cellulose solutions, however, exhibited much higher values than the estimated thermal conductivities for all of the concentrations. As shown in Fig. 6.12, the predicted values were generally outside the 95% confidence region of the estimated values.

The predicted apparent volumetric specific heats of the methyl-cellulose aqueous mixtures generally exhibited significant discrepancies with the estimated values, as shown in Fig. 6.13. The predicted functions are outside the 95% confidence region of the estimated functions. The models tend to overestimate the apparent volumetric specific heat of the methyl-cellulose mixtures at the first part of the freezing process and underestimate them at later stages of the freezing (Fig. 6.13). In addition, at the initial freezing temperature of the solutions, the predicted functions exhibited sudden and large increases due to the immediate release of the latent heat of fusion at the beginning of freezing. However, the estimated function exhibited a more gradual increase. The release of the latent heat is retarded due to large and complex methyl-cellulose molecules and their obstruction of the water molecules during their reorientation to form ice crystals. The discrepancy between the predicted and the estimated volumetric specific heats in the
Figure 6.12 Comparison of Estimated Thermal Conductivities, $k$, and Predicted Thermal Conductivities for Methyl-cellulose Solutions.
Figure 6.13 Comparison of Estimated Apparent Volumetric Specific Heat, \( C \), and Predict Apparent Volumetric Specific Heat for Methyl-cellulose Solutions.
first part of freezing is greater in the case of the more concentrated solutions. However, in the case of the low concentration solutions, the predicted volumetric specific heat deviated further from the estimated volumetric specific heat during the later stages of the freezing process (Fig. 6.13).

The freezing process of the methyl-cellulose is a more complex process than the freezing process of sucrose solutions. Due to the large size and complexity of the molecules of this carbohydrate, the various assumptions used in the mathematical models are not valid in this case. For instance, the ideal binary solution assumption is a fundamental concept in the formulation of the models. In most of the concentrations used in this study, the methyl-cellulose aqueous mixtures were very viscous compounds. In these cases, the ideal binary solution assumption is not valid. The structural characteristics of the mixture are very different from a regular solution; in fact, water molecules are inbedded between methyl-cellulose molecules and hence methyl-cellulose serves as a medium of suspension for water instead of having water as a dispersing medium for methyl-cellulose in an ideal solution.

6.3.3 Estimated and Predicted Thermal Properties of Wheat Gluten Solutions

The predicted thermal properties of wheat gluten aqueous solutions exhibited similar overall behavior as the estimated thermal properties. However, large discrepancies were observed with both the thermal conductivity and apparent volumetric specific heat. The predictive models overestimated the thermal conductivities of wheat gluten mixtures at all concentrations (Fig. 6.14). At higher concentrations, the difference between the
Figure 6.14  Comparison of Estimated Thermal Conductivities, $k$, and Predicted Thermal Conductivities for Wheat Gluten Solutions.
predicted and estimated conductivities increased. The predicted apparent volumetric specific heats of the wheat gluten aqueous solutions were higher than the estimated values during the first stage of freezing (Fig 6.15). In the later stages of freezing, the models underestimated the apparent volumetric specific heat of the mixtures.

Wheat gluten is formed by very large protein molecules and form instable colloidal dispersions when mixed in water. At high concentrations, water is mixed with wheat gluten to form a viscous mixture called "dough". Due to the characteristics of the wheat gluten mixtures, the predicted thermal properties of the mixtures exhibit large discrepancies from the estimated thermal properties. The mixing of water with proteins is a very complex process. This process includes the bonding of protein molecules using water molecules to form long protein chains. The mathematical models employed for the estimation of thermal properties do not account for this process, and therefore, the ideal solution assumption is not an appropriate description of the wheat gluten mixtures analyzed in this investigation.

Due to the complex protein chains in the wheat gluten mixtures and their chemical bonding with water, the ideal binary solution assumption is not applicable. The ideal solution assumption also assumes that the molecules in the mixture move freely and hence water molecules are very easily aligned to form ice crystals as the temperature of the material reaches the initial freezing temperature. However, in wheat gluten mixtures, water molecules are trapped between protein molecules and are therefore prevented from bonding with other water molecules to form ice crystals. Hence, a significant amount of the water present in the wheat gluten is not freezable.
Figure 6.15  Comparison of Estimated Apparent Volumetric Specific Heat, $C$, Predicted Apparent Volumetric Specific Heat for Wheat Gluten Solutions.
In conclusion, the assumptions used in the mathematical models were generally unsuitable for the description of the freezing process in aqueous wheat gluten mixtures, and as a result, the predicted thermal properties using these models exhibited large discrepancies with the estimated thermal properties in all concentrations, as shown in Figs. 6.14 and 6.15.

6.4 Comparison of Experimental and Simulated Temperatures

The estimated thermal properties were used to simulate the temperature history of the food materials during freezing. The simulated temperatures were then compared to the experimental temperatures to test the accuracy of the estimation process.

The simulated temperature exhibited good agreement with the experimental measurements especially at the first part of the experiment, as shown in Fig 6.16. The discrepancy between the two temperatures gradually increased as the freezing process continued. This increase in the difference between the two temperatures is due to the accumulation of errors in the simulated temperatures. These errors are primarily caused by inherent inaccuracies in the estimated thermal properties.

6.5 Summary of Results

In this research study thermal properties of different food solutions were estimated using experimental measurements. The thermal properties of the same food materials
Figure 6.16 Comparison of Measured Temperature with Temperature Simulated Using the Estimated Thermal Properties.
were predicted using models from the literature. The predicted thermal properties were then compared with the estimated properties of the aqueous mixtures.

Overall, the predicted thermal properties of the food materials, analyzed in this study, exhibited behavior similar to the thermal properties predicted using models from the literature. For instance, the predicted thermal conductivities of the various food mixtures were constant above freezing and increased with decreasing temperature below the initial freezing temperatures of the food mixtures. In addition, the apparent volumetric specific heats of the food materials exhibited large increases at the initial freezing temperatures and decreased as the temperature of the food decreased. The deviations of the estimated thermal properties from the mathematical models were anticipated due to the nonideality of the food mixtures. In fact, as expected, the predicted properties deviated further from the models as the concentrations of the food mixtures increased. Although the overall behavior of the predicted thermal properties could be physically interpreted, these properties contain inherent inaccuracies since they were estimated based on the predictive models from the literature. In fact, the initial guesses for the thermal properties in the estimation process were determined using the models.

Although the estimated and the predicted thermal properties exhibited overall similar behavior throughout the freezing process, there were very significant discrepancies between them in most of the cases. The predicted thermal conductivities of the sucrose presented good agreement with the estimated values at the lower sucrose concentrations (4.8% and 28.6%). However, at higher concentrations, the predicted thermal conductivities of sucrose solutions were outside the 95% confidence regions of the
predicted values. Furthermore, the predicted apparent volumetric specific heats of the sucrose solutions were generally outside the 95% confidence regions of the estimated ones. However, at lower concentrations (4.8% and 28.6%), the estimated apparent volumetric specific heats of sucrose solutions exhibited sudden and large increases, similar to the increases in the predicted values, at the initial freezing temperature. At 50% sucrose concentration, the estimated apparent volumetric specific heat of sucrose solution increased gradually at below the initial freezing point; however, the predicted value exhibited sharp and large increase. Furthermore, the predicted thermal conductivities and the apparent volumetric specific heats of the methyl-cellulose solutions and the wheat gluten solutions also exhibited large discrepancies with the estimated values at all concentrations.

The large discrepancies between the estimated thermal properties and the predicted values are generally due to the ideal binary solution assumption used in the mathematical models. Especially in the case of the methyl-cellulose and wheat gluten, the aqueous mixtures of these materials is very far from being ideal due to their complex molecular structures. The sucrose solutions also deviated further from an ideal solution as the concentration of sucrose increased. The models used to predict the thermal properties of these food mixtures fail to account for the chemical characteristics of each of the food substances and also the diffusion process of the water molecules to align and form ice crystals. In fact, these models assume a continuous chemical balance between the solutes and the solvent of the solutions without accounting for the inherent physical processes of the freezing process.
In conclusion, the mathematical models studied fail to accurately predict the thermal properties of food materials during freezing. This is mainly due to the oversimplification of the freezing process by assuming an ideal binary solution and the assumption of free molecular motion within the food matter. Also, these models do not account for the chemical and physical properties of the ingredients present in the mixture and the various other processes that occur during freezing such as mass diffusion. Consequently, these models need to be modified using results of more profound analyses of the freezing process, such as microscopic examination of the food during freezing.
Chapter 7

SUMMARY AND CONCLUSION

The freezing process is one of the most important methods of preserving food products during processing, transportation and storage. This process has been studied over the last few decades using different kinds of methods. Due to the large variations of the thermal properties of the food materials, the freezing process is a very complex physical problem which translates into a highly nonlinear mathematical problem. Consequently, researchers have not been successful in finding an analytical solution for the freezing problem and numerical methods have been employed for the simulation of the process. Due to the simplicity of experimental methods used to determine the properties of food materials, experimental data for temperature dependent thermal properties of foods during freezing have been scarce in the literature. Hence, mathematical models have been used to predict thermal properties of food materials used in simulation processes. These models are generally built on the assumption of an ideal binary solution and a continuous chemical equilibrium between the solvent and the solutes during the freezing process.

The main goal of this research study was to conduct a comprehensive analysis on the freezing process of food materials. Three primary objectives have been accomplished:
1. Analysis and evaluation of the numerical methods used for the simulation of the freezing process of food materials, 2. Estimation of the thermal properties of basic food materials during freezing using the Modified Box-Kanemasu minimization method and experimental temperature measurements, and 3. Comparison of the estimated thermal properties with thermal properties predicted using models from the literature.

7.1 Accuracy Analysis

The Crank-Nicolson and the Two-Step finite difference methods were analytically evaluated for the simulation of the freezing process using an accuracy analysis procedure. The accuracy evaluation of the two numerical methods was conducted using an analytical problem which is a nonhomogeneous modification of the freezing problem with an exact solution. The numerical solutions of the analytical problem were compared to the exact solution for various time steps and grid sizes. The two numerical methods were also used to simulate temperature in codfish during one-dimensional freezing experiments. The numerical solutions were then compared with actual experimental temperature measurements presented by Lescano (1973).

Several conclusions were deduced from the particular accuracy analysis implemented in this study:

1. The Two-Step numerical method exhibited better results than the Crank-Nicoison method in the analytical accuracy analysis.

2. Both numerical methods presented better accuracy for the dimensionless time steps
and grid sizes smaller than 0.2 and larger than 0.05, respectively.

3. The Two-Step numerical simulations of the temperature in codfish during freezing showed better agreement with the experimental results (Lescano, 1973) than the Crank-Nicolson numerical solutions.

4. The Two-Step method is also a more efficient numerical method than the Crank-Nicolson method because it does not require any iterations.

5. The accuracy analysis, presented in this study, is a very useful tool to evaluate the accuracy and stability of numerical methods for the simulation of the freezing problem and could be applied to other highly nonlinear problems.

7.2 Estimation and Comparison of Thermal properties

To accomplish the second objective of this study, an experimental apparatus was built to carry out one-dimensional freezing experiments on basic food substances. Temperature measurements obtained from these experiments were then employed for the estimation of the thermal properties of the food materials during freezing using the Modified Box-Kanemasu minimization method. In this estimation process, the thermal conductivity and the apparent volumetric specific heat of the food materials were determined as piecewise linear functions of temperature. Three basic food materials were used in this analysis: sucrose, methyl-cellulose, and wheat gluten. Aqueous solutions of these food ingredients with various weight concentrations were used in this analysis. The thermal properties of these food solutions were also predicted using models from the
literature and the predicted thermal properties, namely thermal conductivity and apparent volumetric specific heat, were compared to the estimated thermal properties using experimental measurements with the Modified Box-Kanematsu estimation process.

The comparison between the predicted thermal properties using models from the literature and the estimated thermal properties using experimental data provided very useful insights on the freezing process in the different food materials used. Several important observations were concluded:

1. The estimated and the predicted thermal properties exhibited overall similar behavior. The thermal conductivities steadily increased as the freezing process proceeded and the apparent volumetric specific heat suddenly increased at the initial freezing temperature, and steadily decreased for the remainder of the process.

2. The predicted thermal conductivities of sucrose solutions were close to the estimated thermal conductivities at low concentrations. However, at higher concentrations, larger discrepancies between the predicted and the estimated values were observed.

3. The predicted apparent volumetric specific heats of sucrose solutions exhibited significant discrepancies with the estimated values at all concentrations. However, slightly better agreement between the predicted and estimated values was observed at lower concentrations.

4. The predicted thermal properties (i.e. thermal conductivity and apparent volumetric specific heat) of methyl-cellulose and wheat gluten aqueous solutions did not
agree well with the estimated thermal properties at all concentrations. The discrepancies for these two materials were larger than those of sucrose. Overall, the mathematical models studied failed to accurately predict the thermal properties of the three types of food materials used in this research study. This is mainly due to the oversimplification of the food mixture by assuming an ideal binary solution and the assumption of the continuous chemical equilibrium between the solutes and the solvent. Furthermore, these models do not account for the chemical and physical properties of each of the different ingredients present in the food material and exclude the various processes that occur in the food mixture such as mass diffusion and chemical reaction upon mixing. Thus, the mathematical models examined in this research study need to be modified to include the chemical and physical properties of the food mixture.
Chapter 8

RECOMMENDATIONS

The accurate simulation of the freezing process requires reliable numerical methods as well as accurate predictions of the temperature dependent thermal properties of the food material. The methodologies employed in this study have been proven to be effective in improving the prediction of the freezing process in foods. Thus, this research study could be used as a building block for future work in the area of freezing or related fields. Recommendations for future research studies are presented in two subsections:

8.1 Accuracy Analysis

These following recommendations are deduced from the accuracy analysis procedure employed in this research study:

1. The use of the accuracy analysis method should be extended to examine the numerical simulation of multi-dimensional freezing problem and other highly nonlinear problems such as sublimation and curing of composite materials.
2. The accuracy of various numerical methods need to be examined as a function of grid size, time step, and other parameters such as the eigenvalues of the mathematical problem.

8.2 Estimation and Comparison of Thermal properties

These recommendations are deduced from the estimation and comparison process of the thermal properties of food materials presented in this research study:

1. The estimation of the same food materials using different freezing rates is highly recommended. It is expected that the models would agree better with estimated thermal properties for slower freezing rates since these models are based on chemical equilibrium between solutes and solvent during freezing.

2. The use of minimization methods, such as the Modified Box-Kanemasu Method, is recommended for the simultaneous estimation of varying thermal properties, such as thermal properties of composite materials during curing.

3. Further examination of the freezing process is very important. More profound analysis of the process is needed to understand the effect of freezing on the thermal and structural properties of food materials.
4. The mathematical models for predicting the thermal properties of food materials need to be modified based on more extensive analysis of the freezing process. These models must reflect the structural changes and the various physical and chemical processes that occur during freezing.
REFERENCES


Engineers, New York.


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APPENDIX A

ONE-DIMENSIONAL FREEZING PROGRAM

This section will include the "FREEZE" program. A description of the various subroutines and function of the program will be first presented in Table A.1. Then, a listing of Program "FREEZE" will follow. The input and output files will be defined in the last two sections of the appendix.
<table>
<thead>
<tr>
<th>Subroutine Title</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subroutine PROPER</td>
<td>Allows the user to interactively set the thermal properties of the food product and saves them in a file.</td>
</tr>
<tr>
<td>Function MOIST(x)</td>
<td>Determines the unfrozen water fraction as a function of temperature below the initial freezing point of food material.</td>
</tr>
<tr>
<td>Function DENS(x)</td>
<td>Determines the density of food material as a function of temperature below the initial freezing point.</td>
</tr>
<tr>
<td>Function KI(x)</td>
<td>Determines the thermal conductivity of ice as a function of temperature.</td>
</tr>
<tr>
<td>Function CONDUC(x)</td>
<td>Determines the thermal conductivity of food material as a function of temperature below the initial freezing point.</td>
</tr>
<tr>
<td>Function SPHEAT(x)</td>
<td>Determines the specific heat of food material as a function of temperature below the initial freezing point.</td>
</tr>
<tr>
<td>Block Data CONST</td>
<td>Defines constant thermal properties of water and ice.</td>
</tr>
<tr>
<td>Subroutine INPUT1</td>
<td>Allows the user to interactively set the freezing conditions and the geometry of the food sample and saves information into a file.</td>
</tr>
<tr>
<td>Subroutine SOLN</td>
<td>Solves for temperature history in the food material throughout the freezing process.</td>
</tr>
<tr>
<td>Subroutine COEFF</td>
<td>Calculates coefficient matrix of the finite difference algorithm.</td>
</tr>
<tr>
<td>Subroutine PFIND</td>
<td>Determines the thermal properties of the food material as a function of temperature required for the finite difference procedure.</td>
</tr>
<tr>
<td>Subroutine OUTPUT</td>
<td>Write input parameters and the temperature history to an output file.</td>
</tr>
</tbody>
</table>
A.1 Computer Program "FREEZE"

PROGRAM FREEZE

One Dimensional Freezing Program

Written by Elaine P. Scott and extensively modified by Zoubeir Saad
Mechanical Engineering Depaimeent
VPI&SU (January, 1994)

Variables used in each subroutine are defined at the beginning
of the subroutine.

The integer variables appearing in the main program "FREEZE" are:

AVGC - Average specific heat (<0C) (J/kgK)
AVGD - Average density (<0C) (kg/m^3)
AVGK - Average thermal conductivity (<0C) (W/mK)
CP - Food specific heat (>0C) (J/kgK)
DP - Food density (>0C) (kg/m^3)
DS - Food solids density (kg/m^3)
KP - Food thermal conductivity (>0C) (W/mK)
MS - Molecular weight of the solids (kg/mole)
T0 - Initial freezing temperature (C or K)
WF0 - Unfrozen product moisture content
YNAV - Yes or no (1 or 0)

The character variables appearing in the main program "FREEZE" are:

filyn1 - ="y" if property data are stored on file (="n" if not)
filyn2 - ="y" if boundary condition data are stored on file (="n" if not)
fldat - File name for property data file
inpdat - File name for boundary condition data file
title - Title of run
ttlfil - Key word for file containing boundary conditions (4 characters)
tlprp - Key word for file containing thermal properties (4 characters)
The logical values appearing in the main program "FREEZE" are:
The parameters values appearing in the main program "FREEZE" are:

```
parameter(maxp=20,maxm=101,maxd=101,maxc=51,maxs=201)
```

Declare variables in common blocks:

```
integer model,
& prpfil,EEND

double precision ds,
& wf0,ms,dp,kp,cp,t0,
& th,tl,avgd,avgk,avgc,ynavg

character fildat*12,inpdat*12,kindat*12,
& title*20,ttlfil*4,ttlprp*4,ttlkin*4,
& filyn1*1,filyn2*1,filyn*1
```

Declare common blocks:

```
common/mod/model,
&/profil/prpfil,
&/d/ds,
&/prop/wf0,ms,dp,kp,cp,t0,
&/avgd/th,tl,avgd,avgk,avgc,ynavg,
&/datfil/fildat,inpdat,kindat,
&/ttl/title,ttlfil,ttlprp,ttlkin
```

```
write(5,1000)
1000 format(',72(*)',',0',',9', 'One Dimensional Freezing Program',/
 & ',72(*)')
write(5,200)
200 format( ',j', ',Title: ')
READ(5,200)TITLE
write(5,300)'Key word for product property data file:'
300 format(/,1X,A,j,1X,(4 characters))
READ(5,(A4))TTLPRP
write(5,300)
& 'Key word for input boundary conditions and geometry data file:'
READ(5,(A4))TTLFI
20 FORMAT(A)
```
write(5,400)
& 'Are product properties (<0C) stored on file? (y/n)'
400 format(' ',',','A)
   read(5,20)filyn1
   write(5,500)
& 'Are input initial and boundary conditions and geometrical',
& 'dimensions stored on file? (y/n)'
500 format('/',',','A','/','A)
   read(5,20)filyn2
if(filyn1.eq.'n'.or.filyn1.eq.'N')then
   call proper
endif
   if(filyn2.eq.'n'.or.filyn2.eq.'N')then
      call input1
   endif
   call soln
end

******************************************************************************
SUBROUTINE PROPER

This subroutine provides the input for the property functions.
Input values include unfrozen product moisture content, initial
freezing point or molecular weight of solids, and unfrozen
product density, thermal conductivity and specific heat.

Output includes a printout of unfrozen water (percent), density
thermal conductivity and specific heat as functions of temper-
ature. These values may be stored in a separate file. Averaged
values over small temperature ranges are used in the finite
difference calculations for computational efficiency; these values
c are determined in the subroutine CONSPR.

The integer variables used in this subroutine are:

TYPE - =1 if entering initial freezing temperature; =2 if entering
molecular weight of solids

The real variables appearing in this subroutine are:

Constants-
C1 = 18.015 kg/kmole (molecular weight of water)
C2 = 1./273.15 1/K
C3 = 6003./8.314 K (latent heat of ice/R)

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c  C6 = 273.15 K

C CONDUC- Thermal conductivity function (of temperature < 0°C)
c CP - Food specific heat (>0°C) (J/kgK)
c CPI - Specific heat of ice (J/kgK)
c CPW - Specific heat of water (J/kgK)
c DENS - Density function (of temperature < 0°C)
c DI - Density of ice (J/kgK)
c DW - Density of water (J/kgK)
c DP - Food density (>0°C) (kg/m^3)
c DS - Food solids density (kg/m^3)
c ETA - Array used in numerical integration

c KI - Thermal conductivity of ice (W/mK)
c KP - Food thermal conductivity (>0°C) (W/mK)
c KW - Thermal conductivity of water (J/kgK)
c MOIST - Moisture content function (of depressed freezing point)
c MS - Molecular weight of the solids (kg/mole)
c SPHEAT- Specific heat function (of temperature < 0°C)
c T0 - Initial freezing temperature (C or K)
c T0INV - Inverse of T0 (1/C or 1/K)
c TAVG - Average of TH and TL (C or K)
c TC - Temperature for printout.
c W - Array of weighting coefficients in numerical integration

c WFO - Unfrozen product moisture content

c XX - Array of integrated temperatures

c YNAV - Intermittent value in determining Ms or T0.
c YNAVG - Yes or no (1 or 0)

c The character variables appearing in this subroutine are:

c title - Title of run
c tlfil- Key word for file containing boundary conditions (4 characters)
c tlprr- Key word for file containing thermal properties (4 characters)
c Yn - Character- Y or N

c Declare variables not in common blocks:

t integer type,prpscr,EEND

double precision c6,conduc,dens,eta(20),ki,moist,spheat,t0inv,
& tavg,tc,tdif,w(20),x(20),xx

c character yn*1,prpf12*12,fildat*12
c Declare variables in common blocks:

    integer model,
    & prpfil

    double precision c1,c2,c3,
    & wf0,ms,dp,kp,cp,t0,
    & ds,
    & di,dw,
    & kw,
    & cpl,cpw,
    & tl,th,avgd,avgk,avgc,yavg

    character title*20,tllfil*4,tlprp*4,tllkin*4

c Declare external functions

    external moist,dens,condc,spheat

c Declare common blocks

    common /mod/model,
    & /prof/prpfil,
    & /COND/KW,
    & /cons/c1,c2,c3,
    & /d/ds,
    & /densi/di,dw,
    & /pavg/th,tl,avgd,avgk,avgc,yavg
    & /prop/wf0,ms,dp,kp,cp,t0,
    & /SPH/CPI,CPW,
    & /ttl/title,tllfil,tlprp,tllkin

------------------------------------------------------------------
c1=18.015d0
c2=1.0d0/273.15d0
c3=6003.0d0/8.314d0
c6=273.15d0

    write(5,2000)
2000    format(1,'.','/','0',t27,'Product Properties','/','0',',27('')
      5    write(5,100)
100    format( '/',' ',Enter initial moisture content(%): ')
READ*,WF0
if(wf0.LT.1..OR.WF0.GT.100.)THEN
  print*,'Try again!!'
  go to 5
ENDIF
10 WRITE(5,300)
300 FORMAT('0','Choose: 1, 2. Initial freezing temperature
                & 2. Molecular weight of solids'
READ(5,*))type
if(type.NE.1)THEN
  WRITE(5,400)
400 FORMAT('1, Molecular weight of solids: ')
  READ(5,*))MS
ELSE
  WRITE(5,500)
500 FORMAT('2, Initial freezing temperature (C): ')
  READ(5,*))T0
ENDIF
write(5,600)
600 format('Enter unfrozen product property values: 1.
                & 2. thermal conductivity (W/mK): ')
  READ(5,*))DP
  WRITE(5,700)
700 FORMAT('2, thermal conductivity (W/mK): ')
  READ(5,*))KP
  WRITE(5,800)
800 FORMAT('2, specific heat (kJ/kgK): ')
  READ(5,*))CP

  WRITE(5,900)
900 FORMAT('Are these values correct? (y/n) '
  read(5,200)yn
200 FORMAT(A)
    if(yn.ne.'y'.and.YN.NE.'Y')go to 5
20 wf0=wf0/100.0d0
    if(type.NE.1)THEN
C Initial freezing point

  t0=1.0d0/(c2-log(wf0/c1/(wf0/c1+(1.0d0-wf0)/ms))*1.0d0/c3)
ELSE
  t0=t0+273.15d0

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C Molecular weight of solids

\[
t_0inv = 1.0d0/t0 \\
x = exp(c3*(c2-t0inv)) \\
Ms = (1.0d0-wf0)*xx*c1/(wf0*(1.0d0-xx))
\]

ENDIF

WRITE(6,908)
C Density, thermal conductivity and specific heat
C are stored in 'TLTFLPrp.dat'

WRITE(FILDAT,310)tlprp,'PRP.DAT'
310 FORMAT( 'a,A')
OPEN(UNIT=12,FILE=FILDAT(1:16))
WRITE(12,62)WF0,T0,MS
WRITE(12,62)DP,KP,CP
908-format(' ',72('-'))//','END OF PROPERTY DATA INPUT')
90 return
CLOSE(12)
END

c**********************************************************************

double precision function moist(x)

c This function determines the unfrozen water

c fraction of a food product below the initial freezing temper-
cature.

c The real variables appearing in this subroutine are:

C Constants-
C C1 = 18.015 kg/kmole (molecular weight of water)
C C2 = 1/273.15 1/K
C C3 = 6003./8.314 K (latent heat of ice/R)
C CP - Food specific heat (>0C) (J/kgK)
C DP - Food density (>0C) (kg/m^3)
C KP - Food thermal conductivity (>0C) (W/mK)
C MS - Molecular weight of the solids (kg/mole)
C T0 - Initial freezing temperature (C or K)
c TINV - Inverse of T (1/C or 1/K)
c WF0 - Unfrozen product moisture content
c XX - Intermittent value in determining Ms or T0.

c Declare variables not in common blocks:

        double precision tinv,xx,X

c Declare variables in common blocks:

        double precision c1,c2,c3,
        & wf0,ms,dp,kp,cp,t0

c Declare common blocks

        common /cons/c1,c2,c3,
        & /prop/wf0,ms,dp,kp,cp,t0

-------------------------------------------------------------------------

        c1=18.015d0
        c2=1.0d0/273.15d0
        c3=6003.0d0/8.314d0
        tinv = 1.0d0/x
        xx=exp(c3*(c2-tinv))
        moist=xx*(1.0d0-wf0)*c1/(ms*(1.0d0-xx))
        return
        end

-------------------------------------------------------------------------

        double precision function dens(x)

        c This function determines the density of a food product
        c below the initial freezing temperature, as a function of un-
        c frozen water fraction.

        c The integer variables used in this subroutine are:

        c PRPFIL= =1 if properties are saved in a file as a F(T) (=0 no save)
        c TYPE = =1 if entering initial freezing temperature; =2 if entering
        c molecular weight of solids

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c PRPSCR- =i if product properties are displayed on screen

c The real variables appearing in this subroutine are:

c CP - Food specific heat (>0C) (J/kgK)
c DENS - Density function (of temperature < 0C)
c DI - Density of ice (J/kgK)
c DW - Density of water (J/kgK)
c DP - Food density (>0C) (kg/m^3)
c DS - Food solids density (kg/m^3)
c KP - Food thermal conductivity (>0C) (W/mK)
c MOIST - Moisture content function (of depressed freezing point)
c MS - Molecular weight of the solids (kg/mole)
c T0 - Initial freezing temperature (C or K)
c WF0 - Unfrozen product moisture content

c Declare variables not in common blocks:

double precision moist

c Declare variables in common blocks:

double precision wf0,ms,dp,kp,cp,t0,
& ds,
& di,dw,X

c Declare external function

external moist

c Declare common blocks

common /d/ds,
& /dens/di,dw,
& /prop/wf0,ms,dp,kp,cp,t0

save

c Solids density

\[ ds = \frac{(1.0d0-wf0)}{(1.0d0/dp-wf0/dw)} \]
\[ \text{dens} = 1.0d0/(\text{moist}(x)/dw+(1.0d0-\text{wf0})/ds+(\text{wf0}-\text{moist}(x))/di) \]

return
end

***************************************************************************************

**double precision function ki(x)**

**DOUBLE PRECISION X**

**c** Thermal conductivity of ice as a function of temperature (k)

\[ \text{ki} = 7.3640d0-0.02850d0*x+3.525d-5*x**2 \]

return
end

***************************************************************************************

**double precision function conduc(x)**

**c** This function subroutine determines the thermal conductivity
**c** of a food product below the initial freezing temperature.
**c** Thermal conductivity is a function of moisture content and
**c** solids content, therefore, 'conduc' is a function of temper-
**c** ature.
**c** The real variables appearing in this subroutine are:
**c** Constants-
**c** \[ C4 = 2.3 \]
**c** \[ \text{CONDUC} - \text{Thermal conductivity function (of temperature < 0C)} \]
**c** \[ \text{CP} - \text{Food specific heat (>0C) (J/kgK)} \]
**c** \[ \text{DENS} - \text{Density function (of temperature < 0C)} \]
**c** \[ \text{DI} - \text{Density of ice (J/kgK)} \]
**c** \[ \text{DW} - \text{Density of water (J/kgK)} \]
**c** \[ \text{DP} - \text{Food density (>0C) (kg/m^3)} \]
**c** \[ \text{DS} - \text{Food solids density (kg/m^3)} \]
**c** \[ k1 - \text{intermittent value} \]
**c** \[ k2 - \text{intermittent value} \]
**c** \[ k3 - \text{thermal conductivity of water-ice phase} \]
**c** \[ k4 - \text{intermittent value} \]
**c** \[ k5 - \text{intermittent value} \]
**c** \[ KI - \text{Thermal conductivity of ice (W/mK)} \]
**c** \[ KP - \text{Food thermal conductivity (>0C) (W/mK)} \]
**c** \[ KW - \text{Thermal conductivity of water (J/kgK)} \]
**c** \[ MOIST - \text{Moisture content function (of depressed freezing point)} \]
**c** \[ MS - \text{Molecular weight of the solids (kg/mole)} \]
c T0 - Initial freezing temperature (C or K)
c va - intermittent value
c va1 - intermittent value
c WFO - Unfrozen product moisture content

c Declare variables not in common blocks:

double precision dens,ki,moot, &c4,va,va1,ks,k1,k2,k3,k4,k5,X

c Declare variables in common blocks:

double precision kw, & ds, & di,dw, & wfo,ms,dp,kr,cp,t0

c Declare external functions

external moist,dens,ki

c Declare common blocks

common /COND/KW, & /d/ds, & /densi/di,dw, & /prop/wfo,ms,dp,kr,cp,t0

-----------------------------------------------
c4=2.0d0/3.0d0

c Solids density
ds=(1.0d0-wfo)/(1.0d0/dp-wfo/dw)

c Thermal conductivity of solids

va=(1.0d0-wfo)/ds
va1=(va/(va+wfo/dw))**c4
ks=kw*(va1-(kw-kr)/kw-kr*(1.0d0-va1**.5)/va1)

c Phase I: ice--water

k1=(wfo-moot(x))/di/(moot(x)/di+(wfo-moot(x))/di)
k2=k1**c4*(1.0d0-ki(x)/kw)
k3 = kw * (1.0d0-k2)/(1.0d0-k2*(1.0d0-k1**(1.0d0/3.0d0)))

c Phase II: solids-water/ice

k4 = va/(va+(wf0-moist(x))/di+moist(x)/dw)
k5 = k4**c4*(1.0d0-ks/k3)
conduc = k3*(1.0d0-k5)/(1.0d0-k5*(1.0d0-k4**(1.0d0/3.0d0)))
return
end

c*********************************************************************

double precision function spheat(x)

c This function determines the apparent specific
heat of a frozen food product as a function of unfrozen water
below the initial freezing temperature.

c The external function moist (unfrozen water fraction) used
to determine the apparent specific heat is a function of
temperature; therefore, 'spheat' is also a function of tempe-
ture.

c the variables used in this function are:

c cp = specific heat product >0C (kJ/kgC)
c cpi= specific heat of ice (kJ/kgC)
c cps= specific heat of solids (kJ/kgC)
c cpw= specific heat of water (kJ/kgC)
c wf0 = moisture content of unfrozen product

c The real variables appearing in this subroutine are:

c Constants-
c C5 - 6003.0d0/18.015d0
c CONDUC- Thermal conductivity function (of temperature < 0C)
c CP - Food specific heat (>0C) (J/kgK)
c CPI - Specific heat of ice (J/kgK)
c CPS - Specific heat of solids (kJ/kgC)
c CPW - Specific heat of water (J/kgK)
c DP - Food density (>0C) (kg/m^3)
c KP - Food thermal conductivity (>0C) (W/mK)
c MOIST - Moisture content function (of depressed freezing point)
c MS - Molecular weight of the solids (kg/mole)
c SPHEAT- Specific heat function (of temperature < 0C)
c T0 - Initial freezing temperature (C or K)
c WF0 - Unfrozen product moisture content

c Declare variables not in common blocks:

double precision c5,cps,dcp,hd,moist

c Declare variables in common blocks:

double precision wf0,ms,dp,kp,cp,t0,
 & cpi,cpw,X

c Declare external functions

external moist

c Declare common blocks

common /prop/wf0,ms,dp,kp,cp,t0,
 & /PH/CP1,CPW

c---------------------------

c5=6003.0d0/18.015d0
dh = 0.0010d0

c solids specific heat

cps=(1.0d0-wf0)/(1.0d0/cp-wf0/cpw)

if(x+dh.ge.t0)then
dcp = (moist(x)-moist(x-dh))*c5/dh
else
dcp = (moist(x+dh)-moist(x-dh))*c5/(2.0d0*dh)
endif
spheat=(1.0d0-wf0)*cps+moist(x)*cpw+(wf0-moist(x))*cpi+dcp

return
end
BLOCK DATA CONST

c The following values are defined in this block data:

c  di = density of ice (917. kg/m^3) } block
c  dw = density of water (998. kg/m^3)} /densi/

c  kw = thermal conductivity of water } block
   (0.569 w/mk) } /cond/

c  cpi = specific heat of ice } block
   (2.1 kJ/kgK) } /sph/
c  cpw = specific heat of water } /sph/
c  (4.187 kJ/kgK) }

double precision DI,DW,KW,CPI,CPW
COMMON /DENS1/DI,DW,COND/KW,SPH/CPI,CPW
SAVE /DENS1/,COND/,SPH/
DATA DI,DW/917.0d0,998.0d0/,KW/0.5690d0/,&
   CPI,CPW/2.10d0,4.1870d0/
END

SUBROUTINE INPUT1

This subroutine provides the input for the boundary conditions on the product for the case where the ambient temperature and surface heat transfer coefficient are known and assumed to be constant over a given storage period.

Input variables include, initial product temperature, symmetry of boundary conditions, number of constant temperature storage periods, length of storage period, and surface heat transfer coefficient.

The integer variables used in this subroutine are:

M - Total number of nodes minus one
c MODEL - Option number from main menu
c MP1 - Total number of nodes
c NCOUNT - Number of printouts per storage period
c NPDT - Total number of time steps per storage period
c PER - Total number of storage periods
   c SHAPE - = 1 for slab geometry
   c = 2 for cylindrical geometry
   c = 3 for spherical geometry
   c STEP - Step size for printing out temperatures at spatial nodes
   c SYM - = 0 if unsymmetric
   c = 1 if symmetric
   c UNIT - = 1 if storage time is in hours
   c = 2 if storage time is in days

c The real variables appearing in this subroutine are:

c DZ - Spatial increment for finite difference calculations
   c H1 - Array for heat transfer coefficients at boundary 1
   c H2 - Array for heat transfer coefficients at boundary 2
   c L - Dimension in the direction of heat transfer (thickness or radius)
   c PDT - Time step for each storage period
   c STOR - Length of each storage period
   c TEMP - Ambient temperature during each storage period
   c TI - Initial food temperature
   c TUNIT - = 3600.0d0 if storage time is in hours
            c = 86400.0d0 if storage time is in days

c The character variables appearing in this subroutine are:

c fildat- File name for property data file
   c inpdat- File name for boundary condition data file
   c kindat- File name for kinetic data file
   c title - Title of run
   c tlfil- Key word for file containing boundary conditions (4 characters)
   c tlkin- Key word for file containing kinetic properties (4 characters)
   c tlrpr- Key word for file containing thermal properties (4 characters)
   c Yn - Character- Y or N

   parameter(maxp=20)

   c Declare variables not in common blocks:

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integer unit,EEND

double precision pdt(maxp)

character yn*1

c Declare variables in common blocks:

    integer per,ncount(maxp),
    & shape,sym,m,mp1,sstep,
    & model,is,bct(maxp,2)

    double precision ti,temp(maxp),stor(maxp),h(maxp,2),
    & tunit(maxp), q(maxp,2),tb(maxp,2),l,dz

    character fildat*12,inpat*12,kindat*12,
    & title*20,ttlfil*4,tlprp*4,ttlkin*4

c Declare common blocks

    common/bound/per,ti,temp,stor,h,tunit,ncount,q,tb,
    & /datfil/fildat,inpat,kindat,
    & /geom/shape,l,dz,sym,m,mp1,sstep,
    & /mod/model,
    & /ttl/title,ttlfil,tlprp,ttlkin

c----------------------------------------------

3   write(5,1)
1   format('1.72(-.),/0',27x,'Storage Conditions)./0',72('-.))
5   write(6,10)
10  format( ';/','Enter number of constant temp. storage ','
    &periods: ')
    read*,per
    write(6,20)
20  format( ';/','Initial product temperature (C): ')
    read*,ti
    write(6,30)
30  format( ';/','Are the boundary conditions symmetrical? ',
    &'(y/n) '/,'(Enter "y" for cylinder & sphere ',
    &'geometries) ')
    read(5,2)yn
    if(yn.eq.'y'.or.,yn.eq.'Y')sym = 1
write(6,40)
40    format(’/’,’Are these values correct? (y/n) ’)
read(5,2)yn
2    format(a)
     if(yn.ne.’y’.and.yn.ne.’y’)
goto 5
write(6,106)

c input boundary conditions for each storage period

do 120 i=1,per
45   write(6,50)i
50   format(’/’,’Enter data for period ’,i3,’:’)
write(6,60)
60   format(’ ,5x,’Storage temperature (C): ’)
read*,temp(i)
70   write(6,75)
75   format(’ ,5x,’Enter units for storage period:’,
&’/’,’ ,7x,’1= hours’,’/’,’ ,7x,’2= days’)
read*,unit
   if(unit.le.0.and.unit.gt.2)
     print*,’try again!’
     goto 70
   endif
   if(unit.eq.1)
     tunit(i)=3600.0d0
   else
     tunit(i)=86400.0d0
   endif
77   write(6,80)
80   format(’ ,5x,’Length of storage period: ’)
read*,stor(i)
   if(stor(i).lt.0)
     print*,’try again!’
     goto 77
   endif
write(6,240)stor(i)*tunit(i)
240   format(’/’,’Enter time step (sec) for each storage’,
&’/’,’Period:’,’/’,’7x’,’(Time step must be evenly divisible into’,
&’/’,’10.0,’))
read*,pdt(i)
npdt = stor(i)*tunit(i)/pdt(i)
write(6,86)npdt
86   format(’ ,5x,’There are a total of ’,i6,’ time steps in ’,
& 'this storage period.')
write(6,84)npdt
84    format(' /', '5x,'Number of printouts per storage period: ',
& '/8x,'(No. printouts must be evenly divisible into ',i6,')')
read*,ncount(i)

write(6,106)
is=1
87 continue
write(6,88)is
88    format(' /', '5x,Enter the boundary conditions type for side',
+ ' i2,'/
+ '/'  Enter 1: Convective and/or Heat flux '/
+ '/' 2: Temperature ')'/
read*, bct(i,is)
if(bct(i,is).eq.1) then
write(6,90)is
90    format(' Enter heat transfer coefficient (W/m^2C) for side',i2)
read*, h(i,is)
write(6,91)is
91    format(' Enter heat flux into the sample (W/m^2) for side',i2)
read*, q(i,is)
elseif(bct(i,is).eq.2) then
write(6,93)is
93    format(' Enter Temperature of the surface (C) for side',i2)
read*, tb(i,is)
tb(i,is)=tb(i,is)+273.15
endif
if(sym.eq.0.and.is.eq.1) then
    is=2
    go to 87
elseif(sym.eq.1) then
    bct(i,2)=bct(i,1)
endif

write(5,40)
read(5,2)yn
if(yn.ne.'y'.and.yn.ne.'Y')goto 45
write(6,106)
106   format(' /', ',72(''))
continue

c input geometry and size

140 write(6,150)
150 format(0,'Enter product geometry: /,5x,1 = slab/,5x,' +,2 = cylinder/,5x,3 = sphere')
    read*,shape
    if(shape.gt.1.and.sym.eq.0)then
        print*, 'Boundary conditions must be symmetrical for cylinder and,
    & sphere; try again!!'
        go to 3
    endif
    if(shape.eq.1)then
        write(6,160)
        format( ' /,5x,Enter dimensions for slab:/,5x, & thickness in direction of heat transfer (m) = ')
        read*,l
        else
            if(shape.eq.2)then
                write(6,180)
                format( ' /,5x,Enter dimensions for cylinder:/, +',5x,'radius (m) = ')
                read *,l
            else
                write(6,200)
                format( ' /,5x,Enter dimensions for sphere (m)/, +',5x,'radius (m) = ')
                read *,l
            endif
        endif
    endif

500 ti = ti+273.150d0

    if(sym.eq.1.and.shape.eq.1) L = L*0.50d0
    do il = 1,per
        temp(il) = temp(il)+273.150d0
        stor(il)=stor(il)*tunit(il)
        if(sym.eq.1.or.shape.ne.1)then
            if(shape.eq.1)then
                h(il,2) = 0.0d0
                q(il,2)=0.0d0
                bct(il,2)=1
            else
                print*, 'shape eq.1
            endif
        endif
        if(sym.eq.1.or.shape.ne.1)then
            if(shape.eq.1)then
                h(il,2) = 0.0d0
                q(il,2)=0.0d0
                bct(il,2)=1
            else
                print*, 'shape eq.1
            endif
        endif

183
h(il,2) = h(il,1)
h(il,1) = 0.0d0
tb(il,2)=tb(il,1)
q(il,2)=q(il,1)
q(il,1)=0.0d0
endif
endif
enddo

write(6,220)
220 format( ' ', 'Enter total number of spatial increments:'/
& ' ', ' (Must be a multiple of four.)' )
read*,m
sstep = m/4

c Check input values

write(6,40)
read(5,2)yn
if(yn.ne.'y'.and.yn.ne.'Y') goto 140
write(6,106)
write(6,580)
580 format( ' ', 'END OF BOUNDARY CONDITIONS AND GEOMETRY INPUT')
c Write data to file.

590 write(inpdat,600)ttlfil,'inp.dat'
600 format( ' ',a,a)
open(unit=12,FILE=inpdat(1:12))
write(12,700)per,sym,ti
700 format( ' ',i2,2x,i1,2x,f6.2)

do i = 1,per
   write(12,750)bct(i,1),bct(i,2)
750 format( ' ',3x,i2,2x,i2)
   write(12,800)temp(i),stor(i),tunit(i),h(i,1),h(i,2),
   + q(i,1),q(i,2),tb(i,1),tb(i,2),pdt(i),ncount(i)
800 format( ' ',2x,f6.2,2x,f18.2,2x,f6.0,7(2x,f8.2),2x,i5)
endo
write(12,900)shape,L
900 format( ' ',i1,2x,f8.4)
write(12,1000)m,sstep
1000 format( ' ',i3,2x,i2)
close(unit=12)
SUBROUTINE soln

parameter(maxd = 101, maxc = 51, maxs = 201)
parameter(maxn=101,maxp=20,tol=0.10d0,r=8.3140d0)

c This subroutine computes the temperature distribution and the
quality distribution (for Options 4 and 5) of the food as a func-
tion of time. For Option 3, the solution proceeds until the
highest temperature in the food material is less than the desired
freezing temperature. The Crank-Nicolson finite difference scheme
is used in the solution. The matrix coefficients inherent in this
solution are determined in a subroutine called COEFF, and the results
are stored in a file using a subroutine called OUTPUT.

c The integer variables appearing in this subroutine are:

M    - Total number of nodes minus one
MODEL - Option number from main menu
MP1   - Total number of nodes
NCOUNT- Number of printouts per storage period
NSC   - Total number of constant thermal conductivity values used in
approximating thermal conductivity equations as F(temperature)
NSD   - Total number of constant density values used in approximating
density equations as F(temperature)
NSS   - Total number of constant specific heat values used in
PER   - Total number of storage periods
SSTEP - Step size for printing out temperatures at spatial nodes
SYM   - = 0 if unsymmetric
      = 1 if symmetric
YNAV - Yes or no (1 or 0)

The real variables appearing in this subroutine are:

A    - Array containing coefficients for temperature at (m-1)th
c node

- Average specific heat (<0°C) (J/kgK)
c AVGD - Average density (<0°C) (kg/m^3)
c AVGK - Average thermal conductivity (<0°C) (W/mK)
c B - Array containing coefficients for temperature at mth node
c C - Array containing coefficients for temperature at (m+1)th node
c CC - Array containing C(i)/B(i)
c CONDC - Contains approximations of CONDUC used in finite difference calculations
c CONDT - Contains temperature ranges for constant thermal conductivity approximations (CONDUC) used in finite difference calculations
c CP - Food specific heat (>0°C) (J/kgK)
c D - Array containing boundary conditions and previous temperatures at previous time step
c DD - Array containing D(i)/B(i)
c DENS - Contains approximations of DENS used in finite difference calculations
c DENSST - Contains temperature ranges for constant density approximations (DENS) used in finite difference calculations
c DP - Food density (>0°C) (kg/m^3)
c DQDEA - Derivative of quality with respect to EA
c DS - Food solids density (kg/m^3)
c DSUM - Summation used in determining quality loss
c DT - Time step
c DZ - Spatial increment for finite difference calculations
c EA - Activation energy constant
c EAB - Difference between ambient temperature and product temperature;
c used to determine termination of finite difference calculations
c for that storage period
c EEABS - Difference between ambient temperature and product temperature (like EABS)
c EEEX - Defined as: 1.0d0/T(i,2)-1.0d0/TREF
c H1 - Array for heat transfer coefficients at boundary 1
c HH1 - Heat transfer coefficients at boundary 1 for single storage period at both nth and (n-1)th time steps
c H2 - Array for heat transfer coefficients at boundary 2
c HH2 - Heat transfer coefficients at boundary 2 for single storage period at both nth and (n-1)th time steps
c KP - Food thermal conductivity (>0°C) (W/mK)
c L - Dimension in the direction of heat transfer (thickness or radius)
c MS - Molecular weight of the solids (kg/mole)
c PDT - Time step for each storage period
 c PI - Pi defined as: DACOS(-1.0d0)
 c PR - Number of printouts per storage period
 c PTIME - Time from the beginning of each storage period
 c Q0 - Reference shelf-life
 c QAVG - Average quality at nth time step
 c SPHC - Contains approximations of SPHEAT used in finite difference calculations
 c SPHT - Contains temperature ranges for constant specific heat
 c approximations (SPHC) used in finite difference calculations
 c STOR - Length of each storage period
 c T - Finite difference temperature solution
 c T0 - Initial freezing temperature (C or K)
 c TA - Ambient temperature at time step n and n+1
 c TAVG - Average temperature
 c TEMP - Ambient temperature during each storage period
 c TH - High temperature used in averaging properties (K)
 c TI - Initial food temperature
 c TL - Low temperature used in averaging properties (K)
 c TREF - Reference temperature for initial quality
 c TUNIT - = 3600.0d0 if storage time is in hours
 c = 86400.0d0 if storage time is in days
 c VEA - Variance of activation energy constant
 c VQ0 - Variance of reference shelf-life
 c VQ - Variance of predicted food quality
 c VSUM - Summation used in determining variance of quality
 c WF0 - Unfrozen product moisture content
 c YNAV - Yes or no (1 or 0)

 c The character variables appearing in this subroutine are:

 c filedat- File name for property data file
 c inpdat- File name for boundary condition data file
 c title - Title of run
 c tlfil- Key word for file containing boundary conditions (4 characters)
 c ttlrpr- Key word for file containing thermal properties (4 characters)

 c Declare variables not in common blocks.
    integer icnt

    double precision a(maxm),b(maxm),c(maxm),cc(maxm),
    & d(maxm),dd(maxm),dq(2),dqda,dsum,dt,eabs,eeabs,eex,
    & HH(2,2),qq(2,2),tt(2,2),
& qavg, qual(maxm), pi, pr, ptime, t(maxm, 3),
& ta(2), tavg, vq, vsum

c Declare variables in common blocks.

    integer per, ncount(maxp),
    & shape, sym, m, mp1, sstep, EEND, bct(maxp, 2)

    double precision ti, temp(maxp), stor(maxp), h(maxp, 2),
    & tunit(maxp), q(maxp, 2), tb(maxp, 2),
    & DENST(maxd), DENS(daxd), CONDT(maxc), CONDC(maxc), SPHT(maxs),
    & SPHC(maxs),
    & ds,
    & pdt(maxp),
    & 1, dz,
    & tl, th, avgd, avgk, avgc, ynavg,
    & wf0, ms, dp, kp, cp, t0,
    & ea, q0, vea, vq0, tref

    character fildat*12, inpat*12, kindat*12,
    & title*20, ttlfil*4, ttlprp*4, ttlkin*4

c Declare common blocks:

    common/bound/per, ti, temp, stor, h, tunit, ncount, q, tb,
    & /CONSTP/DENST, DENS, CONDT, CONDC, SPHT, SPHC,
    & /d/ds,
    & /datfil/fildat, inpat, kindat,
    & /delt/pdt
    & /geom/shape, l, dz, sym, m, mp1, sstep,
    & /mod/model,
    & /NCONSTP/NSD, NSC, NSS,
    & /pavg/th, tl, avgd, avgk, avgc, ynavg,
    & /prop/wf0, ms, dp, kp, cp, t0,
    & /shelf/ea, q0, vea, vq0, tref,
    & /ttl/title, ttlfil, ttlprp, ttlkin

c---------------------------------------------------------------
c Read in boundary and initial conditions

    write(inpat, 600) ttlfil, 'inp.dat'
600 format( ' ', a, a)
    open(unit=12, FILE=inpdat(1:12))

188
read(12,*)per,sym,ti
do i = 1,per
   read(12,*)bct(i,1),bct(i,2)
   read(12,*)temp(i),stor(i),unit(i),h(i,1),h(i,2),q(i,1),q(i,2),
   + tb(i,1),tb(i,2),pdt(i),ncount(i)
enddo
C Input geometry and dimensions
read(12,*)shape,L
read(12,*)m,sstep
close(unit=12)
c Read in constant property assumptions
   WRITE(FILDAT,310)TTL,prp,'PRP.DAT'
310 FORMAT(1,A,A)
   OPEN(UNIT=12,FILE=FILDAT(1:12))
   READ(12,*)WF0,T0,MS
   READ(12,*)DP,KP,CP
   CLOSE(UNIT=12)

dt = pdt(1)
write(6,1)
1 format(1,'PROGRAM IS RUNNING!')
pi = dacos(-1.0d0)
dz = L/m
mp1 = m+1
DO k = 1,2
   TA(k)=TEMP(1)
   do i=1,2
      HH(k,i)=H(1,i)
      qq(k,i)=q(1,i)
      tt(k,i)=tb(1,i)
   enddo
   DO I = 1,mp1
      t(I,k)=ti
   enddo
   enddo
tavg = ti
time=0
count=0
time=0
JJJ=0
qavg = q0*86400.0d0
   HEADTQ=1
CALL OUTPUT(NPRINT, HEADQT,T,TAVG, TIME, PTIME, QUAL, QAVG, VQ, I, EEND, 
& DT, BCT)
J=1

C finite difference solution

DO 160 II=1, PER

C Determine number of printouts

DT = PDT(II)
PR = STOR(II)/NCOUNT(II)
EEND = 0
IF(II.NE.1) THEN
TIME = TIME + STOR(II-1)
NPRINT = 2
CALL OUTPUT(NPRINT, HEADQT,T,TAVG, TIME, PTIME, QUAL, QAVG, VQ, II, EEND, 
& DT, BCT)
ENDIF
PTIME = 0.0D0
PTIME2 = 0.0D0
JJI = 0

C

C check if time is > length of storage period

65 IF(PTIME.GE.STOR(II)) GOTO 155
C
C check if product temp. is close to ambient temp.

EABS = ABS(T(1,2)-TEMP(II))
DO 60 I=2, MPI1
EEABS = ABS(T(I,2)-TEMP(II))
60 CONTINUE
C
DTMAX = STOR(II)-PTIME
C
COUNT = COUNT+1

C set ambient temperature = storage temperature
ta(2)=temp(ii)

c boundary conditions
  do i=1,2
    hh(2,i)=h(ii,i)
    qq(2,i)=q(ii,i)
    tt(2,i)=tb(ii,i)
  enddo

c thomas algorithm

c find coefficients for thomas algorithm

  do   i=1,mp1
    t(i,3)=t(i,1)
  enddo
  icnt=1
  continue
  call coeff(ii,hh,qq,tt,ta,t,a,b,c,d,dt,bct,icnt)
  cc(1)=c(1)/b(1)
  dd(1)=d(1)/b(1)
  do k=2,mp1
    kk=k-1
    cc(k)=c(k)/(b(k)-a(k)*cc(kk))
    dd(k)=(d(k)-a(k)*dd(kk))/(b(k)-a(k)*cc(kk))
  enddo
  t(mp1,2)=dd(mp1)
  err=(t(mp1,2)-t(mp1,3))*2.0d0
  tavg = t(mp1,2)
  do k=2,mp1
    kk=m-k+2
    t(kk,2)=dd(kk)-cc(kk)*t(kk+1,2)
    err=err+(t(kk,2)-t(kk,3))*2.0d0
    tavg = tavg+t(kk,2)
  enddo
  err=err/mp1
  if(icnt.ge.100) then
    do i=1,mp1
      t(i,2)=t(i,3)
    enddo
    go to 78
  endif
if(err.ge.err1.and.icnt.ne.1) then
   do  i=1,mp1
      t(i,2)=t(i,3)
   enddo
   go to 78
endif
   do  i=1,mp1
      t(i,3)=t(i,2)
   enddo
if(err.gt.0.1d-5.or.icnt.eq.1) then
   err1=err
   err=0.0
   icnt=icnt+1
   TAVG=0.0
   goto 77
endif
78   continue
   err1=0.0
   err=0.0
   ptime = ptime+dt
   ptime2 = ptime2+dt
   tavg = tavg/mp1

85   continue
   count=count+1
   if(ptime2.ge.pr.and.ptime.ne.stor(ii))then

   c printout
   eend=1
   nprint = 1
   call output(nprint,headtq,t,tavg,time,ptime,qual,qavg,qv,ii,
   &eend,dt,bot)
   ptime2 = 0.0
   endif

   c initial t for next time step

   do i=1,mp1
      t(i,1)=t(i,2)
enddo
   ta(1)=ta(2)
do  i=1,2
   hh(1,i)=hh(2,i)
   qq(1,i)=qq(2,i)
   tt(1,i)=tt(2,i)
enddo
   j=j+1
   ijj=ijj+1
   goto 65

   c end of finite difference calculations

   c **********************************************************************
   c set product temp. = ambient temperature; determine quality

105   tavg = 0.0d0

   nx=4
   dt=(stor(ii)-ptime)/nx
   do 130 ij=1,nx
      ptime=ptime+dt
      if(model.ge.3)then
         eex=1.0d0/temp(ii)-1.0d0/tref
         d1=exp(-(ea/r*eex))
         qavg = 0.0d0
         do  i=1,mp1
            qual(i)=qual(i)-d1*dt
            qavg = qavg+qual(i)
         enddo
         qavg=qavg/mp1
      endif
      if(model.eq.4)then
         dqdea=d1*eex*dt/r
         dq(2)=dq(1)+dqdea
         vq=vq0+dq(2)**2*vea
         dq(1)=dq(2)
      endif
   enddo

   c printout
   eend=1
   nprint = 1
   call output(nprint,headtq.t,tavg,time,ptime,qual,qavg,vq,ii,
&eend,dt,bct)
j=j+1
jj=jj+1
count=0
130 continue
140 do 150 i=1,mp1
150 t(i,1)=t(i,2)

ta(1)=ta(2)
do i=1,2
hh(1,i)=hh(2,i)
qq(1,i)=qq(2,i)
tt(1,i)=tt(2,i)
enddo
155 if(count.ne.0)then
  eend=1
  nprint = 1
  call output(nprint,headtq,t,tavg,time,ptime,qual,qavg,vq,ii,
  &eend,dt,bct)
endif

count=0
if(ii.eq.per)then
  eend=1
  nprint = 2
  call output(nprint,headtq,t,tavg,time,ptime,qual,qavg,vq,ii,
  &eend,dt,bct)
endif
160 continue
return
end

$c**********************************************************************************************

subroutine coeff(ii,hh,qq,tt,ta,t,a,b,c,d,dt,bct,icnt)
  The coefficients of the temperature array associated with the finite
difference solution are determined in this subroutine. Coefficients
c are calculated using a Crank Nicolson approximation for the time
c derivative.
  
  parameter(maxm=101,maxp=20,maxd=101,maxc=51,maxs=201)
c The integer variables appearing in this subroutine are:

c M     - Total number of nodes minus one

 c MP1   - Total number of nodes

 c NCOUNT- Number of printouts per storage period

 c NSC   - Total number of constant thermal conductivity values used in
         approximating thermal conductivity equations as F(temperature)

 c NSD   - Total number of constant density values used in approximating
         density equations as F(temperature)

 c NSS   - Total number of constant specific heat values used in

 c SHAPE - = 1 for slab geometry
         = 2 for cylindrical geometry
         = 3 for spherical geometry

 c SSTEP - Step size for printing out temperatures at spatial nodes

 c SYM   - = 0 if unsymmetric
         = 1 if symmetric

C  The real variables appearing in this subroutine are:

 c A     - Array containing coefficients for temperature at (m-1)th
           node

 c AAR    - Geometry area factor

 c AR     - Array containing areas at node m

 c AR1    - Array containing areas at node m+1/2

 c AVG1   - Area where density-specific heat on the left side of the
           finite difference node is evaluated

 c AVG2   - Area where density-specific heat on the right side of the
           finite difference node is evaluated

 c AVG3   - Area specific heat (<0°C) (J/kgK)

 c AVG4   - Average density (<0°C) (kg/m^3)

 c AVG5   - Average thermal conductivity (<0°C) (W/mK)

 c B      - Array containing coefficients for temperature at mth node

 c BETA   - Weighting coefficient for finite difference solution (=1/2)

 c C      - Array containing coefficients for temperature at (m+1)th
           node

 c CK     - Array for thermal conductivity values associated with all the
           nodes at a given time step (from PFIN)

 c CONDC  - Contains approximations of CONDUC used in finite difference
           calculations

 c CONDT  - Contains temperature ranges for constant thermal conductivity
           approximations (CONDTC) used in finite difference calculations

 c CP     - Food specific heat (>0°C) (J/kgK)
c CSD  - Array for density-specific heat values associated with all the
c      nodes at a given time step (from PFI ND)
c D   - Array containing boundary conditions and previous temperatures
c      at previous time step
c time step
c DA   - Term containing temperature at node m-1 and at time n-1
c DB   - Term containing temperature at node m and at time n-1
c DC   - Term containing temperature at node m+1 and at time n-1
c DDD  - Term containing boundary conditions
c DENSC - Contains approximations of DENS used in finite difference
c      calculations
c DENST - Contains temperature ranges for constant density approximations
c      (DENSC) used in finite difference calculations
c DP   - Food density (>0C) (kg/m^3)
c DS   - Food solids density (kg/m^3)
c DT   - Time step
c DZ   - Spatial increment for finite difference calculations
c DZZ  - 1/DZ
c GAM A - Weight for time n+1
c HH1  - Heat transfer coefficients at boundary 1 for single storage
c      period at both nth and (n-1)th time steps
c HH2  - Heat transfer coefficients at boundary 2 for single storage
c      period at both nth and (n-1)th time steps
c KP   - Food thermal conductivity (>0C) (W/mK)
c L    - Dimension in the direction of heat transfer (thickness or radius)
c MS   - Molecular weight of the solids (kg/mole)
c NU   - Weighting coefficient for finite difference solution (=1/2)
c OMEGA - Weight for time n
c PI   - Pi defined as: DACOS(-1.0d0)
c SPHC  - Contains approximations of SPHEAT used in finite difference
c      calculations
c SPHT  - Contains temperature ranges for constant specific heat
c      approximations (SPHC) used in finite difference calculations
c T    - Finite difference temperature solution
c TA   - Ambient temperature at time step n and n+1
c T0   - Initial freezing temperature (C or K)
c TH   - High temperature used in averaging properties (K)
c TL   - Low temperature used in averaging properties (K)
c WF0  - Unfrozen product moisture content
c YNAV G - Yes or no (1 or 0)

c Declare variables not in common blocks.

integer ii,EEND,icnt,nnn,iii,ic

double precision a(maxm),aar,ar(maxm),ar1(maxm),avg1, & avg2,b(maxm),beta,c(maxm),ck(maxm,2),csd1(maxm,2), & csd2(maxm,2),d(maxm),da,db,time & dc,ddd,dt,dzz,gama,hh(2,2),qq(2,2),tt(2,2), & nu,omega,pi,ia(2),t(maxm,3),qqq1,qqq2,qbc,delt,cof(12)

c Declare variables in common blocks.

integer shape,ym,m,mp1,sstep, & nsd,nsc,nss,bct(maxp,2),ncount(maxp),per

double precision DENST(maxd),DENSC(maxd),CONDT(maxc), & CONDC(maxc),SPHT(maxs),SPHC(maxs), & ds, & 1,dz, & tl,th,avgd,avgk,avgc,ynavg, & wf0,ms,dp,kp,cp,t0, & ti,temp(maxp),stor(maxp),h(maxp,2), & tunit(maxp),q(maxp,2),tb(maxp,2)
double precision spheat,dens,conduc,ddl(maxm),sphh,dnss,ckk, & csd1,csd2,cnd1,cnd2,dum1,dum2,dum3,dum4

c Declare common blocks:
    common/bound/per,ti,temp,stor,h,tunit,ncount,q,tb, & /CONSTP/DENST,DENSC,CONDT,CONDC,SPHT,SPHC, & /d/ds, & /geom/shape,1,dz,ym,m,mp1,sstep, & /NCONSTP/NSD,NSC,NSS, & /pavg/th,tl,avgd,avgk,avgc,ynavg, & /prop/wf0,ms,dp,kp,cp,t0
    external spheat,dens,conduc

data cof /22.1413822d0,-6.602498d-3,3.46666666d-6,-5.677883e-9 & ,3.154852d-12,-8.641076d-16,1.3621d-19,-1.300902d-23, & 7.456489d-28,-2.364877d-32,3.194631d-37,0.0d0/
c------------------------------------------------------
    pi = dacos(-1.0d0)
c weighting functions for finite difference method
c modified crank-nicolson method
c weight. coeff. for d2t/dz2
  c   for time t:
    beta=0.50d0
  c   for time t+1:
    nu=0.50d0

c weight. coeff. for dt/dt
  c   for time t:
    omega=-1.0d0
  c   for time t+1:
    gama=1.0d0

dzz=1.0d0/dz

do 10 i=1,mp1

c slab

  if(shape.eq.1)then
    ar(i)= 1.0d0
    ar1(i)= 1.0d0
  endif
10    continue

CALL PFIND(T,M,CK,CSD2,DT,DZ)
  if(icnt.eq.1) then
    time =time+dt
  do i=1,mp1
    ck(i,1)=ck(i,2)
    csd1(i,1)=csd2(i,1)
    csd1(i,2)=csd2(i,2)
  enddo
ENDIF

c 1st boundary point
  if(bct(ii,1).eq.1) then
    a(1)=0.0d0
    c(1)=0.5d0*dzz*(CK(1,2)+ck(1,1))/2
    dc=-0.5d0*dzz*(CK(1,1)+ck(1,1))/2
    b(1)=-(CSD2(1,1)+csd1(1,1))/2-0.5d0*hh(2,1)-c(1)
    db=-(CSD1(1,1)+csd2(1,1))/2+0.50d0*hh(1,1)-dc

198
c

ddd=-0.5d0*(ta(1)*hh(1,1)+qq(1,1))
& -0.5d0*(ta(2)*hh(2,1)+qq(2,1))

d(1)=db*t(1,1)+dc*t(2,1)+ddd
else
  a(1)=0.0d0
  b(1)=1.0d0
  c(1)=0.0d0
db=0.0d0
dc=0.0d0
ddd=tt(1,1)
d(1)=ddd
eendif

c ************************************************************

c interior points
do 20 i=2,m

  a(i)=0.50d0*dzz*(CK(I-1,2)+ck(i-1,1))/2
  c(i)=0.50d0*dzz*(CK(I,2)+ck(i,1))/2
da=-0.50d0*dzz*(CK(I-1,1)+ck(i-1,2))/2
dc=-0.50d0*dzz*(CK(I,1)+ck(i,2))/2
db=-(CSD1(I,1)+CSD1(I,2)+CSD2(I,1)+CSD2(I,2))/2-da/dc
  b(i)=-(CSD1(I,1)+CSD1(I,2)+CSD2(I,1)+CSD2(I,2))/2-a(i)-c(i)

c

d(i)=da*t(i-1,1)+db*t(i,1)+dc*t(i+1,1)
20 continue

c ************************************************************

c 2nd boundary point
  if(bct(ii,2).eq.1) then
    c(mp1)=0.0d0
    a(mp1)=0.50d0*dzz*(CK(M,2)+ck(m,1))/2
da=0.50d0*dzz*(CK(M,1)+ck(m,2))/2
    b(mp1)=-(CSD2(mp1,2)+CSD1(mp1,2))/2-0.50d0*hh(2,2)-a(mp1)
db=-(CSD1(mp1,2)+csd2(mp1,2))/2+0.50d0*hh(1,2)-da
    ddd=0.50d0*(hh(1,2)*ta(1)+qq(1,2))-
+ 0.50d0*(ta(2)*hh(2,2)+qq(2,2))

199
d(mp1)=da*t(m,1)+db*t(mp1,1)+ddd
else
  a(mp1)=0.0d0
  b(mp1)=1.0d0
  c(mp1)=0.0d0
  da=0.0d0
da=0.0d0
dc=0.0d0
ddd=tt(1,2)
d(mp1)=ddd
endif
return
end

SUBROUTINE PFIND(T,M,CK,CSPD,DT,DZ)

  PARAMETER (MAXm=101, MAXC=51, MAXD=!101, MAXS=201)

  c  This subroutine finds the thermal property values associated with the
  c  nodes in the finite difference solution. These values are in the
  c  coefficients used in the solution.

  c  The integer variables appearing in this subroutine are:

    c  M    - Total number of nodes minus one
    c  MP1  - Total number of nodes
    c  NSC  - Total number of constant thermal conductivity values used in
      approximating thermal conductivity equations as F(temperature)
    c  NSD  - Total number of constant density values used in approximating
      density equations as F(temperature)
    c  NSS  - Total number of constant specific heat values used in

  c  The real variables appearing in this subroutine are:

    c  AVGC  - Average specific heat (<0C) (J/kgK)
    c  AVGD  - Average density (<0C) (kg/m^3)
    c  AVGK  - Average thermal conductivity (<0C) (W/mK)
C1 = 1.0d0/(CC*DZ)
CC = 1000.0d0*DZ/2.0d0
CK - Array for thermal conductivity values associated with all the
  nodes at a given time step (from PFIND)
CK1 -
CONDC - Contains approximations of CONDUC used in finite difference
calculations
CONDUC - Thermal conductivity function (of temperature < 0C)
CONDT - Contains temperature ranges for constant thermal conductivity
  approximations (CONDC) used in finite difference calculations
CP - Food specific heat (>0C) (J/kgK)
CSPD - Array for density-specific heat values associated with all the
  nodes at a given time step (from PFIND)
DC - Array containing density values at time step m and m-1
DENS - Density function (of temperature < 0C)
DENSC - Contains approximations of DENS used in finite difference
calculations
DENST - Contains temperature ranges for constant density approximations
  (DENSC) used in finite difference calculations
DP - Food density (>0C) (kg/m^3)
DS - Food solids density (kg/m^3)
DT - Time step
DZ - Spatial increment for finite difference calculations
KP - Food thermal conductivity (>0C) (W/mK)
L - Dimension in the direction of heat transfer (thickness or radius)
MS - Molecular weight of the solids (kg/mole)
SPC - Array containing specific heat values at time step m and m-1
SPHC - Contains approximations of SPHEAT used in finite difference
calculations
SPHEAT - Specific heat as a function (of temperature < 0C)
SPHT - Contains temperature ranges for constant specific heat
  approximations (SPHC) used in finite difference calculations
T - Finite difference temperature solution
T0 - Initial freezing temperature (C or K)
TAVGK - Temperature used to evaluate thermal conductivity
TAVGSD - Temperatures used to evaluate density and specific heat
TH - High temperature used in averaging properties (K)
TL - Low temperature used in averaging properties (K)
WF0 - Unfrozen product moisture content
YNAVG - Yes or no (1 or 0)

Declare variables not in common blocks.
INTEGER M,MP1,NC(8),EEND

double precision c1,cc,CK(MAXM,2),ck1,condc,CSPD(MAXM,2),
& DC(2),dens,dt,dz,SPC(2),spheat,t(maxm,3),TAVGK,TAVGSD(2)

c Declare variables in common blocks.

INTEGER NSC,NSD,NSS

double precision CONDT(MAXC),CONDCC(MAXC),DENST(MAXD),
& DENSNC(MAXD),SPHT(MAXS),SPHC(MAXS),
& ds,
& th,tl,avgd,avgk,avgc,ynavg,
& wf0,ms,dp,kp,cp,t0

c Declare common blocks:

COMMON /CONSTP/DENST,DENSNC,CONDTC,CONDCC,SPHT,SPHC,
& /d/ds,
& /NCONSTP/NSD,NSC,NSS,
& /pavg/th,tl,avgd,avgk,avgc,ynavg,
& /prop/wf0,ms,dp,kp,cp,t0

external dens,condc,spheat

MP1 = M+1
cc = 1000.0d0*dz/2.0d0
c1 = 1.0d0/(cc*dz)
DO 100 1 = 1,mp1
IF(1.LE.M)THEN
   TAVGK = (T(I,3)+T(I+1,3))*0.50d0
   TAVGSD(1) = 0.750d0*T(I,3)+0.250d0*T(I+1,3)
ENDIF
IF(1.GT.1)THEN
   TAVGSD(2) = 0.750d0*T(I,3)+0.250d0*T(I-1,3)
ENDIF

C DO 10 J = 2,NSC+1
IF(1.Eq.Mp1)go to 10
if(tavgk.ge.t0)then
   ck(i,2) = kp

202
nc(1) = 1
else
c(i,2) = conduc(tavgk)
c(1) = 1
endif
10 continue
if(i.gt.1) then
ck1 = ck(i-1,2)+ck(i,2)+(ck(i-1,2)*ck(i,2))**0.5
endif
C DO 40 J = 2,NSD+1
    DO 30 KK = 1,2
        IF(I.EQ.mp1.AND.KK.eq.1)GO TO 30
        IF(I.EQ.1.AND.KK.eq.2)GO TO 30
        if(tavgsk(kk).ge.0) then
dc(kk) = dp
c(kk+2) = 1
        else
dc(kk) = dens(tavgsk(kk))
c(kk+2) = 1
        ENDIF
30 CONTINUE
C 40 CONTINUE
C DO 60 J = 2,NSS+1
    DO 50 KK = 1,2
        IF(I.EQ.mp1.AND.KK.eq.1)GO TO 50
        IF(I.EQ.1.AND.KK.eq.2)GO TO 50
        if(tavgsk(kk).ge.t0) then
spc(kk) = cp
nc(kk+5) = 1
        else
spc(kk) = spheat(tavgsk(kk))
c(kk+5) = 1
        ENDIF
50 CONTINUE
C 60 CONTINUE
90 continue
    DO KK = 1,2
        CSPD(I,KK) = SPC(KK)*DC(KK)*cc/dt
    ENDDO
100 CONTINUE
RETURN
END

subroutine output(nprint,headtq,t,tavg,time,jj,qual,qavg,vq,
&ii,eend,dt,bct)

c The integer variables appearing in this subroutine are:

c DAY   -
c DEAD  -
c EEND  -
c M     - Total number of nodes minus one
nc MODEL - Option number from main menu
nc MP1   - Total number of nodes
nc NCOUNT- Number of printouts per storage period
nc PER   - Total number of storage periods
nc SHAPE - = 1 for slab geometry
nc = 2 for cylindrical geometry
nc = 3 for spherical geometry
nc SSTEP - Step size for printing out temperatures at spatial nodes
nc SYM   - = 0 if unsymmetric
nc = 1 if symmetric

c The real variables appearing in this subroutine are:

c ABC   -
c ABCD  -
c C7    -
c C8    -
c CP    - Food specific heat (>0C) (J/kgK)
c DP    - Food density (>0C) (kg/m^3)
c DT    - Time step
nc DZ    - Spatial increment for finite difference calculations
nc EA    - Activation energy constant
nc H1    - Array for heat transfer coefficients at boundary 1
nc H2    - Array for heat transfer coefficients at boundary 2
nc HR    -
c JJ    -
c KP    - Food thermal conductivity (>0C) (W/mK)
c L - Dimension in the direction of heat transfer (thickness or radius)
c MS - Molecular weight of the solids (kg/mole)
c PDT - Time step for each storage period
c Q0 - Reference shelf-life
c QAVG - Average quality at nth time step
c STOR - Length of each storage period
c T - Finite difference temperature solution
c T0 - Initial freezing temperature (C or K)
c TAVG - Average temperature
c TAVG1 -
c TEMP - Ambient temperature during each storage period
c TI - Initial food temperature
c TIME -
c TREF - Reference temperature for initial quality
c TUNIT = 3600.0d0 if storage time is in hours
c = 86400.0d0 if storage time is in days
c VEA - Variance of activation energy constant
c VQ0 - Variance of reference shelf-life
c VQ - Variance of predicted food quality
c WF0 - Unfrozen product moisture content

c The character variables appearing in this subroutine are:

  c HH11 -
c HH22 -
c OUTFIL-
c PRUNIT -
c title - Title of run
c ttfile - Key word for file containing boundary conditions (4 characters)
c ttkin - Key word for file containing kinetic properties (4 characters)
c tlpri - Key word for file containing thermal properties (4 characters)

c parameter(maxp=20,maxm=101)

c Declare variables not in common blocks

    integer day,dead,eend

    double precision abc(5),abcd,c7,c8,dt/hr,jj,qavg,
    & qual(maxm),t(maxm,3),tavg,tavg1,vq

    character outfil*12,hh11*29,hh22*21,prunit*6
c Declare variables in common blocks

    integer per,ncount(maxp),
    & shape,sym,m,mp1,sstep,
    & model,bct(maxp,2)

    double precision ti,temp(maxp),stor(maxp),h(maxp,2),
    & tunit(maxp), q(maxp,2),tb(maxp,2),
    & pdt(maxp),
    & l,dz,
    & wf0,ms,dp,kp,cp,t0,
    & ea,q0,vea,vq0,tref,spheat,sp,moist

    character title*20,tulfil*4,ttlprp*4,ttlkin*4

c Declare common blocks

    common /bound/per,ti,temp,stor,h,tunit,ncount,q,tb,
    & /delt/pdt
    & /geom/shape,l,dz,sym,m,mp1,sstep
    & /mod/model
    & /prop/wf0,ms,dp,kp,cp,t0
    & /shelf/ea,q0,vea,vq0,tref,
    & /ttl/title,tulfil,ttlprp,ttlkin
    external spheat,moist

C-------------------------------------------------------------------------------------

C NPRINT = 0 if printing input parameters and headings
C NPRINT = 1 if printing temperature distribution and/or
C quality distributions
C NPRINT = 2 if printing period no. and end line
IF(NPRINT.EQ.0)THEN
   GO TO 1100
ELSE
   if(nprint.eq.1)then
      go to 1200
   else
      go to 1300
   endif
endif
1100 write(outfil,1000)tulfil,'out.dat'
1000 format( 'a,a)
   open(unit=12,FILE=outfil(1:12))
   write(12,1)title
format( '///3x,Title: ',a20,'/3x,'-----'//,14x,'Input Para', +meters',/,'14x,16(')'//)
write(12,10)
10 format( ' /','Unfrozen Product Properties,'/)
     abcd=wf0*100.0d0
     write(12,11)abcd
11 format( '2x,'Moisture content (%)...............','f6.2)
     abcd=t0-273.150d0
     write(12,12)abcd
12 format( '2x,'Initial freezing temperature (C)......','f6.2)
     write(12,13)ms
13 format( '2x,'Molecular weight of solids (kg/mole)...','f8.2)
     write(12,14)dp
14 format( '2x,'Unfrozen product density (kg/m^3).....','f8.2)
     write(12,15)kp
15 format( '2x,'Thermal conductivity (W/mK)...........','f6.3)
     write(12,16)cp
16 format( '2x,'Specific heat (kJ/kgK).............','f7.3)
     abcd=ti-273.150d0
     write(12,17)abcd
17 format( ' /','Initial Condition: /','2x,'Product temp., + ('C) at time=0 ..........','f6.2)

c product geometry

if(sym.eq.1) = 1*2.0d0
     write(12,18)
18 format( ' /','Slab Geometry: /','2x,'thickness (m), +26(''),f10.6)

c boundary conditions

do 40 i=1,per
     write(12,24)i
24 format( ' /','boundary conditions for period ','i2,':'//
     abcd=stor(i)/tunit(i)
     if(tunit(i).eq.3600.0d0) then
     write(12,25)abcd
25 format( '4x,'storage time (hours).........','f7.2)
     else
     write(12,26)abcd
26 format( '4x,'storage time (days).........','f7.2)
endif
write(12,45)print(i)
45 format( ' ,4x,'time step (seconds).........',f8.2)
       abcd=temp(i)-273.150d0
write(12,27)abcd
27 format( ' ,4x,'storage temperature (C)......',f6.1/)
28 format( ' ,4x,'convective heat transfer coeff. (W/m^2K):',f7.2)
228 format( ' ,4x,'heat flux (W/m^2):',f7.2,/)
328 format( ' ,4x,'boundary condition temperature (C)',f7.2,/)
       write(12,29)
29 format( ' ,4x,'side 1:')
if(bct(i,1),eq.1) then
   write(12,28)h(i,1)
   write(12,228)q(i,1)
elseif(bct(i,1),eq.2) then
   write(12,328)tb(i,1)-273.15
endif
if(sym.ne.1)then
   write(12,30)
30 format( ' ,4x,'side 2:')
if(bct(i,2),eq.1) then
   write(12,28)h(i,2)
   write(12,228)q(i,2)
elseif(bct(i,2),eq.2) then
   write(12,328)tb(i,2)-273.15
endif
endif
40 continue

write(12,100)title
100 format( ' ///// ,',Title= ',a20,/)
   if(sym.eq.1)then
      write(12,110)
110 format( ' ,Note: Distribution is symmetrical;/',6x,'results',
       +' are shown for half-thickness only./)
   endif
   hh22='DISTRIBUTION HISTORY'
   if(headq.eq.1)then
      hh11=' TEMPERATURE (C) '
   else
      hh11='TEMPERATURE (C) & QUALITY (%)'
   endif
   write(12,120)hh11,hh22

208
120 format( ' ,',19x,a,/,23x,a,/,19x,27(''),/)
   write(12,130)
130 format( ',',28x,'position (m)',/ ',',5x,'time',5x,'(',',',40x, & ' lAvg Temp')
   do i = 1,5
      abc(i)=(i-1)*step*dz
   enddo
   write(12,137)abc(1),abc(2),abc(3),abc(4),abc(5)
137 format( ',',14x,'(',',',5(f8.4))
   write(12,155)
155 format( ',',72('='))
   write(12,160)
160 format( ',',586400.0d0
   tavg1 = tavg-273.150d0
   do i = 1,5
      abc(i)=t((i-1)*step+1,2)-273.150d0
   enddo
   if(tunit(ii),eq,3600.0d0)then
      prunit = 'hours:'
   else
      prunit = 'days :'
   endif
   write(12,190)(time+jj)/tunit(ii)*3600,prunit,abc(1),abc(2),abc(3), & abc(4),abc(5),tavg1
190 format( ',',7.2,2x,a,2x,5(f6.2,2x),'",f6.2,'C")
   return
   c Printout end line
1300 write(12,300)
300 format( ',',65(''))
   if(eend,eq,0)then
      write(12,310)i1
310 format( ',',period',i3)
   else
      close(unit=12)
   endif
   return
end
A.2 Input Files

A.2.1 Properties of Unfrozen Material File

\[
\begin{array}{ccc}
9.000E-001 & 272.15000 & 205.0841 \\
1000.00000 & 5.00E-001 & 3.50000 \\
\end{array}
\]

Such that,

Moisture content | Initial Freezing Temp. (K) | Molecular Weight of Solids
Density (kg/m³) | Thermal Conductivity (W/m K) | Specific Heat (kJ/kg K)

A.2.2 Input File

```
1 1 278.15
1 1
253.15 7200.00 3600.10.00 10.00 .00 .00 .00 .00 40.00 40 .0250
20 5
```

Such that:

Line 1 includes the number of freezing periods, symmetry of the sample (if 0 the freezing experiment is symmetric, if 1 it is symmetric), and the initial temperature of the food sample.

Line 2 includes the types of boundary conditions of side 1 and 2 of the food sample; 1 indicates convective or/and heat flux boundary condition, and 2 indicates constant temperature boundary condition.

Line 3 includes the ambient temperature, total time of freezing, time unit (3600. is hours and 86400. is days), heat transfer coefficient (h) of boundary 1, h of boundary 2, heat flux (q") of boundary 1, q" of boundary 2, Temperature boundary condition 1, Temperature boundary condition 2, time step, and the number of printouts in the output file.

Line 4 includes the thickness of the food sample.

Line 5 includes the number of grid points, and the number of the printout points in the output file.
A.3 Output File

Title: Sample Run

Input Parameters

Unfrozen Product Properties

Moisture content (%).......................... 90.00
Initial freezing temperature (°C).......... -1.00
Molecular weight of solids (kg/mole)... 205.08
Unfrozen product density (kg/m^3)...... 1000.00
Thermal conductivity (W/mK)............. .500
Specific heat (kJ/kgK)...................... 3.500

Initial Condition:
Product temp. (°C) at time=0.......... 5.00

Slab Geometry:
thickness (m).............................. .050000

boundary conditions for period 1:

  storage time (hours)........... 2.00
  time step (seconds)......... 40.00
  storage temperature (°C).... -20.0

  side 1:
  convective heat transfer coeff. (W/m^2K): 10.00
  heat flux (W/m^2): .00

Title= Sample Run

Note: Distribution is symmetrical;
results are shown for half-thickness only.

<table>
<thead>
<tr>
<th>TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DISTRIBUTION HISTORY</td>
</tr>
<tr>
<td>position (m)</td>
</tr>
<tr>
<td>time :</td>
</tr>
</tbody>
</table>

---

211
| Period 1          | .00000 hours | .05556 hours | .11111 hours | .16667 hours | .22222 hours | .27778 hours | .33333 hours | .38889 hours | .44444 hours | .50000 hours | .55556 hours | .61111 hours | .66667 hours | .72222 hours | .77778 hours | .83333 hours | .88889 hours | .94444 hours | 1.00000 hours | 1.05556 hours | 1.11111 hours | 1.16667 hours | 1.22222 hours | 1.27778 hours | 1.33333 hours | 1.38889 hours | 1.44444 hours | 1.50000 hours | 1.55556 hours | 1.61111 hours | 1.66667 hours | 1.72222 hours | 1.77778 hours | 1.83333 hours | 1.88889 hours | 1.94444 hours | 2.00000 hours |
|------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
|                  | 5.0000       | 5.0000       | 5.0000       | 5.0000       | 5.0000       | 5.0010       | 5.03096C     | -9.436       | 1.1384       | 2.6024       | 3.4595       | 3.7402       | 2.15927C     | -1.2715      | -1.3170      | -1.3601      | -1.4004      | -1.4394      | -1.4772      | -1.5143      | -1.5498      | -1.5842      | -1.6178      | -1.6507      | -1.6829      | -1.7142      | -1.7449      | -1.7749      | -1.8042      | -1.8329      | -1.8611      | -1.8888      | -1.9159      | -1.9425      | -1.9688      | -2.0199      | -2.0448      | -2.0694      |
APPENDIX B

THE ESTIMATION PROGRAM

This section will include the "NLINA" program. A description of the various subroutines and function of the program will be first presented in Table B.1. Then, a listing of Program "NLINA" will follow. A sample input file will then be included.

Table B.1 Subroutines of the Modified Box-Kanemasu Estimation Program

<table>
<thead>
<tr>
<th>Subroutine Title</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subroutine MODEL</td>
<td>Calculates the temperature of the food material.</td>
</tr>
<tr>
<td>Subroutine SENS</td>
<td>Calculates the Sensitivity coefficients of the parameters, which are the thermal properties of the food material in this case.</td>
</tr>
<tr>
<td>Block Data CONST</td>
<td>Defines the temperature intervals for the piecewise linear thermal properties and the temperature boundary as a function of time.</td>
</tr>
<tr>
<td>Function TK(x)</td>
<td>Determines the thermal conductivity of the food material as a function of temperature.</td>
</tr>
<tr>
<td>Function CT(x)</td>
<td>Determines the volumetric specific heat of food material as a function of temperature.</td>
</tr>
<tr>
<td>Function QQ(x)</td>
<td>Defines the heat flux boundary condition as a function of time.</td>
</tr>
<tr>
<td>Function TB(x)</td>
<td>Determines the temperature boundary condition as a function of time.</td>
</tr>
<tr>
<td>Subroutine TMP</td>
<td>Solves for the temperature history in food material using the boundary conditions and the initial temperature by employing finite difference algorithm.</td>
</tr>
</tbody>
</table>
B.1 "NLINA" Computer Program (written by James V. Beck, 1993)

PROGRAM NLINA
CCCCCCCCC PROGRAM DESCRIPTION CCCC
C  C
C PROGRAM NLINC C
C WRITTEN BY JAMES V. BECK C
C LAST REVISED FEB. 25, 1993 C
C**********************************************************************C
C
CVCCCCCCC VARIABLE IDENTIFICATION CCCC
C  C
C
C**********************************************************************C
C
CDCCCCCCC DIMENSION BLOCK BLOCK 0000
C  C
C
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION T(300,5),Y(300),SIG2(300),B(100),
1 Z(100),A(100),BS(100),
1 VINV(5,5),BSS(100),CG(100),BSV(100),
1 R(100,100),EXTRA(20),
1 ERR(500), PS(100,100),P(100,100),PSV(100,100),
1 XTX(100,100),XTY(100),SUM(100)
CHARACTER*40 DFILE,OUTFIL
C  C
C**********************************************************************C
C
CCCCCCC COMMON BLOCK BLOCK 0100
C  C
C
COMMON T,N,Z,BS,I,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP,EXTRA
COMMON N,MODL,NP,T,Z,BS,ETA,PS,P,B,A,Y,SIG2,VINV,EXTRA
COMMON ERROR/ERR
COMMON/MOD/AA,TL,SUM
external ct,tk
C  C
C
C**********************************************************************C
C
CACC CCCCC DATA BLOCK BLOCK 0200
C  C

214
DATA EPS,EPSS,IIN,IOUT/1.0D-30,0.0001D+0,5,7/
C
C***************************************************************************************************************************************C
C
CICCCCCCCC initialization block block 0400
C
open(11,file='junk')
C
WRITE(*,*)'ENTER THE NAME OF THE DATA FILE'
READ(*,'(A40)') DFILE
c dfile='s5p15f2.inp'
OPEN(8,FILE=DFILE)
WRITE(*,*)'ENTER THE NAME OF THE OUTPUT FILE'
READ(*,'(A40)') OUTFIL
c outfil='s5p15f2.out'
OPEN(7,FILE=OUTFIL)

C***************************************************************************************************************************************C
C
CPCCCCCCCCC process block block 0500
C
C
C --- start input
C
BLOCK 1
WRITE(7,*),'BEGIN LISTING INPUT QUANTITIES'
200 READ(8,*),N,NP,NT,ITMAX,MODL,IPRINT
WRITE(7,*)
WRITE(7,*),'BLOCK 1'
WRITE(7,*),'N = NO. DATA POINTS, NP = NO. PARAMETERS'
WRITE(7,*),'NT = NO. OF INDEPENDENT VARIABLES'
WRITE(7,*),'ITMAX = MAXIMUM NO. OF ITERATIONS'
WRITE(7,*),'MODEL = MODEL NUMBER, IF SEVERAL MODELS IN
 SUBROUTINES:
    1 MODEL AND SENS'
WRITE(7,*),'IPRINT = 1 FOR USUAL PRINTOUTS, 0 FOR LESS'
WRITE(7,*)
IF(N.LE.0) THEN
    STOP
END IF
WRITE(*,'(7I10)') N,NP,NT,ITMAX,MODL,IPRINT
+
'"MODEL",4X,"PRINT")'
WRITE(7,'(7I10)') N,NP,NT,ITMAX,MODL,PRINT
IOPT=0
C --- IF IOPT=0 THEN ON THE 2ND AND SUCCEEDING STACKED CASES,
THE DATA IS
C --- NOT REPRINTED.
C --- IF IPRT=1, EXTRA PRINT OUT OF ETA, RESIDUALS B(1),... ARE
GIVEN.
C    BLOCK 2
WRITE(7,*)
WRITE(7,*)'BLOCK 2'
WRITE(7,*)'B(1),B(2),...B(NP) ARE INITIAL PARAMETER ESTIMATES'
WRITE(7,*)
READ(8,*)B(I),I=1,NP
WRITE(7,'(10X,"B","I3;">"F16.5")') (I,B(I),I=1,NP)
C
DO 150 J1=2,100
   BS(J1) = 0
150  CONTINUE
C
IF(IOPT.LE.0) THEN
C    BLOCK 3
WRITE(7,*)
WRITE(7,*)'BLOCK 3'
WRITE(7,*)'J = DATA POINT INDEX, Y(J) = MEASURED VALUE'
WRITE(7,*)'SIGMA(J) = STANDARD DEVIATION OF Y(J)'
WRITE(7,*)'T(J,1) = FIRST INDEPENDENT VARIABLE'
WRITE(7,*)
WRITE(7,'(/9X,"J","6X,"Y(J)",3X,"SIGMA(J)",6X,"T(J,1)"
+6X,"T(J,2)")')
   DO 10 I2=1,N
      READ(8,*)Y(J),SIG2(J),(T(J,KT),KT=1,NT)
      y(j)=y(j)+273.15d0
      WRITE(7,'(10I1,7F12.5)') J,Y(J),SIG2(J),(T(J,KT),KT=1,NT)
      SIG2(J) = SIG2(J)*SIG2(J)
10  CONTINUE
END IF
C
313  DO 2 IP=1,NP
   DO 2 KP=1,NP
      PS(KP,IP) = 0
      P(KP,IP) = 0
2  CONTINUE
C WRITE(7,'(/,5X,"P(1,KP)",9X,"P(2,KP)",9X,"P(3,KP)",9X,
C +"P(4,KP)",9X,"P(5,KP)")')
C DO 6 IP=1,NP
C
C READ(8,*) (PS(IP,KP),KP=1,NP)
C WRITE(7,'(5D16.5)') (PS(IP,KP),KP=1,NP)
6 CONTINUE
C BLOCK 4
DO 88 IP=1,NP
88 PS(IP,IP)=B(IP)*B(IP)
READ(8,*)IEXTRA
C IEXTRA=0 FOR NO EXTRA INPUT WHICH COULD BE FOR CONSTANTS
C IN MODELS
C =1 FOR ONE INPUT, NAMELY: EXTRA(1), ETC.
WRITE(7,*)
WRITE(7,'*') BLOCK 4'
WRITE(7,*)IEXTRA = NO. OF EXTRA(I) PARAMETERS, 0 IF NONE'
WRITE(7,*)
WRITE(7,'(10X,"IEXTRA = ",10I0)')IEXTRA
IF(IEXTRA.LT. 1) GOTO 21
WRITE(7,*)
WRITE(7,'*') BLOCK 5'
WRITE(7,*)EXTRA(1),... ARE EXTRA CONSTANTS USED AS DESIRED'
WRITE(7,*)
READ(8,*)(EXTRA(IE),IE=1,IEXTRA)
WRITE(7,'("EXTRA("I2," = ",F16.5)') (IE,EXTRA(IE),IE=1
  1,IEXTRA)
21 CONTINUE
C
C --- ADD BLANK CARD AFTER LAST INPUT CARD
C ---END INPUT
   WRITE(7,'*')END INPUT QUANTITIES - - BEGIN OUTPUT
CALCULATIONS'
   WRITE(7,*)
   WRITE(7,'*') SY = SUM OF SQUARES FOR PRESENT PARAMETER
VALUES'
   WRITE(7,*) SYP = SUM OF SQUARES FOR GAUSS PARAMETER VALUES,
SHOULD
   1 BE SMALLER THAN SY'
   WRITE(7,*') SYP DECREASES TOWARD A POSITIVE CONSTANT'
   WRITE(7,*') G = MEASURE OF THE SLOPE, SHOULD BECOME
SMALLER AS
   ITERATIONS PROCEED'
WRITE(7,*),' G SHOULD APPROACH ZERO AT CONVERGENCE'
WRITE(7,*),'H = FRACTION OF THE GAUSS STEP, AS GIVEN BY THE'
WRITE(7,*),'IBOX-KANEMASU METHOD'
WRITE(7,*)
c    write(*,*),'$
WRITE(7,*)
DO 18 IL=1,NP
   BS(IL)=B(IL)
   CG(IL) = 0
18 CONTINUE
DO 19 IP=1,NP
   XTY(IP)=0.0D+0
   DO 19 KP=1,NP
      P(KP,IP) = PS(KP,IP)
      XTX(IP,KP)=0.0D+0
19 CONTINUE
   I = 0
   MAX = 0
C
99 MAX = MAX + 1
C --- START BASIC LOOP GIVES B(I) AND SY
C
   SY = 0.0D+0
   DO 100 I3=1,N
      I = I3
      CALL MODEL
      CALL SENS
       CALL MODEL
      RISD = Y(I)-ETA
      SY = SY + RISD*RISD/SIG2(I)
      SUMX= 0.0D+0
      DO 20 K=1,NP
         XTY(K)=XTY(K)+Z(K)*RISD/SIG2(I)
      DO 20 L=1,NP
         SUMX= SUMX+ Z(L)*P(K,L)*Z(K)
         XTX(K,L)= XTX(K,L) + Z(L)*Z(K)/SIG2(I)
20 CONTINUE
   DELTA = SIG2(I) + SUMX
   DO 29 JJ=1,NP
      A(JJ) = 0.0D+0
29 CONTINUE
   DO 30 JA=1,NP
      DO 30 KA=1,NP

       218
A(JA) = A(JA) + Z(KA)*P(JA,KA)

30 CONTINUE
CS = 0.0D+0
DO 40 JC=1,NP
   CS = CS + Z(JC)*(B(JC)-BS(JC))
   CG(JC) = CG(JC) + Z(JC)*RISD/SIG2(I)
40 CONTINUE
C = Y(I) - CS - ETA
DO 50 IB=1,NP
   B(IB) = B(IB) + (A(IB)*C)/DELTA
50 CONTINUE
DO 41 ISV=1,NP
   DO 41 JSV=1,NP
      PSV(JSV,ISV) = P(JSV,ISV)
41 CONTINUE
DO 52 IV=1,NP
   DO 52 IU=IV,NP
      SUMP = 0.0D+0
      DO 51 KP=1,NP
         DO 51 JP=1,NP
            IF(KP-IV,EQ.0.OR.JP-IU,EQ.0) GOTO 51
            PSQ1 = PSV(KP,JP)*PSV(IU,IV)
            PSQ2 = PSV(IU,KP)*PSV(IV,JP)
            PSQ = PSQ1 - PSQ2
            IF(DABS(PSQ1)+DABS(PSQ2),LT,1.D-15) THEN
               RP = PSQ * 1.D15
            ELSE
               RP = PSQ / (DABS(PSQ1)+DABS(PSQ2))
            END IF
            RP = ABS(RP)
            RPP = RP - 1.0D-12
            IF(RPP,LE,0.0D+0) THEN
               PSQ = 0.0D+0
            END IF
         END DO
      SUMP = SUMP + Z(JP)*Z(KP)*PSQ
51 CONTINUE
P(IU,IV) = (PSV(IU,IV)*SIG2(I)+SUMP)/DELTA

52 CONTINUE
DO 53 IV=2,NP
   IVM = IV - 1
   DO 53 IU = 1,IVM
      P(IU,IV) = P(IU,IV)
53 CONTINUE
IF(IPRINT.GT.0) THEN
  IF(IEQ.1) THEN
    WRITE(7,*)
    WRITE(7,*)'SEQUENTIAL ESTIMATES OF THE PARAMETERS GIVEN BELOW'
    WRITE(7,'(1.I,3X,"I",6X,"ETA",5X,"RESIDUALS",7X,
    1"B(1)",8X,"B(2)",8X,"B(3)",8X,"B(4) ...")')
  END IF
  WRITE(7,'(14,9.2E12.5)')I,ETA,RISD,(B(JC),JC=1,NP)
END IF
100 CONTINUE
C --- END BASIC LOOP, GIVES B(I) AND SY
C --- START BOX-KANEMASU MODIFICATION
C
C START BOX-KANEMASU MODIFICATION
IF(MAX-1)104,104,103
103 SS=SY/2.0D+0
   IF(SS-SYP)104,104,105
105 DO 210 IBS=1,NP
  B(IBS)= BSV(IBS)
210 CONTINUE
   WRITE(IOUT,212)
212 FORMAT(7X,'USE BSV(IBS)')
   GOTO 211
104 CONTINUE
   DO 102 IBS=1,NP
  BSS(IBS)= BS(IBS)
102 CONTINUE
    ALPHA= 2.0D+0
    AA= 1.1D+0
110 ALPHA= ALPHA/2.0D+0
    DO 116 IBS=1,NP
  BS(IBS)= BSS(IBS) + ALPHA*( B(IBS)-BSS(IBS) )
  BSV(IBS)= BS(IBS)
116 CONTINUE
   INDEX=0
   G= 0.0D+0
   DO 115 IP=1,NP
  DELB= BS(IP)-BSS(IP)
  G= G + DELB*CG(IP)
  RATIO= DELB/( BSS(IP)+EPS )
  RATIO= ABS(RATIO)
   IF(RATIO-EPSS)113,113,114

220
113 INDEX= INDEX+1
WRITE('IOUT,314)
314 FORMAT(7X,'MAX',8X,'NP',5X,'INDEX',8X,'IP')
WRITE(7,'(71I0)) MAX,NP,INDEX,IP
114 CONTINUE
WRITE(7,122) I,Y(I),ETA,RISD,Z(IP),XYP,DELB,SIG2(I)
115 CONTINUE
SYP= 0.0D+0
DO 117 I3=1,N
  I=I3
  CALL MODEL
  RISD= Y(I)-ETA
  SYP= SYP + RISD*RISD/SIG2(I)
117 CONTINUE
IF(NP-INDEX)106,106,107
106 H=1.0D+0
GOTO 132
107 CONTINUE
SYN= SYP*0.999D+0
IF(SYN-SY)112,112,111
111 IF(ALPHA-0.01D+0)109,109,110
109 WRITE(7,108) ALPHA,SYP,SY
108 FORMAT(3X,'ALPHA TOO SMALL,ALPHA=',F12.6,2X,'SYP=',E15.6,2X,
  1'SY',E15.6)
WRITE(7,1001)
1001 FORMAT(8X,'Z(1)',10X,'Z(2)',10X,'Z(3)',10X,'Z(4)',10X,'Z(5))
1002 FORMAT(6E13.4)
  DO 1003 I=1,N
  CALL SENS
  WRITE(7,1002) (Z(IBM),IBM=1,NP)
1003 CONTINUE
GOTO 1000
112 CONTINUE
SKSUM= SY - ALPHA*G*( 2.0D+0-1.0D+0/AA )
IF(SYP-SKSUM)131,131,130
130 H= ALPHA * ALPHA*G/( SYP-SY+2.0D+0*ALPHA*G )
GOTO 132
131 CONTINUE
H= ALPHA*AA
132 CONTINUE
DO 118 IBN= 1,NP
  B(IBN)= BSS(IBN) + H * ( B(IBN)-BSS(IBN) )
118 CONTINUE
211   CONTINUE
   WRITE(IOUT,121)
   WRITE(*,121)
121   FORMAT(5X,'MAX',10X,'H',13X,'G',12X,
     1'SY',11X,'SYP')
   WRITE(7,122) MAX,H,G,SY,SYP
   WRITE(*,122) MAX,H,G,SY,SYP
122   FORMAT(18,I1,F13.6,4E14.6)
   WRITE(7,'(10X,'B("I,"="E16.6")') (I,B(I),I=1,NP)
   WRITE(*,'(10X,'B("I,"="E16.6")') (I,B(I),I=1,NP)
C END BOX-KANEMASU MODIFICATION
   WRITE(7,'(/,5X,"P(1,KP)"9X,"P(2,KP)"9X,"P(3,KP)"9X,
     1"P(4,KP)"9X,"P(5,KP)"))')
   DO 206 IP=1,NP
      WRITE(7,207) (P(IP,IP),KP=1,NP)
206   CONTINUE
207   FORMAT(5D15.7)
   WRITE(7,135)
135   FORMAT(5X,'CORRELATION MATRIX')
   DO 136 IR=1,NP
      DO 136 IR2=1,IR
         AR= P(IR,IR) * P(IR2,IR2)
         R(IR,IR2)= P(IR,IR2)/SQR(T(AR))
136   CONTINUE
   DO 137 IR=1,NP
      WRITE(7,'(5E15.7)') (R(IR,III),III=1,IR)
137   CONTINUE
   DO 126 IPS=1,NP
      PS(IPS,IPS)= (1.0E+7) * P(IP,IP)
126   CONTINUE
   WRITE(7,*')XTX(I,K),K=1,NP'
   DO 220 K=1,NP
220   WRITE(7,'(5E15.7)')(XTX(K,III),III=1,NP)
   WRITE(7,*')XTY(I),I=1,NP, WHERE Y IS RESID'
   WRITE(7,'(5E15.7)')XTY(I),I=1,NP)
127   FORMAT(3X,'IPS=',I4,3X,'PS(IPS,IPS)=',D15.8)
   WRITE(7,*')XTY(I),I=1,NP, WHERE Y IS Y, NOT RESID'
   WRITE(7,'(5E15.7)')(SUM(I),I=1,NP)
   DO 119 IP=1,NP
      XTY(IP)=0.0D+0
   DO 119 KP=1,NP
      P(IP,KP)= PS(IP,KP)
      XTY(IP,KP)=0.0D+0
119 CONTINUE
   DO 120 IP=1,NP
      BS(IP)= B(IP)
      CG(IP)= 0.0D+0
120 CONTINUE
   WRITE(7,314)
   WRITE(7,'(1110,4F10.4)') MAX,NP,INDEX,IP
   IF(NP-INDEX)101,101,123
123 CONTINUE
   M=ITMAX
   IF(MAX-M)99,99,101
101 CONTINUE
   IF(IPRINT)133,133,134
133 IPRINT=IPRINT+1
   GOTO 99
134 CONTINUE
C
1000 CONTINUE
   CLOSE(IIN)
   CLOSE(OUT)
   close(11)
C
CECCCCCCCC ERROR MESSAGES       BLOCK 0900
C
CFCCCCCCC FORMAT STATEMENTS       BLOCK 9000
C
STOP
END
SUBROUTINE MODEL
C  THIS SUBROUTINE IS FOR CALCULATING ETA, THE MODEL VALUE
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION T(300,5),Y(300),SIG2(300),B(100),Z(100),
+A(100),BS(100),VINV(5,5),EXTRA(20)
DIMENSION P(100,100),PS(100,100),SUM(100)
dimension ttk(10),ttc(10)
COMMON T,N,Z,BS,I,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP,EXTRA
COMMON N,I,MODL,NP,T,Z,BS,ETA,PS,P,B,A,Y,SIG2,VINV,EXTRA
COMMON/MODL/AA,TL,SUM

EXTERNAL CT,TK

C WRITTEN BY JAMES V. BECK

PI=4.0D+0*DATAN(1.0D+0)
IF(MDL .EQ.2) GOTO 100
IF(MDL .EQ.3) GOTO 300
IF(MDL .EQ.4) GOTO 400
IF(MDL .EQ.5) GOTO 500
IF(MDL .EQ.6) GOTO 600
IF(MDL .EQ.7) GOTO 700
IF(MDL .EQ.8) GOTO 800
IF(MDL .EQ.9) GOTO 900
AL=0.03

C EXTRA(2)=Q=HEAT FLUX

C EXTRA(3)=T AT X = L

QZ=EXTRA(2)
TL=EXTRA(3)
XDL=T(I,1)
THCOND=BS(1)
AA=BS(2)
ARG=TL+0.5*TL*TL*AA+QZ*AL*(1.0-XDL)/THCOND
ETA=(-1.0+SQRT(1.0+2.0*AA*ARG))/AA

C WRITE(*,*)'MODEL I ETA,I,ETA

GOTO 200

100 CONTINUE

C MODEL 2, FOR CHEMICAL REACTION

200 CONTINUE

C AA1=10.6=BS(1)

C AA2=9.1=BS(3)

A1=EXP(BS(1))
A2=EXP(BS(3))
E1=BS(2)
E2=BS(4)

C UNITS OF E'S ARE kJ/MOLE

R=8.31434D-3

C R IS GAS CONSTANT

TEMP=273.15D+0+T(I,2)

BET1=A1*EXP(-E1/(R*TEMP))

BET2=A2*EXP(-E2/(R*TEMP))

C T(I,1) IS TIME

224
C T(I,2) IS TEMPERATURE
  EXX=EXP(-T(I,1)*(BET1+BET2))
  ETA=BET1*(1.0D+0-EXX)/(BET2*EXX+BET1)
  GOTO 1000

300 CONTINUE
C MODEL 3
C TZ=81.55
C T(I,1) IS TIME
C T(I,2) IS X
  ETA=TZ+BS(1)*T(I,1)+BS(2)*((1.0D+0/3.0D+0)-T(I,2)+.5D+0*T(I,2))
  I*T(I,2))
  GOTO 1000
C BELOW FOR PROB. 6.18, 1993, POWER EXPRESSION
400 IF(NP, EQ, 3) ETA=BS(1)+BS(2)*T(I,1)+BS(3)*T(I,1)*T(I,1)
    IF(NP, EQ, 2) ETA=BS(1)+BS(2)*T(I,1)
    IF(NP, EQ, 1) ETA=BS(1)
    GOTO 1000

500 CONTINUE
C MODEL 5: FOR TRANSIENT HEAT CONDUCTION, TABLE 7.14
  TZ= Y(1)
  Q0=30300.0D+0
  AL=0.0254D+0
  BB1=Q0*AL/BS(1)
  BB2=BS(2)*T(I,1)/(AL*AL)
  SUMM=BB2+(1.0D+0/3.0D+0)-T(I,2)+.5D+0*T(I,2)*T(I,2)
  I=1
549 ARG=III*IIB2*PI*PI
    IF( ARG .GT. 16.0D+0) GOTO 550
    SUMM=SUMM-(2.0D+0/(PI*PI))*COS(III*PI*T(I,2))/(III*III*EXP(ARG))
  III=III+1
    IF(III .GT. 50) GOTO 550
    GOTO 549

550 CONTINUE
    EXTRA(1)=-Q0*AL*SUMM/(BS(1)*BS(1))
    ETA=TZ+BB1*SUMM
    GOTO 1000

600 CONTINUE
C PROBLEM 6.14 TEXT
  ETA=BS(1)+BS(2)*SIN(2.0*PI*T(I,1))
  GOTO 1000

700 CONTINUE
  ETA=100.0 +100.0/EXP(BS(1)*T(I,1))
  GOTO 1000

225
CONTINUE
MODEL 8: FLASH DIFFUSIVITY TESTS
BETA 1 = STRENGTH OF LASER
BETA 2 = ALPHA
MODEL 5: FOR TRANSIENT HEAT CONDUCTION, TABLE 7.14
TZ= EXTRA(1)

AL= EXTRA(2)
BB2=BS(2)*T(I,1)/(AL*AL)
SUMM=0.0D+0
IF(BB2 .LT. 0.01) GOTO 850
SUMM=1.0D+0
III=1

ARG=III*PI*BB2*PI
IF( ARG .GT. 16.0D+0) GOTO 850
SUMM=SUMM+2.0D+0*COS(III*PI)/EXP(ARG)
III=III+1
IF(III .GT. 50) GOTO 850
GOTO 849

CONTINUE
ETA=TZ+BS(1)*SUMM
Z(1)=SUMM
GOTO 1000

MODEL 9 is for freezing of a slab shaped food solution
with heat flux bc at x=0 and temperature bc at x=1 (w/m^2)
T(i,1) is time (second)
T(i,2) is location x (m)
t0 initial temperature of the slab (K)
 thick is the thickness of the slab (m)

CONTINUE

thick=0.02d0

call tmp(t0,t(i,1),t(i,2),thick,eta)
goto 1000

CONTINUE
RETURN
END
SUBROUTINE SENS
C THIS SUBROUTINE IS FOR CALCULATING THE SENSITIVITY
COEFFICIENTS
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION T(300,5),Y(300),SIG2(300),B(100),
   +Z(100),A(100),BS(100),VINV(5,5),EXTRA(20)
DIMENSION P(100,100),PS(100,100),SUM(100)
C COMMON T,N,Z,BS,J,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NS,EXTRA
COMMON N,J,MODL,NP,T,Z,BS,ETA,PS,P,B,A,Y,SIG2,VINV,EXTRA
COMMON/MOD/A,A,TL,SUM
PI=4.0D+0*DATAN(1.0D+0)
C
IF (I.GT.1)GOTO 313
DO 312, IPP=1,NP
312 SUM(IPP)=0.0D+0
313 CONTINUE
TZ=0.0
IF(MODL.EQ.2)GOTO 100
IF(MODL.EQ.3)GOTO 300
IF(MODL.EQ.4)GOTO 400
IF(MODL.EQ.5)GOTO 500
IF(MODL.EQ.6)GOTO 600
IF(MODL.EQ.7)GOTO 700
IF(MODL.EQ.8)GOTO 800
IF(modl.eq.9) goto 900
CALL MODEL
DENOM=1.0D+0+AA*ETA
Z(1)=-(ETA-TL)*(1.0+0.5*AA*(ETA+TL))/(DENOM*BS(1))
Z(2)=-(ETA**2-TL**2)*0.5/DENOM
C WRITE(7,*)I,ETA,Z(1),Z(2),I,ETA,Z(1),Z(2)
C
GOTO 200
100 CONTINUE
CALL MODEL
DELTA=1.000001D+0
DO 150 JJ=1,NP
BS(JJ)=BS(JJ)*DELTA
A1=EXP(BS(1))
A2=EXP(BS(3))
E1=BS(2)
E2=BS(4)
R=8.31434D-3
TEMP=273.15D+0+T(I,2)
BET1=A1*EXP(-E1/(R*TEMP))
BET2=A2*EXP(-E2/(R*TEMP))
EXX=EXP(-T(I,1)*(BET1+BET2))
ET=BET1*(1.0D+0-EXX)/(BET2*EXX+BET1)
BS(JJ)=BS(JJ)/DELTA
Z(JJ)=(ET-ETA)/((DELTA-1.0D+0)*BS(JJ))

150 CONTINUE
200 CONTINUE
GOTO 1000
C BEGIN MODEL 3, HEAT CONDUCTION, LINEAR CASE
300 CONTINUE
TZ=81.55
Z(1)=T(I,1)
Z(2)=(1.0D+0/3.0D+0)-T(I,2)+.5D+0*T(I,1)*T(I,2)
GOTO 1000
400 CONTINUE
Z(1)=1.0D+0
Z(2)=T(I,1)
Z(3)=T(I,1)*T(I,1)
GOTO 1000
C BELOW FOR MODEL 5
500 CONTINUE
Z(1)=EXTRA(1)
TZ= Y(1)
Q0=30300.0D+0
AL=0.0254D+0
BB1=Q0*AL/BS1
BB2=BS(2)*T(I,1)/(AL*AL)
SUMM=BB2/BS(2)
III=1
549 ARG=III*III*BB2*PI*PI
IF( ARG GT. 16.0D+0) GOTO 550
SUMM=SUMM +2.0D+0*COS(III*PI*T(I,2))*T(I,1)
1/(AL*AL*EXP(ARG))
III=III+1
IF(III .GT. 50) GOTO 550
GOTO 549
550 CONTINUE
Z(2)=SUMM*BB1
GOTO 1000
600 CONTINUE
Z(1)=1.0
Z(2)=SIN(2.0*PI*T(I,1))

228
GOTO 1000
700 CONTINUE
Z(1)=-100.0*T(I,1)/EXP(BS(1)*T(I,1))
GOTO 1000
800 CONTINUE
C FILL IN THE SENSITIVITY COEFFICIENT FOR ALPHA HERE
ccc
model 9 is for freezing of a slab shaped food solution
ccc
with heat flux bc at x=0 and temperature bc at x=1 (w/m^2)
ccc
T(i,1) is time (second)
ccc
T(i,2) is location x (m)
ccc
t0 initial temperature of the slab (K)
ccc
thick is the thickness of the slab (m)
ccc
z(i) is the sensitivity coefficient of parameter i (BS(i))
ccc
900 continue
ccc
delta=1.00001d0
ccc
t0=y(1)
ccc
write(*,*) i, bs(1),bs(2)
ccc
thick=0.02d0
ccc
do jj=1,np
ccc
bs(jj)=bs(jj)*delta
ccc
call tmp(t0,t(i,1),t(i,2),thick,et)
ccc
bs(jj)=bs(jj)/delta
ccc
z(jj)=(et-eta)/((delta-1.0d0)*bs(jj))
ccc
donendd
ccc
write(11,'(8e15.7)') (z(jj),jj=1,np)
ccc
GOTO 1000
ccc
1000 CONTINUE
ccc
C IF(I .LT. N)GOTO 2000
ccc
DO 1001 JPP=1,NP
ccc
1001 SUM(JPP)=SUM(JPP)+Z(JPP)*(Y(I)-TZ)/SIG2(I)
ccc
2000 CONTINUE
ccc
RETURN
ccc
END
ccc
BLOCK DATA CONST
ccc
implicit double precision (a-h,o-z)
ccc
dimension tk(10),ttc(10),cfp(12)
ccc
common /intervals/ nik,nic,tk,ttc
ccc
common /polyn/ cfp,npl
The following values are defined in this block data:

data nic, ttc
& /1.00d0,-0.50d0,-1.0d0,-1.5d0,-2.0d0,-3.0d0,-5.0d0,
& -10.0d0,-20.0d0,-30.0d0/
data nik, ttk
& /1.00d0,-0.5d0,-1.0d0,-1.5d0,-2.0d0,-3.0d0,
& -5.0d0,-10.0d0,-20.0d0,-30.0d0/
data npl, cfp /12, 22.1413822d0,-6.602498d-3,3.466666d-6,
& -5.677883e-9
& ,3.154852d-12,-8.641076d-16,1.3621d-19,-1.300902d-23,
& 7.456489d-28,-2.364877d-32,3.194631d-37,0.0d0/

END

Double precision function tk(x)

This subroutine will calculate the thermal properties
(k, C) given the temperature using the parameters
ni: # of temperature intervals used
nt: the boundaries of the temperature intervals
kp : thermal conductivity before freezing
kf : thermal conductivity after freezing

implicit double precision (a-h,o-z)
DIMENSION T(300,5),Y(300),SIG2(300),B(100),Z(100),
+A(100),BS(100),VINV(5,5),EXTRA(20)
DIMENSION P(100,100),PS(100,100)
dimension ttk(10),ttc(10)
C COMMON T,N,Z,BS,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP,EXTRA
COMMON N,I,MODL,NP,T,Z,BS,ETA,PS,P,B,A,Y,SIG2,VINV,EXTRA
common /intervals/ nik,nic,ttk,ttc
c Find the interval to which the temperature belong to
go to 1000
if(x.gt.ttk(1)) then
c    tk=bs(1)
tk=0.50d0
go to 1000
else if(x.le.ttk(nik)) then
c    write(*,*),x,'ha'

230
tk=bs(nik)
go to 1000
else
do ii=1,nik-1
   if(x.lt.ttk(ii).and.x.ge.ttk(ii+1)) then
      tk=bs(ii)-(bs(ii)-bs(ii+1))*(ttk(ii)-x)/
      & (ttk(ii)-ttk(ii+1))
c      write(*,*) '2'
go to 1000
endif
enddo
write(*,*) "no case in k ",x
stop
endif
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
1000 continue
c   tk=.50d0
   tk=bs(1)
   return
end
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc

Double precision function ct(x)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
   This subroutine will calculate the thermal properties
c   (k, C) given the temperature using the parameters
c   ni: # of temperature intervals used
c   tt: the boundaries of the temperature intervals
c   kp and cp : Volumetric specific before freezing
c   kf cf : Volumetric specific after freezing
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
   implicit double precision (a-h,o-z)
   DIMENSION T(300,5),Y(300),SIG2(300),B(100),Z(100),
    +A(100),BS(100),VINV(5,5),EXTRA(20)
   DIMENSION P(100,100),PS(100,100)
   dimension ttc(10),ttk(10)
   COMMON T,N,Z,BS,I,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP,EXTRA
   COMMON N,LMODL,NP,T,Z,BS,ETA,PS,P,B,A,Y,SIG2,VINV,EXTRA
   common /intervals/ nik,nic,ttk,ttc
   C Find the interval to which the temperature belong to
go to 1000
write(*,*) ttc(nic), nik, bs(nik+nic+2)
if(x.gt.ttc(i)) then
c   ct=bs(nik+2)
c   ct=5.0d0
go to 1000
elseif(x.le.ttc(nic)) then
c   ct=bs(2)
go to 1000
else
do ii=1,nic
   iic=nik+ii+1
   if(x.lt.ttc(ii).and.x.ge.ttc(ii+1)) then
      ct=bs(iic)-(bs(iic)-bs(iic+1))
   endif
enddo
write(*,*) "no case in c ",x
stop
endif
continue
ct=bs(2)
ct=ct*1.0d6
return
end

double precision function qq(t)
implicit double precision (a-h,o-z)
c
dtq: time interval with the heat flux on
c
dnq: time interval with the heat flux off
c
dqm: magnitude of the heat flux
c
d: time

qm=645.834620d0
dtq=180.0d0
dnq=360.0d0
dtp=dtq+dnq
n=int(t/dtp)
if(t-dtp*n.le.dtq) then
  qq=qm
elseif(t-dtp*n.gt.dtq) then
  qq=0.0d0
endif
return
end

double precision function tb (time)
implicit double precision (a-h,o-z)
dimension cfp(12)
common /poly/ cfp,npl
 tb=273.150d0
do ii=1, npl+1
 tb=tb+cfp(ii)*time**(ii-1)
endo
do
return
end

subroutine tmp(t0,ttime,x,thick,eta)
	parameter(maxm=101,maxp=20,maxd=101,maxc=51,maxs=201)

The integer variables appearing in this subroutine are:
M - Total number of nodes minus one
MP1 - Total number of nodes

The real variables appearing in this subroutine are:
A - Array containing coefficients for temperature at (m-1)th node
B - Array containing coefficients for temperature at mth node
C - Array containing coefficients for temperature at (m+1)th node
CK - Array for thermal conductivity values associated with all the nodes at a given time step (from PFIND)
c CP    - Food specific heat (>0C) (J/kgK)
c CSD   - Array for density-specific heat values associated with all the
         nodes at a given time step (from PFIND)
c D    - Array containing boundary conditions and previous temperatures
         at previous time step
c time step
 c DA   - Term containing temperature at node m-1 and at time n-1
 c DB   - Term containing temperature at node m and at time n-1
 c DC   - Term containing temperature at node m+1 and at time n-1
 c DDD  - Term containing boundary conditions
c DT   - Time step
 c DZ   - Spatial increment for finite difference calculations
 c DZZ  - 1/DZ
 c KP   - Food thermal conductivity (>0C) (W/mK)
c L    - Dimension in the direction of heat transfer (thickness or radius)
c PI   - Pi defined as: DACOS(-1.0d0)
c T    - Finite difference temperature solution

implicit double precision (a-h,o-z)

dimension a(maxm),b(maxm),c(maxm),d(maxm),t1(maxm),
 & cc(maxm),dd(maxm),t2(maxm),t3(maxm)
 external ct,tk,qq

c----------------------------------------------------------------------------------
thick=0.02d0

c number of nodes = number of intervals + 1

c grid size
  m=10
  mp1=m+1
  dz=thick/m
  dzz=1.0d0/dz
  if(x.ne.0) then
    write(*,*) 'location x is not equal to zero!!!!!!'
    stop
  endif

c number of time steps
  dt=20.0d0
  nt=time/dt
  write(*,*) 'time=',time,nt
time=0.0d0

c set the initial temperature
  do il=1,mp1
\begin{verbatim}
t1(ii)=t0
t2(ii)=t0
t3(ii)=t0
eend

do ii=1,nt
  write(*,*) 'time=',time
time=time+dt
  icnt=1
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dumtl = 0.75d0*t1(i)+0.25d0*t1(i+1)
dumt2 = 0.75d0*t3(i)+0.25d0*t3(i+1)
dumt3 = 0.75d0*t1(i)+0.25d0*t1(i-1)
dumt4 = 0.75d0*t3(i)+0.25d0*t3(i-1)
ct = 0.25d0*(ct(dumtl)+ct(dumt2)+ct(dumt3)+ct(dumt4))
db = ctt*dx(2*dt)-da-dc
b(i) = ctt*dx(2*dt)-a(i)-c(i)
ccccceccccccccccccccccccccccccccccccccccccccccccccc

d(i) = da*t1(i-1)+db*t1(i)+dc*t1(i+1)
c write(*,*) a(i), b(i), c(i), d(i)
20 continue

c *******************************************************
c 2nd boundary point
a(mp1) = 0.0d0
b(mp1) = 1.0d0
c(mp1) = 0.0d0
da = 0.0d0
db = 0.0d0
dc = 0.0d0

ddd = tb(time)
d(mp1) = ddd
c write(*,*) a(mp1), b(mp1), c(mp1), d(mp1)
c

c use thomas algorithm to solve the temperature

c(1) = c(1)/b(1)
dd(1) = d(1)/b(1)
do k = 2, mp1
   kk = k - 1
   cc(k) = c(k)/(b(k) - a(k)*cc(kk))
   dd(k) = (d(k) - a(k)*dd(kk))/(b(k) - a(k)*cc(kk))
endo
t2(mp1) = dd(mp1)
do k = 2, mp1
   kk = m - k + 2
   t2(kk) = dd(kk) - cc(kk)*t2(kk+1)
err = err + (t2(kk) - t3(kk))**2
do k = 2, mp1
   err = err/mp1

c iteration criteria
do i=1, mp1
t3(i)=t2(i)
enddo
if(icnt.gt.20) go to 222
if(err.ge.1.0d-6.or.icnt.eq.1) then
err=0.d0
icnt=icnt+1
go to 111
endif

222 continue

do i=1,mp1
t1(i)=t2(i)
enddo

78 continue

c write(11,55) time, t2(1),t2(2),t2(6)
c55 format(2x,f10.2,3x,f10.4,3x,f10.4,3x,f10.4)
enddo
c stop
c do iii=1,1001
c tt=-10-0.2d0*(iii-1)
c time=10.0d0*(iii-1)
c write(11,*) time,qq(time)
c write(11,55) tt, tk(tt),ct(tt)
c55 format(2x,f10.2,3x,f10.4,3x,f20.4)
c enddo
c stop
c eta=t2(1)
c write(*,*) 'time ',time, 'eta ',eta,'qq ',qq(time),tb(time)
return
d
### B.2 Sample Input File

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Such that,

Row 1 includes the number of data points, the number of parameters to be estimated, the number of independent variables, the maximum number of iterations, the model number, and the printout mode, respectively.

Row 2 and 3 include the initial guesses for the parameters, which in this case are the thermal conductivity and the apparent volumetric specific heat, to be estimated.

Column 1 includes the index number of each data point, Column 2 includes the temperature measurements, Column 3 includes the standard deviation of the measurement errors, Column 4 is the first independent variable which is time, Column 5 is the second independent variable which is the location on the slab. At the end of the columns, the number of the extra parameters and the parameters are included (in this case, there are no extra parameters).
APPENDIX C

ACCURACY ANALYSIS PROGRAM

This program is a modification of the "FREEZE" program. The modified subroutines and added functions are listed Table C.1. Also, a listing of these subroutines and functions is presented in Section C.1.

Table C.1 Subroutines Added for the Accuracy Analysis

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<tr>
<th>Subroutine Title</th>
<th>Description</th>
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<tbody>
<tr>
<td>Function EXT(x,t)</td>
<td>Determines the exact solution as a function of time, t, and location, x. This function was added to FREEZE.FOR program for the accuracy analysis.</td>
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<tr>
<td>Function DEXT(x,t)</td>
<td>Determines the derivative of the exact solution with respect to the location, x. This function was added to FREEZE.FOR program for the accuracy analysis.</td>
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<tr>
<td>Subroutine COEFF</td>
<td>Calculates coefficient matrix of the finite difference algorithm. This subroutine was modified for the accuracy analysis.</td>
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C.1 Modified Subroutines and Functions (by Zoubir Saad, 1994)

double precision function ext(x,tm)
double precision x,tm,al,pi
pi = dacos(-1.0d0)
al=5.0d-4
ext=25.0d0*sin(12.50d0*pi*x+pi*0.43750d0)
& *exp(-tm*al)+253.150d0
return
end

double precision function dext(x,tm)
double precision x,tm,al,pi
pi = dacos(-1.0d0)
al=5.0d-4
dext=25.0d0*12.50d0*pi*cos(12.50d0*pi*x+pi*0.43750d0)*exp(-tm*al)
return
end

subroutine coeff(ii,hh,qq,tt,ta,ta,b,c,d,dt,bct,icnt)

c The coefficients of the temperature array associated with the finite
c difference solution are determined in this subroutine. Coefficients
c are calculated using a Crank Nicolson approximation for the time
c derivative.

parameter(maxm=201,maxp=20,maxd=201,maxc=51,maxs=201)

c The integer variables appearing in this subroutine are:

c M - Total number of nodes minus one
c MP1 - Total number of nodes
c NCOUNT- Number of printouts per storage period
c NSC - Total number of constant thermal conductivity values used in
c approximating thermal conductivity equations as F(temperature)
c NSD - Total number of constant density values used in approximating
c density equations as F(temperature)
c NSS - Total number of constant specific heat values used in
c SSTEP - Step size for printing out temperatures at spatial nodes
c SYM = 0 if unsymmetric

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\[ c = 1 \text{ if symmetric} \]

The real variables appearing in this subroutine are:

- Array containing coefficients for temperature at \((m-1)\)th node
- Geometry area factor
- Array containing areas at node \(m\)
- Array containing areas at node \(m+1/2\)
- Area where density-specific heat on the left side of the finite difference node is evaluated
- Area where density-specific heat on the right side of the finite difference node is evaluated
- Average specific heat (<0°C) \((J/kgK)\)
- Average density (<0°C) \((kg/m^3)\)
- Average thermal conductivity (<0°C) \((W/mK)\)
- Array containing coefficients for temperature at \(m\)th node
- Weighting coefficient for finite difference solution \((=1/2)\)
- Array containing coefficients for temperature at \((m+1)\)th node
- Array for thermal conductivity values associated with all the nodes at a given time step (from PFIND)
- Contains approximations of CONDUC used in finite difference calculations
- Contains temperature ranges for constant thermal conductivity approximations (CONDRC) used in finite difference calculations
- Food specific heat (>0°C) \((J/kgK)\)
- Array for density-specific heat values associated with all the nodes at a given time step (from PFIND)
- Array containing boundary conditions and previous temperatures at previous time step
- Term containing temperature at node \(m-1\) and at time \(n-1\)
- Term containing temperature at node \(m\) and at time \(n-1\)
- Term containing temperature at node \(m+1\) and at time \(n-1\)
- Term containing boundary conditions
- Contains approximations of DENS used in finite difference calculations
- Contains temperature ranges for constant density approximations (DENSC) used in finite difference calculations
- Food density (>0°C) \((kg/m^3)\)
- Food solids density \((kg/m^3)\)

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c Declare variables not in common blocks.

    integer ii,EEND,iext
    double precision a(maxm),aar,ar(maxm),arl(maxm),avg1,
    & avg2,b(maxm),beta,c(maxm),ck(maxm,2),csd1(maxm,2),
    & csd2(maxm,2),d(maxm),da,db,
    & dc,ddd,dt,dzz,gama,hh(2,2),qq(2,2),tt(2,2),
    & nu,omega,pi,ta(2),tt(maxm,3),junk
    &,ext,dext,dens,conduc,spheat,etp,detp,xx,time,dkdt
    &,sph,dsn,nd,dt,dii,dsphh,ddns,sphh,dsnss

c Declare variables in common blocks.

    integer shape,sym,m,mp1,sstep,
    & nsd,nsc,nss,bct(maxp,2),per,ncount(maxp)
double precision DENST(maxd),DENSC(maxd),CONDT(maxc),
& CONDC(maxc),SPHT(maxs),SPHC(maxs),
& ds,
& l,dz,
& tl,th,avgd,avgk,avgc,ynavg,
& wf0,ms,dp,kp,cp,t0,
& ti,temp(maxp),stor(maxp),h(maxp,2),
& tunit(maxp),q(maxp,2),tb(maxp,2),junk1,ckk,csdd,ttl

c Declare common blocks:

common/bound/per,ti,temp,stor,h,tunit,ncoant,q,th,
& /CONSTEP/DENST,DENSC,CONDT,CONDC,SPHT,SPHC,
& /d/ds,
& /geom/shape,l,dz,sym,m,mpi,sstep,
& /NCONSTEP/NSD,NSC,NSS,
& /pavg/th,tl,avgd,avgk,avgc,ynavg,
& /prop/wf0,ms,dp,kp,cp,t0

external dkdt,condc,spheat,dens,ext,dext,dsph,ddns

c ----------------------------------------

pi = dacos(-1.0d0)
c weighting functions for finite difference method

 c modified crank-nicolson method

 c weight. coeff. for d2t/dz2
 c for time t:
   beta=0.50d0
 c for time t+1:
   nu=0.50d0

 c weight. coeff. for dt/dt
 c for time t:
   omega=-1.0d0
 c for time t+1:
   gama=1.0d0

dzz=1.0d0/dz

CALL PFIND(T,M,CK,CSD2,DT,DZ)
if(icnt.eq.1) then
  time =time+dt

244
do i=1,m
  ck(i,1)=ck(i,2)
  csd1(i,1)=csd2(i,1)
  csd1(i,2)=csd2(i,2)
enddo
endif

1st boundary point
if(bct(i,1).eq.1) then
  AVG1 = (AR(1)+AR1(1))*0.50d0
  a(1)=0.0d0
  c(1)=nu*dzz*CK(1,2)*ar1(1)
  dc=-beta*dzz*CK(1,1)*ar1(1)
  b(1)=gama*CSD2(1,1)*avg1-nu*hh(2,1)*ar(1)-c(1)
  db=omega*CSD1(1,1)*avg1+beta*hh(1,1)*ar(1)-dc
  ddd=-beta*(ta(1)*hh(1,1)*ar(1)+qq(1,1))-
   & nu*(ta(2)*hh(2,1)*ar(1)+qq(2,1))
  d(1)=db*t(1,1)+dc*t(2,1)+ddd
else
  a(1)=0.0d0
  b(1)=1.0d0
  c(1)=0.0d0
  db=0.0d0
  dc=0.0d0
  ddd=ext(0.0d0,time)
  d(1)=ddd
endif

interior points
do 20 i=2,m
  AVG1 = (AR(i)+AR1(i))*0.50d0
  AVG2 = (AR(i)+AR1(i-1))*0.50d0
  a(i)=nu*dzz*CK(i-1,2)*ar1(i-1)
  c(i)=nu*dzz*(CK(i-1,2)+ck(i-1,1))*ar1(i-1)/2
  c(i)=nu*dzz*CK(i,2)*ar1(i)
  c(i)=nu*dzz*(CK(i,2)+ck(i,1))*ar1(i)/2
  da=-beta*dzz*CK(i-1,1)*ar1(i-1)
  dc=-beta*dzz*(CK(i-1,1)+ck(i-1,2))*ar1(i-1)/2
  dc=-beta*dzz*CK(i,1)*ar1(i)
  dc=-beta*dzz*(CK(i,1)+ck(i,2))*ar1(i)/2
245
\[ db = \omega_1 \cdot (CSD1(I,1) \cdot \text{avg2} + CSD1(I,2) \cdot \text{avg1}) - \text{da} - \text{dc} \]

\[ c \]

\[ db = \omega_1 \cdot (CSD1(I,1) \cdot \text{avg2} + CSD1(I,2) \cdot \text{avg1} + CSD2(I,1) \cdot \text{avg2}) \]

\[ c & \quad + \frac{CSD2(I,2) \cdot \text{avg1}}{2} - \text{da} - \text{dc} \]

\[ b(i) = \gamma \cdot (CSD2(I,1) \cdot \text{avg2} + CSD2(I,2) \cdot \text{avg1}) - a(i) - c(i) \]

\[ c \]

\[ b(i) = \gamma \cdot (CSD1(I,1) \cdot \text{avg2} + CSD1(I,2) \cdot \text{avg1} + CSD2(I,1) \cdot \text{avg2}) \]

\[ c & \quad + \frac{CSD2(I,2) \cdot \text{avg1}}{2} - a(i) - c(i) \]

\[ xx = dz \cdot (i-1) \]

\[ etp = \text{ext}(xx, \text{time}) \]

\[ \text{if (etp.ge.d0) then} \]

\[ \text{cnd} = kp \]

\[ \text{sph} = cp \]

\[ \text{dns} = dp \]

\[ \text{dkt} = 0.0d0 \]

\[ \text{else} \]

\[ \text{cnd} = \text{condc(etp)} \]

\[ \text{sph} = \text{sheat(etp)} \]

\[ \text{dns} = \text{dens(etp)} \]

\[ \text{dkt} = \text{dkdt(etp)} \]

\[ \text{ENDIF} \]

\[ \text{ccccccccccccccccccccccccccccccccccc} \]

\[ \text{c two step method change} \]

\[ \text{C IF(T(1,1).LT.T0) THEN} \]

\[ \text{C sphh = sheat(t(i,1))} \]

\[ \text{C dnnss = dens(t(i,1))} \]

\[ \text{C ttt = t(i,1) + (ck(i-1,1) \cdot t(i-1,1) - (ck(i,1,1) + ck(i-1,1)) \cdot t(i,1))} \]

\[ \text{C & +ck(i,1) \cdot t(i+1,1)) \cdot dt/(2.0d3 * sphh * dnnss \cdot dz * * 2)} \]

\[ \text{C nnot} \]

\[ \text{ttt = t(i,1) + ck(i,1) \cdot (t(i-1,1) - 2 \cdot t(i,1) + t(i+1,1))/} \]

\[ \text{C nnot & (2 * (csdd1(i,1) + csdd1(i,2)) \cdot dz)} \]

\[ \text{C if(ttt.lt.t0) then} \]

\[ \text{C ckk = condc(ttt)} \]

\[ \text{C csdd = sheat(ttt) \cdot dnnss(ttt) \cdot 1.0d3 \cdot dz/(2 \cdot dt)} \]

\[ \text{C else} \]

\[ \text{C ckk = kp} \]

\[ \text{C csdd = cp * dp \cdot 1.0d3 \cdot dz/(2 \cdot dt)} \]

\[ \text{C endif} \]

\[ \text{C} \]

\[ b(i) = \gamma \cdot (csdd \cdot \text{avg2} + csdd \cdot \text{avg1}) - a(i) - c(i) \]

\[ \text{C db = \omega_1 \cdot (csdd \cdot \text{avg2} + csdd \cdot \text{avg1}) - da - dc} \]

\[ \text{C ENDIF} \]

\[ \text{cccccceccccccccccccccccccccccccccccccccccce} \]

\[ \text{c detp = dext(xx, time)} \]

\[ \text{d(i) = da \cdot t(i-1,1) + db \cdot t(i,1) + dc \cdot t(i+1,1) } \]

246
d(i)=d(i)+dT*dTe*p**2*ar(i)*dz

d(i)=d(i)+(sp*dn*s*5.0d-1)*(etp-253.150d0)*ar(i)*dz

d(i)=d(i)-(cnd*(pi*12.50d0)**2.0d0)*(etp-253.150d0)*ar(i)*dz

c write(*,*) a(i),b(i),c(i),d(i)

20 continue

c ************************************************
c 2nd boundary point

c if(bct(ii,2.eq.1) then

    AVG2 = (AR(mp1)+AR1(M))*0.50d0

    c(mp1)=0.0d0

    a(mp1)=nu*dzz*CK(M,2)*ar1(m)

    da=-beta*dzz*CK(M,1)*ar1(m)

    b(mp1)=-gamma*CSD2(mp1,2)*avg2-nu*hh(2,2)*ar(mp1)-a(mp1)

    db=omega*CSD1(mp1,2)*avg2+beta*hh(1,2)*ar(mp1)-da

    ddd=-beta*(hh(1,2)*ta(1)*ar(mp1)+qq(1,2))-

         + nu*(ta(2)*hh(2,2)*ar(mp1)+qq(2,2))

    d(mp1)=da*t(m,1)+db*t(mp1,1)+ddd

c else

    a(mp1)=0.0d0

    b(mp1)=1.0d0

    c(mp1)=0.0d0

    da=0.0d0

    db=0.0d0

    dc=0.0d0

    ddd=ext(0.010d0,time)

    d(mp1)=ddd

c endif

return

c *********************
APPENDIX D

DATA ACQUISITION PROGRAM

This section will include the data acquisition program used to perform the temperature measurements of the one-dimensional freezing experiments and the control of the heat flux on the boundary. This program was used with the LabWindows data acquisition software from National Instruments. For more information about the various function in this program, see LabWindows manuals.

D.1 "DAQ.LW" Program (by Zoubeir Saad, 1994)

/* Written by Zoubeir Saad
This program was written in C (LabWindows) to configure and execute voltage measurements from 4 channels (channel 0, 1, 2, and 3) of the SCXI 1000 national instruments. It also controls the power output from the HP6024A.*/
static int setup;
static double vt_array[4];
static int hb_array[4];
static int data_buf[8];
static int mio_gain[1];
static int mio_chans[1];
static int strt_chan[1];
static int num_chans[1];
static int mdl_list[1];
static int hb_status;
static int ptr;
static int daq_status;
static int hb_ready;
static int i;
int stscan,mux,db,start,conf,fhand,err,nn,nnn,vout,counter,ii,err1,err2;
int clibr,single,offvlt,disable,sgain,measerr,scale;
double vtout,offset,dlay,t1;
main()
{mdl_list[0] = 2;
num_chans[0] = 4;
strt_chan[0] = 0;
mio_chans[0] = 0;
mio_gain[0] = 10;
dlay=5.0;
counter=0;
vtout=0.0;

/* Open Data File */
fnhand = OpenFile ("data.out", 0, 0, 1);
FmtOut ("fnhand = %i\n", fnhand);

/* Load SCXI Configuration */
conf = SCXI_Load_Config (1);
FmtOut ("conf = %i\n", conf);

/* Set SCXI Gain */
sgain = SCXI_Set_Module_Gain (1, 2, 1);
FmtOut ("sgain = %i\n", sgain);

/* Determine the Offset Voltage
-----------------------------------------------*/
clibr = SCXI_Calibrate_Setup (1, 2, 1);
FmtOut ("clibr = %i\n", clibr);

single = SCXI_Single_Chain_Setup (1, 2, 0, 1);
FmtOut ("single = %i\n", single);

offvlt = AI_VRead (1, 0, 10, &offset);
FmtOut ("offvlt = %i\n", offvlt);
FmtOut ("offset = %f\n", offset);

disable = SCXI_Calibrate_Setup (1, 2, 0);
FmtOut ("disable = %i\n", disable);
/*-----------------------------------------------*/

/* Setup SCXI for Scanning */
stscan=SCXI_SCAN_Setup (1, 1, mdl_list, num_chans, strt_chan, 1, 0);
FmtOut ("stscan= %i\n", stscan);

/* Set SCXI Mux Counter */
mux=SCXI_MuxCtr_Setup (1, 1, 0, 4);
FmtOut ("mux = %i\n", mux);
/* Set MIO Board for Scanning */
setp=SCAN_Setup (1, 1, mio_chans, mio_gain);
FmtOut ("setp = %i\n",setp);

/* Configure MIO Board for Double Buffering */
db=DAQ_DB_Config (1, 1);
FmtOut ("db = %i\n",db);

/* Start Scanning */
start=SCAN_Start (1, data_buf, 8,3,2,5,5);
FmtOut ("start = %i\n",start);

for (i = 0; i < 10000000; i++){

/* Check if Half Buffer is Ready */
err1 = DAQ_DB_HalfReady (1,&hb_ready,&daq_status);
/*FmtOut ("err1 = %i\n",err1);*/

if (hb_ready == 1 )
{nn=nn+1;
 /*FmtOut ("%i\n",hb_ready);*/
 /* Transfer Data from Buffer to Array */
err2 = DAQ_DB_Transfer (1,hb_array,&pttr,&hb_status);
/*FmtOut ("err2 = %i\n",err2);*/
/*FmtOut ("pttr = %i\n",pttr);*/
 /* Scale Data to Voltage */
scale = DAQ_VScale (1, 0, 10, 1.0, 0.0, 4, hb_array, vt_array);
/*FmtOut ("scale = %i\n",scale); */
  /* t1 = Timer();
  FmtOut ("%f", t1);*/

FmtFile (fhand,"%f",counter*dlay);
FmtOut ("Time = %f (minutes)\n", counter*dlay/60);
  for (ii = 0; ii < 4; ii++)
  {FmtFile (fhand,"%s<%f[w15]",vt_array[ii]-offset);
FmtOut ("%s<%f[w10]",vt_array[ii]-offset);
  WriteFile (fhand, "\n", 1);
FmtOut ("\n");}
if(nn==1)
nnn=nn+1;
counter=counter+1;
/*Beep ();*/
/*FmtOut ("\n *** EXPERIMENT IN PROGRESS, DO NOT TOUCH

250
PLEASE!!!! ***\n\nif (nnn<36) {vout= 1.0101525 /* 0.87482 */;
/*FmtOut (" *** HEATER IS ON ***\n\nif (nnn>=36) {vout=0;
/*FmtOut (" *** HEATER IS OFF ***\n
if(nnn==198) {nnn=0;}
vout = AO_VWrite (1, 1, vout);
Delay (dlay);
nn=0;}}
CloseFile (fhand);

DAQ_Clear (1);}
APPENDIX E

COMPARISONS OF THERMAL PROPERTIES

This appendix will include comparisons between the estimated thermal properties (thermal conductivities and volumetric specific heats) and the predicted thermal properties using the models for sucrose, methyl-cellulose, and wheat gluten in solutions at 9.1, 16.7, 37.5, and 44.4% concentrations, as described in Table E.1.

Table E.1 List of Graphs of Comparison between Estimated and Predicted Thermal Properties

<table>
<thead>
<tr>
<th>Substance</th>
<th>Property</th>
<th>% Concentration</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>$k$</td>
<td>9.1, 16.7, 37.5, and 44.5</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>9.1, 16.7, 37.5, and 44.5</td>
<td>244</td>
</tr>
<tr>
<td>Methyl-cellulose</td>
<td>$k$</td>
<td>9.1, 16.7, 37.5, and 44.5</td>
<td>245</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>9.1, 16.7, 37.5, and 44.5</td>
<td>246</td>
</tr>
<tr>
<td>Wheat Gluten</td>
<td>$k$</td>
<td>9.1, 16.7, 37.5, and 44.5</td>
<td>247</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>9.1, 16.7, 37.5, and 44.5</td>
<td>248</td>
</tr>
</tbody>
</table>
Figure E.21 Comparison of Estimated Apparent Volumetric Specific Heat, $C$, and Predicted Apparent Volumetric Specific Heat for 9.1% Wheat Gluten Solution.

Figure E.22 Comparison of Estimated Apparent Volumetric Specific Heat, $C$, and Predicted Apparent Volumetric Specific Heat for 16.7% Wheat Gluten Solution.

Figure E.23 Comparison of Estimated Apparent Volumetric Specific Heat, $C$, and Predicted Apparent Volumetric Specific Heat for 37.5% Wheat Gluten Solution.

Figure E.24 Comparison of Estimated Apparent Volumetric Specific Heat, $C$, Predicted Apparent Volumetric Specific Heat for 44.5% Wheat Gluten Solution.
APPENDIX F

UNCERTAINTIES OF THERMAL PROPERTIES

The uncertainties of thermal properties which are caused by experimental errors can be determined using the estimated errors in the temperature and heat flux measurements and the sensitivity coefficients obtained from the estimation procedure. The uncertainty of an estimated parameter, $R$, can be formulated as follows (Moffat, 1988):

$$\delta R = \left[ \left( \frac{\partial R}{\partial T_1} \delta T_1 \right)^2 + \left( \frac{\partial R}{\partial T_2} \delta T_2 \right)^2 + \left( \frac{\partial R}{\partial q^\prime} \delta q^\prime \right)^2 \right]^{1/2} \quad (F.1)$$

where $\delta R$ is the uncertainty in $R$. $\delta T_1$, $\delta T_2$, and $\delta q^\prime$ are the uncertainties of measured temperatures and heat flux. The uncertainty in the measured temperature was estimated to be approximately 0.1 °C.

For one case study, the uncertainty of thermal conductivity of sucrose was calculated and then compared to the 95% confidence region determined from the estimation procedure. The calculated uncertainty using Eq. F.1 was found to be 0.326 W/m K. The uncertainty for the estimated thermal conductivity for a confidence region of 95% was found to be 0.233 W/m K. The error in the estimated thermal conductivity due to experimental inaccuracies was higher than the estimated uncertainty from the estimation procedure.
VITA

The author, Zoubeir Saad, the son of Mr. Moncef Saad and Mrs. Fatima Saad, was born on December 1st, 1966, in Gafsa, Tunisia. He obtained his high school diplomat in Menzel-Bourguiba, Tunisia, in June 1985. He received a scholarship to attend Michigan State University where he received a Bachelor of Science Degree in Mechanical Engineering, on June 9th, 1989. On August 30th, 1991, he graduated with a Master of Science in Mechanical Engineering with a heat transfer emphasis from Michigan State University.

In the fall of 1991, he started his PhD program under the direction of Dr. Elaine P. Scott at Michigan State University. After a year, he transferred to Virginia Polytechnic Institute & State University due to the relocation of his advisor to Virginia Tech. He completed his PhD program in Mechanical Engineering in the area of heat transfer on April 15th, 1994 at Virginia Polytechnic & State University.

Zoubeir Saad