ON THE RATE OF FREEZING IN FISH MUSCLE.—By G. O. LANGSTROTH,*† McGill University.

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ABSTRACT.

The fundamental equation for the flow of heat is applied to the case of the freezing of fish muscle. The resulting equation, obtained by assuming the solution in the form of a transcendental equation and finding the constants involved from the boundary conditions, connects the time of freezing with the thickness and the thermal and physical constants. The freezing of an additional thickness, on removal from the bath, due to the redistribution of the temperature gradient, is investigated.

The problem of the flow of heat in a homogeneous body has been thoroughly worked out by different investigators, and the question of the rate of freezing has also necessarily received some attention. Neumann[1] has worked out a general expression for the rate of ice formation, in terms of the physical and thermal constants of water and ice. His method is quite general, and can be applied to cases where conditions vary over a wide range. Stefan[2] has developed a treatment by assuming certain conditions which render it only a special case of Neumann's treatment. Both these methods involve only very slight approximations, and the resulting equation in series form can be made to hold to almost any desired degree of accuracy. King[3] has treated the problem from the standpoint of the progress of frost into concrete, by assuming a linear temperature gradient throughout the frozen material[4]. This introduces only a small error (about 4%), and simplifies the procedure enormously.

The following treatment of the problem of the rate of freezing of fish muscle will follow that given by Stefan for ice formation.

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1. Franz Neumann, Weber-Riemann, "Part. Diff. Gleichungen".
2. J. Stefan, Wied. Ann. 42. 269.
3. L. V. King, Proc. Roy. Soc. Canada. 3. 12. 1918.
4. See also Barnes, "Ice Engineering".
For a short discussion of Neumann's and Stefan's methods see Ingersoll and Zobel, "Math. Theory of Heat Conduction".

Let us impose the following conditions in order to simplify the problem. Consider a block of fish with one surface in contact with a bath at temperature T. Let it be just at the freezing temperature, but not frozen at the time $t=o$. Let the temperature scale be so chosen that the zero is at the freezing point of the fish, and let us assume that the block is large enough so that the edge effects may be neglected. The freezing starts immediately and the heat is conducted only through the frozen material.

Let the following symbols apply to the frozen material, k the specific conductivity, c the specific heat, θ the temperature at any point in the frozen material at time t, and ρ the density. Let L be the latent heat of the fish, T the temperature of the bath, ϵ the distance of the "freezing edge" from the bath, ρ' the density of the unfrozen fish, and x the coordinate of any point measured from the edge of the bath.

The fundamental equation for the flow of heat may be written,

$$h^2\Delta^2\theta = \partial\theta/\partial t \quad \text{where} \quad h^2 = k/c\rho.$$

When we consider flow of heat in one direction only we may write $\partial\theta/\partial t = h^2\partial^2\theta/\partial x^2$ (1)

Assume as a solution of this equation some expression of the form,

$$\theta = A\int_{x/2h\sqrt{t}}^{\beta} e^{-z^2}\,dz \qquad (2)$$

which can be shown to be a particular solution of the linear Fourier equation, (1).

It now remains so to adjust the constants "A" and "β" that the equation is consistent with the boundary conditions.

The boundary conditions which must be satisfied are as follows,

(a)...... $k(\partial\theta/\partial x)_{x=\epsilon} = L\rho' d\epsilon/dt$

(b)......when $\theta = T$, $x = o$

(c)......when $\theta = o$, $x = \epsilon$

(d)...... $\partial\epsilon/\partial t = -(\partial\theta/\partial t / \partial\theta/\partial x)_{x=\epsilon}$

Condition (a) arises from a consideration of the material at the freezing edge, i. e.

Heat given out by layer in freezing $= L\rho' d\epsilon$ per cm^2.

Heat conducted away in a time $dt = k(\partial\theta/\partial x)_{x=\epsilon}\, dt$

If we neglect the second order effect due to the establishing of a temperature gradient in the thickness *dx* which would add another term to the last equation given, we have

$$k(\partial\theta/\partial x)_{x=\epsilon} = L\rho' d\epsilon/dt \qquad (3)$$

Condition (d) follows at once from the fact that we may write $\theta = f(x, t)$

and hence $d\theta = \partial\theta/\partial x . dx + \partial\theta/\partial t \cdot dt.$

But when $x = \epsilon,\ d\theta = o$

Therefore, $d\epsilon/dt = -(\partial\theta/\partial t / \partial\theta/\partial x)_{x=\epsilon}$

which is condition (d).

We may now combine conditions (a) and (d) to give the equation

$$(\partial\theta/\partial t)_{x=\epsilon} = -k/L\rho' . (\partial\theta/\partial x)^2_{x=\epsilon} \qquad (4)$$

If we differentiate the solution as given by (2), with respect to x and t, we obtain

$$(\partial\theta/\partial t) = Ae^{-x^2/4h^2t} \cdot x/4ht^{3/2} \qquad (5)$$

$$(\partial\theta/\partial x) = -Ae^{-x^2/4h^2t} \cdot 1/2ht^{\frac{1}{2}} \qquad (6)$$

When we apply condition (c) to equation (2) we see that at $x = \epsilon$, since the integral vanishes, the limits must be equal, and

$$\beta = \frac{\epsilon}{2h\sqrt{t}} \qquad (7)$$

Substitute this value in (5) and (6) and we obtain

$$(\partial\theta/\partial x)_{x=\epsilon} = Ae^{-\beta^2} . \beta/2t \qquad (8)$$

$$(\partial\theta/\partial x)_{x=\epsilon} = Ae^{-\beta^2} \cdot 1/2h\sqrt{t} \qquad (9)$$

Substitute these values in (4),

$$Ae^{-\beta^2}\beta/2t = -k/L\rho' \cdot A^2e^{-2\beta^2} \cdot 1/4h^2t \qquad (10)$$

From which "A" is given as,

$$A = -2L\rho' h^2/k \cdot \beta e^{\beta^2} \qquad (11)$$

Now condition (b) is a particular case of (2) which we may write

$$T = A\int_0^\beta e^{-z^2}dz. \quad \text{i. e.} \quad \beta e^{\beta^2}\int_0^\beta e^{-z^2}dz = -kT/2L\rho' h^2 \qquad (11a)$$

This expression can be easily expanded and integrated and becomes

$$-kT/2L\rho' h^2 = \beta^2[1+2/3\cdot\beta^2+4/15\cdot\beta^4\ldots\ldots\ldots] \qquad (12)$$

Putting in the value of (β) from (7),

$$-kT/2L\rho' h^2 = \epsilon^2/4h^2t.\ (1+2/3\cdot\epsilon^2/4h^2t+4/15\cdot\epsilon^4/16h^4t^2\ldots\ldots)$$

which gives the relation between the time "*t*" and the thickness ϵ of the material frozen.

To a first approximation this becomes

$$\epsilon^2 = -2kTt/L\rho' \qquad (13)$$

while if only powers of ϵ^2/t greater than the third are neglected we get

$$-kT/2L\rho' = \epsilon^2/4t+2/3\cdot\epsilon^4c\rho/16kt^2+4/15\cdot\epsilon^6c^2\rho^2/64k^2t^3\ldots \qquad (14)$$

These equations give the rate of freezing for the conditions named. The effect of experimental boundary conditions will cause a slight discrepancy probably, and for that reason the above will give an upper limit for the time. Note that (13) corresponds to the assumption of a linear temperature gradient The error introduced is of the order of 4%.

Using the following values for the constants of the fish, and the first approximation equation (13), the thickness which is frozen under different conditions is calculated.

L...................60 cal/gm.[1]
k...................0.0014 cal/°C. sec. cm.[2]
ρ'...................0.8 gms/cm.[3]

1. Chipman and Langstroth .... Trans. N. S. Inst. Sci. XVII, Part 3, p. 175, 1929.
2. Langstroth..........................Fish. Exp. Sta. (Atlantic) Report, 1928.

TABLE I.

T.(C°)	ϵ(cm.)	t (hours)
-10	1.0	0.48
-10	2.0	1.90
-10	3.0	4.28
-10	4.0	7.60
- 5	1.0	0.96
- 5	2.0	3.80
- 5	3.0	9.56
- 5	4.0	15.2

These values should not be taken as representing actual fact, in that the values for the constants have not all been accurately determined. The value of ρ' is a purely assumed one since, as far as the author knows, no measurements have been made along these lines. The value assumed for k is one based on some preliminary work done in 1928 over the range 25°-100°. The effect of boundary conditions is probably slight in freezing under practical conditions using methods such as are now in use at the Experimental Fisheries Station, at Halifax, N. S.

The following points should also be noted,

1. If the freezing takes place from both sides then the thickness frozen in a given time is just four times that given by (13).

2. The temperature scale used is one which has its zero at the freezing point of the fish muscle.

An interesting case arises when we consider what happens when a piece of fish is removed from the bath before it is entirely frozen. For convenience assume that on removal from the bath the amount of heat passing to, or from, the surroundings is negligible for a short length of time. Under these conditions the equalization of the temperature throughout the medium provides the sink necessary for the disposal of the small amount of heat liberated in freezing the narrow strip of material which did not freeze in the bath.

The expression for the temperature anywhere through the frozen material is given by (2) i. e.

$$\theta = A\int_{x/2h\sqrt{t}}^{\beta} e^{-z^2}\,dz.$$

We have also the special case as given by (11a)

$$T = A\int_0^{\beta} e^{-z^2}\,dz$$

The constants have been determined for both these equations and are given by (7) and (11). We then arrive at the expression

$$\theta - T = A\int_{x/m}^{\beta} e^{-z^2}\,dz - A\int_0^{\beta} e^{-z^2}\,dz$$

where "m" $= 2h\sqrt{t}$

Hence, $$\theta - T = A\int_{x/m}^{0} e^{-z^2}\,dz \qquad (15)$$

Expanding and integrating,

$$\theta - T = -A[x/m - x^3/3m^3 + x^5/10m^5 \ldots\ldots\ldots] \qquad (16)$$

The conditions under which a thickness d will freeze after removal from the bath are obviously given by the equation,

$$\int_0^{\epsilon} (o - \theta)\,\rho c\,dx = L\rho' d.$$

This becomes on substitution from (16)

$$T\epsilon - A\epsilon^2/2m + A\epsilon^4/12m^3 - A\epsilon^6/60m^5 \ldots\ldots = L\rho' d/\rho c$$

This becomes on substitution for '*A*" from (11)

$$T\epsilon + L\rho' h^2/k.\,\epsilon^2/m \cdot \beta(1+\beta^2+\beta^4/2..) - L\rho' h^2/6k \cdot \epsilon^4/m^3 \cdot \beta(1+\beta^2+\beta^4/2 \ldots + L\rho\, h^2/30k \cdot \epsilon^6/m^5 \cdot \beta(1+\beta^2+\beta^4/2 \ldots) = L\rho' d/\rho c.$$

Neglecting terms in β^3 and substituting from (7)

$$T\epsilon + L\rho' h^2/k \cdot \epsilon^3/4h^2t + 5/96 \cdot L\rho' h^2/k \cdot \epsilon^5/h^4t^2 - 1/480 \cdot L\rho' h^2/k.\ \epsilon^7/h^6t^3 \ldots\ldots = L\rho' d/\rho c$$

or,

$$T\epsilon + L\rho'/k.\ \epsilon^3/4t + 5/96.\ L\rho'\rho c/k^2.\ \epsilon^5/t^2 - 1/480.\ L\rho'\rho^2c^2/k^3.\ \epsilon^7/t^3 \ldots = L\rho' d/\rho c \qquad (18)$$

which is the equation giving the thickness d of material which will be frozen after removal from the bath. Elimination of t or ϵ between equations (18) and (14) gives d as a function of ϵ or t, as may be desired.

To a first approximation, using (18) and (13),

$$T/2 \cdot \rho c\epsilon/L\rho' = d \qquad (19)$$

This is what we would expect from an assumption of a uniform temperature gradient throughout the frozen material. Equation (19) is quite accurate enough for any practical work on account of the small size of the effect with bath temperatures of -15°C or so. A glance at the equation (19) will show, however, that the effect increases with the temperature difference between the bath and the freezing point of the fish. Some idea of its magnitude may be obtained from the fact that with a bath temperature at -10°C. and a thickness of 4 cm. frozen before removal, an additional thickness of approximately 0.2 cm. would freeze after removal.

What has been said of (13) and (14) applies here also. In addition there is the assumption of no heat transfer to or from the surroundings, for the short period of time which is required for the material to come to equilibrium. This is probably not a very dangerous one, when the fish are kept piled together in a room at storage temperature. The effect might become important if very low freezing temperatures such as that obtained with solid Carbon-dioxide were used.

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Author's Note:—This treatment has recently been tested experimentally and has been found to hold to the degree of accuracy of the experimental method. Conductivities are of the order of .0024 cal/°C-sec .cm for the frozen muscle.

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