THERMO-PHYSICAL PROPERTIES OF APPLES AND PREDICTION OF FREEZING TIMES

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
Department of Food Science

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
December 1979

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Date January 3, 1980

ABSTRACT

In two varieties of apples, Golden Delicious and Granny Smith, the temperature dependence of different thermo-physical properties has been investigated. Detailed regression equations are given to cover the variations of thermal conductivity, apparent specific heat and thermal diffusivity of apples with temperature both above and below the freezing point. Tissue density has been studied at four different temperatures.

The thermo-physical properties determined in this study have been employed to predict the freezing times of apples under various conditions of freezing using different models reported in the literature. The freezing conditions included for both variety of apples were: five freezing systems viz., freezing in air at -21 to -25°C and at -28 to -30°C, freezing by immersion in ethylene glycol at -18 to -20°C and -20 to -24°C and by immersion in liquid nitrogen at -197°C; three container sizes, viz., cans of size 300x407, 307x409 and 401x411; two initial product temperatures, 16-25°C and 1-7°C; and two target temperatures, -10° and -18°C.

Two types of prediction methods were used, the analytical methods of Plank (1941), Nagaoka et al. (1955), I.I.R. (1972), Mellor (1976), Cleland and Earle (1979b), and the numerical methods with constant as well as varying thermal properties. The predicted values of freezing times by the different models were compared with experimental values and the relative merits of each model discussed. Based on an analysis of the prediction errors, a modification of Plank's equation to

give the least error was suggested as follows:

$$t = [0.3022\, C_1 (T_i - T_f) + L + 2.428\, C_2 (T_f - T_c)] \frac{\rho_2}{(T_f - T_a)} [\frac{Pd}{h} + \frac{Rd^2}{k_2}]$$

The mean overall prediction error of the suggested model was 6.64% which was less than 5% beyond the experimental error of 2.38%.

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A	Cross sectional area perpendicular to heat flow, m^2
a	constant in eq. 19
B	Dimensionless number = $\bar{h}d/(2k_2)$
Bi	Biot Number = $k_2/(\bar{h}d)$
C	Specific heat capacity, with subscripts 1 and 2 for unfrozen and frozen states, J/kgK°
C	In numerical methods, volumetric specific heat capacity, $J/m^3K°$
D	Constant in eq. 4
d	Diameter of a cylinder or thickness of a slab, m
$\frac{dx}{dt}$	Velocity of the frozen front, m/s
ΔH	Heat content or enthalpy change, J/kg
ΔT	Temperature difference, C°
Δt	Time increment, s
Δr	Radius increment, m
E_T	Calibration constant for DSC, (mg/min)·J/kgC°
erf	Error function
Fo	Fourier's Number = $\frac{\alpha t}{d^2}$
G	Constant in eq. 4
G	Dimensionless number determined by eq. 9
$\bar{h}$	Surface heat transfer coefficient, $W/m^2K°$

i	Time step superscript in finite difference methods
Ko	Kossovitch Number = $L/C_2(T_f - T_a)$
k	Thermal conductivity, with subscripts 1 and 2 respectively for unfrozen and frozen states, W/mK°
L	Latent heat of fusion of ice, J/kg
l	Length of a cylinder, m
ln	Natural logarithm
M	Mass (kg), moisture (%) or a number determined by $R/\Delta r$ in finite difference methods
m	Space step subscript in finite difference methods
P	Constant in Plank's equation
Pk	Plank's Number = $C_1(T_i - T_f)/\Delta H$
Q	Quantity of heat, J
q	Rate of heat flow, W
r,R	Radius of a cylinder, m
S	Dimensionless Number = $A(\frac{d}{V})$
Ste	Stefan's Number = $C_2(T_f - T_a)/\Delta H$
T_a	Ambient temperature adjuce t to the can, °C
T_c	Target temperature, °C
T_f	Freezing point, °C
T_i	Initial temperature, °C
T_s	Temperature at the surface, °C
T_o	Temperature at the center, °C
t*	Dimensionless number determined by equation 14.
t	Freezing time, s
t_e	Experimental freezing time, h

t_{ef}	Effective freezing time, s
$t_{f(-10)}$	Freezing time to reach -10°C, s
t_I	Freezing time (International Institute of Refrigeration, 1972), h
t_P	Freezing time (Plank, 1941), h
t_{NF}	Freezing time (Nagaoka et al. 1955), h
t_{NC}	Freezing time (Nagaoka et al. 1955), h
t_M	Freezing time (Mellor, 1976), h
t_S	Freezing time (Suggested modification of Plank's equation), h
V	Volume, m^3
x	Thickness of the ice front, m
α	Thermal diffusivity with subscripts 1 and 2 respectively for unfrozen and frozen states, m^2/s
β	Dimensionless number = $k_2/(\bar{h}d)$ = Biot Number
γ	Dimensionless number = $C_2(T_f - T_a)/L$
λ	Constant in equations 13, 13a
λ_1	Function of $\bar{h}$ and k_2
μ_1	Function of $\bar{h}$ and k_2
ρ	Density with subscripts 1 and 2 respectively for unfrozen and frozen states, kg/m^3

LIST OF APPENDICES

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. M.A. Tung, Research Supervisor, for his assistance and counsel during this study.

The advice of Professors W.D. Powrie, L.M. Staley, J. Vanderstoep and E.L. Watson is sincerely appreciated.

This research was financed in part by Canadian Commonwealth Fellowship and Scholarship Administration, Ottawa.

INTRODUCTION

Food preservation by freezing is becoming increasingly important as more foods in larger quantities are being preserved, day after day, by freezing. Freezing is a process of bringing down the temperature of the product below its freezing point to a temperature at which it is subsequently stored. It has been generally recognized that the location and size of the ice crystals formed is associated with the rate of freezing. In general, slow freezing results in the formation of large ice crystals located in extra-cellular spaces while rapid freezing results in small ice crystals in both intra- and extra-cellular spaces (Fennema, 1966). Formation of ice crystals, particularly larger ones, damages the cell structure and thus the food material upon thawing will have a poorer texture. This aspect has been reviewed by Fennema and Powrie (1964), Van Arsdel et al. (1969), Tressler et al. (1968), and Fennema et al. (1973).

Food engineers dealing with freezing or defrosting of foods are often faced with the need to predict temperature history curves as well as freezing and thawing times. Therefore, the manner in which the phase change takes place, the freezing times, rates of freezing and temperature history of the material being frozen and subsequently stored are important in the design and optimization of processing equipment , and in exercizing control over the quality of the product during freezing and subsequent storage.

It has been a common practice, however, to rely on emperical experiences for these predictions. Over the years there have been numerous efforts to solve this problem. The complexity of the problem is greatly enhanced by the dependence of the freezing times on different thermo-physical properties which often change during the freezing process. Varietal differences, agricultural practices, seasonal variations, growth locations, and other factors also influence these properties. This complexity has led to many assumptions and approximations. Hence, the accuracy of any prediction model depends on how close the experimental conditions match the assumptions.

The model proposed by Plank (1941) is one of the early and most widely used prediction models. This model, however, does not take into account the initial superheat or the later subcooling since it assumes the material to be at the freezing point. Based on experimental results many modifications have been reported to include these factors (Nagaoka et al., 1955; Levy, 1958; Tanaka and Nishimoto, 1959, 1960, 1964; Cowell, 1967; Mott, 1964; International Institute of Refrigeration, 1972; Cleland and Earle, 1976, 1977, 1979a, 1979b).

Another approach was to obtain solutions for the Fourier equation of heat conduction (Charm and Slavin, 1962). However, Cowell (1967) reported that this method overestimates the freezing time when the Biot number (Bi) is less than 1. Tao (1967) developed charts for estimating the freezing times by numerically solving the Fourier equation. Two types of numerical finite difference schemes have been used. The first kind takes into account the initial superheat as well as the convective boundary condition, but assumes that all the latent heat is released at a unique freezing temperature (Charm et al., 1972). However, foods do not exhibit sharp freezing points. The second way of approaching the problem is to take into account the variation of thermal conductivity and apparent specific heat with temperature thereby completely avoiding the phase change front (Comini et al., 1974). Finite difference schemes of this type are therefore expected to be more accurate. One other aspect of this prediction time problem is the lack of a standardized method for determining the surface heat transfer coefficient. Methods based on dependence of the surface film conductance and the thermal diffusivity on the slope of the heating curve (Charm et al., 1972), cooling curve of a block of high thermal conductivity (Cowell and Namor, 1974; Earle, 1971), and finite difference method using a block of low thermal conductivity (Cleland and Earle, 1976) have been suggested.

The aim of the present research was to study the temperature dependence of the thermal properties of apples and examine the available prediction models for the accuracy of freezing time estimations in order to find an equation which would give the least prediction error. The variables included in the experiment are: variety, initial temperature, freezing temperature, container size, the temperature to which the product is ultimately cooled and the heat transfer coefficient.

LITERATURE REVIEW

Freezing Time Definitions

Lack of a consistent definition for freezing time is one of the major problems in the published literature concerned with freezing of foodstuffs. This apparent lack of information is caused by the fact that the temperature distribution within the product during the freezing process varies significantly and therefore freezing time or rate has to be defined with respect to a given location and between two reference temperatures. The 'thermal center' or the location that cools most slowly is commonly used as the reference point. Foods do not have a well defined freezing point unlike pure systems. Due to soluble components dispersed in the fluids of foods, the latent heat is released over a range of temperature (most of it being released in the region -1 to -5°C, which is referred to as the zone of maximum ice crystal formation). Some authors use the duration of this phase change period as the freezing time while others (Brennan et al., 1976) define it as the duration of the entire process including precooling, phase change and the subsequent cooling to the final temperature. The various methods that have been used by different authors to express freezing rate have been reviewed by Fennema and Powrie (1964). The 'thermal arrest time' (duration to cross the zone 0 to -5°C) has been shown to depend on the initial product temperature (Long, 1955).

Prediction Models

The subject matter of freezing time prediction by different methods has been reviewed by Bakal and Hayakawa (1973), Brennan et al. (1976), Charm (1978), Cleland and Earle (1976, 1977, 1979b), Heldman (1975), and Rebellato et al. (1978).

The prediction models are usually based on many assumptions. The body to be frozen is assumed to have a uniform initial temperature and is cooled by a constant temperature medium, thereby providing a uniform and constant surface heat transfer coefficient between the cooling medium and the surface of the body. It is also assumed in most models that the product will have constant thermo-physical properties in the unfrozen and frozen states, and also possess a defined freezing point at which all the latent heat is liberated.

These assumptions enable the freezing process to be divided into three distinct phases: the precooling period in which the temperature of the product is lowered from its initial temperature (T_i) to the freezing point (T_f), the phase change period in which the latent heat is released and a tempering period in which the temperature is lowered from the freezing point to the target temperature (T_c). Another phenomenon observed during the freezing process is the supercooling period (Fennema and Powrie, 1964) in which the temperature of the product falls well below its freezing point without the occurrence of freezing. Following supercooling, the temperature increases to the freezing point and the normal freezing process continues. None of the freezing time prediction models takes this supercooling period into consideration.

Plank's model

The model proposed by Plank (1941) is one of the early and most widely used methods for freezing time estimations. This model is based on three basic heat balance equations:

Heat conduction: $$q = A(T_o - T_f)\frac{k_2}{x}$$

Heat convection: $$q = A\bar{h}(T_a - T_o)$$

Heat generated at the freezing front:

$$q = AL\rho_2 \frac{dx}{dt}$$

where q is the rate of heat flow, x is the thickness of the ice front, dx/dt, the velocity of the ice front, A, area of cross section perpendicular to the direction of heat flow, T_a and T_o, the ambient and the surface temperatures, T_f, the freezing point, L, the latent heat, ρ_2 and k_2, the density and thermal conductivity of the frozen product and $\bar{h}$, the surface heat transfer coefficient. These three equations are combined to get the most general form of Plank's equation (Plank, 1941)

$$t = \frac{\rho_2 L}{(T_f - T_a)} \left[\frac{Pd}{\bar{h}} + \frac{Rd^2}{k_2}\right] \tag{1}$$

where d is the thickness of a slab or diameter of a cylinder or sphere, P and R are constants depending on the product geometry. The values of P are 0.500, 0.250 and 0.167 for an infinite slab, cylinder and sphere respectively; and the corresponding values of R are 0.125, 0.0625 and 0.0417. A chart for providing P and R when applied to a brick or block geometry is given by Ede (1949).

Plank's model assumes that the product is initially at its freezing point and hence does not take into account the precooling or tempering period. Hence the value predicted will be generally low when used under conditions involving precooling or tempering periods.

However, Ede (1949) and Earle and Fleming (1967) reported that this formula gives fairly accurate estimation of freezing times.

Based on experimental results many modifications have been reported to include the precooling and tempering periods in Plank's equation.

Nagaoka Modification

Nagaoka et al. (1955) suggested the following modification to Plank's equation:

$$t = [1 + 0.00445(T_i - T_f)]\frac{\rho_2 \cdot \Delta H}{(T_f - T_a)}[\frac{Pd}{\bar{h}} + \frac{Rd^2}{k_2}] \tag{2}$$

where $\Delta H = [C_1(T_i - T_f) + L + C_2(T_f - T_c)$

Levy Modification

Levy (1958) suggested that the L in Plank's equation be replaced by ΔH, the enthalpy change at the thermal center over the entire process to get the nominal freezing time, t . Then the effective freezing time is calculated as

$$t_{ef} = t\ [1 + 0.0081(T_i - T_f)] \tag{3}$$

I.I.R. Modification

The International Institute of Refrigeration, 1972 recommended only replacing L in Plank's equation by the enthalpy change over the entire process to get the freezing time.

Mellor modification

Mellor (1976) suggested replacing L by a factor $[\frac{1}{2} C_1(T_i - T_f) + L + \frac{1}{2} C_2(T_f - T_a)]$ in Plank's equation to predict the freezing time.

Cleland and Earle Modifications

Plank's equation has been expressed in terms of dimensionless numbers by Cowell (1967).

$$\frac{Fo}{Ko} = D[\frac{1}{Bi} + G] \tag{4}$$

where Fo is the Fourier Number $= \frac{\alpha t}{d^2}$, Bi, Biot Number $= \frac{\bar{h}d}{k_2}$ and Ko is the Kossovitch Number $= \frac{L}{C_2(T_f - T_a)}$ and D and G are constants determined by the product geometry.

More recently, Cleland and Earle (1976, 1979a, 1979b) expressed Plank's equation in the dimensionless form

$$Fo = P\left(\frac{1}{Bi \cdot Ste}\right) + R\left(\frac{1}{Ste}\right) \qquad (5)$$

where Ste is Stefan Number = $\dfrac{C_2(T_f - T_a)}{\Delta H}$. Defining the sensible heat during the precooling period by a dimensionless number, Plank's Number, Pk = $\dfrac{C_1(T_i - T_f)}{\Delta H}$, the authors suggested modifications of the constants P and R in Plank's equation to predict the freezing times more accurately.

Slab:

$$P = 0.5072 + 0.2018\ Pk + Ste\ (0.3224\ Pk + \frac{0.0125}{Bi} + 0.0681)$$

$$R = 0.1684 + Ste\ (0.2740\ Pk - 0.0135)$$

Cylinder:

$$P = 0.3751 + 0.0999\ Pk + Ste\ (0.4008\ Pk + \frac{0.0710}{Bi} - 0.5865)$$

$$R = 0.0133 + Ste\ (0.0415\ Pk + 0.3957)$$

The freezing times predicted, using these values for P and R, were reported by the authors to be in very good agreement with experimental values as well as those predicted by finite difference numerical methods. Cleland and Earle (1979a) also found that even after the above modifications, the predicted values for freezing in rectangular bricks were very low. They reported, therefore, that the assumptions made by Plank (1941) in arriving at the geometric factors are unjustified and hence the methods using these factors (Nagaoka et al., 1955; Mellor, 1976) can certainly be expected to give erronous results. The authors have modified the equations to find P and R further, to cover rectangular bricks.

Gutschmidt Equation

For products of irregular shape Gutschmidt (1964) suggested the equation:

$$t = \frac{\Delta H}{(T_f - T_a)k_2} \frac{V}{A} \left(\frac{d}{2} + \frac{k_2}{h}\right) \tag{6}$$

For other geometrics such as parallelipiped, right circular cone and others, equations have been given by Lorentzen and Rosvik (1960) and Tanaka and Nishimoto (1959, 1960, 1964).

Mott's Procedure

Mott (1964) developed several tables, to get the thermo-physical data needed to use Plank's prediction model, by dimensional analysis of experimental data which included different product and package characteristics and various conditions of freezing. In this procedure, a functional relationship among three dimensionless groups is utilized for freezing time calculation. The different equations are given below.

$$S = \frac{(B + 1)}{G} = A(\frac{d}{V}) \tag{7}$$

$$B = \frac{\bar{h}d}{2k_2} \tag{8}$$

$$G = \frac{t\ \bar{h}(T_f - T_a)}{\rho_2 Qd} \tag{9}$$

where S, B and G are the three dimensionless groups.

Fourier Models

A different approach in solving the prediction time problem is to obtain solutions for Fourier's heat conduction equations under suitable boundary conditions. The validity of Fourier's equation has been proven and this equation has been widely used in engineering sciences. However, the solutions are rather complicated, and therefore, not many are available in the published literature. Carslaw and Jaeger (1959) and Muehlbauer and

Sunderland (1965) gave excellent reviews on the formulas for estimating heat conduction in a solid when there is a phase change in the sample.

Newman 's Solution

The Newman's solution published in Carslaw and Jaeger (1959) utilizes a unidimensional heat transfer in a semi-infinite slab. The assumptions which hold good for Plank's equation are made here also. The partial differential equations representing the temperature distribution in the unfrozen and frozen regions are represented as:

$$\frac{\partial^2 T_1}{\partial x^2} = \frac{1}{\alpha_1}\frac{\partial T_1}{\partial t} \qquad \text{Unfrozen region} \qquad (10)$$

$$\frac{\partial^2 T_2}{\partial x^2} = \frac{1}{\alpha_2}\frac{\partial T_2}{\partial t} \qquad \text{Frozen region} \qquad (11)$$

The equation expressing the heat flux between the frozen and the unfrozen portion which must be equal to the heat liberated at the freezing front is

$$k_2\frac{\partial T_2}{\partial x} - k_1\frac{\partial T_1}{\partial x} = \rho_2 L\frac{\partial x}{\partial t} \qquad (12)$$

The Newman's solution utilizes several boundary conditions such as

$$T_1(x, 0) = T_i$$

$$T_1(0, t) = T_s(t)$$

$$T_2(x, t) = T_1(x, t) = T_f$$

$$\frac{\partial T_1(\frac{d}{2}, t)}{x} = 0$$

Using these assumptions the equation expressing temperature as a function of time and position in an infinite slab is given below.

$$T_2 = \frac{T_f}{\operatorname{erf}\lambda} \operatorname{erf} \frac{x}{2[\alpha_2 t]^{1/2}} \tag{13}$$

Where $T_2 = T_f$, equation 13 reduces to

$$x = 2\lambda(\alpha_2 t)^{1/2} \tag{13a}$$

suggesting that the location of the freezing front can be linearized on a log log plot with a slope of 0.5 and λ can be calculated from the intercept (Bakal and Hayakawa, 1970). Charm and Slavin (1962) used equation 13 for calculating the freezing time of cod fillets by using a modified thickness equal to $(\frac{d}{2} + \frac{k_1}{\bar{h}})$. However, Cowell (1967) reported that this modified thickness results in over-estimating the freezing time when the Biot number is less than 1.

Tao's Charts

Tao (1967) developed charts for estimating the freezing times in an infinite slab, cylinder and a sphere by numerically solving the Fourier heat conduction equations using three dimensionless groups.

$$t^* = t\, k_2 (T_f - T_a)/d^2 \rho_2 L \tag{14}$$

$$\beta = k_2/\bar{h}d \tag{15}$$

$$\gamma = C_2 (T_f - T_a)/L \tag{16}$$

The charts show a relationship between t^* and β at different values of γ.

Numerical Methods

The different methods discussed so far assume constant thermal properties. But the actual situation requires solution of the equation of type

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} (\alpha(T) \frac{\partial T}{\partial x}) \tag{17}$$

which is a partial differential equation of one dimensional heat conduction in a slab with thermal diffusivity as a function of temperature. The more general way of expressing the relationship is as follows for a slab, cylinder, and a sphere.

Slab:

$$C(T) \frac{\partial T}{\partial t} = k(T) \frac{\partial^2 T}{\partial x^2} \tag{18}$$

Cylinder (a=1)
Sphere (a=2)

$$C(T)\frac{\partial T}{\partial t} = \frac{\partial}{\partial r}[k(T) \frac{\partial T}{\partial r}] + \frac{ak(T)}{r} \frac{\partial T}{\partial r} \tag{19}$$

The most common boundary condition is that with a surface heat transfer coefficient, sometimes referred to as Newton's law of cooling or as a boundary condition of the third kind that uses the convective heat transfer coefficient between the cooling medium and the surface of the product. This is represented as

$$\bar{h}(T_a - T_s) = [k(T) \frac{\partial T}{\partial x}]_{x = 0 \text{ for slabs}} \tag{20}$$

$$\bar{h}(T_a - T_s) = [k(T) \frac{\partial T}{\partial r}]_{r = \frac{d}{2} \text{ for cylinders or spheres}} \tag{21}$$

The solution of the above equations (17-21) are difficult without the use of numerical methods. Two types of numerical finite difference schemes have been used. The first type takes into account the precooling and tempering periods as well as the third kind of boundary condition but assumes all the latent heat to be released at a unique freezing temperature (Charm et al., 1972). However, foods do not exhibit sharp freezing points, so the solutions of this type depart substantially from the actual situation. The second way that phase change in freezing foods can be accommodated is to take into account the variations of thermal conductivity k(T), and apparent specific heat capacity C(T). This completely avoids the need to define a phase change front. The versatility of this method has been demonstrated by Bonacina and Comini (1973), Rebellato et al. (1978), Cleland and Earle (1976, 1977, 1979a, 1979b). The finite element methods are more complex. For unidimensional heat transfer it offers no distinct advantage over the finite difference schemes (Cleland and Earle, 1979b). For a radial heat transfer, a three time-level finite difference scheme proposed by Cleland and Earle (1979b) is given below.

$$C_m^i \frac{T_m^{i+1} - T_m^{i-1}}{2\Delta t} = \frac{1}{3(\Delta r)^2} [k_{m+1/2}^i (T_{m+1}^{i+1} - T_m^{i+1} + T_{m+1}^i - T_m^i$$

$$+ T_{m+1}^{i-1} - T_m^{i-1}) - k_{m-1/2}^i (T_m^{i+1} - T_{m-1}^{i+1}$$

$$+ T_m^i - T_{m-1}^i + T_m^{i-1} - T_m^{i-1})] +$$

$$\frac{k_m^i}{3m\Delta r\, 2\Delta r} (T_{m+1}^{i+1} - T_{m-1}^{i+1} + T_{m+1}^i - T_{m-1}^i$$

$$+ T_{m+1}^{i-1} - T_{m-1}^{i-1}) \qquad (22)$$

At the center (m = o),

$$\lim_{r \to o} \frac{1}{r} \frac{\partial T}{\partial r} \to \frac{\partial^2 T}{\partial r^2} \qquad (23)$$

$$C_o^i \frac{T_o^{i+1} - T_o^{i-1}}{2\Delta t} = \frac{1}{3(\Delta r)^2} [2k_{m+1/2}^i (T_o^{i+1} - T_o^{i+1} + T_1^i - T_o^i$$

$$+ T_1^{i-1} - T_o^{i-1})] \qquad (24)$$

At the surface (m = M), $h(T_a - T_s) = k_M^i \left(\frac{\partial T}{\partial r}\right)_{=M\Delta r}$, and setting $k_{M+1/2}^i = \bar{h}\Delta r$ and $T_{M+1}^i = T_a$,

$$C_M^i \frac{T_M^{i+1} - T_M^{i-1}}{2\Delta t} = \frac{1}{3(\Delta r)^2} [k_{M+1/2}^i (3T_a - T_M^{i+1} - T_M^i - T_M^{i-1})$$

$$- k_{M-1/2}(T_M^{i+1} - T_{M-1}^{i+1} + T_M^i - T_{M-1}^i +$$

$$T_M^{i-1} - T_{M-1}^{i-1})] + \bar{h} (3T_a - T_M^{i+1} -$$

$$T_M^i - T_M^{i-1})/3R \qquad (25)$$

where

$$k_{m+1/2}^i = \frac{1}{2}(k_m^i + k_{m+1}^i) \qquad (26)$$

$$k_{m-1/2} = \frac{1}{2}(k_m^i + k_{m-1}^i) \qquad (27)$$

These numerical methods require the use of a computer. Charm (1978), Cordell and Webb (1972), Bonacina and Comini (1973), Fleming (1971), Cleland and Earle (1977, 1979a, 1979b) have used computer programs to solve the above equations, some using constant thermal properties (Charm, 1978) while others using variable thermal properties. Rebellato et al. (1978) extended the finite element analysis to include irregular shaped products also. Albin et al. (1976, 1979) used Goodman's integral technique (Goodman, 1964) to solve the partial differential equations (17-21) using four dimensionless numbers.

Surface Heat Transfer Coefficient Determinations

One of the major problems involved in prediction models is the lack of a standard method for determining the surface heat transfer coefficient. A commonly used approach is the so-called heat penetration method where the cooling curve of a block of metal of high thermal conductivity is found under the conditions that will apply in the freezing system. This method has been used by Cowell and Namor (1974) in plate freezing and Earle (1971) in air blast freezing. Charm (1971) suggested the use of an equation employed by Ball and Olson (1957) describing the effect of surface conductance and thermal diffusivity on the slope of the heating curve,

$$\frac{2.303}{\alpha_2 f} = \lambda_1^2 + \mu_1^2 \tag{28}$$

where f is the negative reciprocal of the slope of the heating curve obtained by using a Jackson Plot, λ_1 = first root of $\cot \lambda(1/2) = (k_2/\bar{h})\lambda$ μ_1 = first root of $J_o(\mu r) = \mu(k_2/\bar{h})\ J_1(\mu r)$, 1 represents the the depth of a slab or cylinder, r = radius of cylinder. Use of the finite difference methods using gel samples of thermal properties close to those of food materials is recommended by Cleland and Earle (1976). This method involves the determination of surface temperatures and then use of an explicite finite difference scheme with the third kind of boundary conditions to get an estimate of $\bar{h}$ at each step.

Thermo-physical Properties of Apples

Very little work has been published on the evaluation of thermo-physical properties or prediction of freezing times for apples. One of the earliest reports on the thermal conductivity of apples comes from Gane (1936) who gave values for thermal conductivity, apparent density, mean specific heat and thermal diffusivity at 15.6°C for apples, apple juice, apple juice concentrate and apple sauce. In a survey of thermal conductivity of fruits and vegetables, Sweat (1974) reported values for density and thermal conductivity at 28°C for green and red apples

(ρ = 790 and 840 kg/m^3 and k = 0.422 and 0.513 W/mK° respectively). He also gave a regression equation expressing the relationship between thermal conductivity and moisture content (% wet basis) at room temperature.

$$k = 0.148 + 0.00493\ (\%\ \text{Moisture}) \qquad (29)$$

Lozano et al. (1979) expressed the relationship between the moisture content (fraction, X, dry basis) and thermal conductivity of Granny Smith apples in the following equation

$$k = [0.283 - 0.256\ \exp(-0.206X)] \times 1.731\ \text{W/mK°} \qquad (30)$$

Values obtained by Sweat (1974) were significantly higher than those reported by Lozano et al. (1979). Riedel (1951) has given tables for the enthalpy of apple juice, apple juice concentrate and apple sauce at different temperatures. Riedel (1949) expressed a general relationship between k and moisture content at temperatures above freezing point by the quadratic equation (with temperature in F°)

$$k_1 = [307 + 0.645T - 0.00105T^2]\ [0.46 + 0.054\ (\%\ \text{Moisture})] \times 10^{-3}\ \text{BTU/h ftF°} \qquad (31)$$

EXPERIMENTAL

Material

Two varieties of apples, viz., Golden Delicious and Granny Smith, obtained from the local market, were used in the study. The apples were stored at 1-2°C until use.

Methods

Thermal Conductivity [k(T)]

Thermal conductivity was measured by the transient method using a thermal conductivity probe 3.81 cm long and 0.0813 cm diameter as described by Sweat and Haugh (1972). Apples were mechanically peeled and sliced into octets. The probe was inserted into a slice in the longitudinal direction, the slice with probe was placed in a long closely fitting retort pouch (12 μm polyester/9 μm Al foil/50 μm polypropylene) and clamped at both the ends to secure the position. The slices were then cooled to different temperatures in a constant temperature bath, and held at least for $\frac{1}{2}$ h for equilibration. Each measurement was made as follows: when the temperature of the sample was steady, a current of 160 mA was applied to the probe. The resulting temperature rise was recorded as the thermocouple millivolt output using a Digitec data logger (United Systems Corp.) The millivolt record thus obtained was used to provide temperatures occurring at one second intervals up to 40 s of the heating time. The time-temperature data [in the form $\ln(\frac{t_2}{t_1})$ vs T] were subjected to a linear regression through a least squares procedure using the University of British Columbia computer (Amdahl 470V/6-II). To avoid points which do not fall in a straight line, the first 10 s of heating time was not used in the calculation of the slope. Further, the data with a correlation coefficient of less than 0.90 were rejected. The thermal conductivity was calculated using the relationship

$$k = \frac{Q \ln (\frac{t_2}{t_1})}{4\pi \ (T_2 - T_1)} \tag{31a}$$

where Q is the power consumed by the probe heater, T_1 and T_2 are the temperatures of the probe thermocouple at time t_1 and t_2 respectively. With the calculated slope, the equation reduces to the form $k = Q(\text{slope})/4\pi$. Experiments were conducted in 3 replicates at different temperatures between 25 and -25°C.

Apparent Specific Heat [C(T)]

Differential thermal analysis (DTA) is a technique for recording the difference in temperature, ΔT, between a test substance and an inert reference material as samples of the two are warmed or cooled, at a constant rate. If the test substance is thermally active, then the curve obtained by plotting ΔT, against temperature shows irregularities or peaks or valleys. These peaks indicate the occurrence and measure the extent of energy-involving reactions, transitions or phase changes within the test sample. When techniques to measure these changes directly in energy units are available, the measurement is referred to as differential scanning calorimetry (DSC). The different aspects of DSC and DTA have been discussed in detail in the book of MacKenzie (1970).

The Dupont 900 DSC was used to obtain the warming thermograms. This instrument was calibrated to obtain the calibration constant, E_T, using zinc (purity 99.999%). Samples of apple tissues [8 to 14 mg] were cooled in the DSC cell to -100°C using liquid nitrogen. The cooling curves were not recorded. The samples were held for sufficient time ($\frac{1}{2}$ to 1 h) to achieve equilibration. The warming thermograms were recorded while heating at 20C°/min.

The specific heat data were obtained as follows: Two empty pans were first warmed at 20C°/min on the DSC from -100 to 80°C to obtain a blank thermogram. Then the sample was placed in one of the pans and the sample and reference pans were again warmed from -100 to 80°C. From the resulting thermograms of sample and blank, the apparent specific heat at any temperature is calculated by measuring the ΔT values for sample and blank at that temperature, and using the following equation:

$$(C)_T = \frac{(\Delta T_{Blank} + \Delta T_{Sample})_T \; E_T}{(\text{Heating Rate})\ (\text{Mass})} \tag{32}$$

Density (ρ)

For determining density, apples were cut into cylinders of 1.9 cm diameter and 1.6 cm length and weighed (M) individually. Density was then calculated using the equation:

$$\rho = \frac{M}{V} = \frac{4M}{\pi d^2 l} \tag{33}$$

The temperatures used were 2 and 25°C. For determining density in the frozen state, the apples were cut into brick shaped slices of approximate dimensions 1.0 x 1.0 x 3.0 cm , frozen to -20 and -35°C in freezer rooms, where they were left packaged for 1 wk for equilibration. Six of the above slices were placed in a measuring cylinder previously tared with a sinker and weighed (M). To this, 50 ml of water at 2-3°C were added and the volume recorded. From this volume, the volume of 50 ml water plus the sinker was subtracted to yield the volume (V) of the slices and the density was determined using equation 33. Eight replicates were used at each temperature.

Thermal diffusivity [$\alpha(T)$]

Thermal diffusivity (α) was calculated using the equation,

$$(\alpha)_T = \left(\frac{k}{C\rho}\right)_T \tag{34}$$

Moisture (M)

Moisture was estimated by drying a known weight of the sample in a vacuum oven at 70°C for 24 h. Twelve replicates were used each time.

Latent Heat (L)

Latent heat of fusion (L) was calculated based on the moisture content (% wet basis) using the equation:

$$L = \frac{\%\ \text{Moisture}}{100} \times 334.9 \times 10^3 \ \ \text{J/kg} \tag{35}$$

Texture

Texture of whole apples was measured using a Magness-Taylor puncture probe attached to an Instron tester. Two readings were taken on each fruit and eight fruits were sampled at each time. The load (kg) required to puncture the apple tissue (with a thin section of the skin removed at the point of puncture before the measurement) was taken as an index of the texture.

Total Soluble Solids and Acidity

Total soluble solids and titratable acidity were determined using the juice obtained from two slices taken from eight different fruits by the methods suggested by Ruck (1969).

Moisture, total soluble solids, acidity and texture values were determined four times during the period of study for each variety as a measure of the quality of the apples.

Freezing Conditions

Freezing experiments were carried out under five freezing systems, three container sizes, two distinct initial and final temperatures for both varieties of apples. The different conditions are described below:

1. Freezing Systems:
   a) Freezer room at -21 to -25°C
   b) Freezer room at -28 to -30°C
   c) Immersion in ethylene glycol (60%) at -18 to -20°C
   d) Immersion in ethylene glycol (100%) at -20 to -24°C
   e) Immersion in liquid nitrogen at - 197°C

2. Container: Tin-plate cans of three different sizes
   a) 300 x 407
   b) 307 x 409
   c) 401 x 411

3. Initial Temperatures (T_i)
   a) 16-25°C
   b) 1-7°C

4. Final Temperature (T_c)
   a) -10°C
   -18°C

For freezing, apples were peeled and sliced into octets, dipped in a potassium metabisulfite solution containing approximately 200 ppm of sulfur dioxide. The slices were orderly and tightly packed into the cans so as to minimize the extent of empty spaces inside the can.

The can ends were insulated with 3 cm thick cardboard planks. A needle type Eklund copper-constantan thermocouple was inserted into the can in such a way that the tip of the thermocouple was at the geometric center of the can, embedded inside one of the apple slices. Temperature at the center of the can as well as that of the freezing medium were recorded as the thermocouple millivolt output using a Digitec data logger (United Systems Corp.) at 2 min. intervals. These data were used to evaluate the experimental freezing times to cool the material to -10°C and -18°C and also to determine the time taken to cross the zone of maximum ice crystal formation (-1 to -5°C).

Surface Heat Transfer Coefficient

Surface heat transfer coefficients were determined using Plank's equation as well as by the method of Charm (1972). For using Plank's equation, the apples were packed into cans as in the freezing experiments, stored in a room at 1 to 2°C until equilibration was reached, and then frozen in the different freezing systems. Using the freezing time to reach -10°C ($t_{f(-10)}$), the heat transfer coefficient ($\bar{h}$) was calculated by the equation

$$\bar{h} = \frac{Pd}{\left[\frac{t_{f(-10)}(T_f - T_a)}{\rho_2 \Delta H} - \frac{Rd^2}{k_2}\right]} \tag{36}$$

When using Charm's (1972) method the slope of the heating curve was calculated both from the freezing data and by allowing the frozen sample to warm up in the freezing system.

Freezing Time Predictions

Freezing time predictions were made using the models suggested by Plank (1941), Nagaoka et al. (1955), International Institute of Refrigeration (1972), Mellor (1976), Cleland and Earle (1979b), and a suggested modification of Plank's equation. Numerical finite difference methods for a radial heat transfer with a two time level scheme with constant as well as varying thermal properties were also used to predict the freezing times. The schemes were similar to that proposed by Cleland and Earle (1979b) using a three time level scheme.

RESULTS AND DISCUSSION

Thermo-Physical Properties

The different physico-chemical properties, moisture, total solids and the Magness-Taylor texture values for the two varieties of apples did not change significantly during the period of study (Table 1). Golden Delicious was, however, higher in moisture content and lower in total solids, acidity as well as texture value as compared to Granny Smith. From the observed moisture and texture values it was presumed that the quality of the apples remained essentially constant throughout the period of study (approximately two months).

Thermal Conductivity

The probe method of conductivity measurement was found to give accurate and consistent results. The thermal conductivity values for a 0.4% agar gel in eight different runs were found to be 1.48, 1.51, 1.57, 1.53, 1.54, 1.41, 1.43 and 1.45 W/mK^{o} with a mean value of 1.49 W/mK (and a standard deviation of 0.057) as compared to the expected value of 1.52 W/mK^{o}. Thus, the experimental value was found to be within 2% of the actual value. With food samples, the accuracy of the probe methods have been reported to $\pm$5% at temperatures above freezing and

Table 1. Physio-chemical properties of apples during storage at 1-2°C.

PROPERTY	Golden Delicious				Granny Smith			
	Jul 31	Aug 2	Aug 14	Sep 29	Aug 7	Aug 9	Aug 16	Oct 5
Moisture (%)[a]	86.21	87.81	87.89	87.52	85.46	85.64	86.31	85.40
Total Soluble Solids (%)[b]	11.55	11.00	10.40	10.20	12.10	12.10	11.75	12.65
Acidity (mg malic/100 g)[b]	190	170	150	96	506	481	453	480
Texture (Magness-Taylor puncture probe, kg)[c]	2.45	2.32	2.34	2.30	2.98	2.87	2.86	2.66

a average of nine replicates

b average of duplicates from pooled pulp

c average of 12 replicates

±10% at temperatures below freezing point (Sweat and Haugh, 1972). Vos (1955) reported that only when the expression $\frac{4\alpha t}{a^2}$ was greater than 0.6 the error due to finite sample size was noticeable. In the present set of experiments α varied from 1.342 to 9.422 x $10^{-7} m^2/s$; t, the heating time considered was 25 s; and a, the shortest distance from the thermocouple to the boundary = 1.5 cm or .015 m. Hence the factor ranged from 0.0596 to 0.418. Therefore, the boundary influence was taken to be negligible.

The variations in the thermal conductivity of Golden Delicious and Granny Smith apples with temperature are shown in Figures 1 and 2. A comparison of the two figures indicates that the two varieties showed similar conductivity variations with temperature. The thermal conductivity values of both the varieties showed a more consistent variation with temperature above freezing point (correlation coefficient of 0.735 and 0.815 respectively for Golden Delicious and Granny Smith respectively). The linear regression equations for thermal conductivity at temperatures above freezing were:

Golden Delicious:

$$k(T) = 0.394 + 0.00212T \ (W/mK^{o}), \ T > T_f \qquad (37)$$

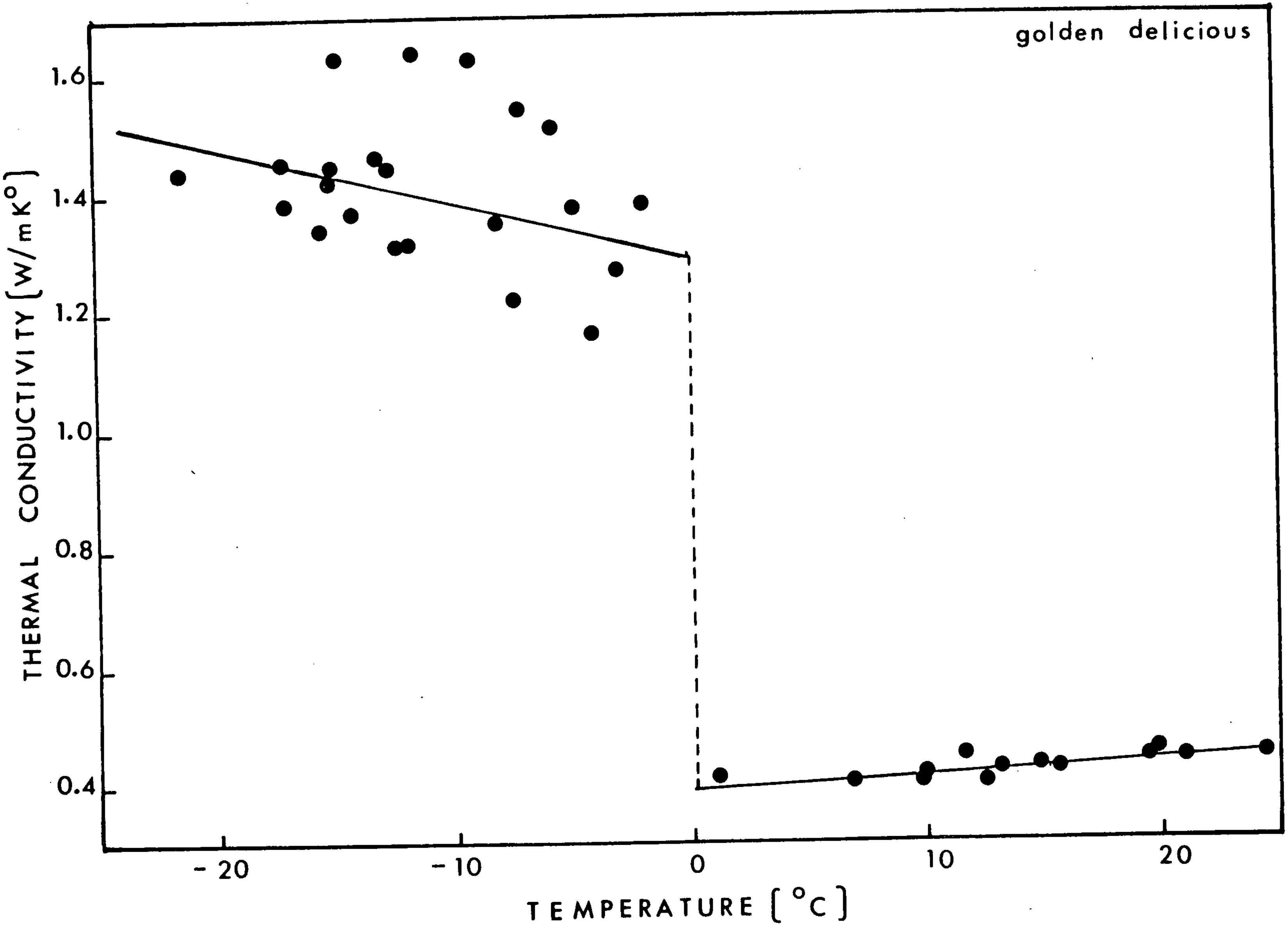

Figure 1. Thermal conductivity of Golden Delicious apples at various temperatures.

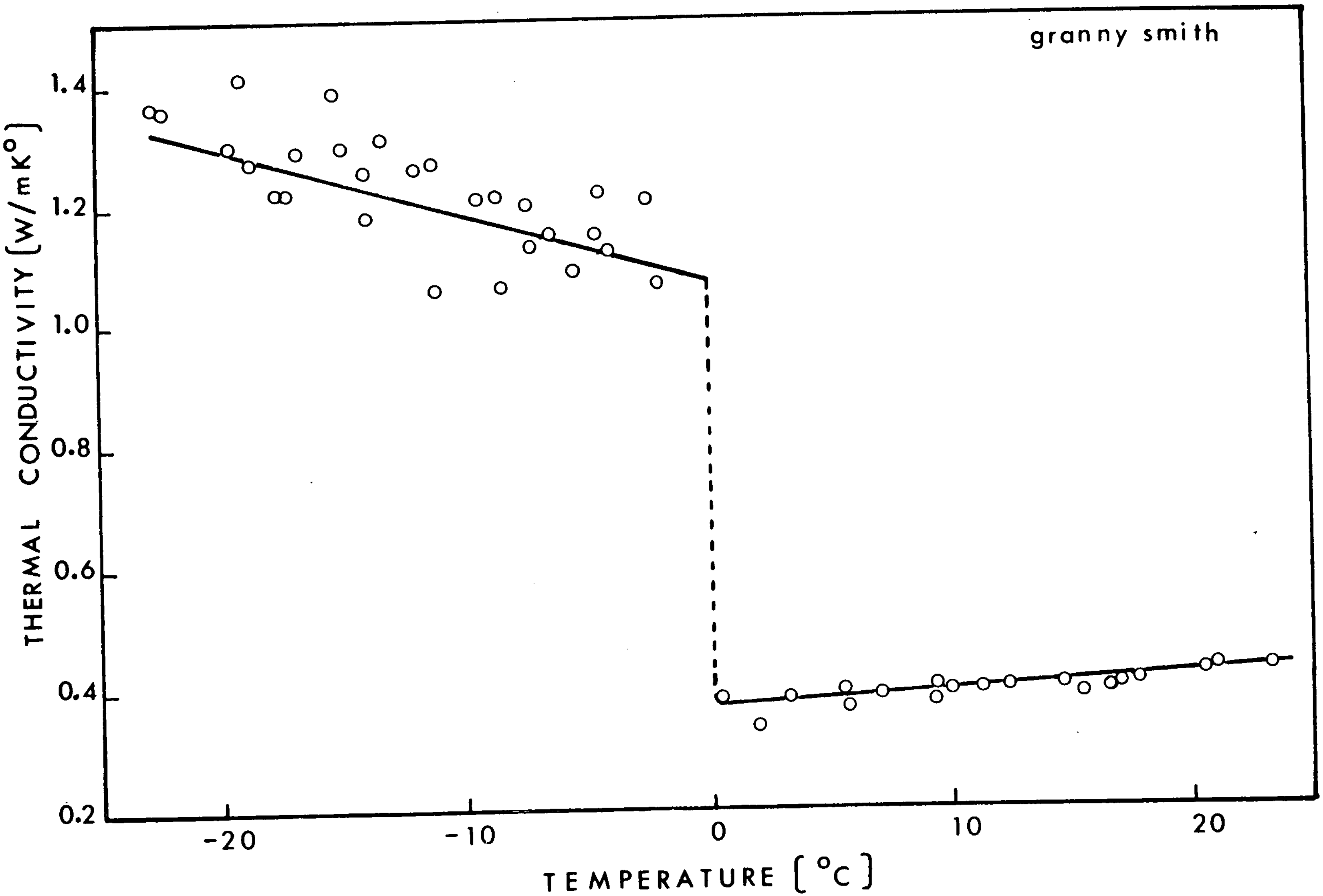

Figure 2. Thermal conductivity of Granny Smith apples at various temperatures.

Granny Smith:

$$k(T) = 0.367 + 0.00250T \quad (W/mK^{o}),\ T > T_f \qquad (38)$$

Below the freezing point, thermal conductivity values showed a larger scattering with temperature. Linear regression analysis of the data gave correlation coefficients of 0.394 and 0.650 for Golden Delicious and Granny Smith respectively, which were however significant at 5% level. The linear regression equations under these conditions were:

Golden Delicious:

$$k(T) = 1.289 - 0.0095T \ (W/mK^{o}),\ T \leq T_f \qquad (39)$$

Granny Smith:

$$k(T) = 1.066 - 0.0111T \ (W/mK^{o}),\ T \leq T_f \qquad (40)$$

For obtaining the mean values of thermal conductivity in the unfrozen and frozen region, all the observed values at temperatures above and below the freezing point (-1°C) respectively were used.

The greater variability observed in the values of thermal conductivities at temperatures below the freezing point are presumed to be related to the complexities of the freezing system, particularly to the varying degree of ice crystallization at different temperatures.

In Figures 1 and 2, the lines represent the regression equations 37 to 40. These data were utilized in prediction of freezing time by finite difference numerical methods. However, for use in other prediction models a mean value of 0.427 and 0.398 W/mK° respectively in the unfrozen state and 1.445 and 1.220 W/mK° respectively in the frozen state for Golden Delicious and Granny Smith were used.

The observed values of thermal conductivity (mean values at temperatures above freezing point) were slightly higher than those computed by equation 30, given by Lozano et al. (1979). Using the equation for moisture contents (g H_2O/g dry matter) of 6.874 and 7.033 corresponding to Golden Delicious and Granny Smith, the thermal conductivities were found to be 0.383 and 0.368 W/mK°, as compared to observed values of 0.427 and 0.398 W/mK°. The values reported by Sweat (1974) were, however, significantly higher (0.578 and 0.571 W/mK°, calculated from equation 29, and 0.513 W/mK° reported for red apples with

84.9% moisture content). The equation of Riedel (1949) also gave a higher value for apples (0.55 W/mK^{o} at 20^{o}C and 85% moisture). There has been no published information on the thermal conductivity of apples at temperatures below the freezing point.

The values of thermal conductivities both below and above freezing point for Golden Delicious were more than those for Granny Smith. Since the slopes of the regression lines for the two varieties were observed to be very close (equations 37 to 40) both at temperatures above and below freezing, it is reasonable to assume that the differences in the thermal conductivity between the two varieties at different temperatures arise mainly because of the differences in moisture content. Golden Delicious had a mean moisture content of 87.3% and Granny Smith, 85.8%. Based on a regression analysis of the thermal conductivity data for the two varieties pooled together, an equation expressing the dependence of thermal conductivity on moisture content and temperature can be written as follows.

$$k(T,M) = 0.667M\,(0.027 - 0.00038T) + 0.0213T - 1.13 \text{ W/mK}^{o}, \quad T > T_f \tag{41}$$

$$k(T,M) = 0.667M\,(0.223 + 0.0016T) - 0.10T - 11.63 \text{ W/mK}^{o}, \quad T \leq T_f \tag{42}$$

Apparent Specific Heat

A typical thermogram recorded using the Dupont DSC for a sample of Golden Delicious apple and a blank are given in Figure 3 and the computed values of apparent specific heat for both the varieties as a function of temperature are given in Figure 4. The values for temperatures above and below freezing were obtained from different thermograms. Each point in Figure 4 represents the mean value of four replicates. The pattern of the apparent specific heat curves for both varieties were similar. However, for Golden Delicious the observed values were higher than those observed for Granny Smith as with thermal conductivity data. This difference presumably arises from the differences in the moisture content of the two varieties.

The regression equations are expressed, here, on the basis of four levels of temperature, below $-25^{\circ}C$, -25 to $-10^{\circ}C$, -10 to $-1^{\circ}C$ and above $-1^{\circ}C$. The equations are:

Golden Delicious:

$$C(T) = 3.36 + 0.0075T \ (kJ/kgC^{o}), \ T > -1^{o}C \qquad (43)$$

$$C(T) = 2.18 - 1.484T \ (kJ/kgC^{o}), \ -1 \geq T > -10^{o}C \qquad (44)$$

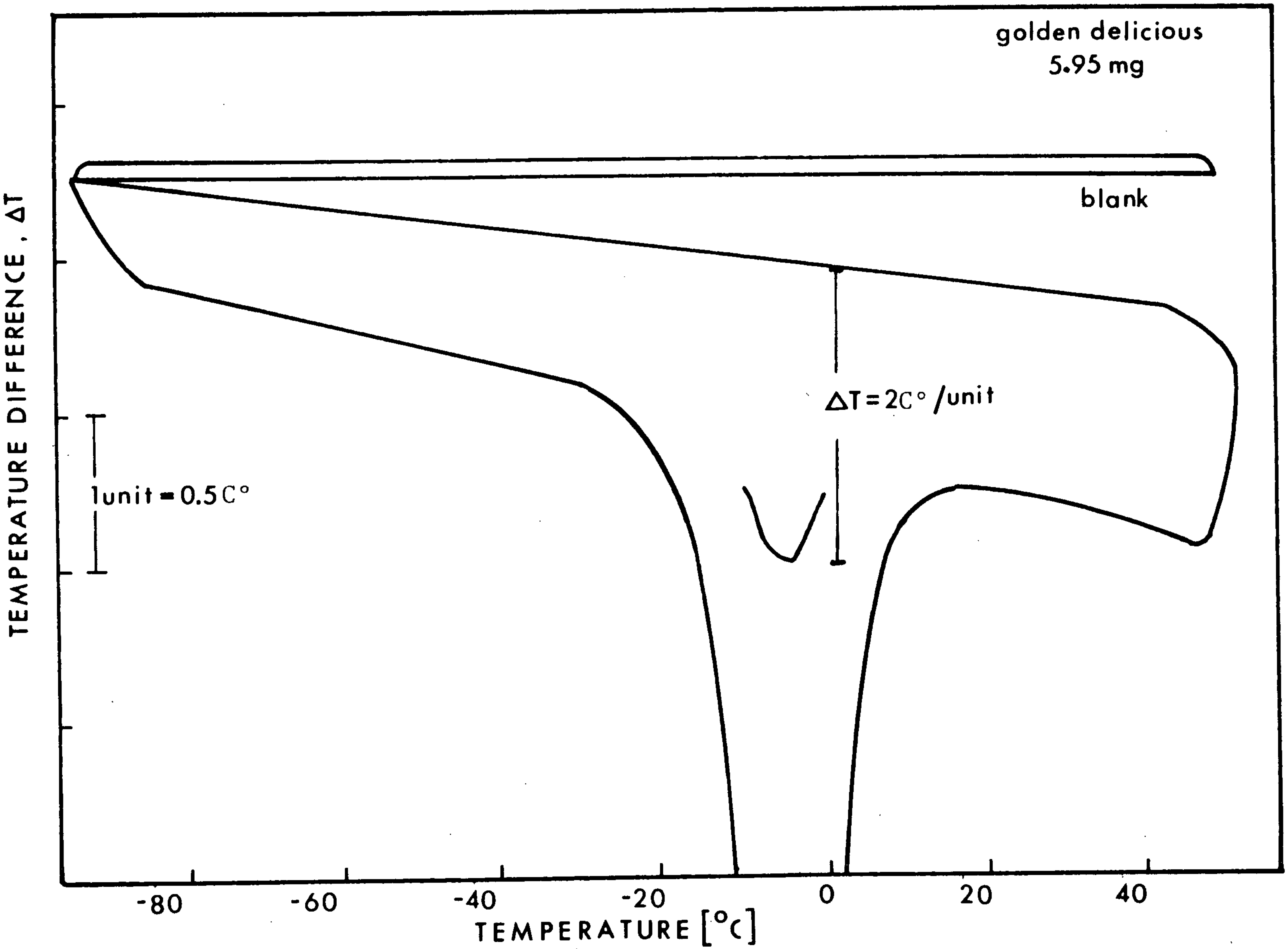

Figure 3. Warming thermogram of frozen Golden Delicious apples and of empty pan (blank) in a Dupont DSC. (ΔT scale of 2C°/unit refers to only the small peak area at the center while 0.5C°/unit refers to the rest of the curve).

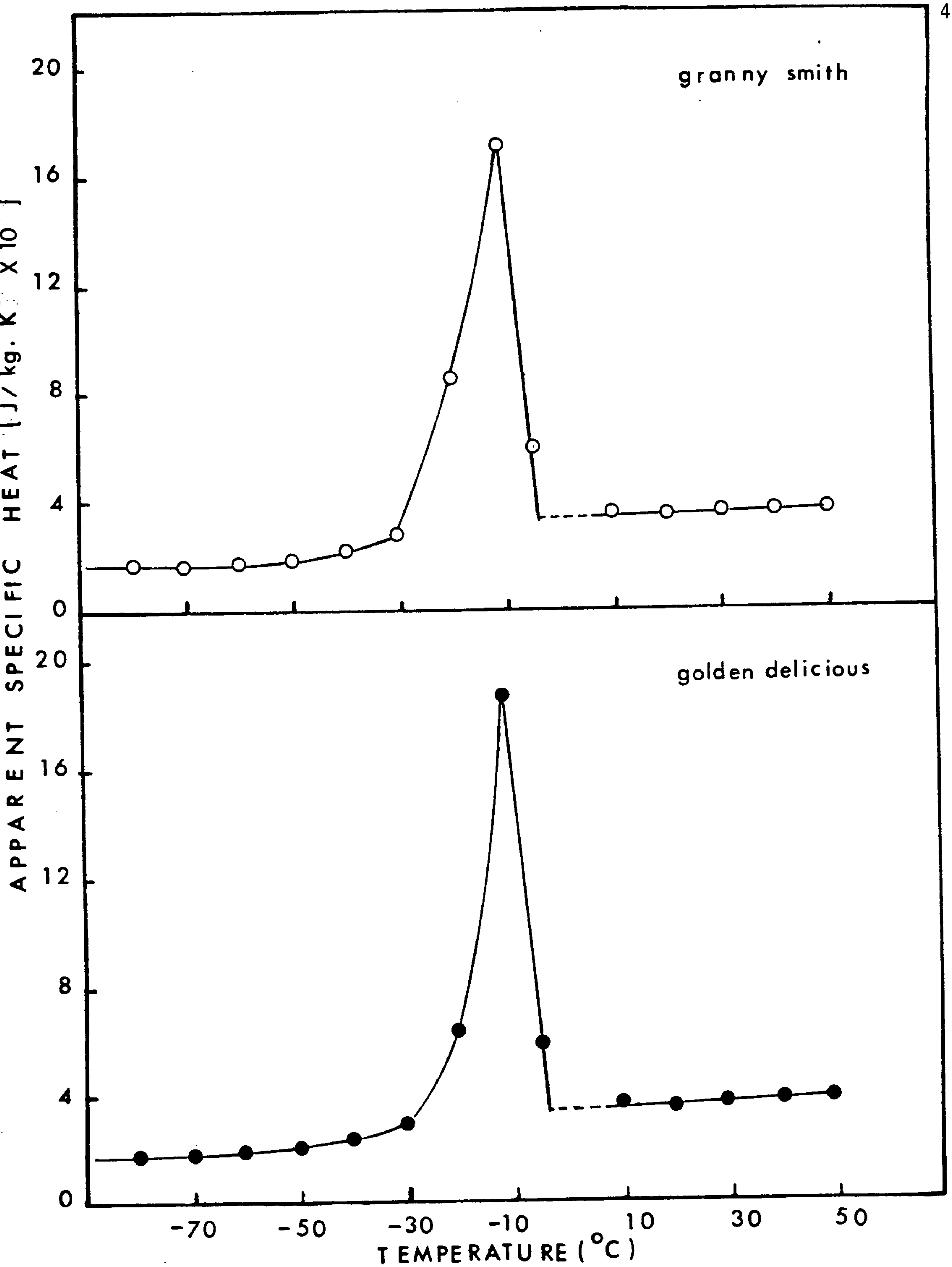

Figure 4. Mean apparent specific heat of apples at various temperatures.

$$C(T) = [24.40+0.791T] \times 10^3 \quad (J/kgC^o), \quad -10 \geq T > -25^oC \qquad (45)$$

$$C(T) = [2.89+0.0138T] \times 10^3 \quad (J/kgC^o), \quad T \leq -25^oC \qquad (46)$$

Granny Smith:

$$C(T) = [3.40+0.0049T] \times 10^3 \quad (J/kgC^o), \quad T > -1^oC \qquad (47)$$

$$C(T) = [2.65=1.421T] \times 10^3 \quad (J/kgC^o), \quad -1 \geq T > -10^oC \qquad (48)$$

$$C(T) = [24.93+0.760T] \times 10^3 \quad (J/kgC^o), \quad -10 \geq T > -25^oC \qquad (49)$$

$$C(T) = [2.50 + 0.0118T] \times 10^3 (J/kgC^o), \quad T \leq -25^oC \qquad (50)$$

These equations expressing the apparent specific heat as a function of temperature are used in the estimation of freezing time by finite difference numerical methods. For the purpose of freezing time computations by other models, the mean value of apparent specific heat between 20 and 60°C was taken for temperatures above the freezing point and the mean value between -30 and -80°C was taken for temperatures below the freezing point. At temperatures between 0 and -25°C, the effect of the release of latent heat was reflected in the apparent specific heat curve and hence were not used for calculating the mean values. The mean specific heats were 1.946 and 1.678 kJ/kgK^{o} below the freezing point and 3.690 and 3.578 kJ/kgK^{o} above the freezing point respectively, for Golden Delicious and Granny Smith apples. The apparent specific heat above freezing point was about 1.9 to 2.1 times more than that below the freezing point. There is not much information available in the published literature regarding the specific heat data for apples. Gane (1936) reported a value of 3.768 kJ/kgK^{o} for apples without mentioning the moisture content. Ordinanz (1946) gave a range of specific heat for apples with moisture contents between 75-85% as 3.73 - 4.02 kJ/kgK^{o}.

It has been generally recognized that the specific heat in foods containing high moisture can be estimated using a simple relationship (at temperatures above freezing point)

$$C = \frac{M}{100} \times 0.8(4187) + 0.2\ (4187) \quad J/kgK^{o} \quad (51)$$

which gives a value of 3.76 and 3.71 kJ/kgK^{o} for Golden Delicious and Granny Smith with 87.3% and 85.8% moisture content respectively. The observed values were slightly lower than the values reported in literature. The observed values of apparent specific heats of apples were consistent with the observations of Short and Bartlett (1944), at temperatures below -7°C. Short and Bartlett (1944), however, reported a constant value of 3.73 kJ/kgK° at temperatures above freezing point.

Density

For determination of density, the methods used were different for frozen and unfrozen samples. For the unfrozen material the method was straight forward. There was no difficulty in cutting the apples into cylinders using a cork borer of known internal diameter and then to cut the cylinders to a known length using two spaced knives. The reproducibility of the results was good. This method was not suitable for frozen samples because of the difficulty in cutting the samples into proper size. The modification suggested to accommodate the frozen samples is simple enough. The main disadvantage of the method was that the temperature of material did not remain constant over the period of measurement, since the volume displacement was measured using water at 1-2°C. The experiment needed only a few seconds and the temperature change estimated during that time was less than 5C°. Hence the temperature of measurement could be taken as ±3C° of the specified temperature. This method was not recommended for use with unfrozen samples because of the porosity of the apple slices. In the frozen state, however, because of the ice formation, the structure would be harder and less porous. The mean values of density for Golden Delicious and Granny Smith respectively were 843 and 837 kg/m^3 at $25^{\circ}C$, 847 and 820 kg/m^3 at $2^{\circ}C$, 785 and 789 kg/m^3 at $-20^{\circ}C$ and 791 and 787 kg/m^3 at $-35^{\circ}C$. The values for the two varieties were more comparable in the frozen state than in the unfrozen state. The changes in the density below and above freezing point with respect to temperatures were not significant. However, the density in the frozen state was approximately 5.2 to 6.8% less than the density in the unfrozen state. For the purpose of computation of freezing times by different models a mean value of 845 and 788 kg/m^3 for Golden Delicious and 829 and 786 kg/m^3 for Granny Smith were taken for temperatures above and below freezing point respectively.

Thermal Diffusivity

Thermal diffusivity of apples was calculated using the relationship given in the equation 34. The mean values of thermal diffusivity above and below freezing point respectively were 1.371×10^{-7} and 9.430×10^{-7} m^2/s for Golden Delicious and 1.342×10^{-7} and 9.257×10^{-7} m^2/s for Granny Smith. The mean value reported by Gane (1936) for unfrozen apples (0 to 32°C) was 1.265×10^{-7} m^2/s. Thermal diffusivity of frozen apples was about 6.9 times that of unfrozen samples. Using equations (37-40, 43-50) which express thermal conductivity and specific heat as functions of temperature, the variations of thermal diffusivity with temperature (assuming density of the material to be constant in unfrozen and frozen states) are shown in the following equations

Golden Delicious:

$$\alpha(T) = (0.00278T+1.389) \times 10^{-7} \ (m^2/s) \quad T > T_f \quad (52)$$

$$\alpha(T) = (-0.109T + 5.085) \times 10^{-7} \ (m^2/s) \quad T \leq T_f \quad (53)$$

Granny Smith:

$$\alpha(T) = (0.00556T+1.309) \times 10^{-7} (m^2/s) \quad T > T_f \quad (54)$$

$$\alpha(T) = (-0.130T + 4.745) \times 10^{-} \ (m^2/\ ) \quad T \leq T_f \quad (55)$$

These equations (52-55) assume the latent heat to be released at the freezing point. Hence the apparent specific heat at temperatures between -30 to -80°C was considered to cover the whole frozen region. To get the more realistic approach of latent heat release over a range of temperature, the apparent specific heat between -1 to -30°C which reflects the latent heat effect had to be considered. The regression equations for thermal diffusivity dependence on temperature in this region are given below:

Golden Delicious

$$\alpha(T) = (0.437T + 4.367) \times 10^{-7}\ (m^2/s) \quad T_f \geq T > -10°C \quad (56)$$

$$\alpha(T) = (-0.187T - 1.215 \times 10^{-7}\ (m^2/s) \quad -10 \geq T > -25°C \quad (57)$$

Granny Smith

$$\alpha(T) = (0.339T + 3.656) \times 10^{-7}\ (m^2/s) \quad T_f \geq T > -10°C \quad (58)$$

$$\alpha(T) = (-0.123T - 0.603) \times 10^{-7}\ (m^2/s) \quad -10 \geq T > -25°C \quad (59)$$

Equations 52 and 54 hold good for $T > T_f$ and 53 and 55 for $T \leq -25°C$ to complete the spectrum of temperature -80 to 60°C.

Surface Heat Transfer Coefficient

Two methods were tried for determining surface heat transfer coefficients associated with the freezing systems. The method suggested by Charm (1972) involved warming up of a material of known thermal properties in the freezing system, thus necessitating cooling of the test material below the temperature of the freezing system. Hence this was not suitable for use in determining the $\bar{h}$ associated with liquid nitrogen. Alternatively, the slope could be determined from the latter part of the freezing data. Experiments carried out in two systems (freezing in air at -21°C and immersion in ethylene glycol at -18°C) showed that the reciprocals of the slopes calculated using the warming and freezing data were fairly close. Further, the mean value of surface heat transfer coefficients for the system of freezing in ethylene glycol (100%) at -20 to -24°C calculated by the method of Charm (1972) was 54.06 $W/m^2K°$ and, by using Plank's formula (equation 35) was 55.59 $W/m^2K°$. Since these two methods gave similar results, for other freezing systems, Plank's method was used. Measurement of surface temperature was not attempted because of the non-homogeneity of the apple pack to have a uniform contact at the surface. Hence, the method suggested by Cleland and Earle (1976) was not employed.

The mean values of four to eight replicates of the surface heat transfer coefficients for the different freezing systems were as follows:

Immersion in ethylene glycol (100%) at -20 to $-24^{\circ}C$, 55.59 W/m^2K°; immersion in ethylene glycol (60%) at -18 to $-20^{\circ}C$, 59.68 W/m^2K°; freezing in air at -21 to $-25^{\circ}C$, 17.83 W/m^2K°; freezing in air at -28 to $-30^{\circ}C$, 13.85 W/m^2K°; and immersion in liquid nitrogen at $-197^{\circ}C$, 68.42 W/m^2K°. The heat transfer coefficient in 100% ethylene glycol was relatively small compared to that for 60% ethylene glycol although the freezing temperature was lower in the latter. This was probably due to higher viscosity associated with 100% ethylene glycol at lower temperatures. Also the heat transfer coefficient associated with the freezer room at -21 to $-25^{\circ}C$ was higher than that provided in the freezer room at -28 to $-30^{\circ}C$ because of a slightly higher air velocity in the former.

Prediction of Freezing Times

Experimental Freezing Times

Thirty three freezing experiments were conducted with each variety of apples. The experimental design was set up to cover a wide range of conditions that are commonly encountered in food freezing. The cooling medium temperature was varied from -18 to -30°C (and -197°C in liquid nitrogen), initial temperature from 1 to 25°C, diameter of the container 0.076 to 0.103m, surface heat transfer coefficient from 13.85 to 68.42 W/m^2K^o.

Tables 2 and 3 show the experimental conditions for each run, the experimental freezing times to reach -10 C and -18°C from the onset of cooling and also the time taken to cross the zone of maximum ice crystal formation (-1 to -5°C) in each run.

Based on forty four replicates of duplicate values under the different experimental conditions shown in Tables 2 and 3, the mean experimental error was estimated to be 2.38%. This low experimental error reflected considerable uniformity in the method of packing the apples into the can.

The freezing curves for the two varieties of apples in 300 x 407 cans in five different freezing systems are given in Figure 5. The initial temperature of the apples varied from 20 to 23°C. Freezing curves for the two varieties under similar conditions with an initial temperature of 3.5 to 7.0°C are given in Figure 6.

Table 2. Experimental data for freezing of Golden Delicious apples.

	Freezing Conditions				Freezing Characteristics		
Code	Can Size	T_i (°C)	T_a (°C)	Mode	Time to reach -10°C (h)	Time to reach -18°C (h)	Time to cross -1° to -5°C (h)
GD1	300x407	21.0	-20	I	2.03	2.33	0.37
GD2	300x407	21.0	-20	I	2.06	2.33	0.40
GD3	300x407	21.0	-27	A	5.13	5.57	2.67
GD4	300x407	21.0	-27	A	5.13	5.63	2.57
GD5	300x407	21.0	-18	I	2.47	2.93	1.00
GD6	300x407	21.0	-18	I	2.27	2.93	1.13
GD7	300x407	23.0	-21	A	5.25	6.08	2.83
GD8	300x407	23.0	-21	A	5.47	6.25	3.05
GD9	300x407	20.0	-197	L	0.242	0.250	0.013
GD10	300x407	20.0	-197	L	0.23	0.23	0.012
GD11	300x407	4.5	-24	I	1.77	1.95	0.90
GD12	300x407	5.5	-24	I	1.70	1.87	0.74
GD13	300x407	4.0	-29	A	4.47	4.90	3.20
GD14	300x407	4.0	-29	A	4.53	4.97	3.20
GD15	300x407	3.5	-20	I	2.13	2.50	1.27
GD16	300x407	3.5	-20	I	2.23	2.53	1.30
GD17	300x407	5.0	-22	A	4.20	5.20	2.53
GD18	300x407	7.0	-22	A	4.33	4.97	2.57
GD19	300x407	6.0	-197	L	0.193	0.205	0.062
GD20	307x409	18.0	-23	I	2.73	3.00	1.23
GD21	307x409	17.0	-23	I	2.83	3.07	1.33
GD22	307x409	18.0	-22	A	5.37	6.03	3.13
GD23	307x409	18.0	-22	A	5.30	5.90	3.20
GD24	307x409	18.5	-197	L	0.325	0.328	0.033
GD25	307x409	2.0	-23	I	2.33	2.60	1.70
GD26	307x409	2.0	-24	A	5.47	6.10	3.97
GD27	307x409	2.0	-197	L	0.267	0.268	0.072
GD28	401x411	19.0	-20	I	3.86	4.27	2.00
GD29	401x411	16.0	-23	A	6.36	7.13	2.90
GD30	401x411	19.0	-197	L	0.360	0.408	0.032
GD31	401x411	2.0	-22	I	3.60	3.97	2.23
GD32	401x411	1.0	-25	A	5.97	6.06	4.10
GD33	401x411	2.0	-197	L	0.310	0.340	0.095

I = Immersion in ethylene glycol
A = Air
L = Liquid Nitrogen Immersion

Table 3. Experimental data for freezing of Granny Smith apples.

Code	Can Size	T_i (°C)	T_a (°C)	Mode	Time to reach -10°C (h)	Time to reach -18°C (h)	Time to cross -1° to -5°C (h)
	Freezing Conditions				Freezing Characteristics		
GS1	300x407	24.5	-22.0	I	2.20	2.43	0.43
GS2	300x407	24.5	-22.0	I	2.10	2.33	0.33
GS3	300x407	24.5	-28.0	A	4.70	5.20	2.60
GS4	300x407	24.5	-28.0	A	4.67	5.17	2.60
GS5	300x407	23.0	-18.0	I	2.30	2.93	1.07
GS6	300x407	23.0	-18.0	I	2.37	2.97	1.10
GS7	300x407	23.5	-21.0	A	5.30	6.43	2.25
GS8	300x407	23.5	-21.0	A	4.80	5.93	1.93
GS9	300x407	23.5	-197	L	0.215	0.222	0.017
GS10	300x407	23.5	-197	L	0.260	0.272	0.025
GS11	300x407	2.0	-21.0	I	2.17	2.47	1.50
GS12	300x407	2.0	-21.0	I	2.17	2.50	1.47
GS13	300x407	1.5	-30.0	A	3.50	3.77	2.63
GS14	300x407	1.5	-30.0	A	4.03	4.43	2.90
GS15	300x407	1.5	-20.0	I	2.30	2.73	1.33
GS16	300x407	1.5	-20.0	I	2.17	2.60	1.50
GS17	300x407	3.0	-22.0	A	4.00	4.83	2.80
GS18	300x407	3.0	-22.0	A	4.47	5.40	2.93
GS19	300x407	4.0	-197	L	0.198	0.208	0.063
GS20	307x409	16.0	-22.0	I	2.90	3.26	1.53
GS21	307x409	18.0	-22.0	I	2.90	3.23	1.50
GS22	307x409	18.5	-22.0	A	5.53	6.33	2.97
GS23	307x409	18.5	-22.0	A	5.70	6.37	3.43
GS24	307x409	18.5	-197	L	0.310	0.322	0.029
GS25	307x409	2.0	-23.0	I	2.33	2.53	1.67
GS26	307x409	2.0	-24.0	A	5.44	6.00	3.73
GS27	307x409	4.5	-197	L	0.270	0.302	0.075
GS28	401x411	19.0	-20.0	I	4.00	4.33	2.03
GS29	401x411	21.0	-23.0	A	6.56	7.70	3.33
GS30	401x411	19.0	-197	L	0.380	0.419	0.035
GS31	401x411	2.0	-22.0	I	3.73	4.20	2.56
GS32	401x411	3.0	-25.0	A	6.17	7.10	3.83
GS33	401x411	2.0	-197	L	0.330	0.362	0.100

I = Immerson in ethylene glycol
A = Air
L = Liquid Nitrogen Immersion

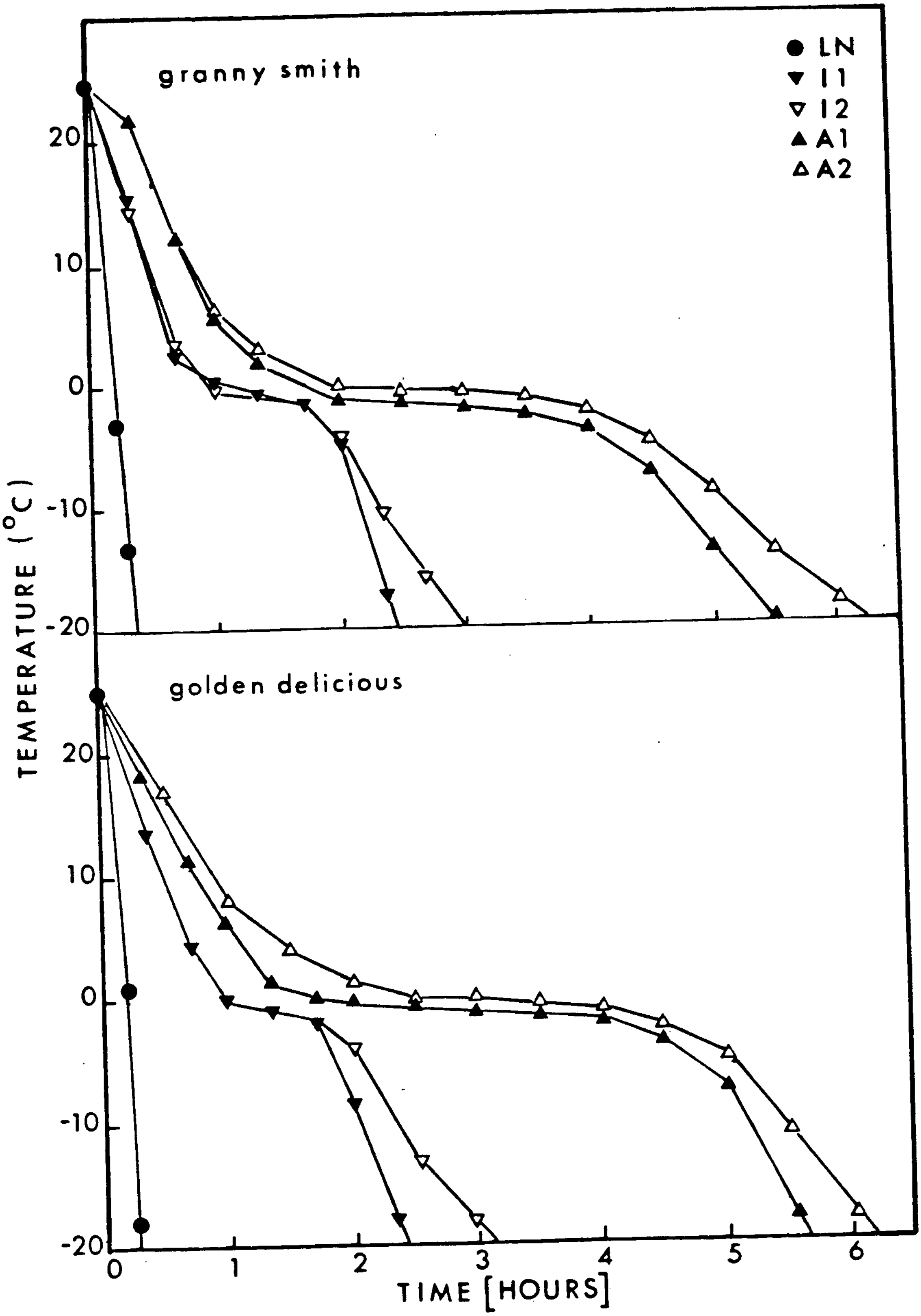

Figure 5. Freezing curves for Golden Delicious and Granny Smith apples under different conditions in a tinplate can of size 300x407, with a product initial temperature of 20-23°C. (LN, Immersion in liquid nitrogen at -197°C, I1, I2, immersion in ethylene glycol at -20 and -18°C, A1 and A2, freezing in air at -27 and -23°C respectively.)

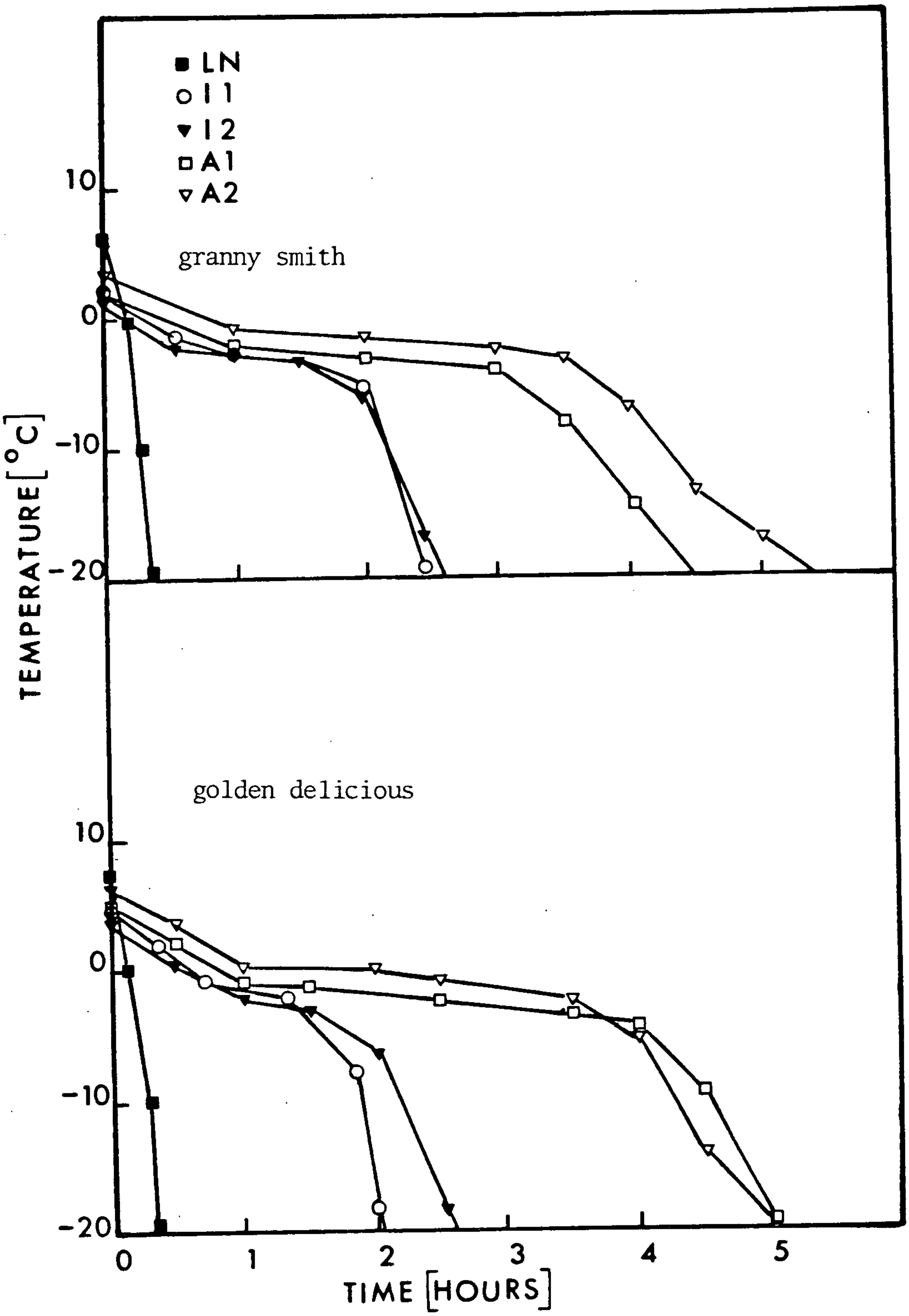

Figure 6. Freezing curves for Golden Delicious and Granny Smith apples under different conditions in a tin-plate can of size 300x407 with a product initial temperature of 2-7°C. (LN, liquid nitrogen freezing at -197°C, I1, I2, immersion in ethylene glycol at -21 and -20°C, A1 and A2, freezing in air at -30 and -22°C respectively).

The Zone of Maximum Ice Crystal Formation

A comparison of Figures 5 and 6 and Tables 2 and 3 indicates that the time required to cross the zone of maximum ice crystal formation (-1 to -5°C) depended on the temperature of the freezing medium, heat transfer coefficient as well as the initial temperature of apples. For higher initial temperature, the time taken to cross the zone was shorter provided the freezing system remained the same This time has been termed the 'thermal arrest time' because the temperature in this zone changes more slowly with time or is arrested until the latent heat is released. This finding is in agreement with the findings of Long (1955) on the freezing of fish. In order to provide a better comparison, the 'thermal arrest time' has been plotted against the freezing time to reach -10°C (a function of freezing temperature as well as the heat transfer coefficient) at two mean initial temperatures, 20.3°C and 3.0°C in Figure 7, for the data of two varieties pooled. The regression equations showed very high linear correlations (0.97 at 20°C and 0.99 at 3°C). The equations were:

$$\text{At } 3^{\circ}\text{C:} \quad t_{(-1 \text{ to } -5)} = \frac{0.70}{3600} t_{f(-10)} - 0.12 \text{ (h)} \qquad (60)$$

$$\text{At } 20^{\circ}\text{C:} \quad t_{(-1 \text{ to } -5)} = \frac{0.57}{3600} t_{f(-10)} - 0.28 \text{ (h)} \qquad (61)$$

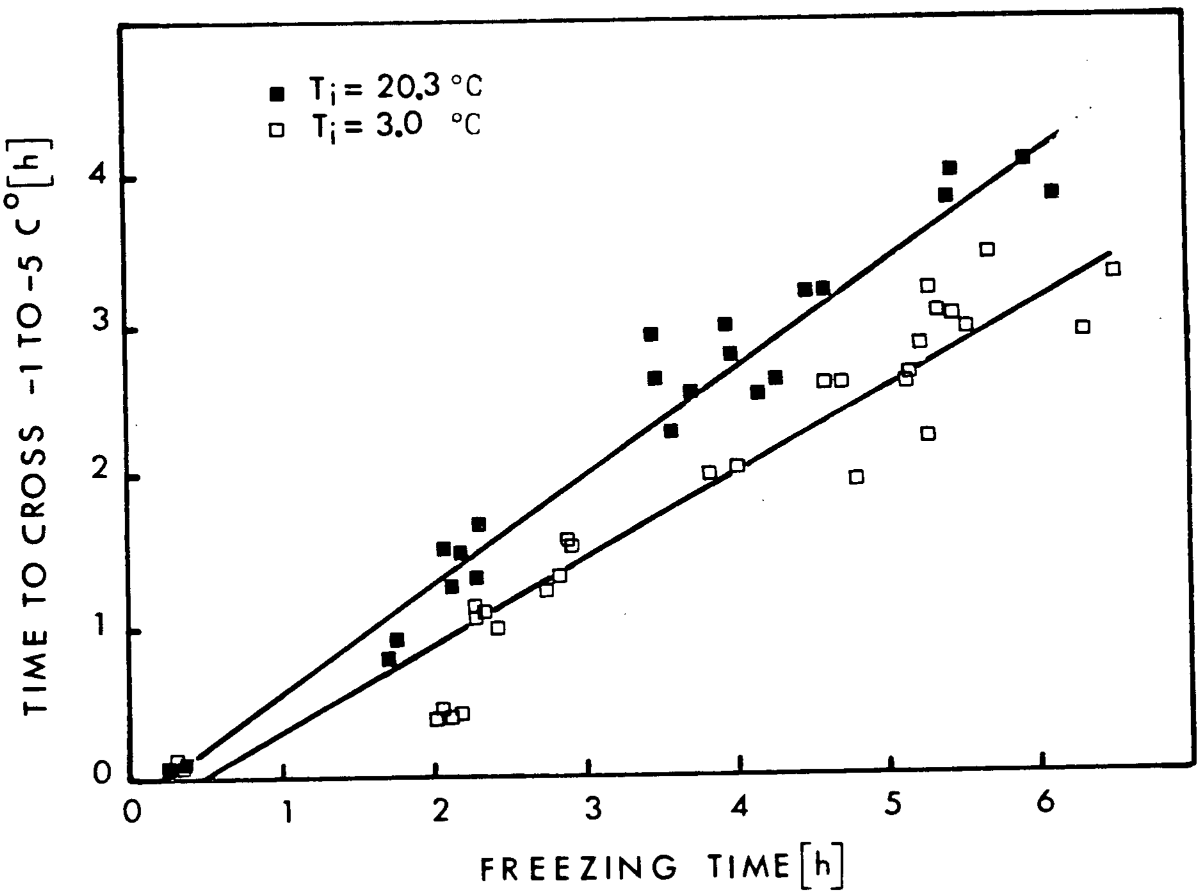

Figure 7. Variations in the time taken to cross the zone of maximum ice crystal formation (-1 to -5°C) with freezing time to reach -10°C, at two mean initial temperatures, 3.0 and 20.3°C.

Predicted Freezing Times: Analytical Methods

Freezing times were calculated using the different methods proposed in the literature and the results compared with the experimental freezing time to calculate the percentage difference between the two which is termed as 'the prediction error' of the particular model. The methods investigated were divided into two groups, those requiring numerical evaluation by a computer and those requiring only a simple calculation.

For all prediction models involving constant thermophysical properties, the data obtained from part A of this investigation were made use of. These values have been summarized in Table 4.

Most of the prediction models (other than the numerical analysis methods) are based on Plank's equation. The predicted freezing times by models proposed by Plank (1941), t_P, Nagaoka et al. (1955), t_{NF}, t_{NC}, I.I.R. (1972), t_I, and Mellor (1976), t_M, along with the prediction errors are summarized in Appendix 1 and 2 for the varieties Golden Delicious and Granny Smith respectively.

When the pooled data from all the experimental conditions for the two varieties of apples were analyzed, the mean prediction errors (taking only the absolute value

Table 4. Thermo-physical data for freezing time computations.

Parameter	Goden Delicious		Granny Smith	
	Unfrozen	Frozen	Unfrozen	Frozen
Thermal conductivity (W/mk°)[a]	0.427	1.445	0.398	1.220
Specific heat $\times 10^3$ (J/kgK°)[b]	3.690	1.946	3.578	1.678
Density (kg/m^3)$\times 10^2$ [c]	8.450	7.880	8.290	7.860
Thermal diffusivity (m^2/s $\times 10^{-7}$)[d]	1.371	9.430	1.342	9.257
Moisture (%)[e]	81.3		85.8	
Latent heat (J/kg $\times 10^3$)[f]	292.4		287.4	
Freezing point (°C)[g]	-1.0		-1.0	
Surface film conductance (W/m^2K°)[h]	12.7-68.4		12.7-68.4	
Initial temperature (°C)	1-25		1-25	
Final temperature (°C)	-10, -18		-10, -18	
Ambient temperature (°C)	-18 to -30		-18 to -30	
Can Size (Diameter) (m)	0.076-0.103		0.076-0.103	

a average of three replicates at different temperatures
b average of four replicates at different temperatures
c average of eight replicates at 4 temperatures
d calculated from a, b and c
e average of 36 replicates
f calculated from latent heat = $\frac{\%\ \text{moisture}}{100} \times 334.9$ kJ/kg
g taken from freezing curves
h average of 4-8 replicates

of the errors) in using the different models were: t_P, 18.2%; t_I, 9.0%; t_{NF}, 17.0%; t_{NC}, 12.9% and t_M, 13.9%. t_{NF} is the freezing time in hours by Nagaoka's model calculated using the British units and t_{NC}, the same using the Metric units. The above-mentioned values, however, do not represent the true performance of the different prediction models in their capacity to predict the freezing times under the different conditions of freezing.

In Table 5, the observations have been grouped into four general freezing conditions for each variety based on the initial and final temperatures as follows

C1 = Freezing from T_i = 16 to 25°C to T_c = -10°C

C2 = Freezing from T_i = 1 to 7°C to T_c = -10°C

C3 = Freezing from T_i = 16 to 25°C to T_c = -18°C

C4 = Freezing from T_i = 1 to 7°C to T_c = -18°C

The mean percentage prediction errors under these four conditions obtained by using the different prediction models on the two varieties of apples are given in Table 5. Under these different conditions significant differences in the prediction errors were observed between the conditions C1 and C2

Table 5. Mean errors in predicting freezing times of apples by different models under different conditions of freezing.

Code	Freezing Conditions		Golden Delicious					Granny Smith				
	T_i (°C)	T_c (°C)	t_P (%)	t_I (%)	t_M (%)	t_{NF} (%)	t_S (%)	t_P (%)	t_I (%)	t_M (%)	t_{NF} (%)	t_S (%)
C1	16-25	-10	17.7	12.3	11.2	28.4	9.2	14.1	15.6	13.2	36.1	7.3
C2	1-7	-10	12.4	7.2	14.0	7.9	6.4	9.7	5.5	13.0	5.9	6.6
C3	16-25	-18	26.7	6.1	12.5	18.2	6.9	24.6	7.2	12.6	23.4	4.8
C4	1-7	-18	20.8	8.3	17.7	7.5	5.3	19.4	9.7	17.3	8.5	6.6

Code	T_i (°C)	T_c (°C)	Two varieties mixed				
			t_P (%)	t_I (%)	t_M (%)	t_{NF} (%)	t_S (%)
C1	16-25	-10	15.9	14.0	12.2	32.3	8.3
C2	1-7	-10	11.1	6.4	13.5	6.9	6.5
C3	16-25	-18	25.6	6.7	12.6	20.8	5.8
C4	1-7	-18	20.1	9.0	17.5	8.0	6.0

t_P Freezing time model, Plank (1941)

t_I Freezing time model, International Institute of Refrigeration (1972)

t_S Suggested model

t_{NF} Freezing time model, Nagaoka *et al.* (1955)

t_M Freezing time model, Mellor (1976) in most of the above-mentioned models and between C3 and C4, C1 and C3, and C2 and C4 in some models (Table 5). This clearly indicates the differences in the capability of the different models in accounting for the precooling and tempering periods.

Plank's Model

Plank's equation assumes that the material is initially at the freezing point and estimates the time required to complete the freezing (to reach a temperature of -10°C). Hence, this method had the least error under condition C2 (T_i = 1-7°C and T_c = -10°C) which was about 11.1%, and maximum error under condition C3 (T_i = 16-25°C and T_c = -18°C) which was about 24.6 to 26.7% (Table 5).

I.I.R. Modification

The prediction error in the model proposed by the International Institute of Regrigeration (1972) was found to be the least among the four models. This model does take into account the precooling as well as the tempering period by replacing the latent heat factor in Plank's equation by the enthalpy from T_i to T_c. Even so, the prediction errors were quite high. Under the condition C1 which had a greater influence due to the precooling period (T_i = 16-25°C, T_c = -10°C), the mean prediction error ranged from 12.3 to 15.6%. Significant differences in the prediction errors were observed only when C1 was compared with C2, C3 and C4 (Table 5).

Nagaoka Modifications

The Nagaoka et al. (1955) modifications resulted generally in a considerable overestimation of the freezing time except under conditions where the initial temperature was low. This model under low T_i, however, was no different from the one proposed by the International Institute of Refrigeration (1972) which had already been shown to give low prediction errors under the condition C2.

Another point worth noticing in the model of Nagaoka et al. (1955) is that an additional dimensional property in the form of $[1 + 0.00445\ (T_i - T_f)]$ has been used as a factor to be multiplied by t_I to get the modified freezing time. Because of the dimensional property (temperature in this case), the factor assumes different values depending on the unit in which the temperature is measured. If $(T_i - T_f)$ is equal to 25 C°, the factor would be 1.111 and for a corresponding temperature difference in F°, the factor would be 1.200. Hence t_{NF} which was obtained by using F° in the above factor was always greater than t_{NC} where temperature was taken in C°. Model t_{NF} resulted in mean prediction errors of 20.8 to 32.3% when T_i was 16-25^{o}C (Table 5).

Mellor Modification

Mellor's (1976) modification showed a consistently higher prediction error under all four conditions for both the varieties. This model suffers from two drawbacks. Firstly, it does not have any factor to account for differences in the tempering period. Hence the freezing time estimated to -10^{o}C would be same as that for -18^{o}C. Secondly, because of the factor $(T_f - T_a)$ C_2 in the ΔH calculation, under conditions when the freezing temperatures were very low (e.g. liquid nitrogen, -197^{o}C), the model resulted in considerable overestimation of the freezing time (as high as 50%). The prediction mean error in this model was 11.2 to 14.0% under C1 to C3 and 17.3 to 17.7% under the condition C4 (Table 5).

General Considerations

In general, between the two varieties there were no significant differences in the mean prediction errors by using the different models under the four different conditions. The mean errors for the two varieties pooled are also included in Table 5.

On the basis of the results given in Table 5, it would not be possible to determine whether the models overestimate the freezing time or underestimate it because the table was based on the absolute values of the prediction errors giving only their magnitudes. Figures 8, 9 and 10 represent the frequency histograms of the prediction errors, under the four different conditions, associated with the different prediction models for Golden Delicious, Granny Smith and the two pooled together respectively. In these diagrams the ordinate scale for frequency is an arbitrary one such that the area under each histogram is the same. These figures could be used to obtain the information on the quality of the prediction error of the different models under the different freezing conditions as to whether it overestimated or underestimated the freezing time.

Plank's equation thus resulted in gross underestimation while Nagaoka et al. (1955) model under T_i = 16-25^{o}C largely overestimated the freezing time, and under condition C4 resulted in considerable underestimation. Mellor's(1976) model showed a larger scatter under all the conditions with a peak frequency at 0% error under conditions where T_c = -10^{o}C. With T_c = -18^{o}C the model largely underestimated the freezing time for obvious reasons.

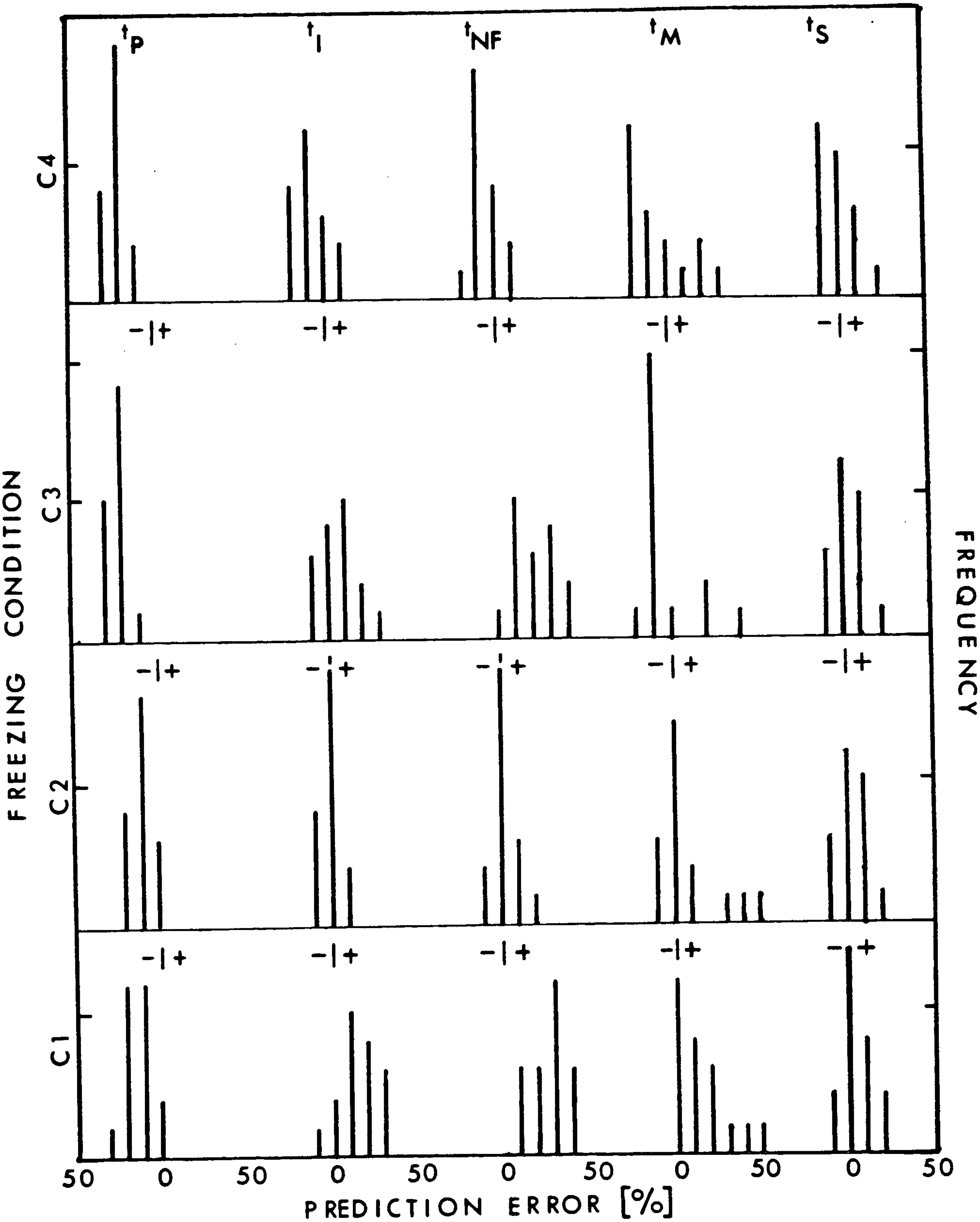

Figure 8. Frequency histograms for prediction error percentage in Golden Delicious apples using different models; Plank (1941), t_P; I.I.R. (1972), t_I; Nagaoka et al. (1955), t_{NF}; Mellor (1976), t_M; author's modification, t_S, under various conditions: C1(T_i = 16-25°C, T_c = -10°C), C2 (T_i = 1-7°C, T_c = -10°C), C3 (T_i = 16-25°C, T_c = -18°C) and C4(T_i = 1-7°C, T_c = -18°C)

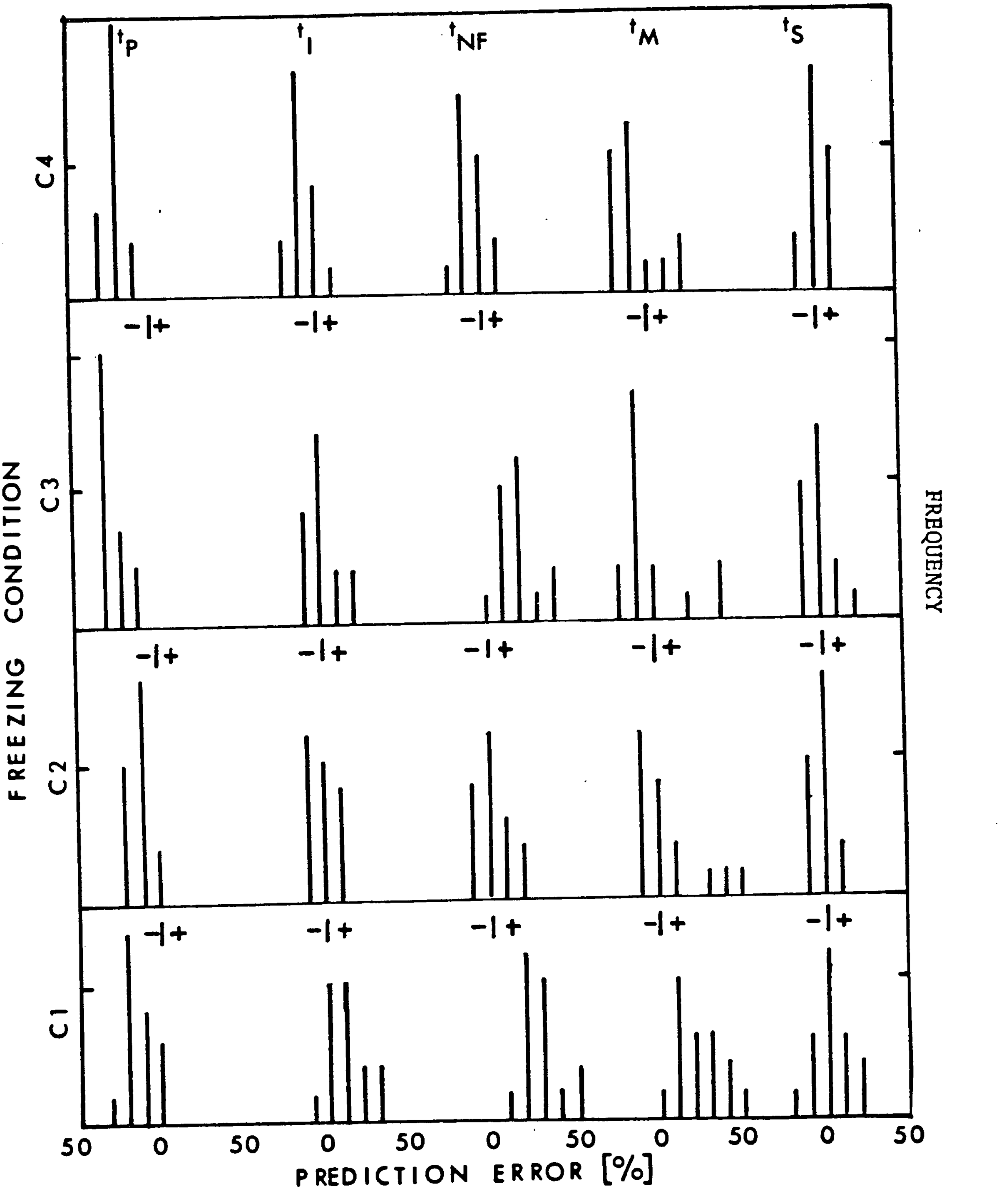

Figure 9. Frequency histograms for prediction error percentage in Granny Smith apples using different models; Plank (1941), t_P; I.I.R. (1972), t_I; Nagaoka et al. (1955), t_{NF}; Mellor (1976), t_M; author's modification, t_S, under various conditions: C1(T_i = 16=25°C, T_c = -10°C), C2 (T_i = 1-7°C, T_c = -10°C), C3(T_i = 16-25°C, T_c = -18°C) and C4(T_i = 1-7°C, T_c = -18°C).

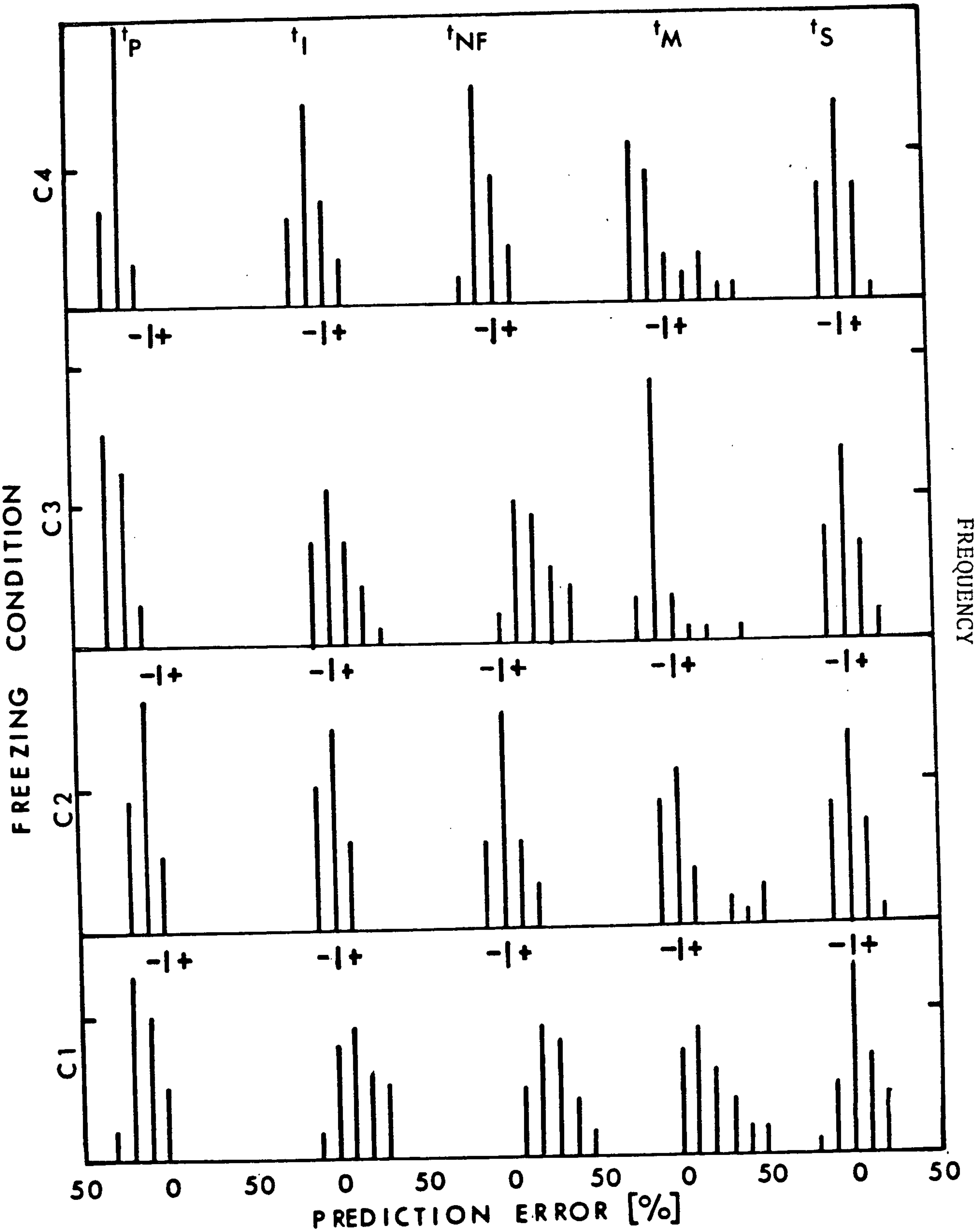

Figure 10. Frequency histograms for prediction error percentage in apples of two varieties using different models; Plank (1941), t_P; I.I.R. (1972), t_I; Nagaoka et al. (1955), t_{NF}; Mellor (1976), t_M; author's modification, t_S, under various conditions: C1(T_i = 16-25°C, T_c = -10°C), C2 (T_i = 1-7°C, T_c = -10°C), C3(T_i = 16-25°C, T_c = -18°C) and C4(T_i = 1-7°C, T_c = -18°C).

A Suggested Modification

Most of the modifications of Plank's equation attempt at altering ΔH, the amount of heat to be released from the material in order that it is cooled from its initial temperature down to the final temperature. This included the latent heat L, the temperature differential (T_i - T_f) and specific heat before freezing (C_1) for the precooling period, and the temperature differential (T_f - T_c) and the specific heat after freezing (C_2) for the tempering period. Taking into consideration the model proposed by International Institute of Refrigeration (1972) in Table 5 and Figures 8 and 9, it can be observed that conditions C1 and C3 resulted in overestimation of freezing time (with mean errors of 14.0 and 6.7 % respectively) and C2 and C4 resulted in underestimation (mean errors of 6.4 and 9.0% respectively). The influencing factor in C1 was essentially the sensible heat during the precooling period and in C4, the sensible heat in the tempering period. These two represent the extreme conditions on either side of the freezing point, thus experience the maximum errors of overestimation of the precooling period and underestimation of the tempering period. The other two intermediate conditions C2 and C3 which have these two influences acting together resulted in intermediate errors.

The correction factor should, therefore, be aimed at minimizing the influence of the factors $C_1(T_i - T_f)$ and $C_2(T_f - T_c)$. This could be achieved by suitably reducing the magnitude of the former and increasing the magnitude of the latter by a multiple regression analysis of the experimental values of $C_1(T_i - T_f)$ and $C_2(T_f - T_c)$ on the expected value of their sum (ΔH - L), obtained by using the actual experimental freezing times in the prediction model of International Institute of Refrigeration (1972) under each of 33 different runs for both the varieties. The regression equation gave a significantly high correlation coefficient (0.635) with 40.3 % of the variance being explained by the two variables.

Based on the above regression equation the suggested modification to take into account the different freezing conditions is given below.

$$t = [0.3022\, C_1(T_i - T_f) + L + 2.428\, C_2(T_f - T_c)] \cdot \frac{\rho_2}{T_f - T_a} \cdot \left[\frac{Pd}{h} + \frac{Rd^2}{k_2}\right] \tag{62}$$

The mean percentage error and the frequency histotrams under the different conditions of freezing for the suggested model are also shown in Table 5 and Figures 8-10.

The mean errors under the four conditions C1 to C4 were 7.3 to 9.2% (C1), 6.4 to 6.6% (C2), 4.8 to 6.9% (C3) and 5.3 to 6.6% (C4) which were more consistent than those observed for any other model. The overall mean error observed was 6.6%. Considering that the mean experimental error was 2.38%, the mean prediction error associated with the suggested model was less than 5% beyond the experimental error.

Figure 11 shows a relationship between the experimental freezing times and the values predicted by the suggested modification (t_S). A least squares regression analysis gave a coefficient of determination of 0.984 with the equation for the fitted line as follows:

$$t_S = 0.986\, t_e + 0.0784 \text{ (h)} \qquad (63)$$

Predicting Freezing Times: Numerical Methods

The numerical methods constitute a second major group of methods used for predicting freezing times of foods. In the present study only one type of numerical

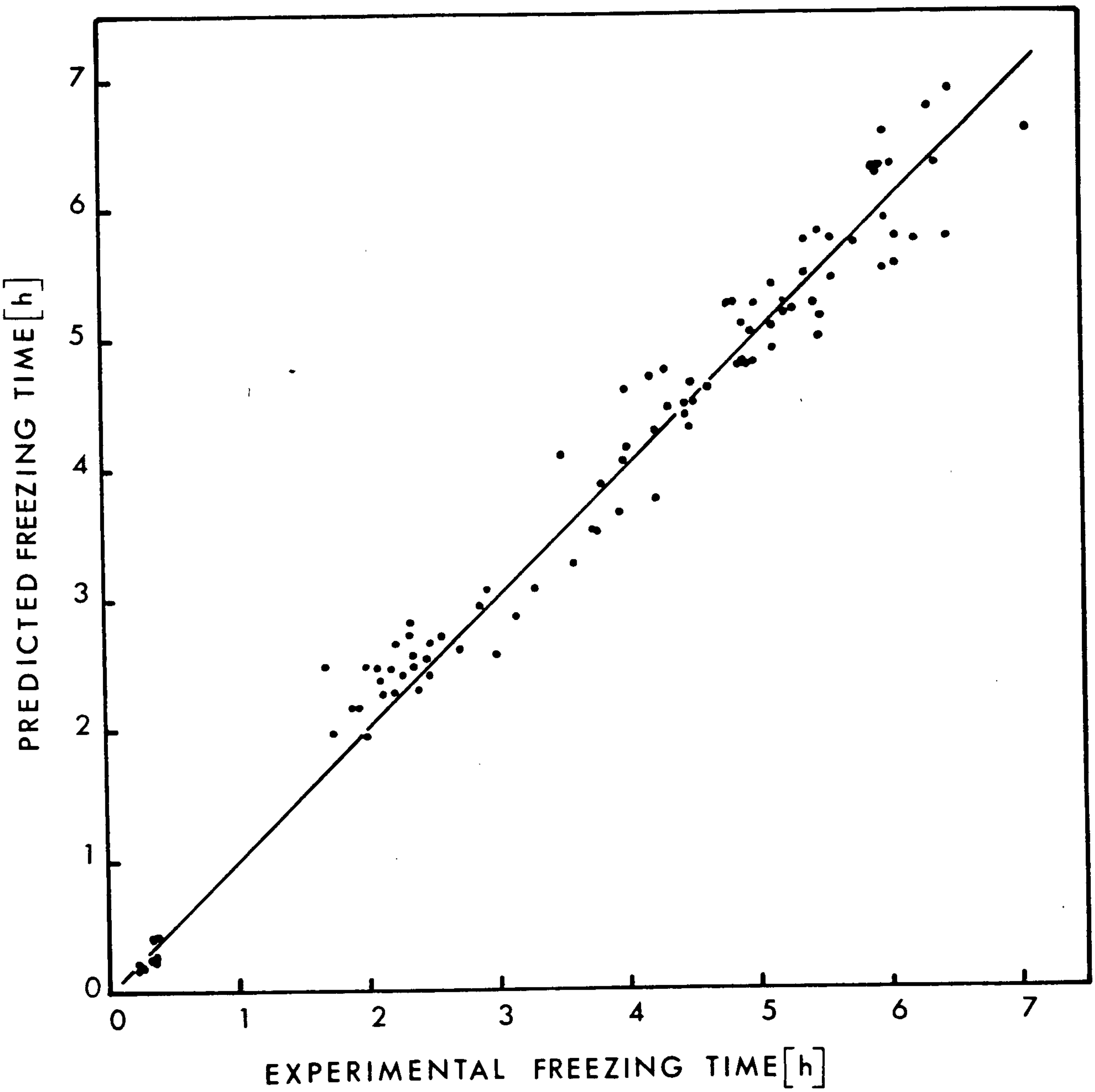

Figure 11. Relationship between the experimental freezing time and the time predicted by using the suggested modification of Plank's equation.

method has been tried, the finite difference method. The finite element methods are also applicable, but are more complex and offer no distinct advantage when used for unidimensional heat transfers as in the case of cylinders (Myers, 1971 and Albasiny, 1956). The finite difference method using constant as well as variable thermal properties has been used in this study.

For calculating the freezing times of slabs, cylinders and spheres, it has been reported that the three time level scheme of Lees (1966) was more accurate than the two time level scheme because of smaller truncation errors (Cleland and Earle, 1979b). However, in this study only the two time level scheme has been employed.

Finite Difference Scheme with Variable Thermal Properties

The general radial heat conduction equation can be approximated by a two level finite difference scheme as follows:

$$C_m^i \frac{T_m^{i+1} - T_m^i}{\Delta t} = \frac{k_m^i(T_{m+1}^i - T_m^i) - k_m^i(T_m^i - T_{m-1}^i)}{(\Delta r)^2} + \frac{k_m^i(T_{m+1}^i - T_{m-1}^i)}{2m(\Delta r)^2} \quad (64)$$

where $m \Delta r = r$ is the distance from the center. This represents the internal nodes.

At the center $(m = 0)$, the equation takes the form:

$$C_o^i \frac{T_o^{i+1} - T_o^i}{\Delta t} = \frac{k_o^i(T_1^i - T_o^i) - k_m^i(T_o^i - T_1^i)}{(\Delta r)^2}$$

because $T_{m+1}^i = T_{m-1}^i = T_1^i$ at $m = 0$ due to the symmetry. This equation can be simplified further to

$$C_o^i \frac{T_o^{i+1} - T_o^i}{\Delta t} = \frac{2k_o^i(T_1^i - T_o^i)}{(\Delta r)^2} \tag{65}$$

At the surface $(m = M)$, the third kind of boundary condition is taken into account by using,

$$C_M^i \frac{T_M^{i+1} - T_M^i}{\Delta t} = \frac{\bar{h}(T_a - T_M^i)(1 + \frac{1}{M})}{(\Delta r)} - \frac{k_M^i(T_M^i - T_{M-1}^i)}{(\Delta r)^2} \tag{66}$$

where $M\Delta r = R$ is the radius of the cylinder. One other assumption that has been made here is that $k_{m+\frac{1}{2}}^i = k_m =$

$k^i_{m-\frac{1}{2}}$ which enables further simplication of the computation program. By selecting Δt and Δr such that the expression $\frac{k^i_m \Delta t}{C^i_M (\Delta r)^2} = \frac{1}{2}$, equations 64 to 66 reduce to

$$\text{(internal node)} \quad T^{i+1}_m = \frac{T^i_{m+1} + T^i_{m-1}}{2} + \frac{T^i_{m+1} - T^i_{m-1}}{4m} \qquad (67)$$

$$\text{(center)} \quad T^{i+1}_o = T^i_1 \qquad (68)$$

$$\text{(surface)} \quad T^{i+1}_M = \frac{T^i_M + T^i_{M-1}}{2} + \frac{\bar{h}\Delta r}{k^i_M} (T_a - T^i_M) \qquad (69)$$

The computer program that was used for the above finite difference scheme has been given in Appendix 3 (see also Appendix 4 for a schematic diagram of the finite difference method).

Finite Difference Scheme with Constant Thermal Properties

The equations used in this method were similar to the ones used in the scheme with varying thermal properties. Constant values of thermal conductivity (k_1, k_2) and specific heat (C_1, C_2) were plugged into the equations above and below the freezing point. The major problem here was to accommodate the release of the latent heat. For this purpose the latent heat was assumed to be released in a range of temperature (5C° taken arbitrarily) below the freezing point. Then the latent heat was converted into apparent specific heat. The specific heat and thermal conductivity during the phase change period were calculated as

$$C = \frac{L + 5.0 \times C_2}{5.0} \qquad \text{J/kgK}^{\circ} \tag{70}$$

and

$$k = \frac{k_1 + k_2}{2} \qquad \text{W/mK}^{\circ} \tag{71}$$

Other than this modification, the procedure was exactly the same as that described for the scheme with varying thermal properties.

The predicted values of freezing times by the two numerical finite difference methods as well as those by the suggested modification of Plank's equation along with the percentage prediction error calculated on the basis of experimental values of freezing time are given in Table 6 for Golden Delicious and Table 7 for Granny Smith. These tables do not contain all the experimental conditions

Table 6. Comparison between the predicted freezing times and prediction errors of numerical methods and modified Plank's equation under different conditions of freezing of Golden Delicious apples.

Code	$\bar{h}$ ($W/m^2K°$)	t_e (h)	t_S (h)	E (%)	t_{nc} (h)	E (%)	t_{nv} (h)	E (%)
GD1	55.59	2.03	2.46	+21.2	3.54	+74.4	1.49	-26.7
		2.33	2.72	+16.7	3.82	+63.9	3.26	+39.9
GD4	13.85	5.13	4.92	-4.1	6.40	+24.8	2.75	-46.4
		5.57	5.43	-2.5	6.77	+24.7	5.28	-5.2
GD7	17.83	5.25	5.23	-0.3	6.74	+28.4	2.96	-43.6
		6.08	5.77	-5.2	7.34	+20.7	7.02	+15.5
GD11	55.59	1.77	1.93	+9.0	1.25	-29.4	1.00	-43.5
		1.95	2.13	+9.3	1.40	-28.1	1.89	-3.0
GD12	55.59	1.70	1.94	+13.8	1.36	-20.0	1.04	-38.8
		1.87	2.14	+14.3	1.51	-19.3	1.92	+2.7
GD13	13.85	4.47	4.30	-3.8	4.76	+6.5	2.00	-55.3
		4.90	4.80	-2.1	5.08	+4.8	4.12	-15.9
GD16	59.68	2.23	2.24	+0.3	1.47	-34.1	1.14	-48.9
		2.53	2.48	-2.0	1.73	-31.6	2.81	+11.1
GD17	17.83	4.20	4.71	+12.1	5.34	+27.1	2.28	-45.7
		5.20	5.22	+0.3	5.85	+12.5	5.69	+9.4
GD18	17.83	4.33	4.74	+9.4	5.70	+31.6	2.36	-45.5
		4.97	5.25	+5.5	6.21	+24.9	5.77	+16.0
GD20	55.59	2.73	2.56	-6.4	3.21	+17.6	1.55	-43.2
		3.00	2.82	-6.0	3.41	+13.7	2.74	-8.7
GD21	55.59	2.83	2.54	-10.1	3.07	+8.5	1.55	-45.2
		3.07	2.81	-8.5	3.27	+6.5	2.73	-11.0
GD22	17.83	5.37	5.77	+7.4	7.42	+38.2	3.21	-40.2
		6.03	6.37	+5.6	8.01	+32.8	7.14	+18.4
GD25	55.59	2.33	2.42	+4.0	1.09	-53.2	1.18	-49.4
		2.60	2.69	+3.4	1.29	-50.4	2.37	-8.8
GD26	17.83	5.47	5.00	-8.6	4.55	-21.0	2.29	-58.1
		6.10	5.54	-9.2	5.00	-18.0	5.30	-13.1
GD28	55.59	3.86	3.82	-1.0	4.28	+10.8	1.97	-49.0
		4.27	4.23	-0.3	4.64	+8.7	4.23	0.0
GD29	17.83	6.36	6.74	+5.9	7.74	+21.7	3.26	-54.3
		7.13	7.44	+4.3	8.28	+16.1	6.91	-3.1
GD31	55.59	3.60	3.27	-9.0	1.31	-63.6	1.35	-62.5
		3.97	3.62	-8.7	1.55	-61.0	2.85	-28.2
GD32	17.83	5.97	5.88	-1.5	3.83	-35.8	2.34	-60.8
		6.06	6.53	+7.8	4.27	-29.5	5.20	-14.2

Footnote: as in Table 7.

Table 7. Comparison between the predicted freezing times and prediction errors of numerical methods and modified Plank's equation under different conditions of freezing of Granny Smith apples.

Code	$\bar{h}$ ($W/m^2K°$)	t_e (h)	t_S (h)	E (%)	t_{nc} (h)	E (%)	t_{nv} (h)	E (%)
GS1	55.59	2.20	2.35	+6.8	3.37	+53.2	1.48	-32.7
		2.43	2.56	+5.5	3.54	+45.8	2.57	+5.8
GS3	13.85	4.70	4.77	+1.5	6.18	+30.0	2.81	-40.2
		5.20	5.20	0.0	6.49	+24.8	4.96	-4.6
GS7	17.83	5.30	5.25	-1.0	6.64	+25.3	3.05	-42.5
		6.43	5.73	-11.0	7.16	+11.4	6.80	+5.8
GS11	55.59	2.17	2.30	+5.8	1.05	-51.6	1.12	-48.4
		2.47	2.51	+1.8	1.25	-49.4	2.44	-1.2
GS13	13.85	3.50	4.12	+17.6	3.54	+1.1	1.89	-46.0
		3.77	4.51	+19.6	3.80	+0.7	3.73	-1.1
GS15	59.68	2.30	2.32	+0.7	1.05	-54.3	1.12	-51.3
		2.73	2.55	-6.7	1.29	-52.7	2.68	-1.8
GS17	17.83	4.00	4.68	-17.0	4.75	+15.8	2.25	-43.8
		4.83	5.12	+6.0	5.19	+7.5	5.42	+12.2
GS20	55.59	2.90	2.79	-3.8	3.12	+7.6	1.67	-42.4
		3.26	3.05	-6.5	3.32	+1.8	2.96	-9.2
GS21	55.59	2.90	2.81	-3.1	3.42	+17.9	1.72	-40.7
		3.23	3.07	-5.0	3.62	+12.1	3.00	-7.1
GS22	17.83	5.53	5.80	+5.0	7.45	+34.7	3.34	-39.6
		6.33	6.33	0.0	7.96	+25.8	6.96	+10.0
GS25	55.59	2.33	2.54	+8.8	1.05	-58.7	1.21	-48.1
		2.53	2.79	+10.3	1.23	-51.4	2.30	-7.9
GS26	17.83	5.44	5.02	-7.7	4.33	-13.7	2.38	-56.3
		6.00	5.50	-8.3	4.73	-14.0	5.15	-14.2
GS28	55.59	4.00	4.04	+1.0	4.34	+7.4	2.09	-47.8
		4.33	4.40	+1.7	4.66	+7.6	4.20	-3.0
GS29	17.83	6.56	6.92	+5.5	8.10	+17.1	3.55	-48.7
		7.70	7.54	-2.0	8.58	+13.8	6.89	-10.5
GS31	55.59	3.73	3.45	-7.4	1.29	-62.6	1.43	-61.7
		4.20	3.78	-10.1	1.61	-57.4	2.82	-32.9
GS32	17.83	6.17	5.97	-3.2	3.73	-37.5	2.54	-58.8
		7.10	6.55	-7.8	4.01	-38.8	5.18	-27.0

First line under each code refers to freezing time to reach -10°C
Second line under each code refers to freezing time to reach -18°C

t_e Experimental freezing time.
t_S Freezing time by the suggested modification of Plank's equation.
E Prediction error.
t_{nc} t_{nv} Freezing times by numerical finite difference scheme with constant and variable thermal properties respectively.

discussed earlier for the other analytical methods based on Plank's equation for certain reasons which will be discussed later.

Constant Thermal Property Scheme

The prediction error varied from -63.6 to +74.4% for Golden Delicious and -62.6 to +53.2% for Granny Smith by using the numerical method with constant thermal properties, as compared to -10.1% to +21.2% and -17.0 to +19.6% respectively by using the suggested modification (Tables 6 & 7). Examination of the analysis showed that conditions C1 and C3 (T_i = 16-25°C and T_c = -10 and -18°C respectively) resulted in overestimation of the freezing time, while the freezing conditions C2 and C4 (T_i = 1-7°C, and T_c = -10 and -18°C) resulted in underestimating the freezing time. The mean errors (absolute values) of freezing time estimation by this method for conditions T_i = 16-25°C (T_c = -10 or -18°C) and T_i = 1-7°C (T_c = -10 or -18°C) respectively were 25.7% and 30.1% for Golden Delicious and 21.0% and 35.5% for Granny Smith apples. It has been generally recognized that the finite difference schemes with constant thermal properties based on the latent heat being released at a unique freezing point often result in overestimating the freezing times (Charm et al., 1972). The results under conditions C1 and C3 supported this observation in spite of the modification made to accommodate the release of the latent heat uniformly over a temperature range of 5C° below the freezing point. Another important phenomenon that has been frequently encountered with numerical finite difference schemes is commonly known as "jumping" of the latent heat peak. This problem arises where the calculation procedure does not follow the specific heat curve and undercuts a portion of the peak. This problem worsens as the Biot Number increases because the cooling rate also increases. Further, this can also occur when the latent heat is assumed to be released in a short range of temperature and the initial temperature is close to the freezing point with a low ambient temperature. This was probably one of the reasons for the under prediction of the freezing times under conditions C2 and C4. The problem became worse when used to predict freezing times in liquid nitrogen immersion systems (T_a = -197°C). These results were not included because of gross underestimations (up to 100%).

Variable Thermal Property Scheme

The prediction error varied from -62.5 to +12.2% for Golden Delicious and -61.7 to +39.9% for Granny Smith apples by using the numerical method with variable thermal properties. A break up of analysis showed, in this case, however, that there is no significant difference in the freezing times between conditions C1 and C3, contrary to the model with constant thermal properties. However, conditions C1 and C3 (freezing time to reach -10°C) resulted in large underestimations of freezing times (-26.7 to -62.5% for Golden Delicious and -32.7 to -61.7% for Granny Smith) while conditions C2 and C4 (freezing time to reach -18°C) gave fairly accurate predictions (-10.5 to +5.8% for Granny Smith and -14.2 to 16.0% for Golden Delicious except in two cases where the values were -32.9% and +39.9%). The mean errors (absolute values) of freezing time estimations by this method were 47.6% and 11.7% for Golden Delicious and 46.8% and 8.6% for Granny Smith respectively under conditions of T_c = -10°C (T_i = 16-25°C or 1-7°C) and T_c = -18°C (T_i = 16-25°C or 1-7°C). Thus the mean error for the two varieties in estimating freezing time to reach -18°C was approximately 10% predominantly towards underestimation. This error could have been caused probably by the partial skipping of the latent heat peak or the incomplete release of latent heat at -18°C. However, the phenomenal underestimatimation of about 45% in freezing time computation to reach -10°C was obviously due to incomplete liberation of latent heat at -10°C. The apparent specific heat curve (Figure 4) clearly shows that the release of latent heat is complete only at temperatures below -25°C. Up to -10°C probably one half of the latent heat was not accounted for, and hence the underestimation of about 45%. This problem does not arise in the finite difference scheme with constant thermal properties because of the assumption made that the entire latent heat was released within 5C° below the freezing point (-1°C) or in the other prediction models where the total latent heat was considered.

Further, for the conditions involving freezing at an ambient temperature of -18°C (GD5, GD6, GS5 and GS6), the numerical methods were not used because the freezing times to reach -18°C would be become a very large number. The method was also not useful for estimating of freezing times when the ambient temperature was very low (liquid nitrogen freezing at -197°C).

Under conditions similar to those in which the numerical methods were used, the suggested modifications of Plank's model gave mean errors of 6.67% for Golden Delicious and 6.2% for Granny Smith with a mean value of 6.46% for the two varieties pooled, which was much better than 10% for the numerical method with variable thermal properties and 23.4% for the numerical method with constant thermal properties.

CONCLUSIONS

There has not been much published information available on the thermo-physical properties of apples. In this study, the temperature dependence of the thermo-physical properties of two varieties of apples, Golden Delicious and Granny Smith, have been investigated.

Detailed regression equations by the method of least squares fitting to cover the variations of thermal conductivity, thermal diffusivity and apparent specific heats with temperature have been presented. Density variations at four different temperatures are given. The thermo-physical properties determined in this study have been used to predict freezing times of apples under different conditions of freezing by using the various prediction models available in the literature.

The predicted values of the freezing times by the different models have been compared with the experimental values of the freezing times and based on the prediction error analysis, an equation which gives the least error has been suggested.

Plank's model (1941) has been the basis for the determination of freezing times of foods. However, this model assumes that the material is initially at its freezing point and hence does not take into account the precooling or tempering periods. Hence, this model results in considerable underestimation of the freezing time when used under the conditions of initial temperatures higher than the freezing point and final temperatures below the zone of maximum ice crystal formation (-1 to -5°C).

Over the years, many modifications have been suggested to Plank's model to include the precooling and tempering periods. All these modifications are based on some empirical relationships used to accommodate the deviations of the value predicted by Plank's model from the experimental values. Most of these modifications (Nagaoka et al., 1955; International Institute of Refrigeration, 1972; Mellor, 1976; Levy, 1958) are aimed at substituting the latent heat (L) in Plank's equation by different proportions of the total amount of heat to be removed from the body in order to bring it down from its initial temperature to the final temperature. The present suggested modification also belongs to this category. The simple fact that the performance of the different models is so different under the different conditions of freezing indicates that no such simple empirical modification can be used to cover all the practical situations. Each of the suggested modifications to Plank's equation must have been the optimum solution when used under the conditions tested by the respective authors. Obviously, the differences in the behavior of the different models appear to be due to the fact that only the properties of the frozen material (ρ_2 and k_2) are used even to consider the situations where the product is initially at temperatures much higher the freezing point. A model which accounts for all the three distinct phases: precooling, phase change and tempering periods, on the merits of the thermal properties of these phases should be the ideal one.

After extensive research on a model system as well as food materials under various conditions of freezing, Cleland and Earle (1977, 1979a, 1979b) suggested modifying the values of P and R on the basis of three dimensionless quantities, Biot Number, Plank's Number and Stefan's Number and using the total quantity of heat to be removed over the entire range of temperature instead of L. Even in this model the structure is essentially based on the thermal properties of the frozen material. Hence, it cannot be an ideal one. This model when used under the conditions mentioned in this investigation resulted in about 20-30% overestimation in most cases and as high as 100-150% when used to predict the freezing times in liquid nitrogen freezing at

- 197 °C. The Stefan's Number under the conditions of liquid nitrogen freezing was very large (close to 1.0) and the accuracy of the model has not been verified by the authors (Cleland and Earle, 1979b) to cover this condition.

The numerical methods have the versatility of accommodating any kind of boundary condition as well as variations in the thermal properties of the product. By identifying the nature of the problem these methods could be easily modified to yield accurate freezing time estimations. The major disadvantages of these methods are, however, the absolute necessity of access to a computer, time required to program the computer (packaged programs are rarely available) and the need to have detailed information on the variation of thermal properties with temperature without which the accuracy of the method suffers.

In spite of the disadvantages discussed earlier, the analytical models of Plank's type are very useful because they are so simple and requires only a hand calculator to do the job. The suggested modification estimates the freezing times of apples in tinplate cans under various conditions of freezing with errors less than 5% beyond the experimental error.

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Appendix 1

Comparison between the experimental and predicted freezing times. Golden Delicious

Code	$\bar{h}_2$ ($W/m^2K°$)	t_e (h)	t_p (h)	E (%)	t_I (h)	E (%)	t_{NF} (h)	E (%)	t_{NC} (h)	E (%)	t_M (h)	E (%)
GD1	55.59	2.03	2.00	-1.1	2.68	+32.4	3.16	+55.8	2.95	+45.3	2.41	+18.9
	55.59	2.33	2.00	-13.8	2.79	+19.8	3.28	+40.9	3.06	+31.6	2.41	+3.6
GD2	55.59	2.06	2.00	-2.5	2.68	+30.4	3.16	+53.5	2.95	+43.2	2.41	+17.1
	55.59	2.33	2.00	-13.8	2.79	+19.8	3.28	+41.0	3.06	+31.6	2.41	+3.6
GD3	13.85	5.13	4.01	-21.7	5.36	+4.6	6.31	+23.1	5.89	+14.9	4.91	-4.1
	13.85	5.57	4.01	-28.0	5.57	+0.1	6.56	+17.8	6.12	+10.0	4.91	-11.7
GD4	13.85	5.13	4.01	-21.7	5.36	+4.6	6.31	+23.1	5.89	+14.9	4.91	-4.1
	13.85	5.63	4.01	-28.7	5.57	-1.0	6.56	+16.6	6.12	+8.8	4.91	-12.7
GD5	59.68	2.47	2.15	-12.6	2.88	+16.8	3.39	+37.5	3.17	+28.3	2.57	+4.4
	59.68	2.93	2.15	-26.4	2.99	+2.3	3.52	+20.4	3.29	+12.4	2.57	-12.0
GD6	59.68	2.27	2.15	-4.9	2.88	+27.1	3.39	+49.6	3.17	+39.6	2.57	+13.6
	59.68	2.93	2.15	-26.4	2.99	+2.3	3.52	+20.4	3.29	+12.4	2.57	-12.0
GD7	17.83	5.25	4.23	-19.2	5.77	+10.0	6.89	+31.3	6.39	+21.8	5.16	-1.7
	17.83	6.08	4.23	-30.3	5.99	-1.4	7.15	+17.7	6.64	+9.2	5.16	-15.1
GD8	17.83	5.47	4.23	-22.5	5.77	+5.6	6.89	+26.0	6.39	+16.9	5.16	-5.6
	17.83	6.25	4.23	-32.2	5.99	-4.0	7.15	+14.5	6.64	+6.2	5.16	-17.4
GD9	68.42	0.242	0.172	-28.6	0.228	-5.4	0.267	+10.5	0.250	+3.4	0.308	+27.3
	68.42	0.250	0.172	-30.9	0.237	-4.9	0.278	+11.2	0.260	+4.1	0.308	+23.3
GD10	68.42	0.230	0.172	-24.9	0.228	-0.5	0.267	+16.3	0.250	+8.8	0.308	+34.0
	68.42	0.230	0.172	-24.9	0.237	+3.4	0.278	+20.9	0.260	+13.1	0.308	+34.0

Code	$\bar{h}_2$ (W/m^{2}K°)	t_e (h)	t_P (h)	E (%)	t_I (h)	E (%)	t_{NF} (h)	E (%)	t_{NC} (h)	E (%)	t_M (h)	E (%)
GD11	55.59	1.77	1.65	-6.3	1.87	+5.7	1.95	+10.5	1.91	+8.4	1.84	+4.0
	55.59	1.95	1.65	-15.0	1.95	+0.4	2.04	+4.9	2.00	+2.9	1.84	-5.5
GD12	55.59	1.70	1.65	-2.5	1.89	+11.3	1.99	+17.2	1.94	+14.6	1.85	+8.9
	55.59	1.87	1.65	-11.4	1.97	+5.8	2.08	+11.4	2.03	+9.0	1.85	-0.9
GD13	13.85	4.47	3.72	-16.6	4.18	-6.4	4.35	-2.5	4.27	-4.2	4.19	-6.2
	13.85	4.90	3.72	-24.0	4.37	-10.7	4.55	-7.0	4.47	-8.6	4.19	-14.5
GD 14	13.85	4.53	3.72	-17.7	4.18	-7.6	4.35	-3.8	4.27	-5.5	4.19	-7.5
	13.85	4.97	3.72	-25.1	4.37	-11.9	4.55	-8.3	4.47	-9.9	4.19	-15.7
GD15	59.68	2.13	1.92	-9.4	2.15	+1.1	2.23	+4.9	2.19	-3.2	2.10	-1.1
	59.68	2.50	1.92	-22.9	2.25	-9.8	2.33	-6.5	2.30	-7.6	2.10	-15.8
GD16	59.68	2.23	1.92	-13.5	2.15	-3.4	2.23	+0.1	2.19	-1.3	2.10	-5.5
	59.68	2.53	1.92	-23.8	2.25	-10.9	2.33	-7.6	2.30	-9.1	2.10	-16.8
GD17	17.83	4.20	4.03	-3.9	4.58	+9.1	4.80	+14.5	4.70	+12.1	4.47	+6.4
	17.83	5.20	4.03	-22.4	4.79	-7.8	5.02	-3.3	4.92	-5.3	4.47	-14.0
GD18	17.83	4.33	4.03	-6.8	4.68	+8.2	4.99	+15.2	4.85	+12.1	4.52	+4.4
	17.83	4.97	4.03	-18.8	4.89	-1.5	5.21	+4.9	5.07	+2.1	4.52	-9.0
GD19	68.42	0.193	0.172	-10.5	0.198	+2.7	0.209	+8.6	0.204	+6.0	0.293	+51.8
	68.42	0.205	0.172	-15.8	0.207	+1.1	0.219	+6.9	0.210	+4.3	0.293	+42.9
GD20	55.59	2.73	2.10	-22.9	2.73	+0.1	3.15	+15.4	2.96	+8.6	2.50	-8.0
	55.59	3.00	2.10	-29.9	2.84	-5.2	3.27	+9.3	3.08	+2.8	2.50	-16.3

Code	$\bar{h}_2$ (W/m^{2}K°)	t_e (h)	t_P (h)	E (%)	t_I (h)	E (%)	t_{NF} (h)	E (%)	t_{NC} (h)	E (%)	t_M (h)	E (%)
GD21	55.59	2.83	2.10	-25.6	2.70	-4.3	3.10	+915	2.92	+3.3	2.49	-11.7
	55.59	3.07	2.10	-31.5	2.81	-8.2	3.22	+5.1	3.04	-0.9	2.49	-18.7
GD22	17.83	5.37	4.74	-11.6	6.16	+14.8	7.11	+32.4	6.69	+24.5	5.64	+5.1
	17.83	6.03	4.74	-21.4	6.41	+6.3	7.39	+22.6	6.95	+15.4	5.64	-6.4
GD23	17.83	5.30	4.74	-10.5	6.16	+16.3	7.11	+34.1	6.69	+26.2	5.64	+6.5
	17.83	5.90	4.74	-19.7	6.41	+8.8	7.39	+25.3	6.95	+17.9	5.64	-4.3
GD24	68.42	0.325	0.211	-35.0	0.275	-15.1	0.319	-1.8	0.299	-7.7	0.374	+15.3
	68.42	0.328	0.211	-35.7	0.286	-12.6	0.331	+1.1	0.311	-5.0	0.374	+14.3
GD25	55.59	2.33	2.10	-9.7	2.30	-0.8	2.36	+1.6	2.34	+0.5	2.29	-1.3
	55.59	2.60	2.10	-19.1	2.41	-7.0	2.47	-4.6	2.45	-5.7	2.29	-11.7
GD26	17.83	5.47	4.32	-20.8	4.75	-13.0	4.87	-10.9	4.81	-11.8	4.74	-13.2
	17.83	6.10	4.32	-29.0	4.97	-18.4	5.10	-16.4	5.04	-11.3	4.74	-22.2
GD27	68.42	0.267	0.211	-20.9	0.231	-13.1	0.237	-11.0	0.234	-11.9	0.352	+32.1
	68.42	0.268	0.211	-21.3	0.242	-9.4	0.240	-7.2	0.246	-8.2	0.352	+31.6
GD28	55.59	3.86	3.13	-18.8	4.11	+6.5	4.77	+23.7	4.48	+16.0	3.72	-3.4
	55.59	4.27	3.13	-26.6	4.29	+0.1	4.96	+16.2	4.65	+9.1	3.72	-12.7
GD29	17.83	6.36	5.57	-12.3	7.10	+11.7	8.08	+27.0	7.64	+20.2	6.58	+3.5
	17.83	7.13	5.57	-21.8	7.39	+3.7	8.41	+18.0	7.96	+11.6	6.58	-7.7
GD30	68.42	0.360	0.273	-23.9	0.359	-0.1	0.417	+15.8	0.391	+8.7	0.486	+35.2
	68.42	0.408	0.273	-32.9	0.373	-8.5	0.433	+6.3	0.406	-0.3	0.486	+19.3

Code	$\bar{h}$ ($W/m^2K°$)	t_e (h)	t_P (h)	E (%)	t_I (h)	E (%)	t_{NF} (h)	E (%)	t_{NC} (h)	E (%)	t_M (h)	E (%)
GD31	55.59	3.60	2.83	-21.3	3.11	-13.5	3.18	-11.4	3.15	-12.3	3.08	-14.2
	55.59	3.97	2.83	-28.6	3.25	-17.9	3.33	-15.9	3.30	-16.8	3.08	-22.3
GD32	17.83	5.97	5.10	-14.4	5.54	-7.0	5.64	-5.5	5.59	-6.2	5.58	-6.4
	17.83	6.06	5.10	-15.7	5.81	-4.1	5.90	-2.5	5.86	-3.2	5.58	-7.9
GD33	68.42	0.310	0.273	-11.7	0.300	-3.0	0.308	-0.6	0.304	-1.6	0.457	+47.5
	68.42	0.340	0.273	-19.5	0.314	-7.4	0.322	-5.1	0.319	-6.1	0.457	+34.6

1 First line under each code refers to freezing time to reach -10°C
2 Second line under each code refers to freezing time to reach -18°C
3 t_e represents experimental value of freezing time
4 t_P = value predicted by Plank's equation (Plank, 1941)
5 t_I = value predicted by a modified Plank's equation (International Institute of Refrigeration (1972))
6 t_{NF} and t_{NC}, Nagaoka et al. modification (1955) of Plank's equation
7 t_M, Mellor (1976) modification
8 E is the prediction error based on experimental value.

Appendix 2

Comparison between experimental and predicted freezing times. Granny Smith

Code	$\bar{h}_2$ (W/m^{2}K°)	t_e (h)	t_p (h)	E (%)	t_I (h)	E (%)	t_{NF} (h)	E (%)	t_{NC} (h)	E (%)	t_M (h)	E (%)
GS1	55.59	2.20	1.92	-12.7	2.63	+19.7	3.17	+44.2	2.93	+33.3	2.34	+6.5
	55.59	2.43	1.92	-21.0	2.72	+11.9	3.28	+34.9	3.03	+24.7	2.34	-3.5
GS2	55.59	2.10	1.92	-8.5	2.63	+25.3	3.71	+51.1	2.93	+24.7	2.34	+11.6
	55.59	2.33	1.92	-17.6	2.72	+16.7	3.28	+40.7	3.03	+30.0	2.34	+0.6
GS3	13.85	4.70	3.89	-17.0	5.34	+13.8	6.44	+37.1	5.95	+26.7	4.82	+2.7
	13.85	5.20	3.89	-25.0	5.52	+6.2	6.65	+28.0	6.15	+18.3	4.82	-7.1
GS4	13.85	4.67	3.89	-16.5	5.34	+14.4	6.44	+37.9	5.95	+27.4	4.82	+3.3
	13.85	5.17	3.89	-24.6	5.52	+6.8	6.65	+28.7	6.15	+18.9	4.82	-6.7
GS5	59.68	2.30	2.28	-0.5	3.09	+34.5	3.69	+60.5	3.42	+48.9	2.74	+19.3
	59.68	2.93	2.28	-21.9	3.19	+9.2	3.81	+30.2	3.54	+20.9	2.74	-6.3
GS6	59.68	2.37	2.28	-3.4	3.09	+30.5	3.69	+55.7	3.42	+44.5	2.74	+15.8
	59.68	2.97	2.28	-22.9	3.19	+7.7	3.81	+28.5	3.54	+19.2	2.74	-7.6
GS7	17.83	5.30	4.30	-18.7	5.84	+10.3	6.99	+32.0	6.48	+22.4	5.21	-1.6
	17.83	6.43	4.30	-33.1	6.04	-6.0	7.23	+12.5	6.70	+4.3	5.21	-18.9
GS8	17.83	4.80	4.30	-10.3	5.84	+21.8	6.99	+45.8	6.84	+35.1	5.21	+8.6
	17.83	5.93	4.30	-27.4	6.04	+1.9	7.23	+22.0	6.70	+13.1	5.21	-12.0
GS9	68.42	0.215	0.184	-14.2	0.250	+16.4	0.300	+39.3	0.277	+29.1	0.317	+47.8
	68.42	0.222	0.184	-17.0	0.258	+16.6	0.309	+39.5	0.286	+29.3	0.317	+43.2
GS10	68.42	0.260	0.184	-29.1	0.250	-3.7	0.300	+15.2	0.277	+6.8	0.317	+22.2
	68.42	0.272	0.184	-32.3	0.258	-4.9	0.309	+13.8	0.286	+5.5	0.317	+16.9

Code	$\overline{h}_2$ (W/m^{2}K°)	t_e (h)	t_P (h)	E (%)	t_I (h)	E (%)	t_{NF} (h)	E (%)	t_{NC} (h)	E (%)	t_M (h)	E (%)
GS11	55.59	2.17	2.01	-7.0	2.20	+1.4	2.25	+3.9	2.23	+2.8	2.17	+0.1
	55.59	2.47	2.01	-18.3	2.29	-7.2	2.34	-5.0	2.32	-5.9	2.17	-12.0
GS12	55.59	2.17	2.01	-7.0	2.20	+1.3	2.25	+3.9	2.23	+2.7	2.17	+0.1
	55.59	2.50	2.01	-19.3	2.29	-8.3	2.34	-6.0	2.32	-7.1	2.17	-13.1
GS13	18.85	3.50	3.62	+3.7	3.93	+12.4	4.01	+14.8	3.98	+13.7	3.99	+14.1
	13.85	3.77	3.62	-3.8	4.09	+8.7	4.18	+11.0	4.14	+10.0	3.99	+5.9
GS14	13.85	4.03	3.62	-9.9	3.93	-2.3	4.01	-0.3	3.98	-1.2	3.99	-0.9
	13.85	4.43	3.62	-18.1	4.09	-7.5	4.18	-5.5	4.14	-6.4	3.99	-9.9
GS15	59.68	2.30	2.04	-11.0	2.21	-3.5	2.26	-1.5	2.24	-2.4	2.19	-4.7
	59.68	2.73	2.04	-25.0	2.31	-15.3	2.36	-13.5	2.33	-14.3	2.19	-19.7
GS16	59.68	2.17	2.04	-5.7	2.21	+2.3	2.26	+4.4	2.24	+3.4	2.19	+1.0
	59.68	2.60	2.04	-21.3	2.31	-11.1	2.36	-9.2	2.33	-10.1	2.19	-15.7
GS17	17.83	4.00	4.09	+2.5	4.52	+13.0	4.66	+16.7	4.60	+15.1	4.45	+11.3
	17.83	4.83	4.09	-15.1	4.70	-2.6	4.86	+0.7	4.79	-0.8	4.45	-7.8
GS18	17.83	4.47	4.09	-8.3	4.52	+1.1	4.66	+4.5	4.60	+3.0	4.45	-0.4
	17.83	5.40	4.09	-24.1	4.70	-12.8	4.86	-10.0	4.79	-11.2	4.45	-17.5
GS19	68.42	0.198	0.184	-6.9	0.205	+3.8	0.213	+8.1	0.210	+6.2	0.295	+49.2
	68.42	0.208	0.184	-11.4	0.213	+2.8	0.222	+7.1	0.218	+5.2	0.295	+42.1
GS20	55.59	2.90	2.34	-19.2	2.96	+2.3	3.37	+16.3	3.19	+10.0	2.73	-4.6
	55.59	3.26	2.34	-28.1	3.07	-5.8	3.49	+7.1	3.30	+1.4	2.73	-16.0

Code	$\bar{h}$ ($W/m^2K°$)	t_e (h)	t_P (h)	E (%)	t_I (h)	E (%)	t_{NF} (h)	E (%)	t_{NC} (h)	E (%)	t_M (h)	E (%)
GS21	55.59	2.90	2.34	-19.2	3.02	+4.3	3.48	+20.2	3.28	+13.1	2.76	-4.6
	55.59	3.23	2.34	-27.4	3.13	-3.1	3.60	+11.7	3.39	+5.2	2.76	-14.4
GS22	17.83	5.53	4.83	-12.6	6.26	+13.3	7.25	+31.1	6.81	+23.2	5.72	+3.5
	17.83	6.33	4.83	-23.6	6.48	+2.5	7.50	+18.6	7.05	+11.4	5.72	-9.6
GS23	17.83	5.70	4.83	-15.2	6.26	+10.0	7.25	+27.2	6.81	+19.5	5.72	+0.4
	17.83	6.37	4.83	-24.1	6.48	+1.8	7.50	+17.8	7.05	+10.7	5.72	-10.2
GS24	68.42	0.310	0.226	-26.9	0.293	-5.3	0.339	+9.6	0.319	+2.9	0.383	+23.8
	68.42	0.322	0.226	-29.7	0.303	-5.6	0.351	+9.2	0.330	+2.6	0.383	+19.1
GS25	55.59	2.33	2.23	-4.0	2.43	+4.7	2.50	+7.3	2.47	+6.2	2.42	+4.0
	55.59	2.53	2.23	-11.6	2.54	+0.5	2.60	+3.0	2.57	+1.8	2.42	-4.2
GS26	17.83	5.44	4.41	-18.9	4.81	-11.5	4.93	-9.3	4.87	-10.3	4.79	-11.9
	17.83	6.00	4.41	-26.4	5.01	-16.4	5.13	-14.4	5.08	-15.3	4.79	-20.1
GS27	68.42	0.270	0.226	-16.1	0.254	-5.9	0.265	-1.7	0.260	-3.6	0.363	+34.8
	68.42	0.302	0.226	-25.0	0.264	-12.5	0.276	-8.5	0.270	-10.3	0.363	+20.5
GS28	55.59	4.00	3.35	-16.1	4.37	+9.3	5.07	+26.9	4.76	+19.1	3.96	-0.9
	55.59	4.33	3.35	-22.5	4.52	+4.5	5.25	+21.3	4.92	+13.8	3.96	-8.5
GS29	17.83	6.56	5.71	-12.9	7.58	+15.6	8.92	+36.1	8.33	+27.0	6.86	+4.7
	17.83	7.70	5.71	-25.8	7.84	+1.9	9.23	+19.9	8.61	+11.9	6.86	-10.8
GS30	68.42	0.380	0.295	-22.2	0.385	+1.4	0.447	+17.7	0.419	+10.4	0.502	+32.1
	68.42	0.419	0.295	-29.4	0.398	-4.9	0.462	+10.5	0.434	+3.7	0.502	+19.8

Code	$\bar{h}_2$ ($W/m^2K°$)	t_e (h)	t_P (h)	E (%)	t_I (h)	E (%)	t_{NF} (h)	E (%)	t_{NC} (h)	E (%)	t_M (h)	E (%)
GS31	55.59	3.73	3.03	-18.6	3.31	-11.3	3.39	-9.0	3.35	-10.0	3.27	-12.1
	55.59	4.20	3.03	-27.7	3.44	-17.9	3.53	-15.9	3.49	-16.8	3.27	-21.9
GS32	17.83	6.17	5.23	-15.1	5.77	-6.4	5.96	-3.3	5.88	-4.7	5.73	-7.0
	17.83	7.10	5.23	-26.3	6.01	-15.3	6.21	-12.5	6.12	-13.7	5.73	-19.2
GS33	68.42	0.330	0.295	-10.4	0.322	-2.2	0.330	+0.2	0.327	-0.9	0.470	+42.6
	68.42	0.362	0.295	-18.3	0.336	-7.2	0.344	-4.9	0.340	-5.9	0.470	+30.0

1 First line under each code refers to freezing time to reach -10°C
2 Second line under each code refers to freezing time to reach -18°C
3 t_e represents experimental value of freezing time
4 t_P = value predicted by Plank's equation (Plank, 1941)
5 t_I = value predicted by a modified Plank's equation (International Institute of Refrigeration (1972))
6 t_{NF} and t_{NC}, Nagaoka *et al*. modification (1955) of Plank's equation
7 t_M, Mellor (1976) modification
8 E is the prediction error based on experimental value.

Appendix 3 A computer program for predicting freezing times of foods with variable thermal properties in cylindrical containers.

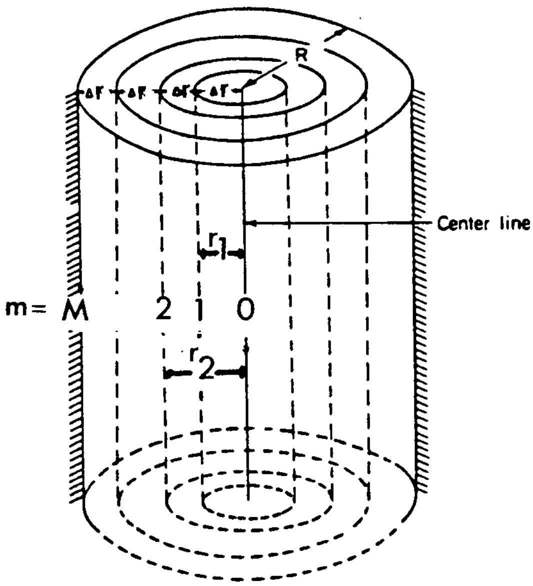
```
C     THIS PROGRAM CALCULATES THE FREEZING TIME IN FOODS IN
C     CYLINDRICAL CONTAINERS BASED ON VARYING THERMAL PROPERTIES
C
C
      IMPLICIT REAL *8(A-H,O-Z)
      DIMENSION T(100),XK(100),C(100)
  500 READ(5,1,END=16)RM,DR,RHO1,RHO2,HTC,TI,TF,TA,TM,TC,ENDT
    1 FORMAT (F5.4,F6.5,2F5.1,F5.2,5F5.1,F3.1)
      N=RM/DR+2
      DO 10 I=1,N
      T(I)=TI
   10 CONTINUE
  990 WRITE (6,2000) TIME,(T(I),I=1,N)
 2000 FORMAT(' TIME(HOURS)',20X,'TEMPERATURE C',/15X,
     2'     T1          T2          T3          T4          T5',/23X,
     3'     T6          T7          T8          T9          T10        T11        TC',
     4///2X,F8.4,5X,5F8.1,/23X,7F8.1)
      XK(I)=3.6*(0.367+0.00250*T(I))
      C(I)=3.40+0.0049*T(I)
      DTH=(RHO1*C(1)*(DR**2))/(XK(1)*2.0)
      K=ENDT/DTH
      TIME=0.0
      DO 19 J=1,K
   11 DO 15 I=1,N
      XK(I)=3.6*(0.367+0.00250*T(I))
      C(I)=3.40+0.0049*T(I)
      XN=XK(1)/(HTC*DR)
C
      IF (T(I)-TF) 20,20,12
   12 IF (I-1) 25,25,30
   30 IF (I-N) 204,40,40
C
   25 T(1)=2.*T(2)-T(1)+(TA-T(1))*(N-1)/(XN*(N-2))
      DTH=(RHO1*C(I)*(DR**2))/(XK(I)*2.0)
      IF(T(1).LT.TF) GOTO 26
      GO TO 15
   26 T(1)=TF
      GO TO 15
  204 T(I)=(T(I+1)+T(I-1))/2.
      TX=(T(I-1)-T(I+1))/(4.0*(N-I))
      T(I)=T(I)+TX
      TY=T(N-1)
      IF(T(I).LT.TF) GOTO 27
      GOTO 15
   27 T(I)=TF
      GO TO 15
   40 T(N)=(T(N-1)+TY)/2.0
      IF(T(N).LT.TF) GOTO 28
      GOTO 15
   28 T(N)=TF
      GO TO 15
```

```
   20 TZ=TM-T(I)
      IF(TZ.GT.0.0) GOTO 220
      XK(I)=3.6*(1.066-0.0111*T(I))
      C(I)=2.65-1.421*T(I)
      XN=XK(1)/(HTC*DR)
      IF(I-1) 125,125,130
  130 IF (I-N) 304,140,140
  125 T(1)=2.*T(2)-T(1)+(TA-T(1))*(N-1)/(XN*(N-2))
      DTH=(RHO2*C(I)*(DR**2))/(XK(I)*2.0)
      GO TO 15
  304 T(I)=(T(I+1)+T(I-1))/2.0
      TX=(T(I-1)-T(I+1))/(4.0*(N-I))
      T(I)=T(I)+TX
      TY=T(N-1)
      GO TO 15
  140 T(N)=(T(N-1)+TY)/2.0
      GO TO 15
C
  220 XK(I)=3.6*(1.066-0.0111*T(I))
      C(I)=24.40+0.7910*T(I)
      XN=XK(1)/(HTC*DR)
      IF (I-1) 225,225,230
  230 IF (I-N) 404,240,240
  225 T(1)=2.*T(2)-T(1)+(TA-T(1))*(N-1)/(XN*(N-2))
      DTH=(RHO2*C(I)*(DR**2))/(XK(I)*2.0)
      GO TO 15
  404 T(I)=(T(I+1)+T(I-1))/2.0
      TX=(T(I-1)-T(I+1))/(4.0*(N-I))
      T(I)=T(I)+TX
      TY=T(N-1)
      GO TO 15
  240 T(N)=(T(N-1)+TY)/2.0
   15 CONTINUE
C
      IF (T(N)-TC) 500,85,85
   85 TIME=TIME+DTH
  999 WRITE (6,2001) TIME,(T(I),I=1,N)
 2001 FORMAT (2X,F8.4,5X,5F8.1/23X,7F8.1)
   19 CONTINUE
   16 STOP
      END



C
C
C
C     RM=RADIUS, DR=RADIUS INCREMENT, RHO1=DENSITY OF UNFROZEN MATERIAL
C     RHO2==DENSITY OF FROZEN MATERIAL, HTC=HEAT TRANSFER COEFFICIENT,
C     TI=INITIAL TEMPERATURE, TF=FREEZING POINT,TA=AMBIENT TEMPERATURE,
C     TM=INTERMEDIATE TEMPERATURE, TC=TARGET TEMPERATURE, ENDT=TIME
C     LIMIT, DTH=TIME I, XK(I) AND C(I) ARE TEMPERATURE FUNCTIONS OF
C     THERMAL CONDUCTIVITY AND APPARENT SPECIFIC HEAT
```

Appendix 4 Schematic diagram of the sections of a cylinder for a finite difference scheme.



$$M = \frac{R}{\Delta r}$$

$$r_m = m\Delta r$$

Centre; $m = 0$

Surface; $m = M$

Interior; $M > m > 0$