# THERMAL PROPERTIES OF SOME FROZEN SUGAR SOLUTIONS

Thesis for the Degree of Ph. D.

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Richard Albert Keppeler

1962

This is to certify that the

thesis entitled

Thermal Properties of Some
Frozen Sugar Solutions

presented by

Richard Albert Keppeler

has been accepted towards fulfillment
of the requirements for

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Carl W. Hall
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THERMAL PROPERTIES OF SOME

FROZEN SUGAR SOLUTIONS

By

Richard Albert Keppeler

AN ABSTRACT OF A THESIS

Submitted to
Michigan State University
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APPROVED: Paul W Hall, August 16, 1962

ABSTRACT

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by Richard Albert Keppeler

The objective of the investigation was to develop a simple method for the determination of specific heat and thermal diffusivity of frozen sugar solutions and to relate these values. The solutions investigated were: sucrose, 12 parts + 61.25 parts water; lactose, 6.528 parts + 61.25 parts water; corn syrup solids (DE 42), 4.5 parts + 61.25 parts water; corn syrup solids-lactose solution, 4.5 parts corn syrup solids + 6.528 parts lactose + 61.25 parts water; and sucrose-lactose solution, 6.528 parts lactose + 12 parts sucrose + 61.25 parts water. The study was conducted at $-20^{\circ}$ to $+20^{\circ}F$, with values determined at $5^{\circ}F$ intervals.

The apparent specific heats for the five solutions are not linear with temperature and, for sucrose, vary between 0.647 Btu/lb$^{\circ}$F at $-20^{\circ}$ to $-15^{\circ}F$ to 2.119 at $+15^{\circ}$ to $20^{\circ}F$. For lactose, values change from 0.516 to 1.065 and, for corn syrup solids (DE 42), from 0.439 to 0.997. Corn syrup solids-lactose solution has an apparent specific heat ranging from 0.531 Btu/lb$^{\circ}$F to 1.618, and sucrose-lactose solution from 0.622 to 2.526.

The apparent specific heat for the two solutions could be predicted by computation using the specific heat of the ingredients of the solutions and the regression equation for each mixture.

The computation equation is analogous to the parallel resistance relationship in electrical circuitry.

The regression equations for apparent specific heat relating the experimental values (Y) and the calculated values (X) are: for corn syrup solids-lactose solution, $Y = 1.9536X - 0.414$ with the regression coefficient of 0.994; for sucrose-lactose solution, $Y = 1.9536X - 0.555$ and the regression coefficient of 0.998.

Apparent thermal diffusivity was determined independently. The two parameters were temperature difference between center and outside of the cylinder and change in center temperature per unit time.

The experimentally determined apparent thermal diffusivities are nearly linear functions. For sucrose the apparent diffusivity ranges from 0.0261 sq ft/hr for $-20^{\circ}$ to $-15^{\circ}$F and 0.0067 sq ft/hr at $15^{\circ}$ to $20^{\circ}$F; for lactose, from 0.0314 to 0.0101; for corn syrup solids, from 0.0365 to 0.0159; for corn syrup solids-lactose solution, from 0.0261 to 0.0062; and for sucrose-lactose solution, from 0.0196 to 0.0035.

The diffusivities for the mixtures could be predicted by calculation using the diffusivities of the ingredients using electrical resistance analogy. The regression equations for experimental (Y) versus calculated (X) diffusivities were for corn syrup solids-lactose solution, $Y = 0.952X - 0.0061$ with the regression coefficient of 0.995, and for sucrose-lactose solution, $Y = 0.829X - 0.0037$ with the regression coefficient of 0.996.

Richard Albert Keppeler

The freezing temperatures of the five solutions were calculated as a function of the percent of water frozen.

August, 1962

# VITA

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## INTRODUCTION

Over 900 million gallons of ice cream, sherbets and ices were hardened prior to sale in the United States in 1960 and 42 million gallons in Michigan alone. In addition, there are many desserts, including fruits and baked goods, which need to be frozen for storage and transportation. The storage of sweetened foods at reduced temperatures comprises a considerable portion of the food processing industry and will continue to expand in number of items and in tonnage.

A large number of items have one feature in common which led to the investigation reported here. The common feature is that they contain sugars or combinations of sugars and they must be frozen or have their temperatures reduced below ordinary atmospheric storage temperatures.

The thermal properties, thermal conductivity, diffusivity, specific heat and density, of all these products are dependent on their ingredients and the water of suspension and solution. Most of the fat, protein and starch fractions will be solids in suspension in the water and, as such, will not contribute appreciably to the change in the thermal characteristics over the span of freezing temperatures. The sugars and salts in solution are completely different and important since the change in freezing point of an aqueous solution from $32^{o}F$ is dependent upon the concentration of sugars and/or salts in the solution. It can and will be shown that these thermal characteristics change differentially with temperature and solution concentration below the freezing point of pure water.

The production of food products is a commercial operation and profits are dependent on the efficiency with which time, materials and energy are used. It would seem necessary to have as much knowledge as possible relative to the production of food products so as to properly engineer the product and the manufacturing facilities. For instance, corn syrup solids are used as an ice cream ingredient for several reasons. It is an economical source of material to increase the solids content. It is only about 40% as sweet as sugar (sucrose) and fair amounts can be used without increasing the sweetness of the ice cream. It will not unduly depress the freezing point of the mix. By knowing the physical and chemical properties of potential ingredients, product enhancement can be incorporated. Gains in freezing efficiency can also be made if thermal characteristics of ingredients are known and if mixture characteristics can be predicted.

Early freezing was accomplished by natural air convection with its low surface heat transfer coefficient--by conduction on coils with its high labor requirements--by high velocity air stream with its high moving and refrigerating costs--and by moving plate type freezer with its high equipment cost. Future innovations and developments might well come from the predicted and fully known thermal characteristics of these ingredients.

## REVIEW OF LITERATURE

Interest in the specific heat of foods is not recent. As early as 1892, Siebel (1892) gave specific heats of some foods and proposed a method for calculation of the specific heat related to the weighted average of the specific heats of the components. He assumed all water to freeze at the initial freezing point and the thermal capacity below that point to be constant, irrespective of temperature.

As late as 1941, Lange (1941) reproduced a table from a publication of Dow (1929) apparently calculated from Siebel's method. These values do not coincide with those of Short, et al., (1942) and Staph (1949) who experimentally determined specific heats of some foodstuffs by calorimetry. Short also reported values for some sugar solutions.

In 1932, Birdseye (1932) suggested that the refrigeration effect be considered to be the same as that needed for causing an equal temperature change in an equal weight of water. This procedure was passable as an estimate of refrigeration loads, but it caused serious discrepancies in use.

Short, et al., noted that in all cases whether for sugar solutions, fruits, meats or vegetables, the specific heats increase sharply as the temperature rises toward the thawing region. He also said that the depression of the freezing point by colloidal material is negligible.

Staph used kerosene in his calorimetry for fruits and vegetables but the method could not be used for fatty materials. D. K. Tressler in the discussion at the end of Staph's article noted that the reported specific heats must include latent heat as well and should be given a different name.

Brunner (1942) found specific heat of butterfat for temperatures above 40$^{o}$F. No reports of thermal characteristics were found for milk-solids-not-fat. Specific heats for corn syrup solutions between 40$^{o}$F and 200$^{o}$F are reported by Torgensen (1950) but none are reported below 40$^{o}$F.

The three sugars commonly used in ice cream are sucrose (cane or beet sugar), corn syrup solids and lactose. Other sugars, such as maple sugar or honey, are used as flavorings and, although they will exert influence on the hardening of the food product, will not be considered here.

Sucrose, which is derived from beets or cane, is the main sweetener and is the familiar table and cooking sugar. Corn syrup solids are the product of partial acid and, sometimes, enzyme hydrolysis of corn starch.

According to a publication of the Corn Industries Research Foundation (1958), cornstarch slurry is acidified, usually with weak hydrochloric acid, and, depending on the time and temperature used, the conversion can progress to 100% or be halted at any point in between all starch and all dextrose (100% conversion). The degree of conversion is classified by dextrose equivalent (DE). DE is the measure of reducing sugar content calculated as anhydrous dextrose and expressed as percent of total dry substance.

Five grades of corn syrup are offered for use which when dried are called corn syrup solids. Table 1 shows these grades and other pertinent information. The higher saccharides have little or no sweetening value so the sweetening depends upon the amount of dextrose and maltose present.

Table 1. Corn syrup classifications.

| Classification | Type of conversion | Dextrose equivalent | Saccharides, percent | | |
|---|---|---|---|---|---|
| | | | Dextrose | Maltose | Poly-saccharides |
| Low conversion | acid | 30 | 10.4 | 9.3 | 80.3 |
| Regular conversion | acid | 42 | 18.5 | 13.9 | 67.6 |
| Intermediate conversion | acid | 54 | 29.7 | 17.8 | 52.5 |
| High conversion | acid | 60 | 36.2 | 19.5 | 44.3 |
| High conversion | acid-enzyme | 63 | 38.8 | 28.1 | 33.1 |

Adapted from Corn Syrup & Sugars (5).

Lactose is a natural part of milk-solids-not-fat and, as such, is sometimes called milk sugar. Leighton (1927) states that it occurs as about 54.4% of the solids-not-fat of milk. Therefore, 12% solids-not-fat times 0.544 equals 6.528% lactose.

Moline, et al., (1961) proposed and used a method for determining specific heat which is used here and is described under Apparatus. They made use of the equation $q = W_s c_{p_s} \frac{\Delta T}{\Delta \theta}$

where: q is the heat leak into the sample, Btu/min

$W_s c_{p_s}$ is the product of the sample and sample tube weight, lb, and specific heat, Btu/lb-$^{o}$F

$\frac{\Delta T}{\Delta \theta}$ is the slope of the warming curve plot of temperature versus time at the temperature where $c_p$ is to be measured.

then: $W_s c_{p_s} = \frac{q}{\Delta T/ \Delta \theta}$ and $W_s c_{p_s} = W_c c_{p_c} + W_x c_{p_x}$

where the subscripts c and x refer to container and sample unknown, respectively.

finally: $c_{p_x} = \frac{W_s c_{p_s} - W_c c_{p_c}}{W_x}$.

The heat leak, q, is determined for each polystyrene insulator by cooling a copper slug of proper size and known specific heat and permitting it to warm inside the insulator while its internal temperature is recorded as a function of time. The heat leak, q, equals $W_{cu} c_{p_{cu}} \left(\frac{\Delta T}{\Delta \theta}\right)_{cu}$ at controlled ambient temperature.

Fourier (1878) discusses the movement of heat in rectangular, cylindrical and spherical coordinates and for each case arrives at a constant, $\frac{k}{c_p \rho}$, which has since been named thermal diffusivity and has units of square centimeter per second or square feet per hour. Schneider (1955) suggests that the reciprocal of thermal diffusivity in hour per square feet is a measure of time required to heat a material to some required temperature and evidently this time is proportional to the square of the conducting path length.

Hall (1957) says the thermal diffusivity is a quantity which is a measure of the rate of temperature change and indicates the speed at which temperature equilibriums will be approached. He visualizes it as though the heat had a point source and the heat front moves as a series of infinitely thin sperical shells away from the source. Then the square feet per hour would be a measure of the expansion of this spherical front.

There was no indication in the literature of any work done on thermal diffusivity of foodstuffs or sugar solutions. The International Critical Tables (1927) quote Neumann in 1868 for a value of 0.0114 sq cm per sec or 0.0442 sq ft per hr for ice at $0^{o}C$. Giedt (1957) gives a value for ice of 0.048 but it appears to be calculated from the values of thermal conductivity, specific heat and density.

Using ice conductivities of 1.21, 0.9434, 0.532 and 1.28 Btu/$^{o}F$ ft hr, specific heats of 0.706, 0.864, 0.954 and 0.46 Btu/lb-$^{o}F$ and densities of 57, 57.25 and 57.5 lb/$ft^3$ from various sources (1927, 1957, 1959) one could calculate thermal diffusivities ranging from 0.0175 to 0.0539 sq ft per hr depending on which values are selected.

Thomas (1957) proposed a method for directly measuring thermal diffusivity in a cylinder in which thermal diffusivity is proportional to the square of the radius and the change in center temperature per unit time and inversely proportional to the temperature difference between the center and outside of the cylinder. The relationship is developed directly from Fourier's equation,

$\frac{\partial T}{\partial \theta} = \alpha \left(\frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}\right)$ in cylindrical coordinates.

## APPARATUS

Two different groups of apparatus were used in the experimental work. One group was designed to determine specific heat and the other group for the thermal diffusivity. To find the specific heat, four similar units were constructed. Each piece, as shown in Figure 1, consisted of a sample tube, a plug cap drilled to receive and carry a thermocouple and centering disk. A polystyrene foam container was used to hold the sample tube during the warming period.

The tubes (A in Figure 1) were made of mild steel, thin-walled electrical conduit (0.6876-in. O.D. and reamed to 0.6250-in. I.D.) 5 in. long with one end closed by a piece of galvanized sheet metal soldered in place and ground smooth. The tubes were closed at the top by a machined Plexiglass plug (B in Figure 1) 0.6250 in. in diameter extending 5/8 in. into the tube. The plug was center bored to pass a copper-constantan thermocouple mounted on an 1/8-in. Plexiglass rod which terminated in a Plexiglass disk mounted normal to the rod. The thermocouple protruded through a hole at the center of the disk. The disk was finished to a diameter just enough under 0.625 in. to slide into the tube and maintain the thermocouple at the center of the tube.

For the warm-up process the tubes were enclosed in a polystyrene foam container (C in Figure 1) 4 in. by 4 in. and 9-3/4 in. high, which was made of two slabs 2 in. x 4 in. x 9-3/4 in. A half-cylinder trough was cut in each slab so that the troughs formed a cylindrical hole just large enough to take the sample

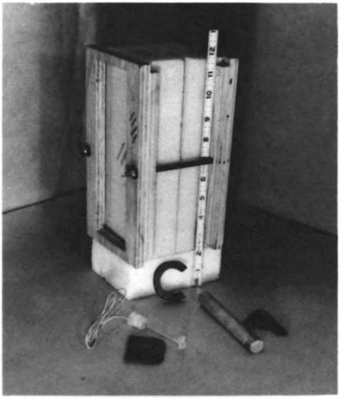

Figure 1. Apparatus for obtaining values to determine specific heats.

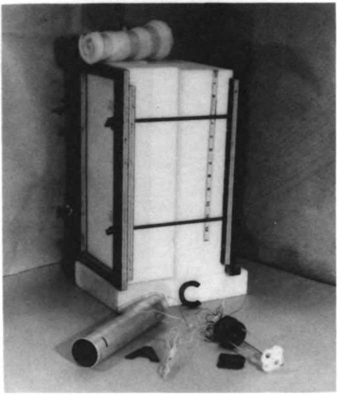

Figure 2. Apparatus for obtaining values to determine thermal diffusivities.

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tube when the slabs were put together. A polystyrene foam plug closed the top of the hole. A light wood frame held the slabs together. The thermocouples were attached to a Brown recording potentiometer ($-40^{o}F$ to $140^{o}F$). The ambient temperature around the insulators was maintained at $69^{o}$ to $71^{o}F$ in an air conditioned room.

Another group of apparatus was used to gather data for the calculation of the thermal diffusivity. It was somewhat similar to the first group but on a larger scale, as shown in Figure 2. The three sample tubes (A in Figure 2) were made of 2-in. O.D. by 1.899-in. I.D. aluminum tubing and were 10 in. long. The bottoms were closed with No. 10 rubber stoppers and the tops were closed with machined bakelite plugs extending 5/8 in. into the tubes.

The plug (B in Figure 2) was drilled in the center to receive two thermocouples which terminated at the geometrical center of the tube in a balsa disk dressed so as to just slide inside the tube. The disk was held parallel to and at a constant distance from the plug by two 1/8-in. Plexiglass rods about 3/8 in. from and diametrically opposed to the centrally-located thermocouples.

One copper-constantan thermocouple was mounted in the center for sensing the center temperature, as in the first group, and was connected to the recording potentiometer. Another thermocouple was placed centrally in the tube but with another junction soldered to the outside of the tube at mid-length. The pair of hot and cold junctions was attached to the manual potentiometer. Since these two junctions were at different temperatures, a small voltage in the order of fifteen to twenty microvolts was generated, determined with the manual potentiometer, and written on the recorder chart at appropriate intervals. Between $0^{\circ}$ and $2^{\circ}F$ temperature difference, 21 microvolts equals $1^{\circ}F$ for copper-constantan.

The polystyrene foam insulators (C in Figure 2) were constructed as were those in the first group except for the size. These insulators were 8 in. x 8 in. x 16 in. and had a hole 2 in. in diameter. After inserting the sample tube, the top was plugged with a roll of polyurethane foamed plastic. These slabs were also held together by a light wood frame.

To determine heat leak the insulators for the small tubes used for specific heat measurements were calibrated with a pure copper slug the same size as the tubes. The specific heat of pure copper was obtained from National Bureau of Standards (1934) for temperatures from absolute zero to $1{,}000^{\circ}C$, and the appropriate values were selected for the temperatures used. The copper slug was chilled on dry ice to below $-40^{\circ}F$, inserted in the insulator and permitted to warm by the heat leaked (gain) through the Styrofoam. The temperature was sensed by a thermocouple at the geometrical center of the slug and recorded on the recording potentiometer. Another thermocouple was soldered to the outside surface of the slug at the middle of the length and its temperature was also recorded but no difference between the two temperatures could be discerned. The heat leak was calculated from $q = W c_p \frac{\Delta T}{\Delta \theta}$

where: q is the heat leak, Btu/min

W is the weight of the slug, lb

$c_p$ is the specific heat of pure copper in the temperature range for which the calculation was made, Btu/lb-$^{o}$F

$\frac{\Delta T}{\Delta \theta}$ is the change in center temperature of the copper per minute in the temperature range, $^{o}$F/min

# PROCEDURE

The investigation was begun with the thought of determining the thermal properties of ice cream in eight 5°F temperature ranges between -20°F and +20°F. A rather representative formula was arrived at which would contain 10% butterfat, 12% milk-solids-not-fat, 12% sugar (sucrose), 4.5% corn syrup solids, 0.25% stabilizer and emulsifier and 61.25% water. The fat and protein portions do not greatly influence the freezing points or the apparent specific heats of ice cream mixes (Brunner and Stine, 1961), so it was decided that only sugar solutions in proportions represented in the above formula would be used.

The five solutions of the three sugars mentioned are as follows:

1. 12 parts sucrose plus 61.25 parts of distilled water or 19.6% solution by weight.

2. 4.5 parts of corn syrup solids (DE 42) plus 61.25 parts of distilled water or 7.3% solution.

3. 6.528 parts of lactose plus 61.25 parts of distilled water or 10.7% solution.

4. Corn syrup solids-lactose solution: 4.5 parts corn syrup solids plus 6.528 parts of lactose plus 61.25 parts of distilled water or 18.0% solution.

5. Sucrose-lactose solution: 6.528 parts of lactose plus 12 parts sucrose plus 61.25 parts distilled water or 30.25% solution.

The first set of determinations was for specific heat so the first group of apparatus with the small tubes and insulators was used. The solutions were proportioned, one at a time, and weighed by difference into the sample tubes. The solution temperature was reduced by placing the four tubes in an alcohol bath with dry ice as the refrigerating agent. When the internal temperature reached $-40^{\circ}F$, the tubes were removed from the alcohol, dried quickly with a dry, clean cloth and locked in the insulator. The warming process began immediately and the changing center temperature was recorded on the potentiometer chart as a function of time.

The second set of determinations was for thermal diffusivity using the second group of apparatus. As before, the solutions were proportioned and weighed into the sample tubes. This time the tubes were packed directly in dry ice, because the large sample size made the freezing in alcohol impracticable. When the center temperature reached $-40^{\circ}F$, the tubes were removed from the dry ice, wiped and placed in the cylindrical cavity in the polystyrene insulators. The top of the cavity was stopped with the rolled polyurethane plug. The single thermocouple sensing the center temperature was connected to the recording potentiometer and the copper leads of paired thermocouples sensing the temperature difference between the outside and center were attached to the manual potentiometer. At appropriate times the voltage difference between those two points was read and noted manually on the recording chart.

## RESULTS AND DISCUSSION

### Apparent specific heat

Since the only experimental parameter involved in the calculation of apparent specific heat was the change in temperature per unit time for each of the temperature ranges, these data were analyzed statistically by two-way analysis of variance. The data for each temperature range were found to be not significantly different for the sucrose, lactose and corn syrup solids-lactose solution, but were just slightly greater than the criterion for corn syrup solids and sucrose-lactose solution. The sum of squares from temperature ranges was very large as would be expected from the differences in values between those ranges and, therefore, the error sum of squares was quite small. The error variances (error mean squares) were quite small also. Since only the means of the data of the ranges were to be used, the standard error of the mean would indicate that these means are good estimates of the true specific heats. The mean squares of replications for the two solutions, corn syrup solids and sucrose-lactose, are in the same range as the mean squares of the other solutions which are not significantly different. The mean square for sucrose-lactose solution is intermediate between those for sucrose and lactose.

Coefficients of variation (mean divided by square root of variance) were calculated for all five solutions for each temperature range and were found to fall between 0.025 and 0.096 for sucrose, lactose and corn syrup solids-lactose which were not significantly different and between 0.016 and 0.072 for corn syrup solids and sucrose-lactose solution which were significantly different. In view of the foregoing, it was decided to use the data without further experimentation. These data means are summarized in Table 2 and plotted in Figure 3.

Table 2. Apparent specific heats, Btu/lb-$^{o}$F

| Temp. ranges $^{o}$F | Experimental | | | | | Calculated | |
|---|---|---|---|---|---|---|---|
| | Sucrose | Lactose | Corn syrup solids | Mixture 1 * | Mixture 2 # | Mixture 1 * | Mixture 2 # |
| -20 to -15 | 0.647 | 0.516 | 0.439 | 0.531 | 0.622 | 0.482 | 0.594 |
| -15 to -10 | 0.715 | 0.571 | 0.522 | 0.637 | 0.725 | 0.550 | 0.657 |
| -10 to -5 | 0.743 | 0.580 | 0.500 | 0.711 | 0.751 | 0.544 | 0.676 |
| -5 to 0 | 0.726 | 0.587 | 0.541 | 0.688 | 0.798 | 0.567 | 0.670 |
| 0 to 5 | 0.908 | 0.688 | 0.598 | 0.824 | 1.042 | 0.648 | 0.816 |
| 5 to 10 | 1.033 | 0.750 | 0.637 | 0.894 | 1.141 | 0.699 | 0.912 |
| 10 to 15 | 1.256 | 0.770 | 0.710 | 1.082 | 1.486 | 0.744 | 1.028 |
| 15 to 20 | 2.119 | 1.065 | 0.997 | 1.618 | 2.526 | 1.036 | 1.571 |

* corn syrup solids-lactose solution.
# sucrose-lactose solution.

Specific heats were calculated for corn syrup solids-lactose and sucrose-lactose solutions using the experimental specific heats from the three ingredient solutions. The calculation was analogous to the resistance in parallel electrical circuitry.

$$\text{Calculated } c_p = \frac{\text{sum of parts of sugars}}{\frac{\text{parts of one sugar}_1}{c_{p_1}} + \frac{\text{parts of other sugar}_2}{c_{p_2}}}$$

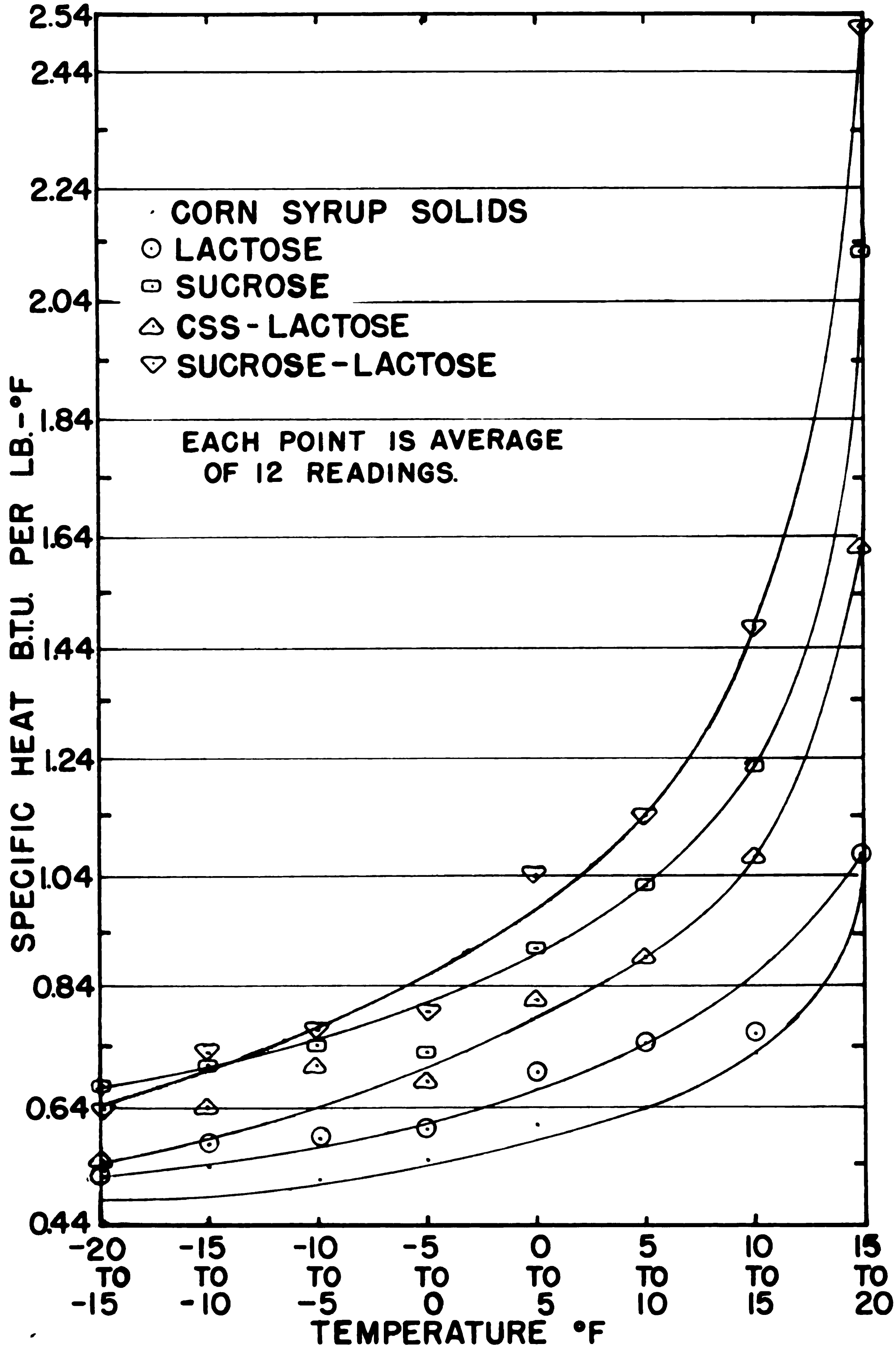



Figure 3. Apparent specific heat versus temperature.

For $-20^{o}$ to $-15^{o}$F and corn syrup solids-lactose solution these were 4.5 parts corn syrup solids with $c_p$ = 0.439 and 6.528 parts of lactose with $c_p$ = 0.516; therefore,

$$c_p = \frac{4.5 + 6.528}{\frac{4.50}{0.439} + \frac{6.528}{0.516}} = \frac{11.028}{10.251 + 12.651} = 0.482$$

While Table 2 shows that the calculated values are smaller than the actual values for each range, a regression equation was computed which indicates that the actual values could be predicted very well by use of the regression equation. For corn syrup solids-lactose solution the equation is Y = 1.9536X - 0.414 where Y is the actual and X the calculated value. The regression coefficient was 0.994 and the criterion is 0.765 at 99%.

The regression equation for sucrose-lactose solution is Y = 1.9536X - 0.555 with a regression coefficient of 0.998, again showing that it can be used as an excellent predictor.

Warming curves are shown for the five frozen solutions in Figure 5. Figure 6 is the graph of solution freezing temperature versus percent of water frozen for the five solutions from the method of Leighton (1927) and using data from Cole and Pickering (1938).

Apparent thermal diffusivity

Two experimental parameters were involved in the computation of the apparent thermal diffusivity. The temperature difference at the center per minute and the temperature difference between the center and the outside were used. The computations were made and then analyzed statistically.

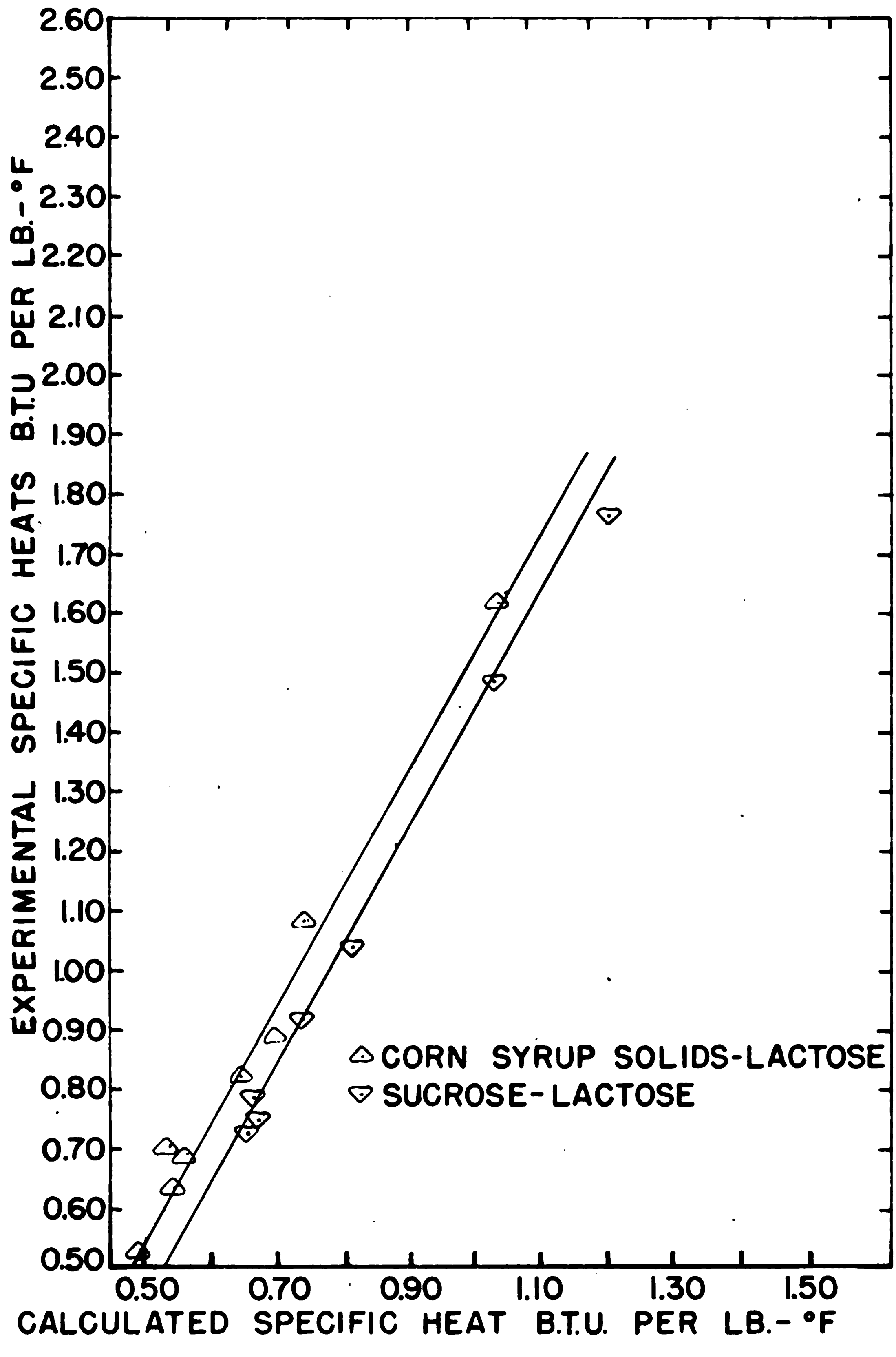



Figure 4. Experimental versus calculated apparent specific heats.

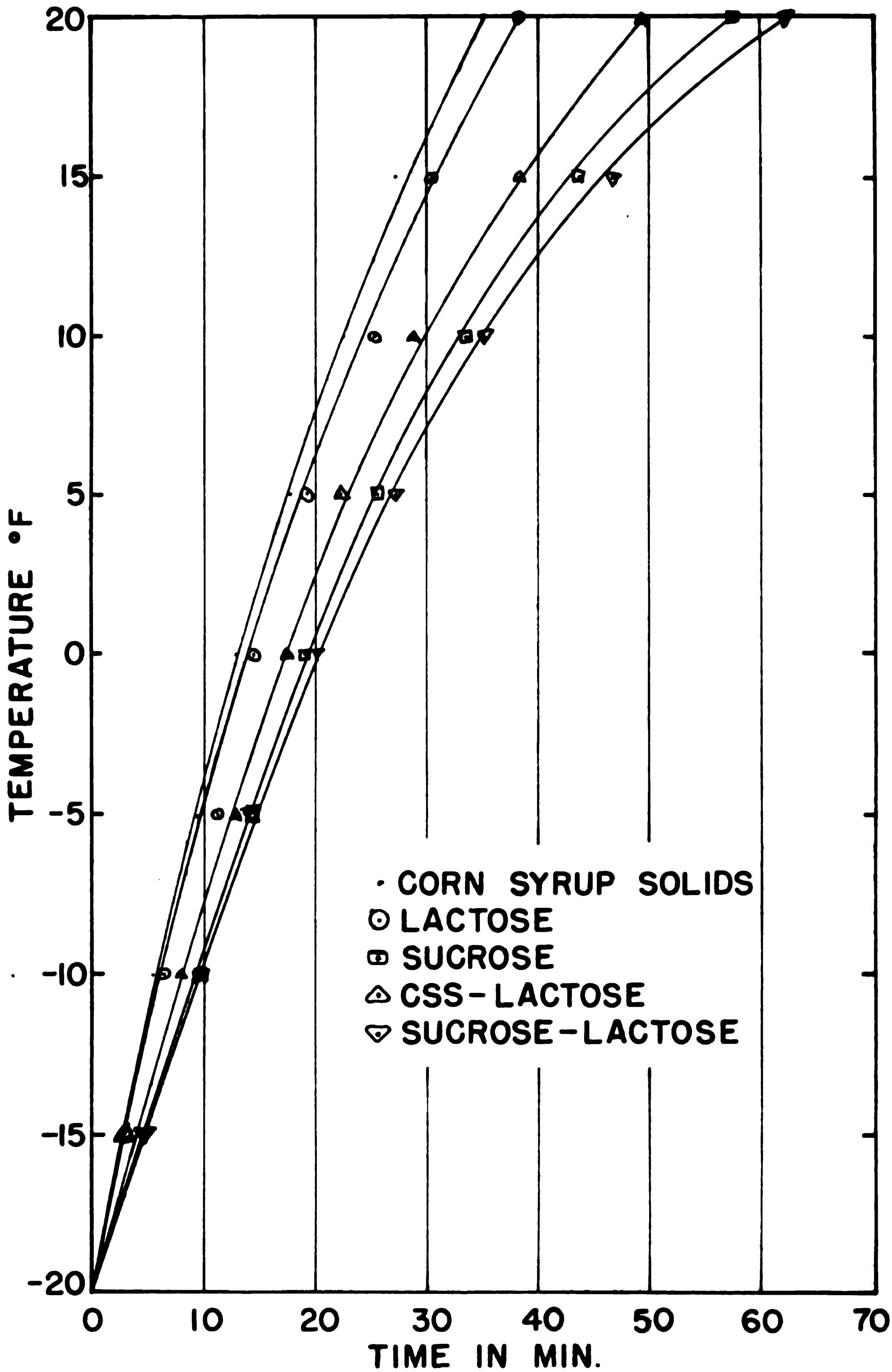



Figure 5. Typical warming curves for small tubes.

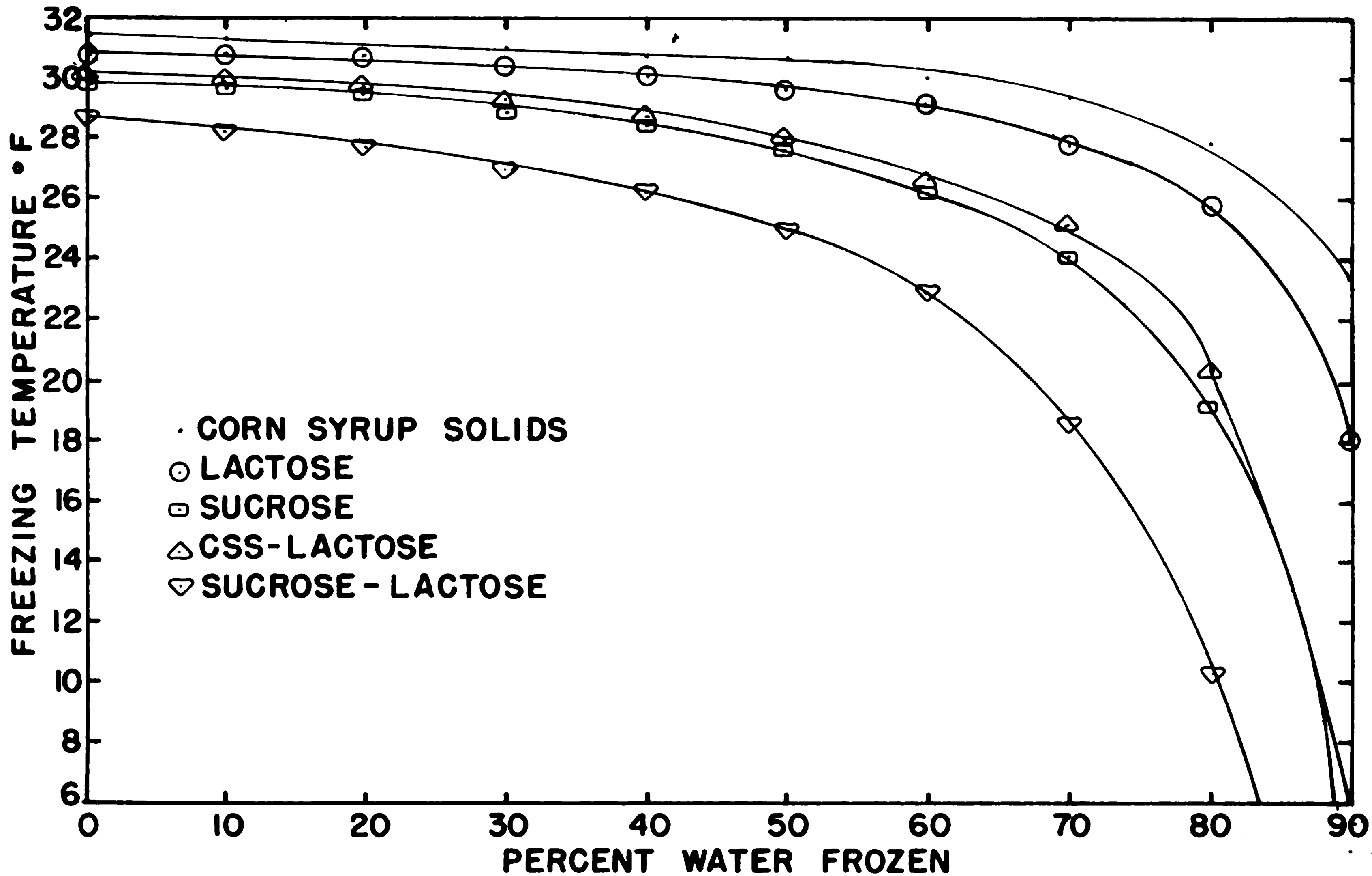



Figure 6. Freezing temperature versus percent water frozen.

Using a two-way classification analysis of variance, the means of the replications for each temperature range of corn syrup solids-lactose and lactose were not significantly different. However, those of sucrose, corn syrup solids and sucrose-lactose were significantly different. Again, the mean squares for replications were in the same range, with the replications mean square for sucrose-lactose solution between those for corn syrup solids-lactose and lactose. The coefficient of variation for sucrose, corn syrup solids and sucrose-lactose ranged from 0.029 to 0.070. As before, it was decided to use the diffusivities as calculated without further experimentation.

Computed diffusivities for corn syrup solids-lactose and sucrose-lactose solutions were generated from the diffusivities of the ingredients using the same analogy that was used in specific heat. The computed values were greater than the actual values from experimental data but their predictor worth was excellent, as shown by the correlation coefficients of 0.990 and 0.996 for corn syrup solids-lactose and sucrose-lactose, respectively. The regression equation for corn syrup solids-lactose solution was $Y = 0.952X - 0.0061$, and for sucrose-lactose solution it was $Y = 0.829X - 0.0037$, where Y is the actual experimental value and X the computed value.

The experimental thermal diffusivities are shown in Table 3 and plotted on Figure 7. Table 3 also contains the calculated diffusivities.

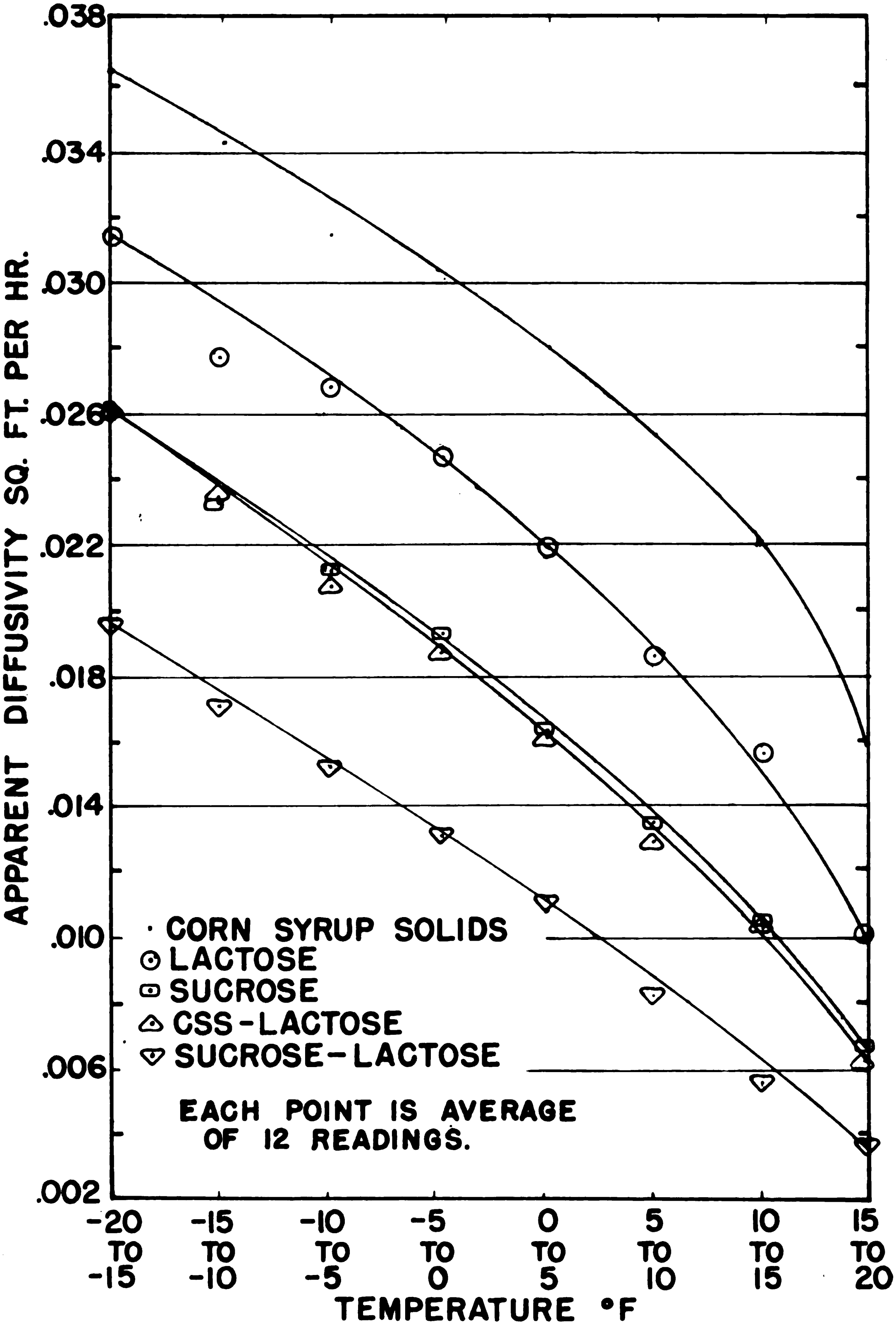



Figure 7. Apparent thermal diffusivity versus temperature.

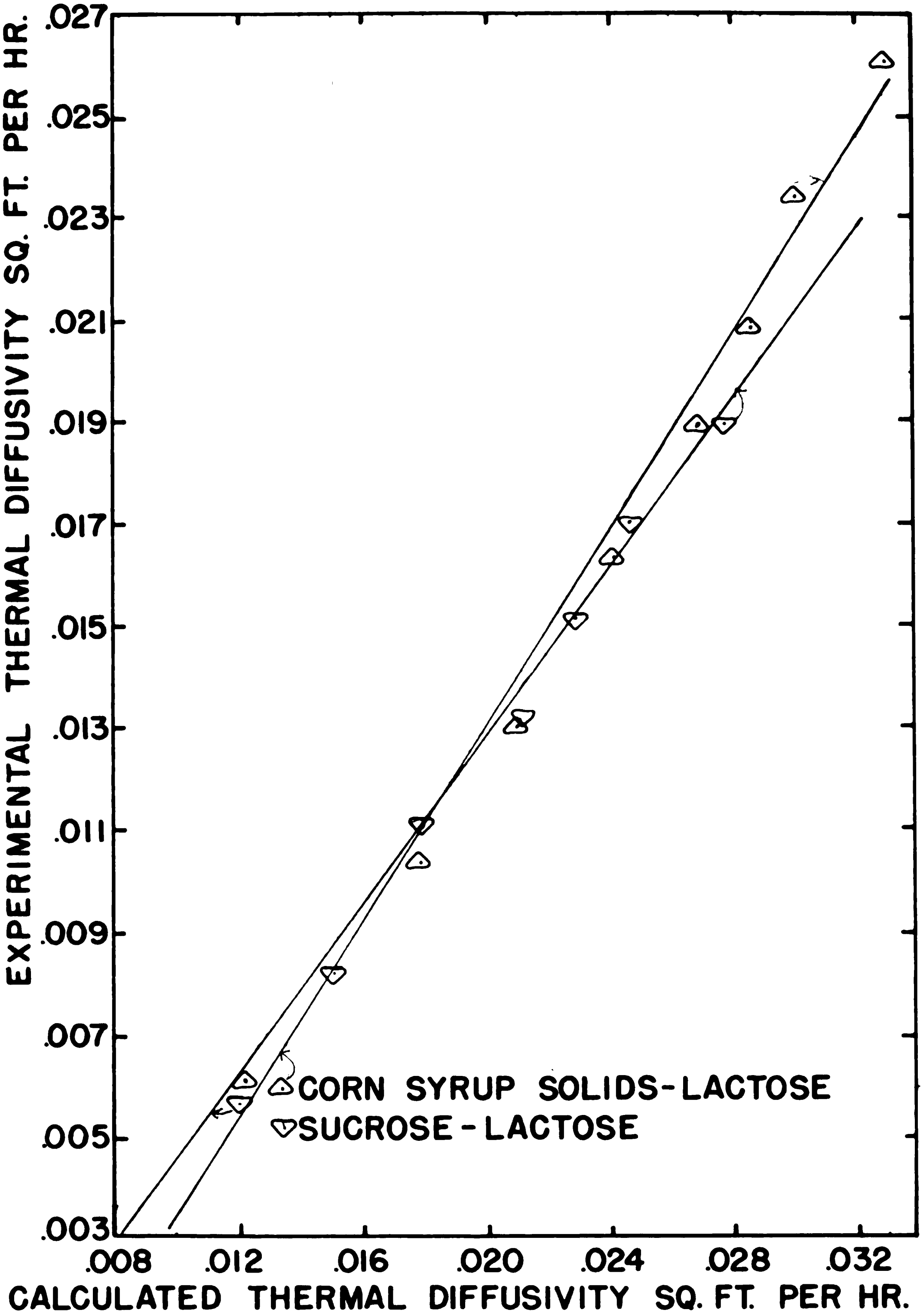



Figure 8. Experimental versus calculated apparent thermal diffusivities.

Table 3. Apparent thermal diffusivities, $ft^2/hr$

| Temp. ranges $^oF$ | Experimental | | | | | Calculated | |
|---|---|---|---|---|---|---|---|
| | Sucrose | Lactose | Corn syrup solids | Mix-ture 1 * | Mix-ture 2 # | Mix-ture 1 * | Mix-ture 2 # |
| -20 to -15 | 0.0261 | 0.0314 | 0.0365 | 0.0261 | 0.0196 | 0.0333 | 0.0278 |
| -15 to -10 | 0.0233 | 0.0278 | 0.0343 | 0.0234 | 0.0171 | 0.0301 | 0.0247 |
| -10 to -5 | 0.0213 | 0.0269 | 0.0315 | 0.0208 | 0.0152 | 0.0286 | 0.0229 |
| -5 to 0 | 0.0193 | 0.0247 | 0.0301 | 0.0188 | 0.0131 | 0.0267 | 0.0209 |
| 0 to 5 | 0.0164 | 0.0220 | 0.0280 | 0.0163 | 0.0111 | 0.0241 | 0.0180 |
| 5 to 10 | 0.0135 | 0.0185 | 0.0255 | 0.0129 | 0.0083 | 0.0208 | 0.0149 |
| 10 to 15 | 0.0105 | 0.0156 | 0.0219 | 0.0104 | 0.0057 | 0.0177 | 0.0119 |
| 15 to 20 | 0.0067 | 0.0101 | 0.0159 | 0.0062 | 0.0035 | 0.0119 | 0.0076 |

* corn syrup solids-lactose solution.
\# sucrose-lactose solution.

Warming curves for the large tubes used in this portion of the work are shown in Figure 9.

**The calculation equation for thermal diffusivity is:**

$$\alpha = \frac{\text{total parts of sugars}}{\dfrac{\text{parts of one sugar}_1}{\alpha_1} + \dfrac{\text{parts of other sugar}_2}{\alpha_2}}$$

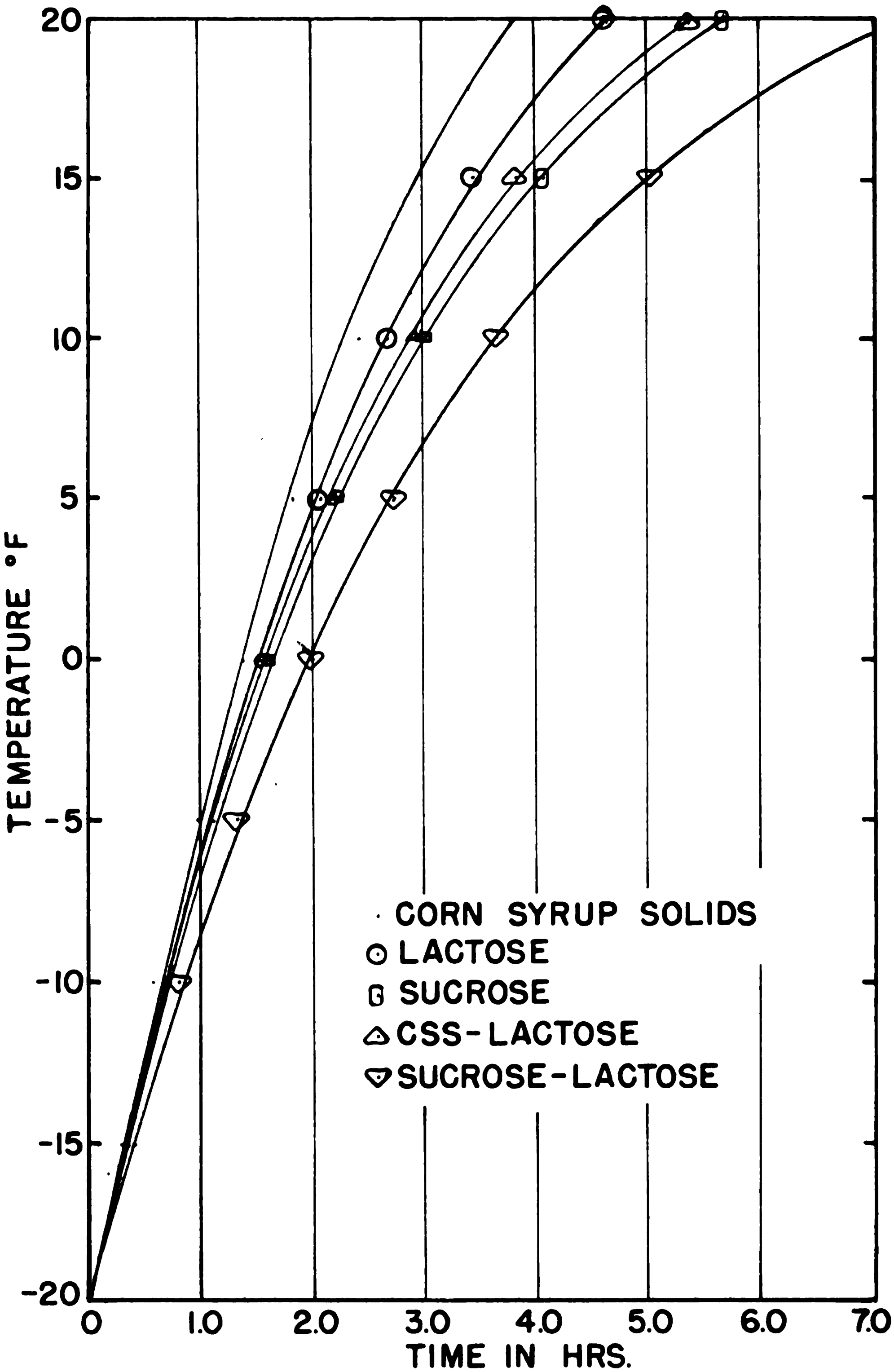



Figure 9. Typical warming curves for large tubes.

## CONCLUSIONS

1. The specific heats determined for the five frozen sugar solutions contain latent heat, are not linear functions with temperature and should be termed "apparent specific heats". The values for each solution rise sharply as the temperature warms to the original freezing point, with a rapid increase at about $5^{\circ}$F. For sucrose, the apparent specific heats range from 0.647 Btu/lb$^{\circ}$F at $-20^{\circ}$ to $-15^{\circ}$F to 2.119 at $+15^{\circ}$ to $20^{\circ}$F. For lactose they vary from 0.516 to 1.065 and for corn syrup solids from 0.439 to 0.997 for the temperature ranges. Corn syrup solids-lactose solution has apparent specific heats going from 0.531 Btu/lb$^{\circ}$F for $-20^{\circ}$ to $-15^{\circ}$F to 1.618 Btu/lb$^{\circ}$F for $+15^{\circ}$ to $20^{\circ}$F, while sucrose-lactose solution has specific heats from 0.622 to 2.526 for the same temperature range.

2. The apparent specific heats for the two mixtures used could be predicted by computation using the specific heats of the ingredients of the solutions and by use of the regression equation for each mixture. The relationship, analogous to the parallel resistance equation in electrical circuitry is:

$$c_p = \frac{\text{total parts of both sugars}}{\dfrac{\text{parts of one sugar}_1}{c_{p_1}} + \dfrac{\text{parts of other sugar}_2}{c_{p_2}}}$$

The regression equations relating the experimental apparent specific heat (Y) versus the calculated apparent specific heat (X) are: for corn syrup solids-lactose, Y = 1.9536X - 0.414 with the regression coefficient equal to 0.994; for sucrose-lactose solution, Y = 1.9536X - 0.555 and a regression coefficient equal to 0.998.

3. The experimentally determined thermal diffusivities are nearly linear functions. For sucrose the diffusivity ranges from 0.0261 sq ft/hr for $-20^{\circ}$ to $-15^{\circ}$F and 0.0067 sq ft/hr at $+15^{\circ}$ to $20^{\circ}$F. For lactose they vary from 0.0314 sq ft/hr at $-20^{\circ}$ to $-15^{\circ}$F to 0.0101 at $+15^{\circ}$ to $20^{\circ}$F and for corn syrup solids from 0.0365 to 0.0159 for the same temperature ranges. Corn syrup solids-lactose solution has diffusivities going from 0.0261 sq ft/hr at $-20^{\circ}$ to $-15^{\circ}$F to 0.0062 at $+15^{\circ}$ to $20^{\circ}$F and for sucrose-lactose solution from 0.0196 to 0.0035.

4. The apparent thermal diffusivities for corn syrup solids-lactose and sucrose-lactose solutions could be predicted by calculation from the diffusivities of the ingredients and by use of the regression equation computed for each mixture. The same relationship as was used in calculation of specific heats is used here. Apparent thermal diffusivity

$$\alpha = \frac{\text{total parts of sugars}}{\dfrac{\text{parts of one sugar}_1}{\alpha_1} + \dfrac{\text{parts of other sugar}_2}{\alpha_2}}$$

The regression equations relating the experimental diffusivities (Y) versus the calculated diffusivities (X) are: for corn syrup solids-lactose solution, Y = 0.952X - 0.0061 with a regression coefficient of 0.995; for sucrose-lactose solution, Y = 0.829X - 0.0037 with a regression coefficient of 0.996.

5. Calculations were made to obtain the relationship of the freezing temperature of the five sugar solutions and the percent of water frozen. The freezing temperature of the solutions reduce about $2^{\circ}$ to $3^{\circ}F$ until 50 to 60% of the water is frozen. Then, generally, the freezing temperature falls quite rapidly. This corresponds to the high apparent specific heats at temperatures approaching thawing where a major portion of latent heat is removed in just a few degrees.

## SUGGESTIONS FOR FURTHER STUDY

1. Extend the work on specific heat and thermal diffusivity to other concentrations of these sugars and other mixed solutions.
2. Determine the thermal conductivities of these frozen solutions.
3. Determine the densities of these frozen solutions.
4. Widen the study to include ice cream and other sweetened frozen foods.
5. Attempt to predict the thermal characteristics of ice cream of different overruns.
6. Find the actual specific heats of these solutions by determining and subtracting the latent heats from the apparent specific heats.

# APPENDIX

## Sample Calculations

Calculation of apparent specific heat

$$q = W\, c_p \frac{\Delta T}{\Delta \theta}$$

where: $q$ = heat leak into the sample tube, Btu/min

$W$ = weight of sample and/or tube, lb

$c_p$ = specific heat of sample and/or tube, Btu/lb$^{o}$F

$\frac{\Delta T}{\Delta \theta}$ = temperature difference at center of sample per unit time, $^{o}$F/min

$$W_s c_{p_s} = \frac{q}{\Delta T / \Delta \theta}$$

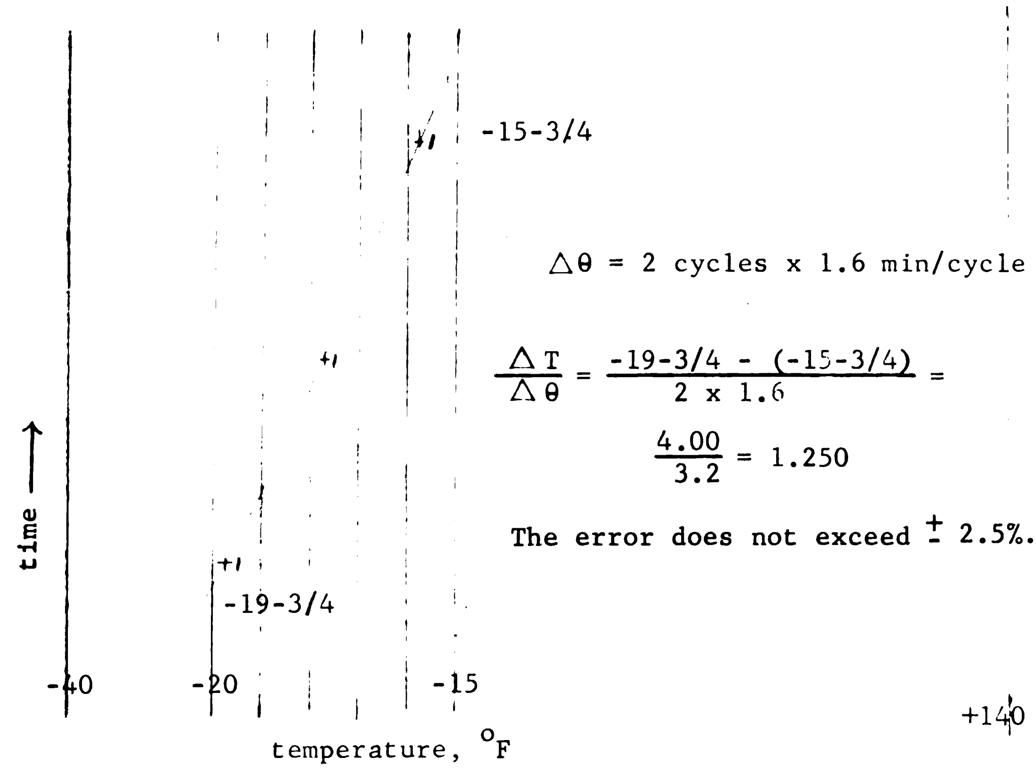
subscript s refers to sample plus tube

$$W_s c_{p_s} = W_t c_{p_t} + W_x c_{p_x}$$

subscripts t and x refer to tube and sample, respectively

$$c_{p_x} = \frac{W_s c_{p_s} - W_t c_{p_t}}{W_x}$$

A representation of a recording chart from which the calculation values would be taken would look like this:




$$\Delta\theta = 2 \text{ cycles} \times 1.6 \text{ min/cycle}$$

$$\frac{\Delta T}{\Delta \theta} = \frac{-19\text{-}3/4 - (-15\text{-}3/4)}{2 \times 1.6} =$$

$$\frac{4.00}{3.2} = 1.250$$

The error does not exceed $\pm$ 2.5%.

Within the temperature range of -20° to -15°F thermocouple No. 1 printed at -19-3/4°F and the other points printed in turn through 16 points for two cycles. Thermocouple No. 1 again printed at -15-3/4°F at the end of two cycles. The temperature difference, T, would be 4°F and the time, $\Delta\theta$, would be 2 cycles x 1.6 min/cycle or 3.2 min. $\frac{\Delta T}{\Delta \theta} = \frac{4.00}{3.2} = 1.250$ °F/min. The heat leak, q, already was determined from the calibration with the copper slug and was known to be 0.0553 Btu/min for this temperature range. The product of the tube weight and specific heat of steel, $W_t c_{p_t}$, is 0.0137 Btu/lb°F. Therefore,

$$\frac{q}{\Delta T / \Delta \theta} = W_s c_{p_s} = \frac{0.0553}{1.250} = 0.0442 \text{ Btu/}^{\circ}\text{F}$$

$$c_{p_x} = \frac{0.0442 - 0.0137}{0.0450} = 0.678 \text{ Btu/lb }^{\circ}\text{F}$$

## Development of the Calculation Equation for Apparent Thermal Diffusivity

To the Fourier differential heat transfer equation in cylindrical coordinates, $\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} = \frac{1}{K}\frac{\partial v}{\partial t}$, apply LaPlace trans- (1) formation $\left[\text{by definition } L(u) = \int_0^\infty e^{-ux} f(x)dx\right]$ to equation 1 with respect to t

$$\int_0^\infty e^{-pt} \frac{\partial^2 v}{\partial r^2} dt + \int_0^\infty e^{-pt} \frac{\partial v}{\partial r}\frac{1}{r} dt = \frac{1}{K}\int_0^\infty e^{-pt} \frac{\partial v}{\partial t} dt. \quad (2)$$

The right side can be integrated to obtain

$$\frac{1}{K}(p\ L(v) - v\ (r,\ 0^+)).$$

Now assume function will behave and that we may change the order of differentiation and integration, then the left side of (2) becomes

$$\frac{\partial}{\partial r^2}\int_0^\infty v(r,\ t)\ e^{-pt}\ dt + \frac{1}{r}\frac{\partial}{\partial r}\int_0^\infty v(r,\ t)e^{-pt}dt,$$

where the integral is recognized to be the LaPlace transformation of $v(r,\ t)$. Let $L\ v(r,\ t) \equiv \bar{v}$, then equation 1 is written as

$$\frac{d^2\bar{v}}{dr^2} + \frac{1}{r}\frac{d\bar{v}}{dr} = \frac{1}{K}\left[p\ L(v) - v(r,\ 0^+)\right], \quad (3)$$

where $v(r,0^+) = 0$, or $\frac{d^2\bar{v}}{dr^2} + \frac{1}{r}\frac{d\bar{v}}{dr} - q^2\ \bar{v} = 0$ (4)

where $q^2 = \frac{p}{K}$. Now equation (4) is an algebraic equation with $\bar{v} = \bar{v}(r)$ only and $\bar{v} \equiv L(v)$.

Equation (4) can be rewritten in the form

$$r^2 \frac{d^2\bar{v}}{dr^2} + r\frac{d\bar{v}}{dr} - q^2 r^2 \bar{v} = 0. \tag{4a}$$

Let $\eta = qr$, then equation (4a) becomes

$$\eta \frac{d^2\bar{v}}{d\eta^2} + \eta \frac{d\bar{v}}{d\eta} - \eta \bar{v} = 0 , \tag{5}$$

which has the general solution

$$\bar{v} = c_1 I_o (\eta) + c_2 K_o (\eta), \text{ or} \tag{6}$$

$$\bar{v} = c_1 I_o (qr) + c_2 K_o (qr) \tag{6a}$$

Where $I_o$ and $K_o$ are the modified Bessel functions of zero's order; $c_1$ and $c_2$ are constants and $\bar{v} = L(v)$.

Remember that $K_o \to \infty$ as $r \to o$, or

$$\lim_{r \to o} K_o (qr) = \infty \tag{7}$$

and this is quite inconvenient, then the general solution, equation (6), becomes (with $c_2 = 0$)

$$\bar{v} = c_1 I_o (qr). \tag{8}$$

Now the boundary conditions are given by

$$F = K \frac{\partial v}{\partial r} + W \frac{\partial v}{\partial t} , \text{ at } r = a \tag{9}$$

transform $\frac{F}{p} = K \frac{d\bar{v}}{dr} + W\bar{v}p$ , or

$$K \frac{d\bar{v}}{dr} = \frac{F}{p} - Wp\bar{v} , \tag{10}$$

but $\bar{v} = c_1 I_o (qr)$ or, at $r = a$, (8)

$$\bar{v} = c_1 I_o (qa) \tag{8a}$$

$$\text{and } \frac{d\bar{v}}{dr} = c_1 \left. \frac{d\, I_o\,(qa)}{dr} \right|_{r=a} = q\, c_1\, I_1\,(qa). \tag{11}$$

Substitute equation (8a) and (11) into (10)

$$K\, q\, c_1\, I_1\,(qa) = \frac{F}{p} - Wpc_1\, I_o\,(qa).$$

$$\text{Therefore, } c_1 = \frac{F}{p} \left[ K\, q\, I_1\,(qa) + Wp\, I_o\,(qa) \right] \tag{12}$$

$$\text{and then } \bar{v} = \frac{F}{p} \left[ Kq\, I_1\,(qa) + Wp\, I_o\,(qa) \right] I_o\,(qr) \tag{13}$$

v is found from $\bar{v}$ by using the inversion integral

$$v = \frac{F}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{I_o\,(qr)\, e^{zt}\, dz}{z \left[ Kq\, I_1\,(qa) + Wz\, I_o\,(qa) \right]} \tag{14}$$

where $q^2 = z/K$.

This has a double pole at $z = 0$ and single poles at the roots of $Kq\, I_1\,(qa) + Wz\, I_o\,(qa) = 0$.

Since $I_o$ and $I_1$ are positive functions, it follows that all the roots are negative and consequently the terms in v corresponding to these roots will each contain a negative exponential which tends to zero as t increases.

On expanding the various functions in power series and taking the limit $z \to 0$ it will be found that the residue (coefficient of $1/z$) is

$$\frac{F}{2\pi i} \left[ t + r^2/4K - \frac{a^2}{8K} \left( \frac{4KW + Ka}{2KW + Ka} \right) \right] (W + Ka/2K) \tag{15}$$

and by the Cauchy residue theorem it follows that this (multiplied by $2\pi i$) is the term in v corresponding to $z = 0$.

From the expansion comes

$$K = \frac{1}{4} a^2 \frac{\partial v}{\partial t} \Big/ v_s - v_c \ . \tag{16}$$

Equation (16), translated into the parameters used in this thesis, becomes

$$\alpha = \frac{1}{4} r^2 \frac{\Delta T}{\Delta \theta} \frac{1}{\Delta T^1}$$

The author is indebted to Mr. Gad Hetsroni for this derivation after Thomas (1957).

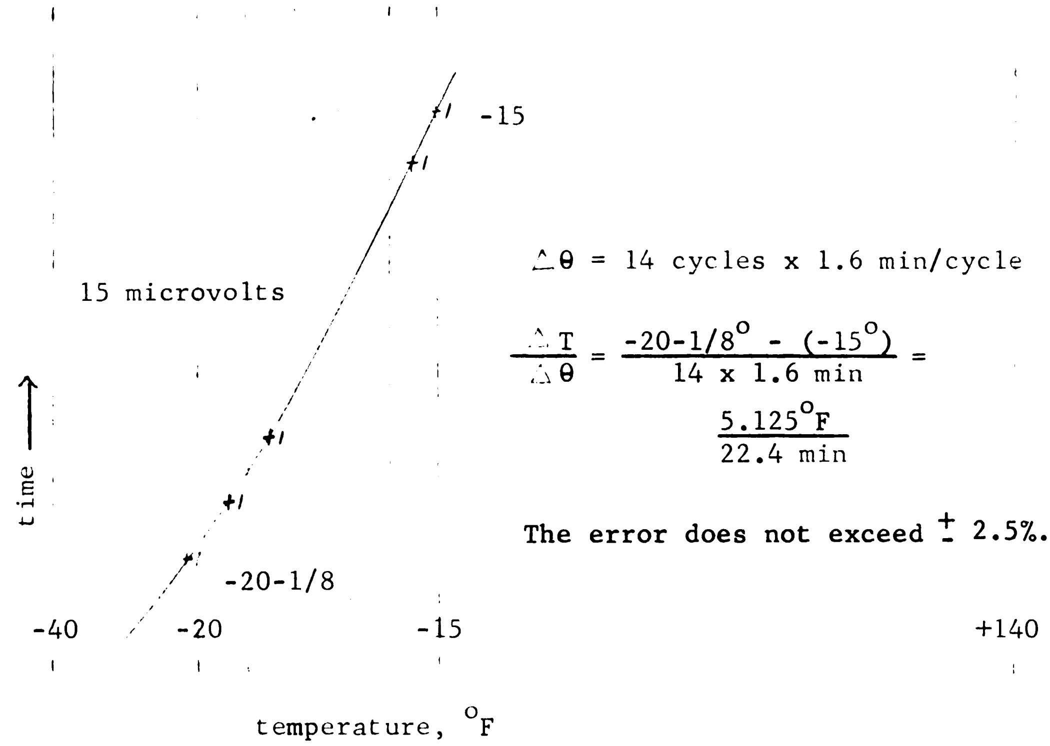
Calculation of apparent thermal diffusivity

$$\alpha = \frac{1}{4} r^2 \frac{\Delta T}{\Delta \theta} \frac{1}{\Delta T^1}$$

where: $r$ = inside radius of the tube, ft

$\frac{\Delta T}{\Delta \theta}$ = temperature difference at center of sample per unit from the recording chart, Btu/min

$\Delta T^1$ = temperature difference between the center and outside of the sample read on the manual potentiometer and written on the recording chart, microvolts (21 microvolts - $1^\circ F$ for copper-constantan at this temperature)




$\Delta\theta$ = 14 cycles x 1.6 min/cycle

$$\frac{\Delta T}{\Delta \theta} = \frac{-20\text{-}1/8^\circ - (-15^\circ)}{14 \times 1.6 \text{ min}} = \frac{5.125^\circ F}{22.4 \text{ min}}$$

**The error does not exceed $\pm$ 2.5%.**

The above is representative of the chart from which the following values were taken.

$$r = \frac{1.899}{2} \text{ in.}$$

$$\frac{\Delta T}{\Delta \theta} = \frac{5.125 \ ^{o}F}{14 \times 1.6 \text{ min}}$$

$$\Delta T^{1} = \frac{15}{21} \ ^{o}F$$

$$\alpha = \frac{1}{4} \left(\frac{1.899}{2 \times 12}\right)^{2} \left(\frac{5.125}{14 \times 1.6} \times 60\right) \frac{1}{15/21} = 0.0301 \text{ ft}^{2}/\text{hr}$$

## REFERENCES


Anonymous

1929. Dow Calcium Chloride for Refrigeration. Midland, Michigan. Dow Chemical Co. 11 pp

Birdseye, C.

1932. Refrigerating Data Book, 1st Ed, pp 339-40. New York: American Society of Refrigerating Engineers. 625 pp

Brunner, J. R.

1942. The physical state of fat in cream and its relation to churning time. Unpublished thesis for MS. University of California, Davis. Department of Dairy. 107 pp

Brunner, J. R. and C. Stine

1961. Personal conversation.

Cole, W. C.

1938. Use of the dilatometer is measuring the extent of freezing in ice cream and related products. Journal of Agricultural Research 56(2):137-53, February.

Corn Industries Research Foundation, Inc.

1958. Corn Syrups and Sugars, Washington, D.C.: Technical Service Committee. 45 pp

Fourier, Joseph

1878. The Analytical Theory of Heat. New York, N.Y.: Dover Publications, Inc. 466 pp

Giedt, W. H.

1957. Principles of Engineering Heat Transfer. Princeton, N.J.: D. Van Nostrand Co., Inc. 372 pp

Hall, C. W.

1957. Drying Farm Crops. Ann Arbor, Michigan: Edwards Brothers, Inc. 335 pp

Handbook of Chemistry and Physics

1959-60. 41st Ed. pp 2121, 2285, 2437. Cleveland, Ohio: Chemical Rubber Publishing Co.

Hodgman, C. D.

1932. Handbook of Chemistry and Physics, 17th Ed. p 1448. Cleveland, Ohio: Chemical Rubber Publishing Co. 2372 pp

International Critical Tables
1927. Volume II p 316. New York, N.Y.: McGraw-Hill Book Co. 616 pp

Lange, N. A.
1941. Handbook of Chemistry, 4th Ed., p 1206. Sandusky, Ohio: Handbook Publishers, Inc. 1875 pp

Leighton, A.
1927. On the calculation of the freezing point of ice cream mixes and the quantities of ice separated during the freezing process. Journal of Dairy Science 10(4):300 July.

Moline, S. W., Sawdye, J. A., Short, A. J., and Rinfret, A. P.
1961. Thermal properties of foods at low temperatures. Food Technology 15(5): 228-31, May.

National Bureau of Standards
1934. Copper. Circular No. 73, Washington, D.C. p 29.

Schneider, P. J.
1955. Conduction Heat Transfer. Cambridge, Mass.,: Addison-Wesley Publishing Co., Inc. 395 pp

Short, B. E., Woolrich, W. R. and Bartlett, L. H.
1942. Specific heats of foodstuffs. Refrigerating Engineering, 50(12):385-88, December.

Siebel, J. E.
1892. Specific heat of various products. Ice and Refrigeration 2(4): 256-257, April.

Staph, H. E.
1949. Specific heats of foodstuffs. Refrigerating Engineering 57(8): 767-71, 829-30, August.

Thomas, T. S. E.
1957. A method of measuring the thermal constants of granular materials. British Journal of Applied Physics 8(10): 403-405, October.

Torgensen, J. L.
1950. Quarterly Report Research Project. Washington, D. C.; National Bureau of Standards, Physics-Chemistry Section, December.