

THE FREEZING OF PLANT TISSUE

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Summary

A theory of the freezing process of the tissue of pear fruit is presented, based on the cell permeability theory and on the thermodynamics of moisture in porous media. According to this theory the nature of the temperature *v.* time curve during freezing is determined by the speed of advance of the ice front into the tissue. Curves for freezing and thawing calculated from the theory are compared with experimental curves.

Using the theory to interpret the experimental freezing curves, further experiments enabled the true freezing point of the tissue to be deduced. In most cases the true freezing point, defined as the highest temperature at which ice can propagate through the tissue, coincided with the freezing point of the expressed juice. In some cases, however, the true freezing point was as much as 1°F below the juice freezing point.

The theory provides an explanation for a number of points raised in the literature which are either unexplained or the subject of dispute.

I. INTRODUCTION

As part of an investigation into the freezing point of pear fruit, a detailed study has been made of the temperature *v.* time curves followed by intact pears and pieces of their tissue during freezing and thawing. The practical purpose of this work was to examine the relationship between the maximum freezing temperature exhibited by the freezing curves (Fig. 1) and the true freezing point, which is defined as the highest temperature at which ice may form throughout the tissue. A theory is put forward, based on the cell permeability theory and on the thermodynamics of moisture in porous media, from which freezing and thawing curves can be calculated and compared with the experimental curves. This theory is presented here together with a discussion of its bearing on current ideas on the freezing of plant tissue—an account of the more practical implications of this work, and further investigations of the practical problem will be published elsewhere.

II. EXPERIMENTAL

Temperatures were measured with a recording thermistor thermometer developed by Melville (1958), which uses a probe consisting of a 20-gauge hypodermic needle with a thermistor bead set in the tip. The output is recorded on a 1-mA Esterline Angus recorder. The instrument was adjusted and calibrated against a standard thermometer for the range 22–32°F, but temperatures beyond this range could be read by reducing the sensitivity in known ratios.

The pears were frozen in the modified freezing chamber of a domestic refrigerator. A plywood lining opening at the top was fitted, leaving a 1-cm air gap between

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it and the metal evaporator. This in conjunction with a Danfoss thermostat enabled the air temperature to be controlled within a range of 0.4°F .

For thawing experiments a double-walled container with ice-water in the outer jacket was used.

In preliminary experiments many freezing curves were recorded, typical examples of which are shown in Figures 1 and 2. Features of the curves for intact pears are that there is always some supercooling, quite often as much as 10°F (Fig. 1, *B*); when freezing does begin it may take as long as 1 hr for the temperature to rise to its maximum; after this the temperature falls steadily, the rate of fall increasing gradually, or sometimes fairly suddenly after 6 or 8 hr as in Figure 1, *A*. A conspicuous feature in every case is a sharp pulse which very often rises above the maximum freezing temperature, and which may occur anywhere during the

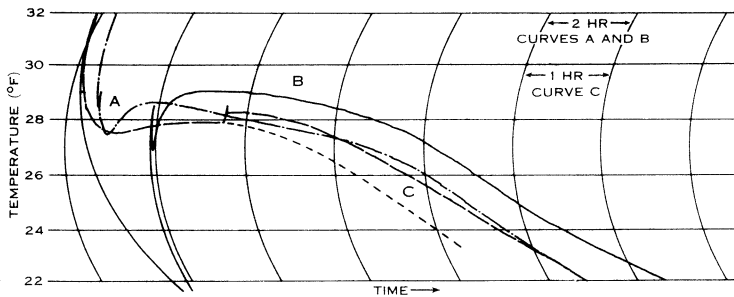


Fig. 1.—Experimental records showing freezing curves for intact pears, placed in an environment at 15°F . (The dashed curve in *C* is an addition to the record which is referred to later in the text.)

supercooling stage, although very occasionally it may occur as late as in Figure 1, *C*. If the pear is dissected when the curve is at the maximum, it is found that only a comparatively thin layer of tissue just under the skin is frozen—about 0.5 cm thick or less. If the pear is not dissected until the temperature has fallen 1 or 2°F below the maximum, there will usually still be found a small region of unfrozen tissue. The presence of freezing is shown by the translucent appearance of the tissue, but if the pear has been frozen in an environment colder than about 20°F the distinction of the frozen from the normal, white, opaque, unfrozen tissue is not very clear immediately after dissection. After $15\text{--}30\text{ min}$ at room temperature, however, a sharp division between the two regions (which one may call the “ice front”) is apparent. The thickness of the frozen layer is usually quite uniform, although in some cases it has a spotty appearance, the centre of some of the spots coinciding with the vascular bundles. The frozen region also extends around the thermistor probe, in a cylinder of radius comparable with the thickness of the surface layer.

If an intact pear is placed in a comparatively warm environment, at say 25°F , it is not practicable to obtain a freezing curve at all, as the pear will remain supercooled at this temperature for 24 hr or more. If the fruit is peeled first, however, a curve such as that in Figure 2, *A* is obtained. The characteristics of such curves

are only slight supercooling, a sudden temperature rise of about 1°F , followed by a temperature fall which settles down after about an hour to a very steady rate. In this case when the tissue is dissected the translucent frozen region is immediately distinguishable from the unfrozen tissue.

When peeled fruit or pieces of tissue are frozen at lower temperatures, the main difference from the curves of Figure 1 is that deep supercooling never occurs. In some cases in fact curves like Figure 2, *C* are obtained, in which, apart from the sharp pulse, the curve never becomes horizontal.

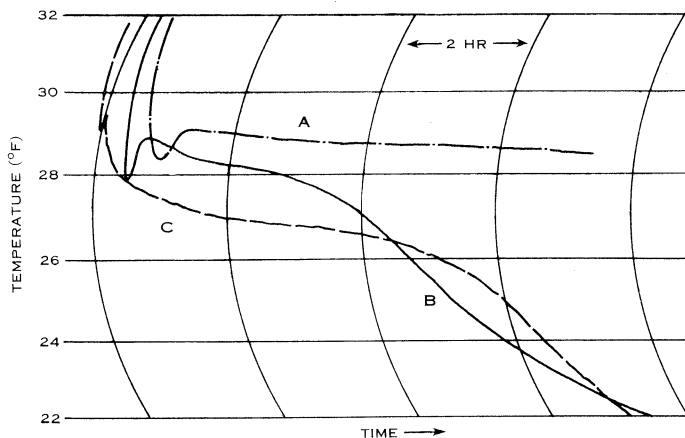


Fig. 2.—Experimental records showing freezing curves for peeled fruit and pieces of tissue. The environment temperatures were: *A*, 24°F , *B*, 19°F , and *C*, 17°F .

These experiments showed that the freezing temperatures were dependent on the temperature of the environment, the recorded curve deviating from its general trend to follow variations in the environment temperature. The variations in the temperature of the tissue, however, were only about 5% of those of the air in the freezing chamber.

To provide a temperature characteristic of the tissue, against which freezing temperatures could be compared, the freezing point of the juice was measured. The “juice freezing point” is here defined to be the measurement obtained by freezing tissue hard overnight (at 15°F or lower), thawing it, and then refreezing it, preferably at the same low temperature. A piece about 1 by 1 by 2 cm freshly cut is used for the second freeze. With a piece this size or larger, the resulting freezing curve has a reasonably flat top which is repeatable and can be measured to 0.1°F accuracy. It was confirmed that this value is identical with the freezing point obtained for the expressed juice. This refreezing method is very simple to use for routine measurements, and will measure the juice from a restricted locality.

The maximum freezing temperature of intact fruit held at fairly low temperatures may be about 2°F below the juice freezing point—a well-known result. While this freezing temperature was evidently not the highest temperature at which

the tissue could freeze, it was a principal aim of the investigation to determine whether the true freezing point was as high as the juice freezing point.

III. PREVIOUS WORK

There is a vast literature dealing with the freezing of plant tissue which has been extensively reviewed by Levitt (1941, 1958). This literature is mostly concerned with the nature of frost injury. The present investigation, however, was limited to determining the highest temperature at which freezing can occur—whether or not the freezing was injurious was not considered.

Levitt concludes that the evidence supports the permeability theory. Briefly this theory states that at comparatively mild freezing temperatures ice formation is confined to the intercellular spaces, supercooled water from inside the cell diffusing through the cell wall to freeze on the ice outside. Only when the temperature falls below a certain limit does intracellular freezing occur.

The various modes of ice formation are shown very graphically in the cinemicrographs of Modlibowska and Rogers (1955) which the author was fortunate enough to see. The growth of ice by withdrawal of water through cell wall or membrane could be observed under various circumstances. Of particular interest was the progress of intracellular freezing along a staminal hair of *Tradescantia*. The wall between successive cells was stretched sometimes to four or five times its original size before ice crystals were able to pass through it, after which the cell contents froze very quickly and the process was repeated at the next intercellular barrier. The same process is described in detail by Asahina (1956).

A physical explanation of why ice crystals may not pass through the porous cell wall to the supercooled water on the other side has been given by Jackson and Chalmers (1958). Their work is concerned with soil moisture but is equally applicable to plant tissue. They show that the interfacial free energy of the ice-water interface has the effect of lowering the freezing point of water in a capillary by an amount inversely proportional to the radius of the capillary (provided the other interfacial free energies obey a certain condition). One can see that if the cell wall is stretched, enlarging the pores, a stage will be reached at which the water in the pores can freeze, and the ice crystals grow into the supercooled liquid beyond.

Concerning actual freezing temperatures, the literature is not conclusive. Levitt (1941) remarks "Many recent workers have confirmed the claim that dead tissues freeze at a higher temperature than living tissues. The lower the temperature of the freezing bath the lower was the freezing point of the tissue." And again, "Thus, though the freezing point of living tissue varies with the conditions, it has not been possible to obtain real agreement with the freezing point of the same tissue when dead." Maximov (1914) was evidently the first to point out that a consequence of the permeability theory is that the freezing temperature of plant tissue must be below that of the free cell sap.* Thus (as quoted by Levitt) "The freezing point of living tissue depends on a complicated interaction between the rate of cooling,

* I am indebted to the late E. W. Hicks, Division of Food Preservation, C.S.I.R.O., for first drawing my attention to Maximov's work and the permeability theory.

the resistance of the protoplasm to the exit of water, and the speed of ice formation in the intercellular spaces." ". . ., there must be a steady drop (in temperature), slow at first, then more rapid, due to the progressively smaller quantity of ice formed and of heat liberated thereby." E. W. Hicks (personal communication) had suggested that the true freezing point of living tissue should not be more than 0.1°C below the freezing point of disrupted tissue.

Our preliminary observations were generally consistent with the permeability theory. The appearance of the translucence on dissection, for instance, is in agreement with the occurrence of extracellular ice formation during mild freezing and intracellular ice formation during more rapid freezing. The translucence is evidently caused by the replacement of the air in the intercellular spaces by water, and the consequent removal of the air-water interfaces round each cell and the refraction of light which they produce. In the case of the more severe freezing, it takes some minutes for the melting ice inside the cell to seep through the walls into the spaces, whereas after mild freezing the ice is already in the spaces and translucence appears immediately.

To explain the details of the freezing curves, however, a more precise formulation of the theory is needed. The very existence of the ice front shows that the cells do not all freeze at the same temperature in a given case, and the presence of unfrozen tissue when the temperature has fallen 2°F below the minimum freezing temperature shows that either some mechanism comes into play which progressively lowers the freezing point, or that supercooling of the tissue may be very persistent. In the latter case Levitt's suggestion that intracellular ice results when "the temperature of the cell sap falls below its undercooling point" cannot hold. A full understanding of the freezing curve must take into account the flow of heat through the pear tissue.

IV. THEORETICAL

The theory proposed here is an elaboration and quantification of the permeability theory. It asserts that the shape of the freezing curve is determined by the speed of advance of the ice front, or more fundamentally, by the factors which determine this speed. In the case of a single body of liquid the speed of the solidification front is determined by the balance between the rate of heat loss from the front and the rate of latent heat release. This balance occurs when the temperature remains steady at the freezing point of the liquid—the temperature at which the specific free energies of the liquid and the solid are equal. If the speed were to decrease, the balance would be disturbed in the direction which would make the temperature fall, which would result in the liquid having a greater free energy than the solid. This energy difference would cause a force tending to restore the balance.

In a cellular tissue, however, the speed of the ice front is dependent on the rate at which water diffuses through the cell wall, which in turn depends on the degree of supercooling (since this provides the driving force). It is an essential postulate of the present theory that once freezing has begun the remaining intact cells do not freeze until they come within the influence of the ice front.* During

* Both Modlibowska and Rogers (1955) and Asahina (1956) emphasize the stability of cells under supercooling.

extracellular freezing a layer of ice is visualized as growing over the cell wall, regularly bringing new cells within its water-extracting influence as it comes in contact with them. When the freezing is intracellular it is visualized as being transferred from cell to cell in the manner filmed by Modlibowska and Rogers. In this case not only must water diffuse through the cell wall, but the ice formed must stretch the wall until the pores are sufficiently enlarged for the water in them to be able to freeze. It can be seen that more energy will be needed for this process than for the straightforward diffusion in extracellular freezing, and therefore the temperature must be lower. This explains why even if a cell should freeze internally, it will not cause adjacent cells to freeze in a similar manner unless they are supercooled beyond a certain limit. This is discussed in more detail below.

It will now be shown that by assuming a suitable relation between the speed of the ice front and its temperature, freezing curves can be calculated which have the same general characteristics as the experimental curves shown in Figures 1 and 2. These theoretical curves enable meaningful comparisons to be made between experimental curves of different shapes, which in turn give an indication of the true freezing point of the tissue.

Calculation of the Freezing Curve

In applying mathematical methods to phenomena in biological material which displays so much variety that no two samples are ever identical, it is necessary to make numerous generalizations and simplifications. This approach has been ably expounded and justified by Rashevsky (1948) in the preface of his book "Mathematical Biophysics". In the present case we begin by assuming that the pear or piece thereof is spherical and that the ice front lies on a concentric sphere. We will be satisfied if the values of the physical constants used are only approximately correct.

The temperature of the environment is taken as zero and the following temperatures defined (in Centigrade degrees):

V_0 = the ice point,

V = the true freezing point of the pear tissue,

v_F = the temperature of the ice front (a function of time),

v = the temperature of any point in the pear (a function of radius and time).

Also let

a = radius of the pear (in cm),

ρ = radius of the ice front (in cm, a function of time).

At this stage we make the arbitrary assumption that:

$$\text{Speed of ice front} = -d\rho/dt = S(V_0 - v_F) \quad \text{cm/sec for } v_F < V, \quad (1)$$

where S is a constant. The reasons for this assumption will be discussed later. In the meantime it may be remarked that the speed increases with the supercooling as desired.

When a cell at the ice front freezes, whether externally or internally, it will be assumed that it takes negligible time for all the water which can freeze at the temperature v_F to do so. It then follows (see Appendix I) that the latent heat l

(cal/g) released is given by:

$$l = L[(V - v_F)/(V_0 - v_F)], \quad (2)$$

where L = latent heat when all the water is frozen. This expression implicitly assumes that the effect of anything other than dissolved material which causes a depression of freezing point remains constant for all values of the temperature v_F .

After the ice front has reached a particular cell and it has become a part of the frozen region between the surface of the pear and the ice front, it will undergo thawing or further freezing according as the local temperature rises above or falls below the temperature at which it originally froze. If it is assumed that the freezing point of the unfrozen solution takes negligible time to adjust itself to the local temperature, the effect of this marginal freezing and thawing is equivalent to a temperature-dependent specific heat of magnitude:

$$-dl/dv = L(V_0 - V)/(V_0 - v)^2 \text{ cal/g } ^\circ\text{C}. \quad (3)$$

The shape of the cooling curve before freezing begins shows that it is a good approximation to assume that the heat loss from the surface of the pear is proportional to the difference between the temperatures of the surface and the environment—sometimes called the “radiation” boundary condition (Carslaw and Jaeger 1948, pp. 13–16):

$$\text{Rate of heat loss} = H v_s \text{ cal/cm}^2 \text{ sec}, \quad (4)$$

where v_s is the temperature of the surface (the temperature of the environment being defined as zero), and H is a constant.

In common with most heat flow problems involving latent heat, the present one cannot be solved analytically. The alternative method is to use numerical analysis, the usual method for a partial differential equation like the heat equation being to use a space lattice of points and calculate the temperature distribution at successive time intervals. This method was not used here, however, as without an electronic computer the labour involved is usually prohibitive.

A simpler though somewhat less accurate method is to consider the heat balance of the pear as a whole:

$$\begin{aligned} & (\text{Rate of heat loss at surface}) - (\text{rate of latent heat release}) \\ & = \text{Net rate of heat loss from pear} \\ & = (\text{Volume}) \times (\text{density}) \times (\text{average specific heat}) \times (\text{rate of temperature drop}). \end{aligned} \quad (5)$$

This approach leads to an ordinary differential equation which can be solved more easily. The details are given in Appendix I.

A family of solutions to the equation is shown in Figure 3. A family rather than a single curve is obtained because the temperature at which freezing begins can be chosen arbitrarily. In curve *A* freezing begins when the temperature has fallen 0.9°F below the true freezing point of the tissue, V . Nevertheless, the temperature continues to fall quite rapidly for another $1\frac{1}{2}^\circ\text{F}$. Note the resemblance between this curve and the experimental one in Figure 2, *C*.

In curve *D* the tissue was considerably supercooled before freezing was assumed to begin. The temperature immediately rose to a rounded maximum similar to the majority of the experimental records for intact fruit (Fig. 1). Curve *B* may be

regarded as the most fundamental one from a theoretical point of view. In this case the rate of heat loss and the rate of heat release are equal at the instant when freezing begins. The temperature at the point *B* will be defined as the "initial freezing temperature".

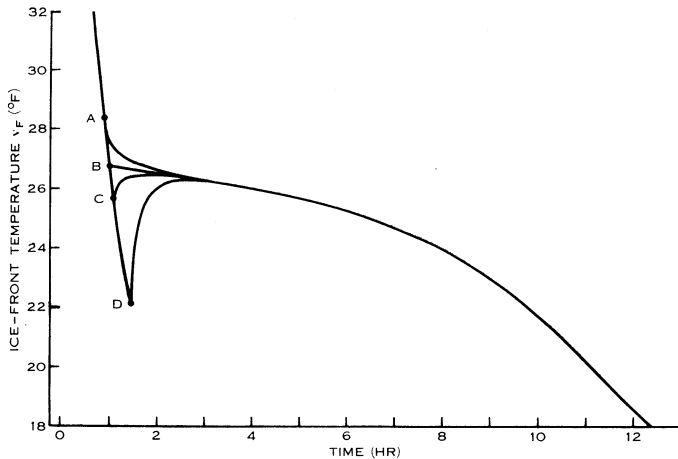


Fig. 3.—Theoretical curves for the temperature of the ice front in a pear of radius 3 cm having a true freezing point of 29.3°F , frozen in an environment at 14°F . The ice-front speed factor, S , was taken as 2×10^{-5} cm/sec $^{\circ}\text{C}$. The values of other constants used are given in Appendix I.

One of the points of detail in which the experimental records differ from the theoretical curves in Figure 3 is that the bottom of the supercooling minimum may be gently rounded. Part of the explanation for this lies in the time required for the

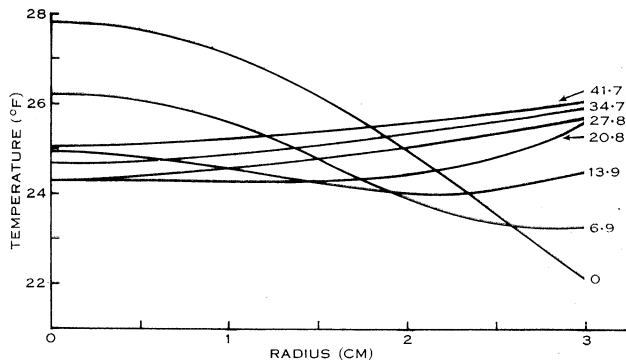


Fig. 4.—Theoretical temperature distributions within the pear at certain times after the instant represented by point *D* in Figure 3. Times (in minutes) are indicated on the figure.

latent heat released from the ice front at the surface to penetrate to the centre of the fruit. The temperature distribution within the pear at successive times for the case *D* of Figure 3 is shown in Figure 4. The temperature at the core continues to

fall for 21 min after it has begun to rise at the surface. The variation with time of the temperature at radius 1 cm may be compared with the temperature of the ice front in Figure 5. The "dashed" part of the curve is an estimate based on the fact that the interior temperatures follow that of the ice front closely when the temperatures are not changing rapidly. At the point *P* the ice front is at radius 1 cm and the curves coincide. At later times the points at 1 cm are in the frozen region and the temperature falls below that of the ice front. The curve of ice-front temperatures is thus the pattern from which the temperature at any particular point differs in a predictable way.

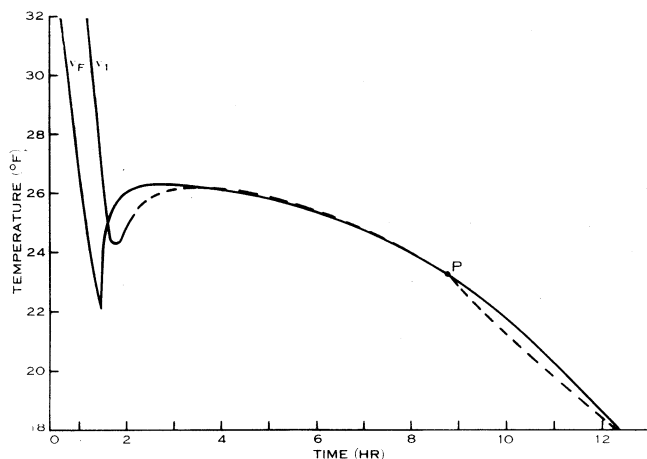


Fig. 5.—Theoretical curves for the ice front temperature, v_f , and the temperature at radius 1.0 cm, v_i , for case *D* of Figure 3.

Another reason for the rounded minimum is that once freezing has begun at a comparatively few (or perhaps only one) points at the surface, it takes a certain length of time for the freezing to spread and form a continuous ice front. Since the supercooling is deepest at the surface and rapidly increases at areas which have not frozen, the ice front tends to grow round the surface initially rather than into the warmer interior. It is only when the ice front is almost complete that the latent heat begins to raise the temperature of the interior. In the case of peeled fruit or pieces of tissue the surface is covered with a layer of juice from the damaged cells, which may be expected to freeze throughout very quickly. As would be expected, deep supercooling does not often occur in these cases and when it does the temperature rises rapidly once freezing begins. A further effect which will be discussed in more detail below is due to the freezing of the tissue immediately surrounding the probe.

With the use of only a desk calculator the number of solutions of the differential equation had to be restricted to a few typical cases. It would be highly desirable to run this problem on an electronic computer and to observe the effect of varying the constants. One variation which has been calculated is to double the value of the speed factor S (see Fig. 6). The general shape of the curve has not changed, but as the ice front travels from the surface to the centre its temperature falls by only 4.2°F instead of 6.8°F as in the first case.

Another case which has not been treated concerns the freezing point of the tissue, V , which has been taken as constant throughout the volume. In practice, however, one finds that the juice freezing point is almost always higher at the core than just under the skin, the difference frequently being as much as 0.8°F . Since the freezing point of the tissue must be closely related to, if not identical with, the juice freezing point, it would be desirable to know the theoretical effect of making V decrease with the radius. Presumably the temperature would not fall quite so rapidly from the maximum freezing temperature.

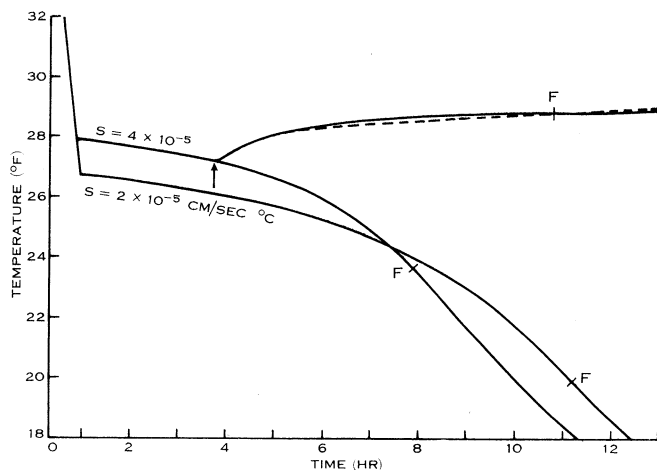


Fig. 6.—Theoretical curves showing the effect of doubling the value of the speed factor, S ; and also the thawing curve when the pear is transferred to an environment at 32°F at the moment when the ice front is at radius 2.0 cm . The points marked F show the moment at which the ice front reaches the centre; the full lines represent the ice-front temperature (or the temperature at the centre after the points F). The dashed line represents the temperature at radius 1.5 cm during the thaw.

Although the full possibilities of this theory have not been explored in detail, it is clear that it can account for the main features of the experimental records. The basic physical meaning of the freezing curve is that the rate at which the temperature changes is determined by the difference between the heat lost and the heat released. The heat loss falls quite slowly, since the area of the surface of course remains constant while the rate of heat loss falls with the surface temperature. On the other hand the latent heat released falls quite rapidly as the ice front moves in towards the core, since the decrease in area with the square of the radius predominates over the increase of speed of the ice front with falling temperature. The exact rate of temperature change which results from a particular heat loss or gain depends on the average equivalent specific heat of the pear. At first this specific heat rises as the frozen region increases in volume, but eventually it decreases again as the specific heat due to marginal freezing (eqn. (3)) decreases with falling temperature. This means that for a constant net heat loss the rate of temperature drop would gradually decrease at first and then speed up again.

One of the more puzzling experimental observations was the presence of unfrozen tissue when the temperature had fallen well below the maximum freezing temperature. On the present theory this is not to be attributed to any mechanism which causes an actual depression of freezing point of the tissue, but to the high stability of the cell sap in the supercooled state. A particular cell can be made to freeze only by inoculation with ice crystals from an adjacent cell. Confirmation of this view is provided by a study of the thawing process treated below.

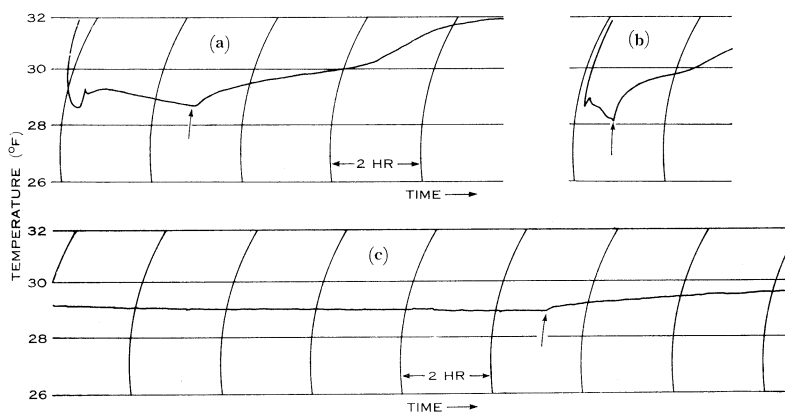


Fig. 7.—Experimental records showing thawing curves. The temperatures of the freezing environment were: (a) 26°F, (b) 11°F, and (c) 26°F. The arrows indicate when the pieces of tissue were transferred to the thawing chamber (32°F).

It will be noticed that according to this theory the maximum freezing temperature has no direct relation to the true freezing temperature of the tissue, V . It still had to be determined, however, whether V was identical with the juice freezing point. Some light could be thrown on this question by studying the relation between the initial freezing temperature and the temperature of the freezing environment, which is considered below. The theoretical curves in Figure 3 are of great value here in enabling the initial freezing temperature to be estimated even when freezing did not begin at the point B .

V. THAWING CURVES

If during the freezing process the pear is suddenly transferred to an environment held at 32°F, the temperature follows a course of which typical examples are shown in Figure 7. The features of the thawing curve are a fairly sharp rise in temperature of 0.2–1.2°F, which begins within about $1\frac{1}{2}$ min of the transfer to the thawing chamber; a slow but very steady temperature rise for some hours; followed by a gradual increase in the rate of warming.

The most striking feature of the curves is the sudden initial temperature rise. A brief calculation shows that this cannot be caused by the heat flowing in from the surface; $1\frac{1}{2}$ min is in fact the order of time required for the surface heat to just begin to reduce the temperature gradient which causes heat to flow outwards from the ice front. It would take much longer than this for the gradient to be reversed and

cause heat to flow inwards. The explanation of the effect lies in the fact that, although a thawing process has begun at the surface of the pear, the ice front continues to advance as long as the cells just inside the front are supercooled below their freezing point, V . Rather paradoxically, it is in fact the latent heat of freezing at the ice front which causes the initial temperature rise of the thawing curve.

A theoretical thawing curve has been calculated for one case (Fig. 6). Since there was no alternative to the laborious space lattice method of calculation, only a portion of the curve was calculated. The temperature distribution at various instants is shown in Figure 8. It can be seen that in this particular case the ice front

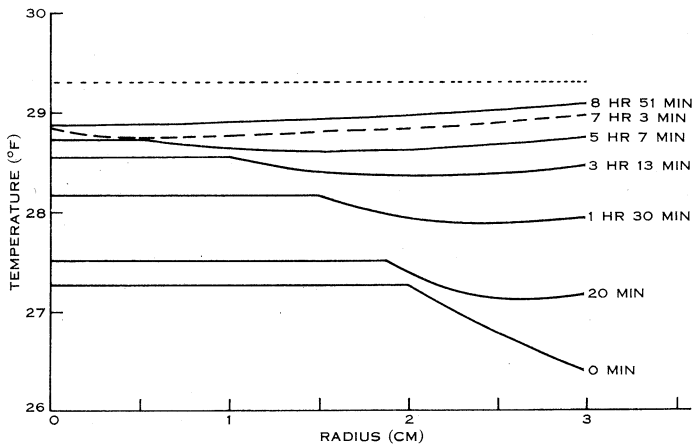


Fig. 8.—Theoretical temperature distributions within the pear at certain times (indicated on the figure) after the moment of transfer to the thawing environment at 32°F. Although the temperature inside the ice front was assumed to be constant as shown here, theory shows that the temperature at the centre would differ from that of the ice front by 0.1°F at the early stages of thawing. The dotted line shows the true freezing point, $V = 29.3^{\circ}\text{F}$.

continues travelling till it reaches the centre although thawing began when the front had reached a depth of only a third of the radius of the pear. (If thawing had begun earlier the temperature would have risen faster, and the ice-front temperature risen to the freezing point V before the front reached the centre.) For the first 7 hr of thawing both freezing and thawing are proceeding simultaneously. The history of any cell near the centre is that as the ice front reaches it, it suddenly freezes. Then as the front passes on it slowly thaws, the latent heat of melting at first coming from the ice front but later coming from the outside.

This interpretation of the thawing curves was confirmed by two experiments. In the first, two pieces of tissue cut from the same fruit were frozen for 1½ hr at 11°F. Then, as the one whose temperature was being recorded was transferred to the thawing chamber, the thickness of the frozen layer in the other was measured. When the first piece was examined after thawing for 3 hr it was found that the thickness of the frozen layer had approximately doubled, confirming that the ice front continued to advance during thawing.

In the second experiment a piece of tissue was frozen overnight at 12°F and then left to reach equilibrium in an environment at 26°F for 24 hr. This ensured that it was evenly frozen throughout, with no ice front. When this piece was transferred to the thawing chamber, there was no sudden temperature rise; in fact, it took from 10 to 15 min for the usual slow temperature rise to become established.

VI. FREEZING ROUND THE PROBE

A conspicuous feature of every experimental record which has not yet been referred to in the theoretical treatment is the sharp pulse which usually occurs at an early stage of the freezing. All the evidence indicates that this pulse is caused by freezing of the ruptured cells at the probe itself, as suggested by Maximov. The very sharpness of the pulse is strong evidence for this view. A heat pulse which originated at a distance from the probe would quickly become diffused in the process of conduction to it.

After the effect of the sharp pulse has disappeared, the expanding ice front round the probe will raise its temperature above that of the surrounding tissue. An approximate idea of the magnitude of this effect can be obtained by considering the temperature of a point from which an ice front expands radially outwards. It is found that if this is the only freezing taking place, the latent heat will not be sufficient to raise the temperature of the point but will simply slow down the rate at which the temperature falls. As suggested above, this is probably one reason for the rounded minimum in freezing curves such as Figure 1, *A*.

If, on the other hand, the frozen shell which grows inward from the surface of the pear has formed, the effect of the freezing round the probe is to lift the temperature of the probe some fraction of a degree above the temperature of the outer ice front. The magnitude of the difference which occurs in practice can be obtained from the few curves like Figure 1, *C* which were recorded. It can be seen that the curve has been displaced upward by about 0.3°F following the sharp pulse. Since calculation shows that this difference must gradually increase, the record which would have been obtained in the absence of freezing round the probe is probably as shown by the dashed line.

The practical importance of this question is that all those records—the vast majority—in which the pulse occurred at an early stage, are displaced upward compared with the theoretical curves. This has been ignored, however, in the experiments described in the next section, since any error will be on the safe side.

In the case of peeled tissue frozen gently (Fig. 2, *A*), the pulse may be quite broad. It is likely that this is due to the infiltration of juice from the ruptured cells into the spaces between the adjacent layers of cells, which increases the speed of the ice front through these layers. The broad pulse has accordingly been ignored in the extrapolation.

VII. RELATION BETWEEN INITIAL FREEZING TEMPERATURE AND ENVIRONMENT TEMPERATURE

The initial freezing temperature has been defined as the temperature at which the rates of heat loss and latent heat release are equal at the instant freezing begins.

An expression for this temperature can be obtained from equation (8) in Appendix I, by equating dv_F/dt to zero with $\rho = a$. This gives:

$$LS(V - v_i) = H v_i, \quad (6)$$

since both v_F and v_s now equal the initial freezing temperature, v_i .

Reverting now to the normal centigrade system with the ice point taken as 0° , we define:

T_0 = temperature of the environment ($= -V_0$),

T = true freezing point of tissue ($= V + T_0$), and

T_i = initial freezing temperature ($= v_i + T_0$).

Equation (6) then becomes:

$$LS(T - T_i) = H(T_i - T_0)$$

or

$$T_i = [H/(H + LS)]T_0 + [LS/(H + LS)]T. \quad (7)$$

Since H , L , and S are constants for a particular pear, this means that if a pear is cut into a number of pieces which are frozen separately at different environment temperatures, the plot of initial freezing temperatures against environment temperatures should give a straight line which intersects the line $T_i = T_0$ at the point $T = T_i = T_0$, i.e. at the true freezing point.

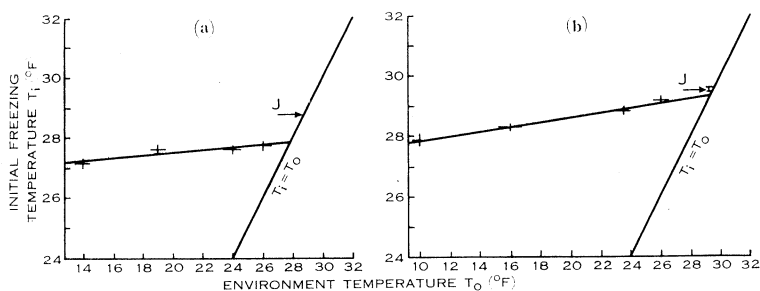


Fig. 9.—Experimental results for two pears, both Winter Nelis. In case (a), which was classed as “reasonably good”, only one juice freezing point measurement, J , was made. In case (b), classed as “very good”, the core and the surface juice freezing points differed by only 0.2°F .

Such an experiment has been carried out on 18 individual pears, typical results being shown in Figure 9. Agreement with the theory has been assessed as very good, reasonably good, or inconclusive according as values of the freezing point T resulting from all straight lines which reasonably fit a set of points, lie within the respective ranges: less than $\pm 0.15^\circ\text{F}$, between ± 0.15 and $\pm 0.25^\circ\text{F}$, and greater than $\pm 0.25^\circ\text{F}$. On this basis 8 results could be classed as very good, 5 as reasonably good, and 5 as inconclusive. The aim of these experiments was to relate the true freezing point T to the juice freezing point. The results for those pears which fell in the first two categories are given in Table 1.

Since the practical purpose of this investigation was to establish the lowest temperature at which a pear could be stored without any danger of freezing, the values in the table have been chosen where necessary, on the safe side. When the juice freezing point, for instance, was higher at the centre than at the surface of the pear, the lowest value has been used. Similarly the initial freezing temperatures were obtained by direct extrapolation from the experimental curve, as the point *B* in Figure 3. The effect of freezing round the probe is probably to make the value so obtained too high if anything.

The practical conclusion to be drawn from Table 1 is that it is not safe to store pears at a temperature below their juice freezing point. In no case was the true freezing point significantly higher than the juice freezing point, and in half the cases these two points were not significantly different. In a third of the cases, however, there is evidently no chance of freezing until the temperature falls about 1°F below the juice freezing point. The reason for this remains a matter for speculation. The validity of the assumption concerning the speed of the ice front which was postulated above in developing the theory has a bearing on this point and will be discussed in the next section.

TABLE 1

TEMPERATURE INTERVALS (°F) BY WHICH THE TRUE FREEZING POINT FELL BELOW THE JUICE FREEZING POINT

Time of Measurement	Variety of Pear Used				
	Beurre Bosc	Packham's Triumph	Peter Barry	Winter Cole	Winter Nelis
Within 1 month of picking	1.4	—	—	0.2	1.0,* 1.2
After at least 4 months in cool storage	0.3	0.1, 0	1.1, 0.4, 0.1	0.1	0.2,* 0.9

* See Figure 9.

VIII. THE SPEED OF THE ICE FRONT

The relation between the speed of the ice front and its temperature (eqn. (1)) is illustrated graphically in Figure 10, curve *W*. This particular expression was chosen partly in order to simplify the mathematics, but the broad agreement between the theory built on it and the experimental findings gives strong support to it. It is desirable, however, to examine the effect on the theoretical curves of adjusting the speed assumption in various ways. It appears likely that the general shape of the freezing and thawing curves would not be greatly altered by quite appreciable variations in the relation between the speed and the temperature. On the other hand the theoretical relation between initial freezing temperature and environment temperature (eqn. (7)) is quite sensitive to such variations. By reversing the procedure used above it is possible to deduce what the speed relation must be to give rise to any

particular curve relating initial freezing temperature and environment temperature. Various possibilities are shown in Figure 10. When the T_i versus T_0 line is 1°F lower (case X) the reason might be that some mechanism is lowering the freezing point of each cell by this amount. In this case the speed curve is also displaced 1°F downward, as at X_1 . If, however, the mechanism concerns the speed alone and not the latent heat released by each cell as it freezes, the speed relation X_2 must hold. If the T_i versus T_0 curve takes an upward turn at the end as at Y (the freezing point T being equal to the juice freezing point as in case W), the speed curve must also take an upward turn. Incidentally, if the speed curve W runs smoothly to zero as at Z this simply causes a local dip in the T_i versus T_0 curve as shown, without altering the extrapolated temperature T .

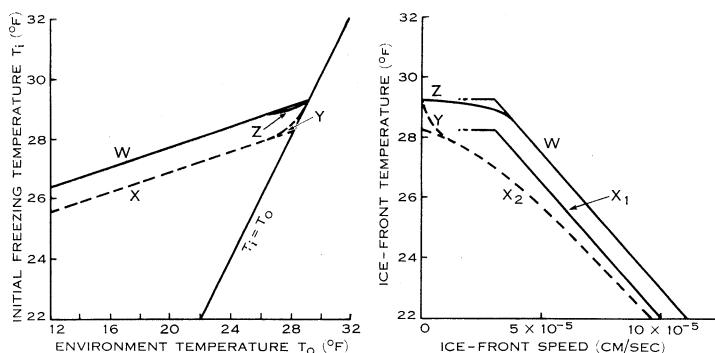


Fig. 10.—Various curves relating initial freezing temperature and environment temperature which would result from particular assumptions regarding the dependence of the speed of the ice front on its temperature.

For explanation see text.

Theoretically one would expect any change in the speed curve to occur at the temperature where extracellular freezing gives way to intracellular freezing. In practice this transition occurred when the environment temperature T_0 was about 20 or 22°F , but the experiments carried out (Fig. 9) give no evidence of any behaviour like Figure 10, Y . Any conclusions, however, which are based on extrapolation as are those presented in Section VII can never be absolutely conclusive.

It may be possible to obtain direct experimental information about the temperature dependence of the ice-front speed. The ice front would be established by beginning the freezing process in the usual way, and then the temperature of the tissue held steady at the desired value by manipulating the environment temperature.

IX. DISCUSSION

It seems worth while to consider in more detail Jackson and Chalmers' (1958) treatment of the freezing of liquids in porous media, since this is not only the basis of the theory presented here but can also explain a number of points which are matters of dispute or mystery in the literature on the freezing of plant tissue.

They consider the various possible relative magnitudes of the interfacial free energies per unit area for the ice-substrate, water-substrate, and ice-water interfaces and conclude that when the substrate is soil the first of these free energies is not less than the sum of the latter two. In this case "the solid (ice) will tend to be separated from the substrate by a layer of liquid (water). In this latter case, the solid cannot nucleate at the substrate."

We may also conclude that the same situation holds when the substrate is plant tissue, since the high stability of cell sap in the supercooled state, which is emphasized by Asahina (1956) and is essential to our theory, indicates no tendency for ice to crystallize out on the surface of the tissue. Asahina's photomicrographs also show that when ice has formed, it does not adhere to the tissue but is surrounded by liquid in which it is frequently quite mobile.

Jackson and Chalmers then derive an expression for the depression of the freezing point of liquid in a capillary. This depression is inversely proportional to the radius of the capillary. For a radius of 0.1μ it is 0.2°C , for instance, and for a radius of 0.01μ , 2.0°C . They go on to point out that when a supercooled liquid is separated from its solid phase by a porous material with the described properties, the solid interface cannot propagate through the porous material, but the free energy of the system will be lowered if the liquid flows through the porous medium to the solid interface and freezes there. Now this is precisely the process which has been observed many times during the freezing of plant tissue. It can be seen that the smaller the size of the pores in the membrane or cell wall which hinders the advance of the ice front, the further must the liquid on the other side be supercooled before the liquid in the pores can freeze and allow the passage of the ice crystals into the supercooled liquid.

Asahina's attempt to explain the phenomenon in terms of the dendritic growth of the ice crystals as they "flash" into the supercooled liquid is inadequate. Dendritic growth is a dynamic effect, as Asahina himself indicates. The transmission of intracellular freezing in *Tradescantia*, however, is preceded by the slow growth of a "very clear ice mass"—the sharp crystals appear only on the far side of the barrier after penetration, and therefore can hardly be put forward as a cause of penetration. Chalmers (1959), incidentally, has written another more descriptive account of these various ways in which water freezes.

When, under constant-temperature conditions, an ice front encounters a porous membrane whose pores are too small to transmit ice crystals at that temperature, it may still be possible for the ice to penetrate the barrier if the membrane can be stretched under the pressure of the ice. Such a process has been observed by Modlibowska and Rogers (1955) and also by Asahina. An important point here is that additional energy is required to cause this stretching, and this is manifest as a depression of freezing point of the ice under the pressure of the stretched wall or membrane. This is the case discussed by Edlefsen and Anderson (1943, Section 30), where the pressure is exerted only on the ice and not on the water, resulting in a freezing point depression of 0.09°C per atmosphere of pressure. This depression is 12 times greater than is the case when the pressure acts equally on both ice and water.

If it happens that the freezing point is lowered in this way until it coincides with the prevailing temperature before the pores have become sufficiently enlarged to enable their contents to freeze, the process will come to a stop, unless the temperature is lowered further. As mentioned above, this explains why the temperature at which freezing can be propagated intracellularly is lower than that at which extracellular freezing may proceed.

If, on the other hand, the stretching proceeds till the second cell can be inoculated through the enlarged pores, the pressurized ice in the first cell will melt to the benefit of the unpressurized ice in the second cell, and the stretched cell wall will contract again—as has been observed experimentally.

In the case of “frost plasmolysis” described by Asahina the barrier membrane, although far more fragile than the cell wall, is protected from stretching by its flexibility, and provided the temperature does not fall below the critical value determined by the size of the pores, the state may continue indefinitely.

The theory is also capable of explaining the reduction in frost resistance caused by immersing cells in hypotonic solutions. Asahina found that there was a critical concentration of the solution below which the capacity of the cell to prevent the penetration of ice crystals into the cell interior was suddenly much reduced. He considers the possibility of “a swelling of the membrane in which the water space is so enlarged that the ice crystallisation in it is no longer disturbed”, but rejects this because the cell interior freezes by “flashing” which implies a considerable degree of supercooling. On the present theory, however, the swelling of the pores in the membrane is not regarded as removing all hindrance to ice penetration, but as steadily raising the temperature at which such penetration can occur. The weaker the hypotonic solution, the greater the quantity of water imbibed by the cell, and the greater the enlargement of the pores. For a particular temperature there will be a critical degree of stretching beyond which the water in the pores can freeze. But if extracellular freezing once begins at some part of the surface of such a cell, the resulting dehydration will immediately cause the pores to begin to shrink and remove any possibility of internal freezing. This is to be contrasted with the case of intracellular freezing considered above where the growth of ice causes further enlargement of the pores.

Conversely the action of hypertonic solutions in increasing frost resistance may be due to a reduction in pore size as well as a decrease in the amount of freezable water.

It may be remarked that in this theory the actual temperature is the important thing, not its rate of change. The preoccupation of much of the literature on the freezing of plant tissue with rates of cooling seems to be misleading. Due to the large size of the pieces of tissue used in the present experiments, the rates of cooling were never more than extremely slow according to the terminology suggested by Levitt (1958). In fact, after deep supercooling, intracellular freezing occurred even though the temperature was rising.

A further conclusion of the present theory is that the moisture in the surface of the cell walls will not freeze first as suggested by Levitt (1941, p. 182). Although

this water may be pure, it cannot have the same freezing point as free pure water, because its specific free energy would then be greater than the cell sap and it would immediately be imbibed into the cell by osmosis. Whereas the free energy of the cell sap is lowered by the solutes it contains, the free energy of the water in the cell wall is lowered by the surface energy effects which become dominant in very thin layers of liquid. Ice on the surface of the cell wall can come only from water extracted from the cell interior following some initial inoculation from elsewhere.

Partly for this reason, the objections which Levitt (1958, p. 21) raises against some of Aoki's interpretations (Aoki 1948, 1950) appear to be invalid. The second part of Levitt's objection is that he claims that rinsing pieces of tissue will effect the turgor of inner cells as well as those on the surface. Some of our own experiments, which admittedly used much larger pieces of tissue than Aoki's, tend to support Aoki's interpretation. These experiments were designed to investigate whether the apparent depression of freezing point during the course of freezing a whole pear might be due to a considerable migration of water from the unfrozen interior cells to the ice front. No evidence for such water movement was detected. A typical experiment was to cut one pear in pieces before freezing hard and thawing, while another similar pear was frozen whole and cut in pieces before thawing. The juice freezing points of tissue at various radii were then compared.

A complete answer to this point must involve a consideration of the rate of water diffusion in the particular tissue under a given free energy gradient in conjunction with the time between rinsing and measurement.

Concerning the differences between hardy and tender plants, one may make certain deductions about the structure of their cell walls or plasma membranes, in so far as the distinction between them lies in these members. It is generally agreed that hardy cells have a high permeability to water while at the same time being resistant to intracellular inoculation with ice. The latter implies pores of small radius, while the former would be favoured by a comparatively large number of pores of comparatively short length—i.e. a thin membrane. In tender cells, conversely, there must be a smaller number of longer and wider pores. Use of Jackson and Chalmers' formula in conjunction with careful observations like Asahina's, of the temperature at which a membrane allows transmission of ice crystals, should give useful information on the radius of the pores.

A puzzling feature of the present experiments has been the evidence that in some cases the true freezing point may be appreciably lower than the juice freezing point. The reason why such a difference should exist in the case of intracellular freezing has been presented, but this explanation can hardly apply to extracellular freezing since ice in the intercellular spaces, which are all interconnected, cannot be subject to much pressure. A possibility which might partially account for the effect is that the juice freezing point of the cells in the immediate vicinity of the initial freezing nucleus may be sufficiently lowered by the growth of ice at this nucleus to separate the ice from cells whose contents are supercooled. This, however, seems unlikely to account for more than a small fraction of a degree.

X. ACKNOWLEDGMENTS

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APPENDIX I

MATHEMATICAL DETAILS

(a) Derivation of Equation (2)

Disregarding the slight change in the absolute temperature, the depression of the freezing point of a solution is proportional to the mole fraction of dissolved material (e.g. Edlefsen and Anderson 1943, section 34). For a dilute solution the mole fraction is approximately proportional to $1/m$, where m is the quantity of water in which a given quantity of solute is dissolved. Thus

$$\text{Freezing point depression} = V_0 - v_F \propto 1/m.$$

Similarly $V_0 - V \propto 1/M$, where M is the original quantity of water before any has frozen. Therefore the fraction of water which freezes at temperature v_F is

$$\frac{M-m}{M} = 1 - \frac{m}{M} = 1 - \frac{V_0 - V}{V_0 - v_F} = \frac{V - v_F}{V_0 - v_F}.$$

(b) *The Freezing Equation*

We substitute in equation (5) the following expressions, which assume for simplicity that the density of the tissue both before and after freezing is 1.0 g/c.c.:

$$\text{Rate of heat loss at surface} = 4\pi a^2 H v_s \quad \text{cal/sec.}$$

$$\begin{aligned} \text{Rate of latent heat release at ice front} &= 4\pi \rho^2 S (V_0 - v_F) L \left(\frac{V - v_F}{V_0 - v_F} \right) \\ &= 4\pi \rho^2 L S (V - v_F) \quad \text{cal/sec.} \end{aligned}$$

$$\text{Right-hand side of equation (5)} = \frac{4}{3} \pi a^3 C \left(-\frac{dv_F}{dt} \right),$$

where C is the average specific heat of the pear. Equation (5) then becomes:

$$dv_F/dt = \{LSp^2(V - v_F) - Ha^2v_s\} / \frac{4}{3}a^3C, \quad (8)$$

and C is given by

$$C = 1 + \{(a^3 - \rho^3)/a^3\} L(V_0 - V)/(V_0 - v_{av})^2, \quad (9)$$

where $v_{av.}$ is an average temperature of the frozen shell. The first term represents the normal specific heat of the tissue, and the second term the effect of the marginal freezing and thawing in the frozen region.

It is necessary to express v_s and $v_{av.}$ in terms of the dependent variable v_F . To do this it was assumed for the moment that the net heat loss comes entirely from the frozen region, and uniformly from each point in it. This leads to the following expression for v_s :

$$v_s = \frac{K(a^2 + a\rho + \rho^2)v_F + LSp^2\{\frac{1}{2}(a + \rho) - a^2/\rho\}(V - v_F)}{K(a^2 + a\rho + \rho^2) + Ha^2\{\frac{1}{2}(a + \rho) - \rho^2/a\}}, \quad (10)$$

where K is the thermal conductivity of the frozen region. Although this is rather a cumbersome expression, the terms involving a and ρ can be tabulated once and for all at the beginning, and are not involved in the successive recalculations which are the most laborious aspect of a numerical solution.

Equation (10) agrees very closely with the exact solution which is available for the case $\rho = 0$ (Carslaw and Jaeger 1947, Section 92). The assumptions make it less accurate as ρ becomes larger, but at the same time $|v_F - v_s|$ becomes smaller so the absolute error should never be very large.

The expression for $v_{av.}$ is even more complicated than equation (10). However, the weighted mean

$$v_{av.} = 0.4v_F + 0.6v_s, \quad (11)$$

is a good approximation to it at selected values of ρ , and has been used accordingly.

Equations (9), (10), and (11) enable the right-hand side of equation (8) to be expressed in terms of the two variables v_F and ρ . It is therefore desirable to use ρ rather than t as the independent variable. By putting

$$\frac{dv_F}{dt} = \frac{dv_F}{d\rho} \cdot \frac{d\rho}{dt} = \frac{dv_F S(v_F - V_0)}{d\rho},$$

equation (8) becomes

$$dv_F/d\rho = \{LS\rho^2(V-v_F) - Ha^2v_s\}/\frac{1}{3}a^3CS(v_F - V_0). \quad (12)$$

This equation can now be solved numerically to give v_F as a function of ρ . Equation (1) can then be integrated numerically to obtain v_F as a function of t as desired. Once the ice front reaches the centre, $\rho = 0$, and the equations are much simplified and can be solved analytically.

The four starting values for the numerical solution were obtained by using Picard's method of successive approximation (e.g. Kunz 1957, Section 8.13). The solution was then continued with an Adams predictor/corrector method (Kunz, Section 9.11). The interval h was taken as 0.05 cm initially and then increased to 0.10 cm at $\rho = 2.60$ cm, and to 0.20 cm at $\rho = 2.20$ cm. (The radius of the pear, a , was taken as 3.0 cm).

Since the main object of the calculation was to observe the general shape of the freezing curve, precise choosing of constants was considered unimportant. The latent heat L was arbitrarily taken as 70 cal/g, a value somewhat less than that for pure water. From a number of measurements of the rate of cooling of pears in the unfrozen state it was deduced that H was approximately 3×10^{-4} cal/cm² sec °C. The value 2.8×10^{-4} was actually used for arithmetical reasons. The speed factor S was chosen to make the time for the ice front to reach the centre about 8 hr as observed in practice when the environment temperature is low. Two values for S were tried, 2×10^{-5} and 4×10^{-5} cm/sec °C. The environment temperature was taken as 14°F, and the true freezing point as 29.3°F. In the units used this makes $V_0 = 10^\circ$ and $V = 8.5^\circ$. The thermal conductivity of the frozen region K was taken as 0.0050 c.g.s. units, slightly less than the value for pure ice, since even in the mildly frozen state the ice is assumed to form a connected network.

(c) *The Thawing Calculation*

In this case the method of finite differences was used. For radial heat flow in a sphere the differential equation is

$$\frac{\partial^2 v}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial v}{\partial r} - \frac{1}{k} \cdot \frac{\partial v}{\partial t} = 0.$$

From this can be obtained the difference equation (cf. Kunz 1957, Section 14.1)

$$v_i^{j+1} = m(1+1/i)v_{i+1}^j + (1-2m)v_i^j + m(1-1/i)v_{i-1}^j,$$

where j is the number of time intervals of length p , and $r = ih$, and $m = kp/h^2$. In the frozen region the specific heat is

$$c = 1 + L(V_0 - V)/(V_0 - v)^2,$$

and since the diffusivity $k = K/\rho c$, where K and ρ are assumed to remain constant, it follows that as the temperature v rises the diffusivity decreases. To allow for this variation m was given the successive values 0.50, 0.48, 0.46, When the lowest temperature corresponded to $m = 0.40$ the time interval p was increased to raise this highest value of m to 0.50 again. The interval h was taken as 0.25 cm.

At the surface of the pear the boundary condition is now:

$$K(\partial v/\partial r)_{r=a} = H(V_0 - v_s),$$

since the environment is now at V_0 , the ice point. Using a differentiation formula involving three points this defines the surface temperature in terms of the two nearest interior points.

At the ice front it was assumed that heat flowed only into the frozen region. Since in the particular case calculated 70% of the pear was frozen when freezing began, and the frozen region had an equivalent specific heat of about 13 compared with unity in the unfrozen region, the error amounted to only a few per cent and decreased rapidly as the ice front advanced. The boundary condition is then:

$$K(\partial v/\partial r)_{r=\rho} = -LS(V - v_F).$$

The ice front was assumed to move in steps of $\frac{1}{4}h$, and four different formulas were used to define the temperature of the lattice point nearest to the ice front in terms of the temperatures of the two nearest points in the frozen region.