The Heat Capacity of Rochelle Salt Between −30° and +30°C

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The heat capacity of Rochelle salt has been measured in the temperature range −30° to +30°C by the method of adiabatic electric heating. Two samples of the salt have been investigated, one consisting of eleven single crystals of total weight about 123 grams, the other of small crystals, almost a powder, of total weight about 58 grams. The heat capacities of the two samples are nearly the same. They are well represented (mean deviation of individual points 0.3 percent) by the straight lines:

$$C_p = 1.290 + 0.0031t \quad \text{(crystals)}$$
$$C_p = 1.289 + 0.0034t \quad \text{(powder)}.$$

The heat capacity is in joule/g·°C; t is in °C. There are indications of anomalies at approximately −18° and possibly +24°C, but the maximum departure from the straight lines is less than 1 percent. The direction of the indicated anomalies and their order of magnitude is in agreement with theory. The small amplitude of the anomaly at +24° is not in agreement with the measurements of previous observers.

INTRODUCTION

THE temperature variation of the heat capacity of Rochelle salt (sodium potassium dextro-tartrate tetrahydrate, $KNaC_4H_4O_6 \cdot 4H_2O$) is of considerable interest since it is connected with the spontaneous polarization[1] of the crystals. By an argument similar to that applied to the analogous magnetic phenomenon[2] it may be shown that the anomalous heat capacity associated with the potential energy of the spontaneous polarization is

$$\Delta C = -\tfrac{1}{2} f \partial P^2 / \partial t \quad \text{erg/cm}^3 \cdot °C \tag{1}$$

where f is a constant ("Lorentz factor;" "coefficient of the inner field") for which various values ranging from about 2 to $4\pi/3$ have been suggested and P is the spontaneous polarization in electrostatic units. To get the anomalous heat capacity in joule/g·°C Eq. (1) must be divided by the density of Rochelle salt and 10^7:

$$\Delta C = -\frac{f}{2\rho 10^7} \frac{\partial P^2}{\partial t} \sim -10^{-7} \frac{\partial P^2}{\partial t} \text{ joule/g·°C.} \tag{2}$$

P has recently been measured by Tarnopol[3] and

Bradford[4] by different methods. From neither set of measurements is it possible to account for an anomaly of much more than +0.003 joule/g·°C at the upper Curie point ($\sim +24$°C) or −0.005 joule/g·°C at the lower Curie point (~ -18°C).

Measurements near the upper Curie point have been made by Kobeko and Nelidow[5] and by Rusterholz.[6] The writer is unaware of any previous measurements near the lower Curie point. Kobeko and Nelidow found a heat capacity of about 92.6 cal./mole·°C and a break of about 7 cal./mole·°C (0.1 joule/g·°C) at 26°. Rusterholz found a heat capacity of 104 cal./mole·°C at 24° and a break of about 6 cal./mole·°C (0.09 joule/g·°C) at 25.8°C.

From measurements of many electrical properties of Rochelle salt made by Mueller[7] one would expect the break to come at about 24° rather than at 26°. The difference in absolute value (~ 11 percent) between the values of Kobeko and Nelidow and of Rusterholz is hardly satisfactory. It was therefore decided to measure the heat capacity of Rochelle salt with three main

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[1] An account of this and other peculiarities of Rochelle salt may be found in reference (7).

[2] See, for example, Pierre Weiss and P. N. Beck, J. de Phys. 7, 249 (1908).

[3] Lester Tarnopol, M. S. Thesis, Massachusetts Institute of Technology, 1934. Fig. 17, reference (7), is based on Tarnopol's work.

[4] Eliot Bradford, B. S. Thesis, Massachusetts Institute of Technology, 1934. As far as the writer knows this has not been published.

[5] P. P. Kobeko and J. G. Nelidow, Physik. Zeits. Sowjetunion 1, 382 (1932).

[6] A. A. Rusterholz, Helv. Phys. Acta 7, 643–644 (1934); 8, 39–54 (1935).

[7] Hans Mueller, Phys. Rev. 47, 175–191 (1935).

intentions: (1) to investigate the variation in the neighborhood of the lower Curie point, (2) to decrease the uncertainty in the absolute value of the heat capacity and (3) to attempt to reconcile the discrepancy between the electric Curie point ($\sim24°$) and the thermal Curie point ($\sim26°$).

METHOD

A modification of the method of adiabatic electric heating developed by Bronson and his students[8-11] was used. The salt was enclosed in a copper calorimeter fitted with a heating coil. The calorimeter was suspended inside a jacket immersed in a stirred oil bath. A differential thermocouple ran between the calorimeter and the jacket. The temperature of the oil bath was regulated so that the temperature difference indicated by the thermocouple was kept small. The temperature of the oil bath was measured by a platinum thermometer.

To obtain the heat capacity of the salt the following procedure was used. The temperature of the calorimeter was measured by measuring that of the bath when the differential thermocouple indicated zero. The calorimeter was then heated a suitable amount (0.2° to 5° depending on circumstances), the energy supplied being measured carefully. The temperature of the calorimeter was again determined. Dividing the energy supplied by the change in temperature gave the heat capacity of the calorimeter plus salt. The (previously measured) heat capacity of the empty calorimeter was subtracted and the difference divided by the mass of the salt to give its heat capacity in joule/g·°C.

APPARATUS

(a) Calorimeters and thermocouples

Two calorimeters were used in the course of this work. The first is shown inside the jacket in Fig. 1. It consisted of an outer cup of copper about 3 mm thick with a cover which screwed firmly into place. Into this fitted an inner cup of $\frac{1}{2}$ mm brass on the outside of which the heating

[8] H. L. Bronson, H. M. Chisholm and S. M. Dockerty, Can. J. Research 8, 282–303 (1933).

[9] S. M. Dockerty, Can. J. Research 9, 84–93 (1933).

[10] H. L. Bronson and A. J. C. Wilson, Can. J. Research, A14, 181–193 (1936).

[11] S. M. Dockerty, Can. J. Research A15, 59–66 (1937).
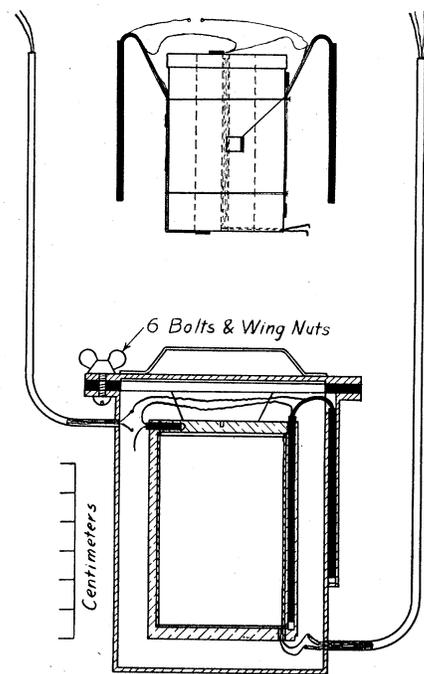
FIG. 1. The calorimeters and jacket.

coil was wound and into which the salt was put. The calorimeter was suspended in the jacket by three wire hooks.

An eight-junction copper-constantan thermocouple was used. The calorimeter junctions were distributed over the surface of the calorimeter in an attempt to get a good average of its surface temperature. There was one junction which fitted into the bottom of the calorimeter, one (shown in Fig. 1) in the top and two groups of three each in the side of the calorimeter. One side group is shown in Fig. 1; the other is omitted in order to show other details. The six side junctions were distributed approximately uniformly along the length of the calorimeter. The jacket junctions were in two groups of four which fitted into tubes soldered on opposite sides of the jacket. The thermocouple was connected by an all-copper circuit to a Leeds & Northrup galvanometer of sensitivity such that one cm deflection corresponded to about 0.001° difference in temperature between calorimeter and jacket. The heat capacity of this calorimeter plus the part of the thermocouple heated by it was about 180 joule/°C.

The second calorimeter (inset, Fig. 1) was of much lighter construction, being a single cup of 0.005″ copper foil. Its interior was divided into six sections by radial fins of copper foil. The heating coil was wound longitudinally in the notches between opposite pairs of fins. The eight thermocouple junctions were cemented permanently into small foil pockets soldered to its outer surface. The distribution of the junctions is fairly clear from the figure. The heat capacity of this calorimeter was about 11 joule/°C.

(b) Oil bath

The oil (kerosene was used in most of the measurements) was contained in an earthenware crock of about four gallons capacity. The crock was insulated on bottom and sides by rock wool. The top could be covered to a great extent with cushions filled with hair felt. Inside the crock there was a brass framework which supported the calorimeter jacket, heating coils, platinum thermometer and stirring motors.

The bath was stirred by two "Economy" stirrers whose original propellers had been replaced by others of larger size. The stirrers were mounted on opposite sides of the bath. There were two heating coils, also on opposite sides of the bath. They had a resistance of about 40 ohms each and were made of bare wire to decrease heating lag. They could be connected in series or in parallel with one another and in series with a variable resistance, ammeter and the 110-volt line.

Cooling the bath was at first accomplished by a rather complicated apparatus which pumped cold oil into the bath. This was reasonably satisfactory at the higher temperatures, but the rapid variations in temperature caused by the injection of the large quantities of cold oil required to maintain, say, −20° made it almost impossible to obtain accurate measurements near the lower Curie point. After some experimenting, the method adopted was to place solid carbon dioxide in direct contact with the crock, the amount used being determined by the temperature desired. The method was not ideal as it produced larger temperature gradients than were desirable but it was fairly satisfactory at all temperatures.[12]

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[12] An oil bath was used instead of a more convenient copper adiabatic jacket of the type described in references

(c) Jacket

The jacket is shown in Fig. 1. It was made of brass; the details of its construction are fairly clear from the drawing. At first there was considerable trouble in making the cover oil-tight. Gaskets of ordinary rubber were tight for a short time but deteriorated rapidly in the oil. A gasket of "Thiokol" was not attacked by the oil but did not make an oil-tight joint. The oil crept in between the brass flanges and the gasket. The method finally adopted was to coat both the flanges and the gasket with rubber cement and allow it to dry before screwing down the cover.

(d) Other apparatus

The rest of the apparatus was of standard construction and requires no description. The platinum thermometer was calibrated at the melting point of mercury, the melting point of ice, sodium sulphate decahydrate transition point and the boiling point of water. Its fundamental interval was found to be 10.010_0 ohms; δ was found to be 1.48 from the mercury point, 1.47 from the sodium sulphate point. The difference is within the limits of error. Each point, except the mercury point, was repeated at intervals.

MEASUREMENTS

The procedure followed in making the measurements has been described. The first measurements were those of the first calorimeter as a function of temperature. Then, to check the ability of the apparatus to give reliable values of the absolute magnitude of heat capacity, the heat capacity of copper was measured. The copper was in the form of small shot intended for analytical work and was stated to contain less than 0.04 percent impurities. The values found were slightly over 0.1 percent greater than those

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(9, 10 and 11) because of two considerations which seemed convincing when the work was started. (1) It was thought that temperature uniformity in the oil bath would be better than in a copper jacket. On testing with a differential thermocouple it was found to be somewhat better than the jacket of reference (10), but not as much better as had been anticipated. (2) The surface of the calorimeter heats up faster than the interior of the salt so that when the heating current is turned off the temperature of the calorimeter falls rather rapidly. The fall was not as fast as had been expected and it now seems likely that a copper jacket would have sufficed.
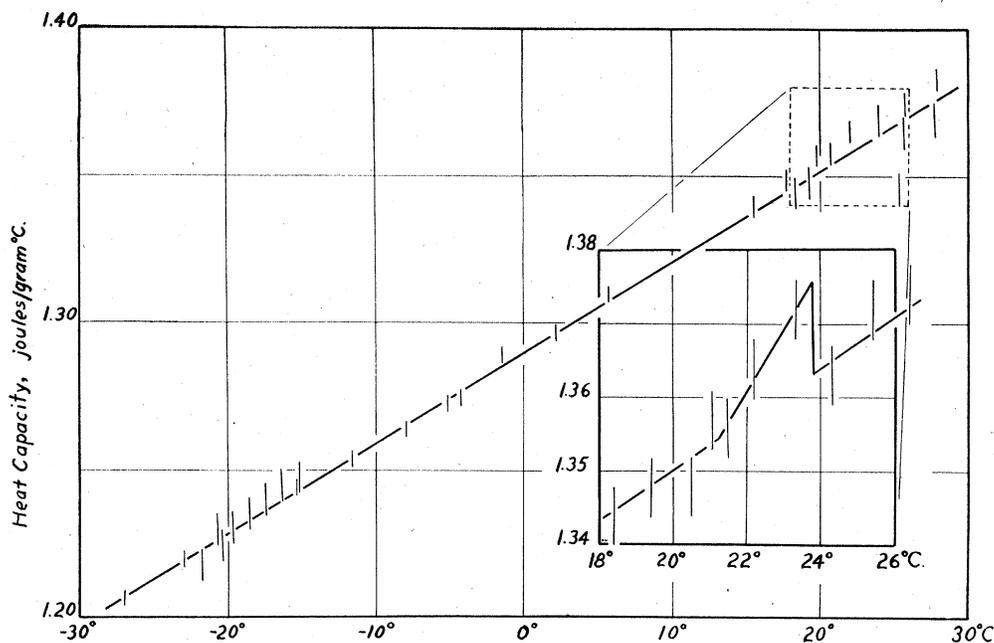
FIG. 2. Heat capacity of the large crystals of Rochelle salt in the range −30 to +30°C.

of Dockerty.[9, 11] The agreement is satisfactory.[13]

The calorimeter was then filled with small crystals of Rochelle salt (Merck). It was found to require about an hour for the calorimeter to reach thermal equilibrium with the result that the measurements scattered badly. More concordant measurements on the same material were obtained later so it does not seem necessary to discuss these.

Eleven single crystals, specially cut by the Brush Development Company to pile into a roughly cylindrical shape which fitted loosely into the calorimeter, were each wrapped in copper foil and put in the calorimeter. The foil served the double purpose of preventing charges produced by the pyroelectric effect from interfering with the normal change of polarization with temperature, and of decreasing the time required to reach thermal equilibrium. Measurements were made over the range −30° to +30°C (Fig. 2). Near the lower Curie point no anomaly was found. At the upper Curie point there were some indications of an anomaly of $\frac{1}{2}$ or 1 percent,

but they were not very convincing. The set of measurements showing the effect most clearly is inset in Fig. 2. It must be emphasized that if all points were shown, no one would draw an anomaly if it were not expected. The straight line $C_p = 1.290 + 0.0031t$ represents the 48 experimental points with a mean deviation of about 0.3 percent.

The measurements with the first calorimeter showed that to obtain greater "resolving power" two things were necessary: The time required to reach thermal equilibrium should be decreased and the heat capacity of the calorimeter should be reduced to a small fraction of that of the salt. These ends were attained with the second calorimeter. A measurement with it with a temperature interval of 0.3° was apparently as reliable as one with an interval of 1° made with the first calorimeter.

After the determination of the heat capacity of the second calorimeter it was filled with small crystals of Rochelle salt and about 120 measurements made. They are plotted in Fig. 3. Space does not permit publishing tables of the measurements. Except in the neighborhood of −18° they are well represented by the straight line $C_p = 1.289 + 0.0034t$. The mean deviation of points

[13] The values in reference (9) are about 0.2 percent low. After it was published it was found that the Leeds & Northrup volt box used had a ratio of about 25.047 : 1 instead of 25.000 : 1 as it should have had. The correction, but not the reason for it, is mentioned in reference (10).
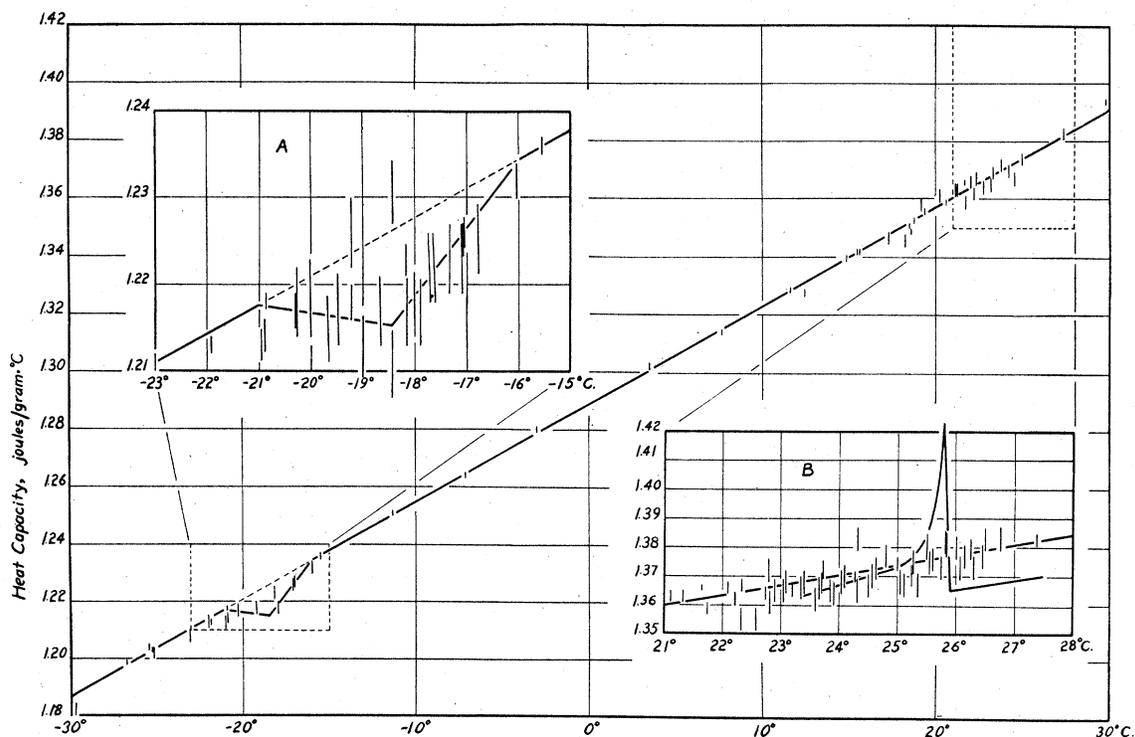
FIG. 3. Heat capacity of the small crystals of Rochelle salt in the range −30 to +30°C.

with temperature intervals of 3° or more from this line is 0.1 percent; the mean deviation of all points is 0.3 percent.

The points near −18° are plotted to a larger scale in inset A of the figure. There is a strong suggestion of an anomaly of amplitude somewhat less than 1 percent. It is of the right sign and order of magnitude to agree with the theory mentioned in the introduction but the uncertainties in C_p and $\partial P^2/\partial t$ are large enough to make closer comparison pointless.

The temperature range +22° to +27° was investigated very carefully in a search for the anomaly reported by Kobeko and Nelidow and by Rusterholz. Over 50 measurements were made in this region, most of them with a temperature interval of less than 0.3°. No anomaly was found and it is considered likely that any which may be present has an amplitude less than 1 percent and probably less than $\frac{1}{2}$ percent. Theory does not suggest a larger one. The measurements are plotted in inset B, Fig. 3. Rusterholz' curve is superposed for comparison.

The absolute value of the heat capacity found agrees within $\frac{1}{2}$ percent with that found by Kobeko and Nelidow and is about 11 percent smaller than that found by Rusterholz. The large anomaly found by him and by Kobeko and Nelidow would seem to indicate some difference in the properties of Rochelle salt of European and American origin. The differences in absolute value may reasonably be attributed to the method used by Rusterholz. It is perhaps worth mentioning that this work was undertaken in the expectation of finding anomalies as large as those previously reported and that the size to be expected from the theory was not worked out until after measurements at the upper Curie point had shown no appreciable anomaly.

Finally, to show that the apparatus was capable of producing something other than a linear variation of heat capacity with temperature, a magnetic substance containing manganese and arsenic was prepared by heating the powdered metals together at about 700°C. After treatment intended to purify it the substance was put in

the calorimeter and measurements made. They are not included in this paper as it cannot be seriously considered that they represent the temperature variation of the heat capacity of any definite manganese-arsenic compound. They do show, however, a rise to a maximum at about 41.5°C and a rather rapid falling off which is roughly the behavior that Rochelle salt was expected to show.

DISCUSSION OF ERRORS

The errors in the measurements are chiefly of two kinds. The first kind ("systematic") affects all measurements made at a given temperature to the same extent and in the same direction; the second ("accidental") introduces a random scattering. The systematic errors are not affected by the temperature interval used in making a measurement; the accidental errors are more or less inversely proportional to it. When the temperature derivative of the heat capacity does not change rapidly with temperature, the accidental errors may be made small by using large temperature intervals, but small intervals must be used in searching for anomalies near the Curie points.

The vertical lines used in Figs. 2 and 3 to represent the measurements are of lengths intended to cover the "probable" accidental error.

(a) Systematic errors

(i) The calibration of the electrical instruments and stop watch and the measurement of the mass of the salt were done with care that the error introduced by each be not much over 0.01 percent. The total, if all errors affect the result in the same direction, is about 0.1 percent.

(ii) The heat capacity of the second calorimeter was not measured at low temperatures, but measurements made between 18° and 33° were extrapolated parallel to the heat capacity curve of the first calorimeter. It was intended at first to use it only for looking for anomalies near the Curie points and for this use the absolute value of its heat capacity was not important. As the curve is nearly a straight line, the error is probably not much over 0.1 percent at any temperature and vanishes above 18°.

(iii) Non-uniformity of the bath temperature can introduce error if the temperature difference between the position of the thermometer and the position of the jacket junctions of the thermocouples varies systematically with temperature. A constant difference of any amount compatible with the small size of the differences found when the bath was tested with a differential thermocouple would have no appreciable effect. The error from any variation is difficult to estimate but it seems unlikely that it was more than 0.1 percent.

(b) Accidental errors

The errors estimated below are those in measurements made with the second calorimeter. Because of the high heat capacity of the first the errors in measurements made with it are about twice as great.

(i) The smallest division on the platinum thermometer bridge was 0.0001 ohm, the smallest division read on the potentiometer was 0.0001 volt and there was probably a variation of about 0.2 of a second in the times of opening and closing switches. These sources introduce accidental errors totaling 0.1 percent into the measurements made with large temperature intervals ($\sim 4°$), 0.6 percent into those made with small ($\sim \frac{1}{4}°$).

(ii) The thermocouple reading could not be kept exactly zero during a measurement. The deflection varied from + to − more or less at random but was rarely more than 0.005°. One may perhaps assume that the effective uncompensated difference in temperature was about 0.002°. A difference of this amount would introduce an error of somewhat less than 0.1 percent in measurements made with large temperature intervals, 0.2 to 0.3 percent in those made with small.

(c) Possible error caused by heat transfer between jacket and calorimeter

One error caused by heat transfer has already been discussed. It is possible, however, that heat transfer could take place even when the differential thermocouple indicated zero. If the transfer is proportional to the rate at which the

calorimeter is heated, it is included in the heat capacity of the empty calorimeter in such a way that it is eliminated in the heat capacity of the salt. If it is independent of the rate of heating the calorimeter, it affects the heat capacity of the salt to an extent depending on the difference between the rate of heating when determining the heat capacity of the empty calorimeter and when determining that of the salt. From observations of the rate of change of temperature of the calorimeter when it was not being heated, it is estimated that the error from this source does not exceed 0.05 percent in measurements made with large temperature intervals, 0.2 percent in those made with small.

It is of some interest to compare the sum of the calculated accidental errors with the mean deviation of the measurements from the straight lines chosen to represent the heat capacities:

	Calculated error	Mean deviation
First calorimeter.		
2° to 4° interval	0.4 percent	0.2 percent
1° interval	1.0 percent	0.3 percent
Second calorimeter.		
3° to 4.5° interval	0.2 percent	0.1 percent
0.2° to 0.5° interval	0.8 percent	0.4 percent

The mean deviations are about half the calculated errors.

ACKNOWLEDGMENTS

Note on the Evaluation of the Earth's Temperatures Arising from Radioactivity*

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IN a previous paper,[1] it was shown that the contribution to the temperatures of the earth, arising from radioactivity, is given by

$$T(r, t) = \frac{2R^3}{\pi^2 K r} \sum_{s=1}^{\infty} \frac{1}{s^2} \sin \frac{s\pi r}{R} \int_0^1 x\phi(Rx)$$

$$\times \sin s\pi x dx - \frac{2R^3}{\pi^2 K r} \sum_{s=1}^{\infty} e^{-s^2 c} \frac{1}{s^2}$$

$$\times \sin \frac{s\pi r}{R} \int_0^1 x\phi(Rx) \sin s\pi x dx$$

$$= T_1(r) - T_2(r, t) \tag{1}$$

[1] A. N. Lowan, Phys. Rev. 44, 769 (1933). This paper will be referred to as A.N.L.

where R is the radius of the earth; r the distance from center; t the time in seconds; K the thermal conductivity in c.g.s. units; k the thermal diffusivity in c.g.s. units; $c = k\pi^2 t/R^2$; and $\phi(r) =$ the heat generated in calories per unit volume per unit time.

It is clear that $T_1(r)$ represents the distribution of temperatures corresponding to the steady state. Accordingly, $T_1(r)$ may be obtained by dropping the term $\partial T(r, t)/\partial t$ in the differential equation of heat conduction, satisfied by $T(r, t)$. Thus, $T_1(r)$ must satisfy the differential equation

$$(\partial/\partial r^2 + 2/r \cdot \partial/\partial r) T_1(r) = -\phi(r) \tag{2}$$

and the boundary condition

$$T_1(R) = 0. \tag{3}$$