

Physics. — “*The Process of Solidification as a Problem of Conduction of Heat*”. By Dr. H. C. BURGER. (Communicated by Prof. W. H. JULIUS).

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§ 1. *Introduction.* The equilibrium between two phases has been fully investigated experimentally and theoretically. Little, however, is known about the cases in which there is no equilibrium, but one phase is converted into another. In the first case the thermodynamic laws may serve as basis of all considerations; in the second case, however, such leading principles are entirely wanting. The researches on the dynamics of the conversion of phases are quite detached, and are often restricted to the collecting of empirical data the meaning of which is not quite clear.

It would be very desirable to develop a general theory of dynamics, which will have to include “thermodynamics” as the special case of its statics. Whether this is possible from a purely phenomenological point of view, further experiment will have to teach.

In what follows I have worked out a general method for the treatment of the special case of the solidification of a chemically simple substance.

On transition of a supercooled melt into the solid condition the following processes should be sharply distinguished:

1. The formation of particles of the solid phase in the supercooled liquid¹⁾.

2. The further growth of each of these particles, and also the growth of a particle of the solid substance put into the liquid purposely²⁾.

Only the second point will be treated in this communication. In this the particularities which are in connection with the anisotropy of the solid substance will not be taken into account. In this way the problem is simplified, but at the same time the idea of accounting for the formation of the crystalline form is abandoned.

¹⁾ G. TAMMANN, *Zeitschr. f. phys. Chem.* 25, p. 442, 1898.

²⁾ D. GERNEZ, *Compt. rend.* 95, p. 1278, 1882.

B. MOORE, *Zeitschr. f. Phys. Chem.* 12, p. 545, 1893.

The question which should be posed when one wishes to examine the course of the process of solidification, is the following:

Given a supercooled liquid, in which there are one or more pieces of the solid substance. At a definite moment the temperature is given as function of the place. Required to determine for every successive moment the temperature as function of the place and the velocity with which the boundary surface of the two phases moves in consequence of the solidification.

When the general principles and methods that may serve to solve this problem, are known, all the cases that present themselves can in principle be treated by the aid of them. This treatment only requires the surmounting of mathematical difficulties. The theory must be developed for a particular case and compared with the experiments. As is the case in every phenomenological theory, certain constants or functions which are characteristic of the substance, remain undetermined a priori here too. Comparison of theory and observations makes us acquainted with these constants or functions.

When the above mentioned questions are answered, it should be borne in mind that in a substance in which the temperature differs from point to point, conduction of heat takes place. The conduction should not be considered as accessory, for without transport of heat solidification cannot take place.

In a substance moving with a velocity V the temperature θ satisfies a generalized differential equation of the conduction of heat

$$c\rho \frac{\partial \theta}{\partial t} = \lambda \Delta \theta - c\rho \operatorname{div}(\theta V) \dots \dots \dots (1)$$

This equation contains the quantities c , ρ , and λ , (resp. specific heat, density, and conductivity of heat), which refer to the phase for which (1) holds. An equation of the shape of (1) exists for the solid as well as for the liquid phase. In these equations there occur constants which are characteristic only of one of the phases separately, and not for the heterogeneous reaction between the two phases.

As in every problem of conduction of heat there are here too, by the side of the differential equation, boundary conditions which the temperature θ must satisfy, viz.:

1. At the boundary plane of two media the temperature is continuous. This refers both to the boundary surface of the solid and the liquid phase and to the surfaces along which each of the phases touches the wall of the vessel in which they are contained.

2. At a boundary surface the normal component of the current of heat is continuous, when no generation of heat takes place at

the surface. If this is the case, the normal components of the current of heat in the two substances at the two sides of the surface together lead off a quantity of heat equal to the generation of heat taking place at this surface.

The boundary conditions 1 and 2, however, together with the equation (1) are not yet sufficient to determine the condition for every successive moment. For one thing, the velocity with which the boundary surface of the solid phase moves is not known, hence it is not known either at a definite moment, at what surface the conditions 1 and 2 are valid. The velocity of the boundary surface of the phases is directed from solid to liquid during the solidification. This velocity can only depend on the condition of the substance at this surface, hence on the nature of the substance and the temperature there. As third limit condition we get, therefore, the relation that must exist between the linear velocity of crystallisation (or solidification) and the temperature at the boundary.

When the value of a quantity in the solid phase is denoted by the index 1, and in the liquid phase by the index 2, and when v is the normal at the boundary surface solid-liquid, we have at this boundary surface the conditions:

$$\bar{\theta}_1 = \bar{\theta}_2 \quad (2a)$$

$$\lambda_1 \frac{\partial \theta_1}{\partial v} - \lambda_2 \frac{\partial \theta_2}{\partial v} = v \rho_1 Q \quad (2b)$$

$$v = f(\bar{\theta}) \quad (2c)$$

When $v \rho_1$ is the mass solidifying per unit of time and per unit of surface, $v \rho_1 Q$ represents the difference of the normal-component of the current of heat on the two sides of the boundary surface, when Q represents the melting heat at the temperature $\bar{\theta}$ prevailing at this surface.

The differential equation (1) with the boundary conditions (2) now determines the course of the process of solidification. (1) and (2) can, however, not be solved, when the function f , which is characteristic of the substance, is not known. It might be tried to make different suppositions about the relation between $\bar{\theta}$ and v , e.g. that $\bar{\theta}$ is equal to the temperature of melting. Every supposition leads to a definite value of the temperature as function of place and time. Each of these results might be compared with the observation, and in this way it might be found what relation there exists between $\bar{\theta}$ and v .

¹⁾ A horizontal line indicates the value at the limit.

²⁾ Of course inversely $\theta = \varphi(v)$.

As we à priori do not even know the form of the relation (2c), the following course is, however, to be preferred. A value is chosen for the velocity v ¹⁾. When further v is considered as given, the temperature can be determined from (1), (2a), and (2b), hence also the temperature $\bar{\theta}$ at the boundary. By causing the solidification to take place under different circumstances, different values of v can be obtained, and for each of these values the corresponding temperature $\bar{\theta}$ can be calculated, and in this way the relation between v and $\bar{\theta}$ can be found. To check the theory, the temperature $\bar{\theta}$ may be determined experimentally, but this is not necessary in order to find the relation given by (2c) for a definite substance.

§ 2. Theory of the solidification in a cylindrical tube.

One of the simplest phenomena of solidification, which has also been studied most fully experimentally, is the crystallisation of a supercooled liquid in a cylindrical tube.

Let the solid substance be in one part (A) of a straight tube, the supercooled liquid in the other part (B). The whole is surrounded by a space of constant temperature, which must also prevail in A and B within the tube at infinite distance from the boundary surface. This temperature must, of course, lie under the melting-point of the substance used, because else no solidification takes place²⁾.

The solidification now proceeds as follows. Heat is liberated at the boundary surface of the phases (heat of melting). It flows off on both sides through the solid substance and the liquid, and finally passes through the wall of the tube to the sphere of constant temperature. In every vertical section of the tube the temperature is highest in the axis of the cylinder and decreases towards the outside. This is also the case at the boundary surface of the phases. Hence the normal velocity at this surface cannot be the same everywhere, but must increase or decrease from within outward as the velocity of solidification v increases or decreases with diminishing temperature. Both cases may occur. The velocity v is, of course, zero at the melting-point, then increases with decreasing temperature, after which it begins to diminish again, as experience teaches, approaching asymptotically to zero at sufficiently low temperature.

Let us suppose the temperature of the surrounding space to be

¹⁾ The velocity v can be determined in a simple way experimentally, and can, therefore, conveniently be used as basis for the calculation.

²⁾ A process of melting, analogous to the process of solidification treated here, is impossible, because a liquid *can* exist under its melting point, but a solid substance cannot exist above its melting point.

only little under the melting-point of the substance, so that the velocity of crystallisation increases with falling temperature. Then the velocity of the boundary surface must be smaller in the axis of the tube than at the periphery, i.e. this surface becomes concave towards the liquid. The form of the surface can, however, not remain unchanged during the increase; as the velocity in normal direction is smallest in the axis of the cylinder, and increases towards the outside, the curvature will always increase, as is easy to understand, and at last a hollow may even arise, which is shut off, and is then filled up. At the same time the more rapid growth has proceeded at the periphery, and the same thing is repeated. The growth will further not be symmetrical round the axis. When through a slight disturbance the substance grows somewhat more rapidly at a point of the circumference than at the other points, the surface gets here further from the places where the crystallisation takes chiefly place, i.e. at points where the temperature is lower and the rate of solidification, therefore, greater. Consequently the growth in the considered point takes place still more rapidly. Hence the condition is unstable. A small accidental disturbance will have great influence on the form of the boundary surface, hence on the process of the solidification. In this case the solidification is a very irregular phenomenon, and a theoretical treatment of the problem proposed on p. 619 is impossible.

This is, however, entirely different when the temperature of the surroundings, hence that of the tube, is chosen lower, so that the velocity of solidification becomes smaller with decreasing temperature. Then the normal velocity is greatest in the axis of the cylinder where the highest temperature prevails. The surface of the solid phase becomes, therefore, convex towards the liquid. This convex surface now begins to move parallel to the axis, and in this it assumes a very definite form. The normal velocity during this displacement is greatest in the axis, and decreases towards the periphery. This decrease must be such that in every point the velocity v has the value that according to (2c) corresponds to the temperature θ prevailing there. There can, and will, arise a condition in which the boundary surface moves uniformly and with constant form parallel to the axis. Every disturbance in this condition will disappear again of its own accord. It is also easy to convince oneself that everything around the axis of the tube must be symmetrical. If this is not the case at a moment, the growth and conduction of heat takes place in such a way that the symmetry is restored.

Though in this way one can see that the differential equation (1)

with the boundary conditions (2) perfectly determine the form of the boundary surface of the phases on solidification in a tube, this determination is attended by great mathematical difficulties. We shall, therefore, suppose for simplification that the surface of the solid phase is a plane at right angles to the axis of the tube¹⁾. The constant velocity v , with which this plane moves, is determined according to (2c) by the temperature θ at this plane.

When there shall actually arise a condition in which the boundary plane, preserving its shape, moves uniformly, the whole distribution of temperature also in solid and liquid phase will have to move with it with this velocity, in other words, the temperature will only depend on the distance from the boundary surface. That a solution of (1) and (2) with this property actually exists, will now be shown.

In the solid substance, where the matter is at rest, and the condition round the axis is symmetrical, the differential equation (1) assumes the form:

$$\frac{\partial \theta_1}{\partial t} = \alpha_1 \left\{ \frac{\partial^2 \theta_1}{\partial \xi^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_1}{\partial r} \right) \right\} \dots \dots \dots (3)$$

in which $\alpha_1 = \frac{\lambda_1}{c_1 \rho_1}$ and ξ is a coordinate, which is measured along the axis of the tube in the direction of the velocity v with which the boundary surface moves, and r the distance from the axis.

On solidification contraction takes place. In consequence of this the liquid moves in a direction opposite to that of the positive ξ -axis with a constant velocity V , which in the densities ρ_1 and ρ_2 of the solid and the liquid phase can be expressed thus:

$$V = - \frac{\rho_1 - \rho_2}{\rho_2} v.$$

Accordingly the differential equation holding in the liquid, becomes:

$$\frac{\partial \theta_2}{\partial t} = \alpha_2 \left\{ \frac{\partial^2 \theta_2}{\partial \xi^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_2}{\partial r} \right) \right\} + \frac{\rho_1 - \rho_2}{\rho_2} v \frac{\partial \theta_2}{\partial \xi} \dots \dots \dots (4)$$

When the temperature in the solid and the liquid phase is supposed only to depend on the distances x_1 resp. x_2 from the boundary surface, the differential quotients according to time may be expressed in those according to place:

$$\frac{\partial \theta_1}{\partial t} = v \frac{\partial \theta_1}{\partial x_1}; \quad \frac{\partial \theta_2}{\partial t} = -v \frac{\partial \theta_2}{\partial x_2} \dots \dots \dots (5)$$

Further:

¹⁾ As in the cases that occur most frequently the velocity v depends only little on the temperature, the boundary surface will generally be only little curved.

$$\frac{\partial}{\partial \xi} = -\frac{\partial}{\partial x_1} \text{ resp. } \frac{\partial}{\partial \xi} = \frac{\partial}{\partial x_2}.$$

When (5) is substituted in the equations (3) and (4), and when in these equations the following form is written:

$$v = v_1; \frac{Q_1}{Q_2} v = v_2,$$

it is found that:

$$v_1 \frac{\partial \theta_1}{\partial x_1} = a_1 \left\{ \frac{\partial^2 \theta_1}{\partial x_1^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_1}{\partial r} \right) \right\} \dots \dots \dots (6)$$

$$-v_2 \frac{\partial \theta_2}{\partial x_2} = a_1 \left\{ \frac{\partial^2 \theta_2}{\partial x_2^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_2}{\partial r} \right) \right\} \dots \dots \dots (7)$$

Besides there are still the limit conditions (2a) and (2b), which are in this case:

$$(\theta_1)_{x_1=0} = (\theta_2)_{x_2=0} \dots \dots \dots (8a)$$

$$-\lambda_1 \left(\frac{\partial \theta_1}{\partial x_1} \right)_{x_1=0} - \lambda_2 \left(\frac{\partial \theta_2}{\partial x_2} \right)_{x_2=0} = Q Q_1 v \dots \dots \dots (8b)$$

The liquid having a normal velocity *V* at the boundary surface, it is not self-evident that (2b) may be applied unmodified. A closer examination, however, teaches that this is, indeed, the case, and that therefore (8b) is correct¹⁾.

Besides the relations (6), (7), and (8) the temperatures must satisfy other conditions which hold at infinite distance and on the wall of the tube. The tube being in surroundings of constant temperature, this temperature in both phases must exist at infinite distance from the boundary surface, where the influence of the generated heat of melting is not felt. The zero-point of the temperature being arbitrary, the temperature of the surroundings is chosen for it, and thus the following conditions are obtained:

$$(\theta_1)_{x_1=\infty} = 0; (\theta_2)_{x_2=\infty} = 0 \dots \dots \dots (9)$$

It is less simple to take the influence of the wall of the tube into account. When one wants to solve the problem accurately, also a differential equation must be drawn up for the temperature in the wall of the tube, and this temperature must be brought in connection with the temperature of the solid and the liquid substance in the tube by means of boundary conditions corresponding to (2a) and (2b). At the outer surface of the wall the temperature must be zero, i.e. equal to that of the surrounding space.

To put this train of reasoning into practice, though not impossible in principle, would lead to very elaborate calculations. In the cases

¹⁾ Compare also W. HERGESELL, Ann. de Phys. u. Chem. 15, 1882, p. 19.

that have been examined experimentally, the conduction of heat through the wall is very great, however, because the wall is not very thick, and consists of a substance (mostly glass) that conducts heat pretty well. Consequently the influence of the resistance to heat of the wall of the tube is slight, and the following approximation may be used. When the current of heat in the wall is supposed to be radial, and when *σ* and *λ₃* represent the thickness resp. the conductivity of this wall, a quantity of heat given by:

$$\frac{\lambda_3 \theta}{\sigma}$$

flows through the wall per unit of time and surface.

In this *θ* is the temperature of the substance on the inner side of the wall of the tube.

When *a* is the radius of the interior width of the tube, we get the boundary conditions:

$$-\lambda_1 \left(\frac{\partial \theta_1}{\partial r} \right)_{r=a} = \frac{\lambda_3}{\sigma} \theta_1 \text{ resp. } -\lambda_2 \left(\frac{\partial \theta_2}{\partial r} \right)_{r=a} = \frac{\lambda_3}{\sigma} \theta_2 \dots (10)$$

Both members of this equation express the current of heat per unit of time and surface.

In order to solve the differential equation (6) with the conditions (8), (9) and (10), we seek a particular solution, which is a product of two factors, one that depends on *x₁* (*X₁*), and one that depends on *r* (*R₁*). When we substitute:

$$\theta_1 = X_1 R_1$$

in (6), we may write for this equation:

$$r \frac{d^2 R_1}{dr^2} + \frac{dR_1}{dr} = \frac{v_1 dX_1}{a_1 dx_1} = \frac{d^2 X_1}{dx_1^2} X_1$$

As in this relation the first member depends only on *r* and the second member only on *x₁*, both members are constant, e.g. — *C*. Then the following equations are obtained for *X₁* and *R₁*:

$$r \frac{d^2 R_1}{dr^2} + \frac{dR_1}{dr} + Cr R_1 = 0 \dots \dots \dots (11a)$$

$$\frac{d^2 X_1}{dx_1^2} - \frac{v_1 dX_1}{a_1 dx_1} - CX_1 = 0 \dots \dots \dots (11b)$$

The solution of (11a) which remains finite for *r* = 0, is the BESSEL function of order zero:

$$R_1 = J_0(r \sqrt{C}) \dots \dots \dots (12)$$

As θ_1 must satisfy (10) for all values of x_1 , this is also the case with each of the products $X_1 R_1$, of which θ_1 is built up, hence also with R_1 . When in (10) the value of R_1 given by (12) is substituted for θ_1 , we find:

$$-\lambda_1 \sqrt{C} J_0(a \sqrt{C}) = \frac{\lambda_2 a}{d} J_0(a \sqrt{C}).$$

When in this

$$a \sqrt{C} = \xi_1,$$

and

$$\frac{\lambda_1 d}{\lambda_2 a} = \gamma_1, \dots \dots \dots (13)$$

is put, this equation assumes the form:

$$\gamma_1 \xi_1 J_1(\xi_1) = J_0(\xi_1) \dots \dots \dots (14)$$

This equation has an infinite number of roots, which ranged according to ascending value may be called:

$$\xi_1^{(1)}, \xi_1^{(2)}, \dots, \xi_1^{(k)}, \dots$$

They depend on the quantity γ_1 defined by (13).

To every root ξ belongs a value of the function R_1 . These functions become:

$$R_1^{(k)} = J_0\left(\frac{r \xi_1^{(k)}}{a}\right), (k = 1, 2, \dots). \dots \dots (15)$$

Like (11a), (11b) has also two particular solutions, one of which becomes zero for $x_1 = \infty$, and the other infinite. In connection with (9) the former must be chosen. Apart from a constant factor, this solution is:

$$X_1 = e^{-p_1^{(k)} x_1} \dots \dots \dots (16)$$

p_1 is the positive root of the equation:

$$\{p_1^{(k)}\}^2 + \frac{v_1}{\alpha_1} p_1^{(k)} - \frac{\{\xi_1^{(k)}\}^2}{a^2} = 0,$$

which is found by substitution of (16) in (11b), and replacement of C by:

$$\frac{\{\xi_1^{(k)}\}^2}{a^2}.$$

The value of $p_1^{(x)}$ is:

$$p_1^{(k)} = -\frac{v_1}{2\alpha_1} + \sqrt{\frac{v_1^2}{4\alpha_1^2} + \frac{\{\xi_1^{(k)}\}^2}{a^2}} \dots \dots (17)$$

The general solution of the problem must be composed of special solutions in the following way:

$$\theta_1 = \sum_{k=1}^{\infty} A_1^{(k)} J_0\left\{\frac{r \xi_1^{(k)}}{a}\right\} e^{-p_1^{(k)} x_1} \dots \dots (18)$$

The constants $A_1^{(k)}$ can only be determined in connection with the value of θ_1 . The expression given by (18) satisfies the boundary condition (10), which holds at the boundary surface of the solid substance and the wall of the tube, and is also in agreement with (9).

The value of the temperature θ_2 prevailing in the liquid is found in an analogous way. It is:

$$\theta_2 = \sum_{k=1}^{\infty} A_2^{(k)} J_0\left\{\frac{r \xi_2^{(k)}}{a}\right\} e^{-p_2^{(k)} x_2} \dots \dots (19)$$

The quantities $\xi_2^{(k)}$ are the roots of the equation:

$$\gamma_2 \xi_2 J_1(\xi_2) = J_0(\xi_2), \dots \dots \dots (20)$$

in which:

$$\gamma_2 = \frac{\lambda_2 d}{\lambda_1 a} \dots \dots \dots (21)$$

From $\xi_2^{(k)}$ follows $p_2^{(k)}$:

$$p_2^{(k)} = \frac{v_2}{2\alpha_2} + \sqrt{\frac{v_2^2}{4\alpha_2^2} + \frac{\{\xi_2^{(k)}\}^2}{a^2}} \dots \dots (22)$$

In conclusion the constants $A_1^{(k)}$ and $A_2^{(k)}$ occurring in (18) and (19), must be determined from the conditions (8) at the boundary surface of the solid and the liquid phase. By the aid of (18) and (19) these conditions become:

$$\sum_{k=1}^{\infty} A_1^{(k)} J_0\left\{\frac{r \xi_1^{(k)}}{a}\right\} = \sum_{k=1}^{\infty} A_2^{(k)} J_0\left(\frac{r \xi_2^{(k)}}{a}\right) \dots \dots (23)$$

$$\sum_{k=1}^{\infty} \left[A_1^{(k)} \lambda_1 p_1^{(k)} J_0\left\{\frac{r \xi_1^{(k)}}{a}\right\} + A_2^{(k)} \lambda_2 p_2^{(k)} J_0\left\{\frac{r \xi_2^{(k)}}{a}\right\} \right] = Q \varrho_1 v_1. (24)$$

Both equations must hold for all values of r .

The difficulty to find the constants $A_1^{(k)}$ and $A_2^{(k)}$ from (23) and (24), consists in this that in these equations there occur two series of normal functions, viz. $J_0\left\{\frac{r \xi_1^{(k)}}{a}\right\}$ and $J_0\left\{\frac{r \xi_2^{(k)}}{a}\right\}$. These series are, indeed, each in themselves orthogonal; but the functions of one series are not orthogonal to those of the other. The most symmetrical way would be to try and find normal functions belonging to the whole space, and not, as had been done up to now, either to space 1 (solid substance) or to space 2 (liquid). There exists, however, a simple — though asymmetrical — method, which leads to the pur-

pose with comparatively little trouble. It is possible to develop the functions for one region into a series of normal functions of the other region. The following development is then obtained:

$$J_0 \left\{ \frac{r \xi_1^{(k)}}{a} \right\} = \sum_{l=1}^{\infty} \alpha_{kl} J_0 \left\{ \frac{r \xi_2^{(l)}}{a} \right\} \dots \dots \dots (25)$$

The constants α_{kl} form a twofold infinite system of values that do not depend on the variables $\frac{r}{a}$, but on the constants γ_1 and γ_2 defined by (13) and (21). As we saw before, they depend on the dimensions of the tube used, and on the conductivity of the substances that play a part in the problem.

For the determination of α_{kl} both members of (25) are multiplied by $r J_0 \left\{ \frac{r \xi_2^{(k)}}{a} \right\} dr$, and an integration is carried out with respect to r from zero to a . When for this purpose use is made of the known properties of the BESSEL functions, and of the equations (14) and (20), the following form is found:

$$\alpha_{kl} = \frac{2 \xi_1^{(k)} \xi_2^{(l)} (\gamma_2 - \gamma_1) J_1 \{ \xi_1^{(k)} \}}{\{ (\xi_1^{(k)})^2 - (\xi_2^{(l)})^2 \} \{ 1 + \gamma_2^2 (\xi_2^{(l)})^2 \} J_1 \{ \xi_2^{(l)} \}} \dots \dots (26)$$

By substitution of (25) in (23), we get:

$$A_2^{(k)} = \sum_{l=1}^{\infty} \alpha_{lk} A_1^{(l)} \dots \dots \dots (27)$$

If this relation between the coefficients $A_1^{(k)}$ and $A_2^{(k)}$ is satisfied, (23) holds for all values of r .

Also in (24) all the occurring functions of r must be developed with respect to $J_0 \left\{ \frac{r \xi_2^{(k)}}{a} \right\}$. For $J_0 \left\{ \frac{r \xi_1^{(k)}}{a} \right\}$ (25) gives this development: we write for the second member of (24):

$$Q \varrho_1 v_1 = \sum_{k=1}^{\infty} \beta_k J_0 \left\{ \frac{r \xi_2^{(k)}}{a} \right\} \dots \dots \dots (28)$$

The coefficients β_k are found by multiplication of both members by $r J_0 \left\{ \frac{r \xi_2^{(k)}}{a} \right\} dr$, and integration with respect to r from zero to a . Then follows from (20) and the properties of the BESSEL functions:

$$\beta_k = \frac{2 Q \varrho_1 v_1 \gamma_2}{\{ 1 + \gamma_2^2 (\xi_2^{(k)})^2 \} J_0 \{ \xi_2^{(k)} \}} \dots \dots \dots (29)$$

When (25) and (28) are substituted in equation (24), it appears that this is identically satisfied when the following relations exist between the still unknown coefficients $A_1^{(k)}$ and $A_2^{(k)}$:

$$A_2^{(k)} p_2^{(k)} + \sum_{l=1}^{\infty} A_1^{(l)} \lambda_1 p_1^{(l)} \alpha_{lk} = \beta_k \dots \dots \dots (30)$$

When finally the constants $A_2^{(k)}$ are expressed in $A_1^{(k)}$ by the aid of (27), then follows from (30):

$$\sum_{l=1}^{\infty} A_1^{(l)} \alpha^{lk} (p_1^{(l)} \lambda_1 + p_2^{(k)} \lambda_2) = \beta_k \dots \dots \dots (31)$$

The equations (31) are infinite in number and contain infinitely many unknowns $A_1^{(l)}$. As we have not used orthogonal normal functions, we do not find the coefficients A_1 expressed explicitly, but as solutions of a system of linear equations. Practically this is, however, not a very serious drawback. For the quantities α_{kl} are small for $k \neq l$; hence they differ only little from one if $k = l$. In the first of the equations (31) all the terms but one can be left out in the first member in first approximation. The value of $A_1^{(1)}$ thus found is substituted in the second equation, in which all the terms following the second, are left out. Thus an approximated value of $A_1^{(2)}$ is obtained from this equation. Proceeding in the same way, an approximation is found for all the values $A_1^{(l)}$. Now the calculation is repeated, but no terms are left out. The terms which were neglected in first approximation, are now replaced by the value which they appeared to have in first approximation. By this method of successive approximation, which quickly converges, the values of the coefficients $A_1^{(l)}$ are found. The values of the constants $A_2^{(l)}$ (or $A_2^{(k)}$) are then found from (27).

The temperature θ_1 in the solid substance and θ_2 in the liquid is found by substitution of the values found of $A_1^{(k)}$ and $A_2^{(k)}$ in (18) and (19); the problem we had proposed to ourselves, has, therefore, been solved.

The above-developed theory becomes of importance when it leads to a clearer understanding of the result and the interpretation of observations. Experiments on solidification in a tube and their relation to the theory will be found in a subsequent communication.

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