THERMOMETRIC LAG

By D. R. Harper 3d

CONTENTS

INTRODUCTION

When a thermometer is immersed in a warmer or in a cooler medium for the purpose of ascertaining the temperature of the latter, it does not immediately indicate this temperature but exhibits a time lag in reaching it. A certain time must elapse after immersion before the reading is correct to within 0°1, still longer before correct within 0°01, etc., when the temperature of the medium remains constant. If the latter be varying, the thermometer follows the variation in a definite way, maintaining a difference which may be large or small, according to the rate of the variation and the form of the thermometer.

It therefore becomes necessary under some conditions to apply a correction to a thermometer reading[1] in order to obtain the simultaneous value of the temperature of the medium in which it is immersed. Thiesen[2] in his elaborate treatise on thermometry devotes a section to the consideration of lag, and Guillaume[3] also, under the title of "Défaut de Sensibilité." Neither of these chapters conveys an adequate impression of the variation of the lag of a particular thermometer under different conditions of immersion, namely, nature of medium and rate at which it is stirred. Also electrical thermometers, thermoelectric and resistance, were not in use as precision instruments when these papers were published and are, of course, not considered. It has, therefore, seemed advisable to prepare a paper supplying some of these omissions, and in so doing to incorporate as much of the general theory as seems necessary for full comprehension of the subject.

I. THE LAG OF A MERCURIAL THERMOMETER

FUNDAMENTAL CONSIDERATIONS

The transfer of heat between a thermometer bulb and the medium in which it is immersed may be expressed in the form usually referred to as "Newton's law of cooling," namely, the rate of heat transfer directly proportional to the difference of temperature between the two. While direct experimental test of this fundamental assumption is difficult, it is very easy to test many of the equations deduced from it, some of which are so closely related to the parent equation that the test possesses all the force of a direct one. For the ordinary or "chemical" form of mercurial thermometer, the agreement between theory and experiment amply justifies the assumption, which analytically expressed is

---

[1] Throughout this paper the assumption is tacitly made, except where explicitly stated to the contrary, that all instrumental errors have been corrected for, i. e., calibration of bore, zero error, etc.

[2] Thiesen: Metronomische Beitrage, No. 3, p. 13; 1881.

[3] Guillaume: Thermometrie de Precision, p. 184; 1889.

$$\frac{\partial\theta}{\partial t}=\frac{1}{\lambda}(u-\theta) \qquad (1)$$

where u = temperature of bath at instant t.

θ = temperature of thermometer at same instant.

λ = constant with respect to u, θ, or t.

The temperature of the bath, u, is assumed to be uniform throughout the neighborhood of the thermometer. No other case would be simple enough for convenient mathematical treatment. The temperature of the thermometer, θ, is the integrated or average temperature on which depends the average density of the thermometric liquid and the volume of the envelope. It defines the position of the meniscus in the capillary, i. e., the reading of the thermometer. λ requires no further definition at present than the placing of the limitation that it shall be independent of θ, u, and t. It will be found to be not independent of form of thermometer, medium surrounding latter, conditions of stirring, etc., a variation of a kind to be carefully distinguished from that denied to it in integrating equation (1).

Integration of (1) leads to relations between quantities all of which may be readily found by direct experiment, serving as a criterion of the validity of the assumption. For the ordinary form of thermometer a numerical value for λ, constant for a particular thermometer in any one medium stirred at a certain rate, may be found and used in applying corrections to any readings made under the same conditions, whenever a lag correction is necessary. For some forms of thermometer, e. g., those having a layer of air separating part of the bulb from the bath, the simple theory employing equation (1) fails.[4] If we endeavor to find numerical values for λ for such a thermometer by the equations deduced from (1), we are led to the conclusion that no single value is obtainable; the various values that might be computed from a few points on a curve of observations will differ according to the temperature or time corresponding to the points chosen. This is inconsistent with the limitation placed on λ in

---

[4] Thiesen, loc. cit.

deducing the equations, nullifying the whole theory for application to such an instrument. Modification of equation (1) by the introduction of additional assumptions leads to a treatment that is satisfactory for some such forms of thermometer; for instance, a calorimetric Beckmann, which has a considerable portion of its mercury in a large inclosed capillary, between the bulb and the fine capillary. (See Sec. II.)

PHYSICAL MEANING OF λ

Physical interpretation of the quantity λ is highly desirable. This is obtained from the equations (see pp. 664–665), but it may be well to anticipate slightly and give two such interpretations at this point. From the fundamental equation, which serves as the definition of λ,

$$\frac{\partial \theta}{\partial t} = \frac{1}{\lambda}(u - \theta) \tag{1}$$

it is seen by inspection that λ has the dimensions of time. Later equations give the following interpretations as a definite number of seconds:

(1) If a thermometer has been immersed for a long time in a bath whose temperature is rising at uniform rate, λ *is the number of seconds between the time when the bath attains any given temperature and the time when the thermometer indicates this temperature.* In other words, it is the number of seconds the thermometer "lags" behind such a temperature.

(2) If a thermometer be plunged into a bath maintained at a constant temperature (the thermometer being initially at a different temperature), λ *is the number of seconds in which the difference between the thermometer reading and the bath temperature is reduced to* ϵ^{-1} *times its initial value.*[5]

FALLING MENISCUS

Considerable attention has been paid to the lag of a thermometer when its temperature is decreasing,[6] and the results published seem liable to misinterpretation. Without entering the very dif-

---

[5] $\epsilon^{-1} = \frac{1}{2.718} = 0.4$, approximately.

[6] Thiesen, loc. cit.; Guillaume, loc. cit.

ficult field of analysis of the surface tension and capillary forces governing the motion of the meniscus, it is sufficient to point out that with falling temperatures one may observe sticking of the meniscus and even separation of the mercury column, indicating that there is no certainty that the forces tending to return mercury to the bulb accomplish the return at a rate proportional to the rate at which the transfer of heat from the bulb takes place. The usual equations of lag, being primarily equations of heat transfer, must not, therefore, be expected to cover all cases of falling meniscus. If a thermometer is plunged into a bath much cooler than itself, the drop of the meniscus is apt to be so erratic that a computation of the lag by the usual methods results in values widely variable under exactly the same conditions and oftentimes quite different from the lag measured with a rising meniscus. The pseudo λ so obtained may or may not be related to the temperature lag of the bulb, and as the conditions are impossible of specification the values thus determined fail of interpretation.

Because of the sticking of the meniscus and possible separation of the mercury column, the readings of a mercury thermometer with falling temperatures are less reliable than with rising ones, and in precision thermometry a falling temperature should be avoided whenever possible. When its use is unavoidable the difficulties are overcome to a considerable extent, in the case of a small rate of fall, by subjecting the thermometer to a series of rapid jars, as by an electric buzzer. There seems to be every reason for believing that under such conditions the position of the meniscus depends on the temperature of the bulb in the same relation as when the meniscus is rising, and the lag corrections to be applied may be computed from the value of λ determined with rising meniscus, for the medium and rate of stirring employed.

PRINCIPAL EQUATIONS

The fundamental equation

$$\frac{\partial\theta}{\partial t}=\frac{1}{\lambda}(u-\theta) \tag{1}$$

suffices to determine the function u if the function θ be known, since $\frac{\partial \theta}{\partial t}$ may at once be determined. The converse problem of determining θ when u is known requires solution of the differential equation.

Solving $\lambda\frac{d\theta}{dt}+\theta=u$ under the conditions that the thermometer reads θ_0 at the time $t=0$, in a medium at temperature u_0; the reading θ at any time t when the medium is at temperature u, is

$$\theta=\theta_0\epsilon^{-\frac{1}{\lambda}t}+\frac{1}{\lambda}\epsilon^{-\frac{1}{\lambda}t}\int_0^t u\epsilon^{\frac{1}{\lambda}t}dt \tag{2}$$

An integration by parts puts this equation in a form showing directly the temperature difference, $\theta-u$.

$$\theta-u=(\theta_0-u_0)\epsilon^{-\frac{1}{\lambda}t}-\epsilon^{-\frac{1}{\lambda}t}\int_0^t\frac{\partial u}{\partial t}\epsilon^{\frac{1}{\lambda}t}dt \tag{3}$$

From this equation the solution for special cases is obtained upon substituting the proper expression for $\frac{\partial u}{\partial t}$. The cases of most importance are (a) constant temperature $u=u_0$; (b) linear rise, $u=u_0+rt$, usually at small rate, r; (c) exponential change of temperature according to formula $u=A+B\epsilon^{\alpha t}$, the constant α being usually small.[7]

(a) When $u=u_0$, $\frac{\partial u}{\partial t}=0$

and equation (3) reduces to

$$(\theta-u_0)=(\theta_0-u_0)\epsilon^{-\frac{1}{\lambda}t} \tag{4}$$

Equation (4) states that an initial temperature difference (θ_0-u_0), between a thermometer and a constant-temperature bath in which it is immersed, decreases logarithmically with time, becoming in λ seconds, ϵ^{-1} times the original difference. From the approximate values, $\epsilon^{-7}=.001$ and $\epsilon^{-9}=.0001$, it will be seen

---

[7] The frequent occurrence of the conditions (a) and (b) is evident. The importance of (c) lies in the fact that whenever one body is exchanging heat with another according to Newton's law, its temperature is expressed by the exponential equation given. When α is very small, nearly always true in calorimetry for instance, the curvature of this exponential function may be so slight that only where high precision is sought need any account be taken of its departure from a linear function (case b)

that times of 7λ and 9λ seconds elapse before a difference of 10° is reduced to 0°.01 and 0°.001, respectively.

(b) $u = u_0 + rt$. —The value of $\frac{\partial u}{\partial t}$ is r, which is to be substituted in equation (3). Reduction and collection of terms gives the relation

$$\theta - u = -r\lambda + (\theta_0 - u_0 + r\lambda)\epsilon^{-\frac{1}{\lambda}t} \qquad (5)$$

The interpretation of equation (5) is very simple, except the exponential term. Consideration of the numerical values which enter will show that this term is usually negligible. From two to six seconds, according to the size of bulb, is the value of λ for an ordinary thermometer in water stirred rather vigorously. Taking, as a mean, four seconds for substitution in the term $\epsilon^{-\frac{1}{\lambda}t}$, the value, for $t =$ one minute, is ϵ^{-15}, about 3×10^{-7}. This multiplies a term $(\theta_0 - u_0 + r\lambda)$ not very large, so the product is insignificant. Accordingly, with a value of λ of four seconds or that order of magnitude, the lag of a thermometer, immersed in a bath the temperature of which is increasing at a constant rate r, is represented less than a minute after immersion, by the equation.

$$\theta - u = -r\lambda \qquad (6)$$

A constant difference of temperature, numerically $r\lambda$ thus exists between the thermometer and the bath. Both rise at the rate r, so that in λ seconds either one increases its temperature by $r\lambda$. Accordingly, λ seconds after the bath attains a given temperature, the same is indicated by the thermometer.

The application of equation (6) to numerical examples will illustrate the magnitude of the corrections necessary for lag in applied thermometry. For a rate of rise of 0°.03 per minute, perhaps the maximum allowable when readings to single thousandths of a degree are taken, the lag correction to any reading if $\lambda = 4$ seconds is +0°.002.

Care must be taken in the application of equations (5) and (6) to any case where λ is large, e. g., in still air, where the value of λ may be 50 to 100 times the value for the same thermometer in stirred water. Computation in this case requires consideration of the term $\epsilon^{-\frac{1}{\lambda}}$, which becomes very small only after a rather long time elapses.

(c) EXPONENTIAL CHANGE OF TEMPERATURE $u=A+B\epsilon^{-at}$.—Before proceeding to the solution for this case, it may be well to give an example of its occurrence and the interpretation of the symbols.

Let a calorimeter, whose temperature may be designated u, be exchanging heat with surroundings at constant temperature A according to Newton's law,

$$\frac{du}{dt}=-\alpha(u-A).$$

the solution of which is $u-A=B\epsilon^{-at}$, the equation written above. B is the initial value of $u-A$, i. e., the value of the temperature difference between the calorimeter and its surrounding at any arbitrary time at which we may choose to start applying the equation. Instead of B, therefore, may be introduced another constant, u_0, which, if defined as the value of u for the time zero, will be in harmony with all the foregoing equations and permit of using them.

If $u=A+B\epsilon^{-at}$; $u_0=A+B$, $u-A=(u_0-A)\epsilon^{-at}$.

Substituting the value of $\frac{\partial u}{\partial t}$, namely, $-\alpha(u_0-A)\epsilon^{-at}$ in equation (3) and collecting

$$\theta-u=\left(\theta_0+\frac{\alpha\lambda A-u_0}{1-\alpha\lambda}\right)\epsilon^{-\frac{1}{\lambda}t}+\frac{\alpha\lambda}{1-\alpha\lambda}(u-A). \qquad (7)$$

Every term in the coefficient of the exponential is a constant, so that some value of t can be found, after which the term will be negligible to any required order. For the values of α, λ, A, and u_0 commonly met with in practice, this time is comparatively short. The "steady state" is then said to be established, and the behavior of the thermometer is given by

$$\theta-u=\frac{\alpha\lambda}{1-\alpha\lambda}(u-A). \qquad (8)$$

The difference $(\theta - u)$ is, therefore, dependent on u; but when α is quite small, the change, with time, in u is small and $u-A$ is almost constant. The temperature of the thermometer then follows that of the bath in a manner almost similar to that expressed by equation (6), namely, with a constant difference.[8]

METHODS OF DETERMINING λ

The equations of which the derivations and applications have just been discussed may be easily transformed into some which can be conveniently employed in the determination of λ.

Absolute Determination.[9]—Equation (4) may be written in the form

$$\frac{\theta_o - u_o}{\theta - u_o} = \epsilon^{\frac{1}{\lambda}t}$$

which, in logarithmic form, is

$$\lambda = \frac{t}{\log \dfrac{\theta_o - u_o}{\theta - u_o}} \tag{9}$$

This linear relation between time and logarithm of temperature differences is very convenient in getting the best mean value from a large number of readings of θ and t, because a graphical plot (time against logarithms of temperature difference) should be a straight line of slope λ.

The experimental details for carrying out the determination are simple. The thermometer is cooled and plunged into a bath

---

[8] From the expansion $\epsilon^{-at} = \left(1-at+\frac{(at)^2}{2}-\ldots\right)$, one can conveniently study the function for values of t less than $1/a$. The expression for u is

$$u=A+B\left(1-at+\frac{(at)^2}{2}-\ldots\right)$$

If the precision of the work in hand permit of neglecting at with respect to unity we have $u=A+B$, or the change in u is insignificant during the time t considered.

If at be appreciable, but its square and higher powers are negligible, we have $u=A+B\,(1-at)=(A+B)-aBt$, which is the linear change $u=u_o+\gamma t$.

Calorimetric work, generally speaking, never permits of neglecting the first power. Ordinary work does permit of neglecting the second and higher powers and the temperature changes, which are really logarithmic, are treated as linear. Precision work requires retention of at least one more term in the series and it may be as convenient to keep the exponential as such as to employ a quadratic expansion for it.

[9] Method given here is the classical procedure, described by Thiesen, Guillaume, and others.

which is stirred at the desired rate, and maintained at constant temperature throughout the experiment. This condition may be secured by the use of a bath of large heat capacity and at room temperature. As the meniscus of the thermometer rises, the times of passing chosen graduations are read off on a watch or recorded on a chronograph. The later thermometer readings serve to give the bath temperature u_0. Any reading may be taken as θ_0 and time reckoned from that of this reading. Corresponding to each reading θ, a value of $\log \frac{\theta_0 - u_0}{\theta - u_0}$ is computed and plotted against time. The slope of the best mean straight line is the numerical value of λ. If logarithms to base 10 instead of the base ϵ be used, the modulus must be taken account of in computing the slope.

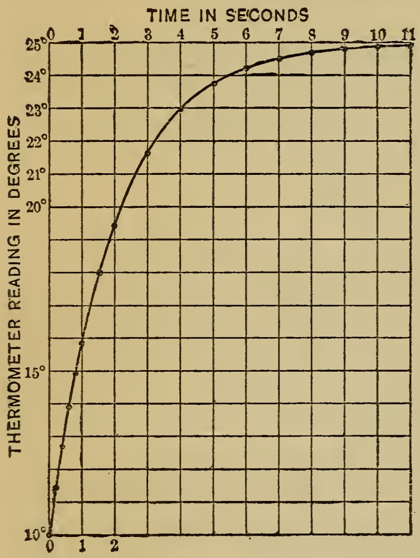

Fig. 1.—*Rise of thermometer cooled below 10° and plunged into bath maintained at 25° (for λ=2 seconds)*

The chronograph should be employed if the λ to be determined is small. Fig. 1 illustrates the rate at which the meniscus of a thermometer rises from 10° to 25° for λ = 2 seconds (small bulb chemical thermometer in well-stirred water). It makes evident the desirability of securing time readings to a fraction of a second.

The agreement of results in a well-stirred water bath when a chronograph is employed has been found to be well within 5 per cent. Observations taken with a watch depart from a straight line, on a logarithmic plot, to an extent making it difficult to determine the slope within this limit of certainty.

Departures of points either side of a straight line (logarithmic plot) in an irregular fashion, indicate the degree of experimental error in making readings, but departures in the nature of a consistent curvature are a warning that the thermometer is one to which the equations just deduced should not be applied other than as first approximations. Slight curvature may be considered to define limits between which lies a mean value that may be used as λ in the equations above, for the approximate computation of lag corrections to readings. Additional assumptions, modifying equation (1), lead to a more perfect representation of the behavior of many such thermometers. (See Sec. II.)

Relative Determinations.—The difference in the values of λ for two thermometers, under the same conditions, can be obtained in a bath whose temperature is uniform and rising linearly. If one be known under the conditions of the intercomparison, the value of the other is thus obtained.

Applying equation (6) to two thermometers read at the same instant

$$\theta_1 - u = -r\lambda_1; \quad \theta_2 - u = -r\lambda_2$$

Subtracting

$$\theta_2 - \theta_1 = -r(\lambda_2 - \lambda_1) \qquad (10)$$

$$\lambda_2 - \lambda_1 = \frac{1}{r}(\theta_1 - \theta_2) \qquad (11)$$

The rate of rise, r, is the same for both thermometers and for the bath (p. 665), and therefore readily determined by observing the progress of either thermometer. The difference $(\theta_1 - \theta_2)$[10] at any

---

[10] θ_1, θ_2, refer here, as elsewhere, to readings corrected for bore, zero error, etc.; i. e., assume a perfect thermometer. Since $\theta_1 - \theta_2$ is generally small and since only the comparative instrumental correction is required, much greater precision can be obtained by direct comparison of the thermometers at the time of the experiment for lag, than by the use of tables of corrections pertaining to the instruments individually.

Convenient procedure is to carry out the lag experiment with the required rate of rise of temperature, and then so diminish the supply of heat to the bath employed that the condition of constant temperature is as nearly attained as may conveniently be, and intercompare the thermometers. The departure from constancy of temperature must be in the direction of a slow rise, never a fall, because the sticking of a falling meniscus vitiates thermometer comparisons.

The working equations will be:

Let θ=reading of thermometer if "perfect."
R=observed reading.
ε=correction for all instrumental errors.

$$\theta_1 - \theta_2 = (R_1 + \varepsilon_1) - (R_2 + \varepsilon_2)$$

so that equation (11) is used in form

$$\lambda_2 - \lambda_1 = \frac{1}{r}[(R_1 - R_2) + (\varepsilon_1 - \varepsilon_2)]$$

where $\varepsilon_1 - \varepsilon_2$ is determined directly from the mean of a number of pairs of readings taken in the inter comparison at a very small rate r. Designating such readings with primes, equation (10) is

$$(R'_2 + \varepsilon_2) - (R'_1 + \varepsilon_1) = 0$$

or

$$\varepsilon_1 - \varepsilon_2 = R'_2 - R'_1$$

because when r is small enough, no matter what λ_1, λ_2, may be, the term $r(\lambda_2 - \lambda_1)$ may be neglected.

instant may be repeatedly obtained to give a reliable mean, and if λ_1 be known the data suffices to give λ_2 with the simplest of computations. λ_1 may be known by a previous application of the method described on p. 667, or it may be computable from other constants of the thermometer (e. g., see Section III on platinum resistance thermometers).

Frequently λ_1 may be neglected, and the method becomes an approximate absolute one for "slow" thermometers and more convenient than the other. For example, if the result of an experiment gives $\lambda_2 - \lambda_1 = 30$ seconds, and λ_1 is surely less than 3 seconds, λ_2 is determined to be 30 seconds (± the experimental error) within 10 per cent. A little familiarity with thermometers and their behavior in baths stirred at various rates enables one to place by inspection an upper limit for λ for many forms of thermometers and thus apply the method just described to "slow" thermometers.

Illustrative Values of λ.—To illustrate the concordance of both final results and the individual readings pertaining to a single result, a short series of experiments performed in vigorously stirred water is tabulated in Table I and plotted on Fig. 2. The method employed was the logarithmic one described on page 667 et seq.

TABLE I

Date	Thermometer number	Brief description of same	Lag in well-stirred water
1909			Sec.
Aug. 30	Chabaud, 77874	0°–50° thermometer divided in 0°.1 (1° about 6.6 mm long). Convenient to read 0°.01. Bulb approximately 4.5 mm diameter and 25 mm long.	2.00 2.13 2.15
Do.	Golaz, 4192	Open-scale calorimetric thermometer divided in 0°.02 (1° about 31 mm long). Convenient to read 0°.001. Bulb approximately 9 mm diameter and 52 mm long.	4.82 4.95 4.96 4.78
Do.	5951	"Einschlusz Faden." Bulb a long narrow thread of mercury, 100 mm × 2.5 mm (diameter) surrounded by an air space of about 3 mm, outer envelope of glass approximately 8 mm in diameter inclosing the whole.	52
Do.	1787	Callendar type platinum resistance thermometer. Fine platinum wire coil wound on a cross of sheet mica and inclosed in a porcelain tube about 30 cm long, 1 cm diameter, and 0.15 cm thick.	15.3 15.7

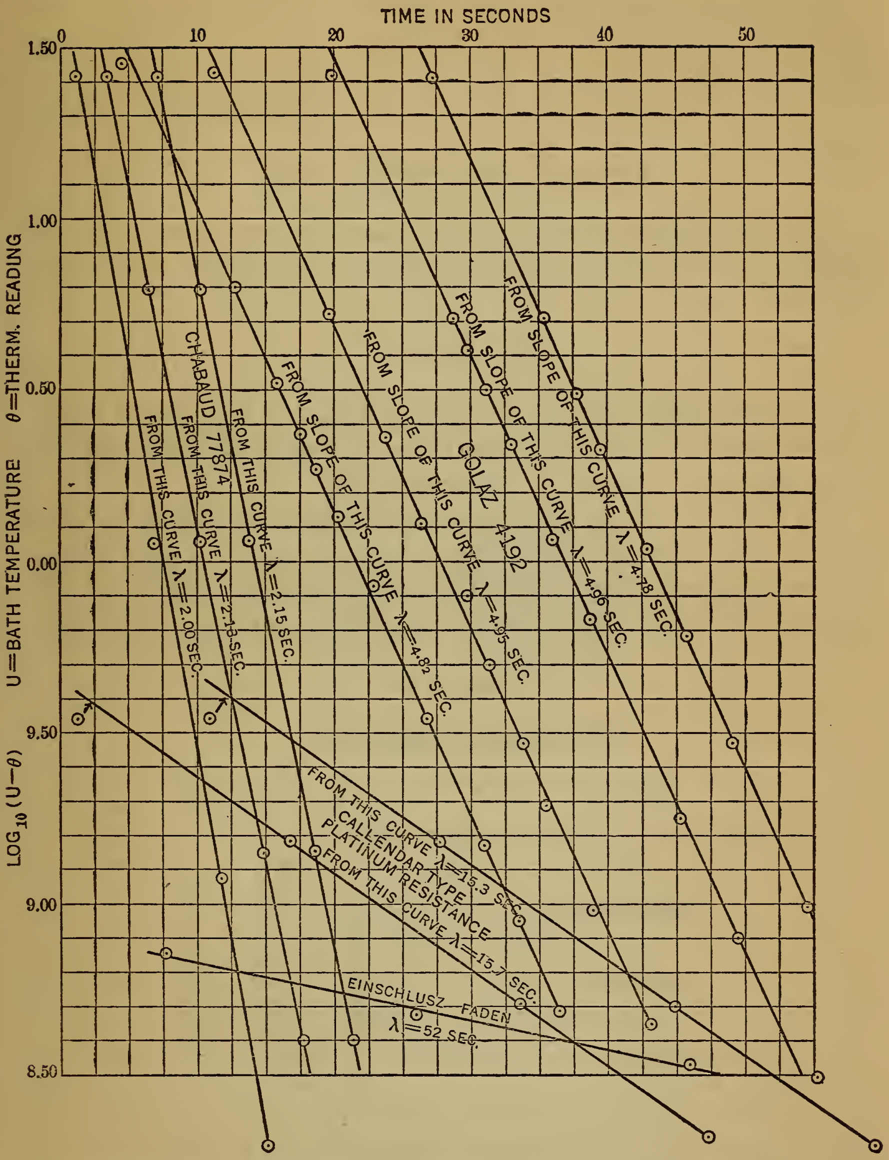

Fig. 2.—*Typical curves obtained in determining* λ (*vigorously stirred water*). *To illustrate degree of concordance obtained for individual readings forming one determination; and also for slopes of the several determinations with a given thermometer*

A brief description of the thermometers is included, giving an idea of the value of λ for different types. The lag of a platinum resistance thermometer of the Callendar type is tabulated with those of the mercurial instruments to show its comparative magnitude.

VARIATION OF λ WITH STIRRING

With a given thermometer of the usual type in a given medium stirred at a certain rate, a definite numerical value for λ in the equation (1)

$$\frac{\partial\theta}{\partial t}=\frac{1}{\lambda}(u-\theta)$$

may be found and applied in this equation, or integrated forms deduced from it. But this same value of λ must not be employed if the medium be stirred at a different rate.

Lag in Water.—As an interesting example arising under conditions of use, the following values were measured in a calorimeter with a propeller stirrer rotated as slowly and as rapidly as the convenience of the calorimeter stirring arrangement would permit.

TABLE II

Thermometer Golaz 4191

	λ	Mean λ
	Sec.	Sec.
Vigorous stirring	4.22 4.34 4.42	4.3
Slow stirring	6.46 6.40 6.57	6.5
No stirring	15.5 14.5 14	14.5

An increase of 50 per cent in the value of λ is thus observed upon decreasing from the normal vigorous stirring of calorimetric use to a propeller speed of one-third the normal. Such an experiment gives no definite relations, however, because the velocity of flow past the thermometer bulb is not known. Accordingly, a special apparatus was assembled in which the velocity of flow could be measured. The schematic drawing, Fig. 3, renders description unnecessary.

The velocity of the current of water past the thermometer bulb was computed from the quantity of water delivered in a definite time and the area of the annular space $\left[\frac{\pi}{4}(\overline{1.19^2}-\overline{0.54^2})=0.88_3\text{cm}^2\right]$ between the thermometer bulb and the surrounding glass tube.

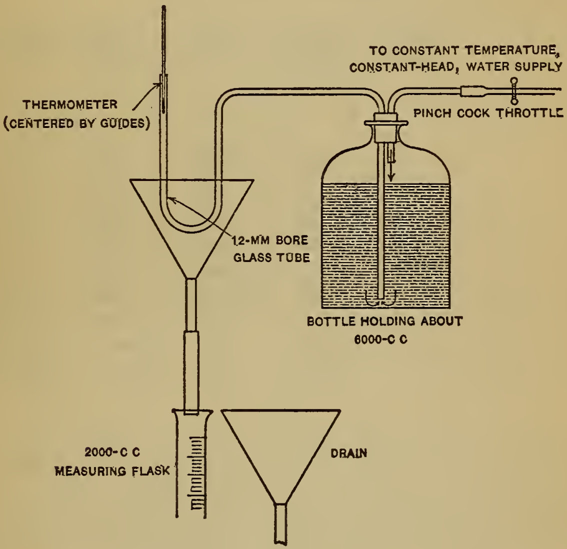

Fig. 3.—*Apparatus for determining lag of thermometer in a stream of liquid flowing at a definite rate*

This does not take account of the "drag" near the walls, but the nature of the problem in hand does not warrant such refinement.

With the stream flowing at the desired rate, and its temperature that of the room (between 30° and 35°) the thermometer was cooled in ice and dropped into place in the tube, centering by guides. As the meniscus passed appropriate graduations between 10° and room temperature the observer made a record chronographically. This was repeated several times for each velocity tested. The results are summarized in the accompanying Table

III and plotted on Fig. 4. The method of computing results was the logarithmic plot method described on page 667, and the individual points lie on a straight line very closely. The results of the several determinations at each rate of stirring are in good agreement, as shown by the table.

TABLE III

Value of λ for Various Velocities of Water Flow Past Bulb (in Apparatus of Fig. 3)

Thermometer Chabaud 80659

Date	Experiments	Mean flow cc per sec.	Av. dev. from mean	Velocity cm per sec.	Mean λ sec.	Av. dev. from mean
1911						
July 13	4	0.62	$\pm 0.01_5$	**0.70**	**5.6**	$\pm 0.1_9$
Do	4	1.14	0.01_6	**1.28**	**4.6**	0.1_6
Do	4	1.6_7	0.01_8	**1.9_0**	**4.2**	0.1_3
Do	6	1.8_7	0.02	**2.1**	**4.1**	0.0_4
Do	5	3.3	(1 obs.)	**3.8**	**3.5_4**	0.0_5
July 6	4	4.9	(1 obs.)	**5.5**	**3.2_4**	0.0_5
July 13	6	5.3	0.0 (2 obs.)	**6.0**	**3.22**	0.04
July 6	5	9.6	0.1	**10.9**	**2.89**	0.03
Do	6	$20._9$	0.2	**$23._6$**	**2.59**	0.06
Do	5	$33._8$	0.1	**37**	**2.37**	0.02
Do	5	$40._0$	0.1	**45**	**2.41**	0.03

As the velocity decreased, the logarithmic plots curved a little, making accurate determination of λ impossible. It is to be noted, however, that considerable latitude in the value of λ (vertical displacement of a point) at the lower velocities would not greatly affect the shape of the curve.

For the determination of lag under conditions approximating infinite velocity the thermometer was plunged into steam and read as above described. The heat supplied instantaneously as steam condenses on the bulb maintains its surface at the temperature of the steam, less the drop through the layer of water formed there. The thickness of this, if uniformly distributed over the bulb, would be less than 0.05 mm at the conclusion of the experiment, a film of the order of one-tenth the thickness of the glass in the bulb. It may be concluded that the behavior of the thermometer under the conditions of this experiment is probably not very different

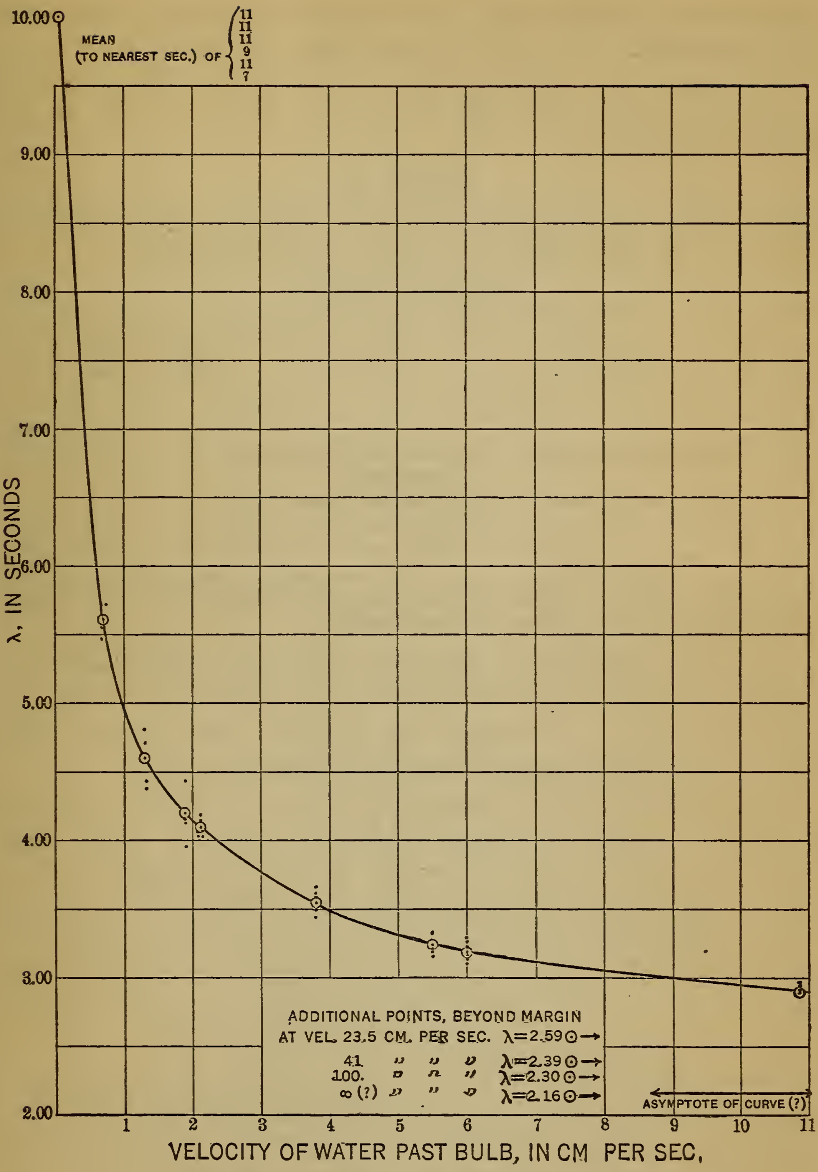

Fig. 4.—*Variation of λ with stirring*
Thermometer Chabaud 80659 in water

from what its behavior might be if an infinite supply of heat could be instantaneously brought to the surface of the bulb.[11]

The values of λ obtained in steam are given in Table IV. Here are also the values obtained in water at rest except for its own natural convection.

TABLE IV

Limiting Values of λ for Curve of Fig. 4 (Zero Velocity of Water Past Bulb; Infinite Velocity (?) of Any Medium Past Bulb)

Thermometer Chabaud 80659

Date	Immersion	Remarks	Experiments	Av. dev. from mean	Mean λ
1911					Sec
July 10...	Slightly superheated steam[12]..	Equivalent of infinite stirring (any medium)?	6	±0.04	2.16
Do...	Still water in calorimeter can..	Lag curves not straight lines. Cf. pp. 668-9.	3	0	11
July 13...	.....do......................	.....do......................	3	1	9

[12] Steam determinations in International Bureau form of steam-point apparatus (due to Chappuis). Pressure of steam about 5 mm of water in excess of atmosphere.

The determinations in unstirred water give wide latitude of variation, probably due to differences in convection currents. A mean value of λ of 10 seconds was obtained, using a large can of water at constant temperature as the immersion bath.

The minimum value of λ obtained in the experiments summarized in Table III being 2.4 seconds, it seemed desirable to test higher velocities and see whether the steam value of 2.2 seconds was more closely approached. Modifications of the apparatus for the purpose of securing a larger flow somewhat impaired the accuracy of measurement. One hundred cm per second was attained and the mean λ found was 2.3 seconds (the statement of a third figure not being warranted by the results).

LAG IN KEROSENE OIL.—On account of the great variation in the rate of change of the lag with the velocity as shown on Fig. 4, a short investigation with another liquid was undertaken to see

---

[11] If this be true, the λ determined in this way should be independent of the medium; i. e., a characteristic constant of the thermometer. Any other vapor of high latent heat should give the same result. An experiment in alcohol gave a value of λ (2.5— seconds) somewhat larger than in steam (2.2 seconds), being about equal to the λ found in water at the highest velocity measured with the apparatus of Fig. 3 (λ=2.4 seconds at 45 cm per second, Table III).

whether the same general form of curve (when the same units of measurement were employed) would be found. A kerosene oil was employed with the same thermometer and gave a very similar plot. As might be expected, the more viscous liquid gives a greater value of λ for a given velocity (Fig. 5). It must be noted that the values given were all obtained in one tube (internal bore 12 mm), and the question of change in the relations at that velocity where the flow through a tube changes from a steady drift to a turbulent motion, involving experiments in tubes of several sizes, would enter into a more complete study of the subject.

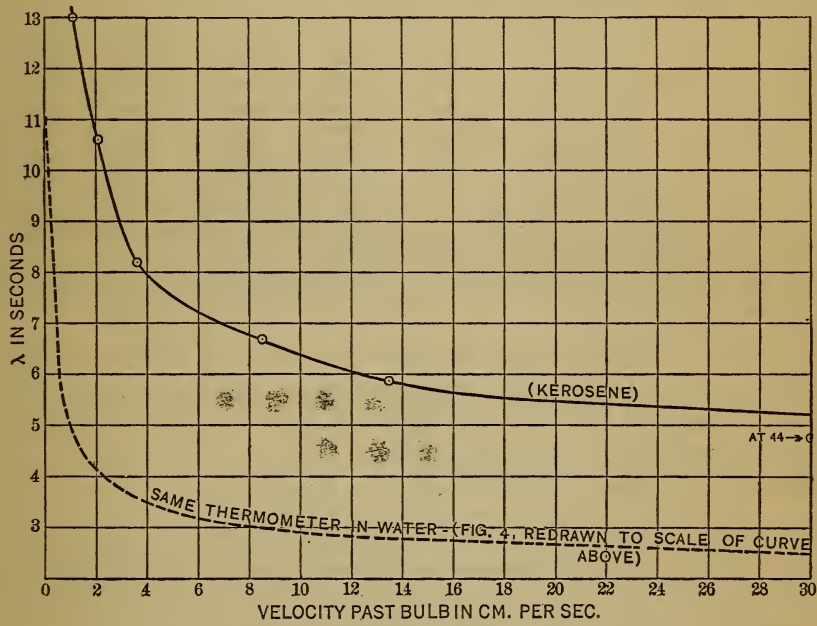

Fig. 5.—*Variation of* λ *with stirring*

Thermometer Chabaud 80659 in a kerosene oil

The data obtained for kerosene oil, including the density and viscosity of the oil at 20° C, are summarized in Table V, and the results plotted as Fig. 5. The discrepancies between individual observations are more likely due to lack of care in obtaining the data than inherent in the method or the heat-convecting properties of the oil. No great pains were taken concerning temperature regulation of oil, and the observations were taken more hastily than for the work in water, as an accuracy of 5 per cent seemed quite sufficient to illustrate what was desired. No observations are discarded in making Table V.

TABLE V

Lag of a Thermometer in Oil. (Apparatus of Fig. 3)

Thermometer Chabaud 80659

[Mixture of kerosene oils: Density, at 20° C, 0.870 g per cc; viscosity, at 20° C, 5° Engler,[13] equivalent to 0.31 dynes per cm^2]

Date	Experiments	Mean flow cc per sec.	Av. dev. from mean	Velocity cm per sec.	Mean λ	Av. dev. from mean
1911					Sec.	
Nov. 13	6	0	....	0	40-50	[14] (20)
Nov. 11	3	0.96	±0.04	1.08	13.0	0.1
Nov. 13	4	1.80	0.15	2.03	10.6	0.2
Nov. 11	4	3.2	0.15	3.6	8.2	0.0_5
Nov. 10	6	7.5	0.3_3	8.5	6.7	0.0_7
Nov. 11	4	11.9	0.2	13.5	5.9	0.0_7
Do	4	38	1.5	44	4.8	0.1_2

[13] A viscosity of 5° Engler means that a fluid of that viscosity runs through the efflux tube of an Engler viscosimeter at a rate one-fifth that for water at same temperature.

[14] Determinations of the lag in this oil unstirred showed large variation, owing probably to the relatively high viscosity of the oil interfering with convective interchange of heat between the liquid near the bulb and the mass of the liquid.

LAG OF A THERMOMETER IN AIR.[15]—The lag of a thermometer employed to measure the temperature of gas has considerable practical interest because it is great enough to affect the results quite appreciably. It is not, however, easy to make proper correction in the usual case, because the thermometer is subject to

---

[15] To this subject a large number of papers have been contributed, chiefly in the meteorological journals. Most of these must be characterized as little more than qualitative investigations, because the experimenters do not more closely specify the velocities employed than as "strong wind," "lightly moving wind," "quiet room," etc. The most complete quantitative papers are by Hergesell, Meteorologische Zeitschrift, **14** pp. 121 and 433, 1897. Simultaneously with this appeared the paper of J. Hartmann, Zeitschrift für Instrumentenkunde, **17**, p. 14 (1897), which is qualitative only.

Wilhelm Schmidt, Meteorologische Zeitschrift, **27**, p. 400 (1910), contributes data for over a dozen thermometers, mercurial, alcohol, toluene, and metallic expansion, under a variety of conditions, but without quantitative specification thereof.

de Quervain, in the same journal, **28**, p. 88 (1911), reviews previous work and deduces therefrom some formulæ for which it appears that he claims great generality. Certainly they are not universal in their application, for they fail to agree with the observed behavior of the thermometer used as an example in the present paper, a thermometer of the ordinary "chemical" type in a current of air. Brief reviews by de Quervain summarize the salient features from the following papers:

Dufour in 1864 (see Meteorologische Zeitschrift, **14** p. 276, 1897); Hartmann, loc. cit.; Hergesell, loc. cit.; Valentin, Meteorologische Zeitschrift, **18** p. 257, 1901; Maurer, ibid., **15** p. 182, 1898, **21** p. 489, 1904.

Rudel, in the same issue of the Meteorologische Zeitschrift, **28**, p. 90, 1911, gives the data for some thermometers and reviews the work of Krell, Zeitschrift für Heizung, Lüftung, und Beleuchtung, **11**, 1906–7.

Marvin, Monthly Weather Review, **27**, p. 458, 1899, gives some data pertaining to the lag of kite thermographs.

drafts of widely different velocities and no single value for λ holds for more than a few moments. To illustrate the magnitudes involved, it may be well to anticipate the data tabulated below and discuss the lag in air of the thermometer whose constants in water and oil have just been given. In still air the mean λ found was 190 seconds. The time of 7λ seconds for an initial difference of 10° between the thermometer and still air in which it might be immersed, to be reduced to 0°.01 (see p. 665) is accordingly over 20 minutes. The reading of a gas temperature to hundredths of a degree with a mercurial thermometer must therefore be undertaken with due lapse of time permitted after immersion. Then, too, in a space warming a degree in 15 minutes (if there be no drafts) the error in any reading of this thermometer after reaching the equilibrium state, would be over 0°.20. In the presence of drafts the numbers cited are considerably reduced, but they are worth consideration as examples of the error under the worst conditions.

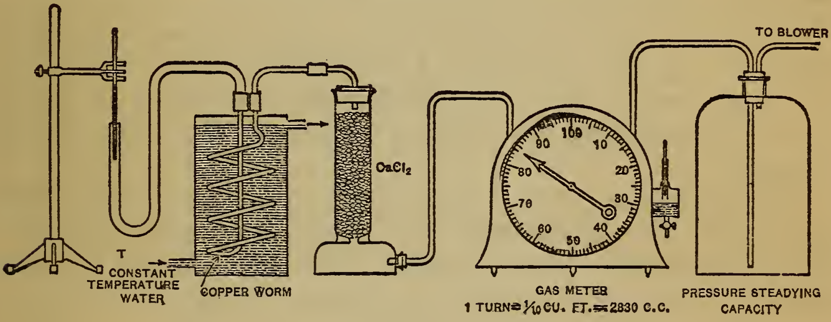

Fig. 6.—*Apparatus for determining lag of thermometer in a stream of gas flowing at a definite rate*

To study the variation of the lag with drafts in air, thermometer Chabaud No. 80659 was immersed in currents of various velocities in the same U tube as that employed for water and oil (Fig. 3). The current of air was measured by a gas meter in series with the tube. The area of the annular orifice past the thermometer being the same as for the experiments with water, the computation on page 673 of 1.13 cm/sec velocity for each cc per second current holds good here. The accuracy claimed for the tabulated velocities is but 5 per cent.

Since the wet meter raised the humidity of the air above the point where dew condensed on the thermometer bulb, when cooled sufficiently for the experiment, a drying tower of $CaCl_2$ was necessary. A copper worm in a thermostatic water bath was introduced to steady temperature fluctuations. The apparatus is shown diagrammatically in Fig. 6.

The resistance of the piping employed placed the upper limit, for the apparatus shown, at a current of about 90 cm per second. To obtain some points on the curve at higher velocity the apparatus was modified by substituting a dry meter, of larger capacity, dispensing with the drying tower and also the copper worm. With this arrangement, velocities up to 1000 cm per second were obtained. The value of λ of the thermometer is, at this velocity, 23 seconds, whence it appears that an almost inconceivably large velocity of gas past the bulb of a thermometer would be necessary to supply heat as fast as the surface can transmit it to the interior, corresponding to a value of 2.2 seconds for λ, the value in steam (p. 674).

The logarithmic method described on page 667 was modified slightly to a more convenient form to avoid plotting lines and computing logarithms. This is possible when the motion of the thermometer meniscus is comparatively slow throughout the scale; i. e., when λ is large. Every λ seconds a given difference of temperature between medium and thermometer is reduced to ϵ^{-1} times its initial value. From tables of ϵ^{-n} we obtain the following data for an initial difference of 10°.

TABLE VI

(ϵ^{-n})	At time t,	Temperature difference equals—	For bath at 30°, thermometer reads—
$\epsilon^{0}=1$	0	10°00	20°00
$\epsilon^{-\frac{1}{2}}=.6065$	$\frac{\lambda}{2}$	6.06	23.94
$\epsilon^{-1}=.3679$	λ	3.68	26.32
$\epsilon^{-\frac{3}{2}}=.2231$	$\frac{3\lambda}{2}$	2.23	27.77
$\epsilon^{-2}=.1353$	2λ	1.35	28.65
$\epsilon^{-\frac{5}{2}}=.0821$	$\frac{5\lambda}{2}$	0.82	29.18
$\epsilon^{-3}=.0498$	3λ	0.50	29.50
$\epsilon^{-\frac{7}{2}}=.0302$	$\frac{7\lambda}{2}$	0.30	29.70
$\epsilon^{-4}=.0183$	4λ	0.18	29.82

Cooling a thermometer and plunging it into a bath at 30° one would read off the times corresponding to the thermometer readings tabulated in the last column. These should occur at equal intervals of half λ. Most of the thermometer readings will be odd valued and not easily carried in mind, no matter what temperature range is chosen, whence the method is hardly to be recommended unless the observation interval be great enough to permit of reference to notes between readings. Also with a rapidly moving meniscus odd values can not be timed as accurately as can coincidences with even graduation lines.

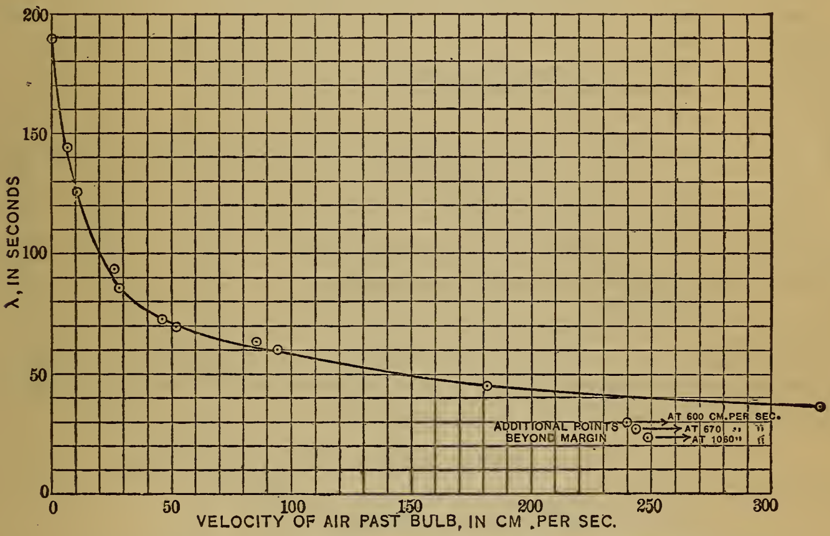

Fig. 7.—*Variation of λ with current, in air. Thermometer Chabaud 80659*

It is very easy to see that a slight change in the bath temperature affects the time-differences for the later readings by a large percentage; consequently the first three or four differences are the more dependable, and it is desirable to employ a table of readings made out for every λ/2 seconds rather than for any greater interval, to secure a number of intervals before the temperature difference grows too small.

The results of the experiments in air are summarized in Table VII and shown graphically on Fig. 7.

TABLE VII

Values of λ in Air Passing Thermometer Bulb at Different Rates

Thermometer Chabaud 80659

Date	Apparatus, etc.	Experiments	Velocity[16] cm per sec.	Mean λ	Av. dev. from mean
1911				Sec.	
July 25	Inclosed space—air at rest except convection	3	0	190	±11
July 27	U tube, etc. (no current)	1	0	190	
Sept. 14	U tube, etc., Fig. 6 (wet meter)	3	6.3	144	5
Do	do	3	11	126	2
Do	do	3	26	94	4
Aug. 19	do	1	$28._5$	86	
Do	do	2	47	73	1
July 27	Dry meter (tower and worm removed)	1	52	70	
Aug. 17	Fig. 6 (wet meter)	4	86	64	2
July 27	Dry meter, etc	2	95	60	0.5
July 26	do	2	18_2	46	0.0
Do	do	2	32_5	37	0.5
Do	do	2	60_0	30	0.5
Do	do	3	67_0	28	0.0
July 28	do	2	106_0	24	0.5
July 25	Suspended vertically in greatest draft of high-speed horizontal fan.	3	?	24	0.5

---

[16] The average deviation from the mean velocity is without significance; as to the precision read, different observations were in exact agreement among themselves. Readings were taken to about 1 per cent, but the gas-meter calibration was slightly uncertain, making a systematic error greater than this possible.

II. LAG OF A BECKMANN THERMOMETER

ADDITIONAL ASSUMPTIONS

It is found that the behavior of the ordinary type of Beckmann thermometer is not completely represented by the equations that have been developed, whence the assumption $\frac{\partial\theta}{\partial t}=\frac{1}{\lambda}(u-\theta)$, equation (1) (see p. 661) is not justifiable. A consideration of the form of the instrument suggests a reason for this. The main bulb is like the bulb of the type of instrument considered above. But in addition the large capillary, which is common in such instruments, between the bulb and the zero of the scale, acts as a second smaller bulb.[17] Inclosed in a tube with an air layer between it and the bath, it is quite slow to assume the bath temperature, yet the amount of mercury in this secondary bulb is sufficient to appreciably affect the position of the meniscus in the small capillary.

There are thus two bulbs, the temperature of each of which may be expressed by the law $\frac{dA}{dt}=\frac{1}{\lambda}(u-A)$ where u is the temperature of the surrounding medium and A is the average temperature of the bulb, as previously defined (p. 661).

$$\frac{dB}{dt}=\frac{1}{\lambda_B}(u-B) \text{ for main bulb} \tag{12}$$

$$\frac{dC}{dt}=\frac{1}{\lambda_C}(u-C) \text{ for large capillary} \tag{13}$$

B and C together define the position of the meniscus in the bore of the thermometer, this being the reading θ. If the relation of θ to B and C be stated (this being equation 14 below) it will be possible to eliminate from the three equations (12), (13), (14) the two quantities B and C, which are not directly determinable, and leave a relation connecting θ with u, quantities in which interest centers.

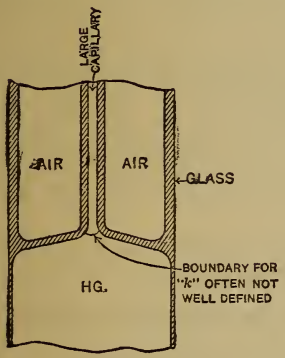

Fig. 8.—*Section through Beckmann thermometer*

In stating the dependence of θ upon B and C one has to bear in mind—

Firstly, that the volume of the mercury originally in the bulb will change proportionately to the change in the temperature B, and the volume of that originally in the large capillary will be likewise related to C.

Secondly, the position of the meniscus in the bore will vary as the sum of these two volumes changes.

---

[17] Total immersion is assumed in this paper, along with the assumption previously mentioned that the thermometer is instrumentally perfect. The difference in the behavior of any thermometer between total and partial immersion must be considered as part of the theory of emergent stem corrections and can not be included here. In the experiments tabulated in this section the thermometer was immersed to the top of the large capillary, the results given being on the basis of total immersion.

Whence $d\theta$ will be the sum of two quantities proportional to dB and dC, respectively, and, since no constant of integration except zero could satisfy the obvious relation $\theta = 0$ when both B and C are 0, θ must be related to B and C exactly as $d\theta$ to dB and dC, although this does not imply that the temperature of the thermometer as a whole is to be thought of as an addition of the temperatures of the several parts.

If unit quantity of mercury be distributed between two bulbs, k in the first and $1-k$ in the second, the effect of each in defining the position of the meniscus will be in the proportion k to $1-k$, besides the effect of the respective temperatures. We may take for the unit of quantity the total amount of mercury in any thermometer and so omit factors of proportionality and state the relation in the simple form

$$\theta = kC + (1-k)B \tag{14}$$

where k is the fraction of the total volume contained in the large capillary.

Omitting the steps of the elimination of B and C from (12), (13), and (14) and collecting, the resulting equation is

$$\lambda_B \lambda_C \frac{d^2\theta}{dt^2} + (\lambda_B + \lambda_C)\frac{d\theta}{dt} + \theta = [k\lambda_B + (1-k)\lambda_C]\frac{\partial u}{\partial t} + u \tag{15}$$

If equations deduced from it are verified by experiment this equation, which can not be directly tested, will be justified. We shall find that a sufficient agreement obtains to do this, the equations developed from it proving to be fairly close approximations to exact statements of the behavior of this type of thermometer. It must be noted that k can not be accurately determined, since the end of the bulb and beginning of the large capillary is not thermally a definite location, even if mechanically it were so. (Fig. 8.)

To obtain the primitive of (15) requires considerable mathematical manipulation, but presents no difficulties as the steps follow common textbook suggestions in [18] order, being type-form

---

[18] See, for instance, A. R. Forsyth: A Treatise on Differential Equations—"General linear equations with constant coefficients," p. 64 (3d ed., 1903); Notes on particular integral and complementary function in the section on General Linear Equations of the Second Order, p. 98; "Method of variation of parameters," p. 110.

processes. The result is

$$\theta = u + A_1\epsilon^{-\frac{1}{\lambda_B}t} + A_2\epsilon^{-\frac{1}{\lambda_C}t} - k\epsilon^{-\frac{1}{\lambda_C}t}\int\frac{\partial u}{\partial t}\epsilon^{\frac{1}{\lambda_C}t}dt - (1-k)\epsilon^{-\frac{1}{\lambda_B}t}\int\frac{\partial u}{\partial t}\epsilon^{-\frac{1}{\lambda_B}t}dt \quad (16)$$

where A_1 and A_2 are the arbitrary constants of integration and must be fixed by assigning two definite conditions. One of these may well be to assign simultaneous values to all the variables, defining for the time 0 that the corresponding bath temperature be u_0 and thermometer reading θ_0. The most convenient second condition to impose is that all parts of the thermometer shall be at the same temperature at this time zero, i. e., $B_0 = C_0$. Since $\theta = kC + (1-k)B$, whenever $B = C$, either of these equals θ, so that this second condition is expressed by the relation

$$\theta_0 = B_0 = C_0 \quad (17)$$

Whenever the thermometer remains in a medium of constant temperature for a considerable time all parts come to this temperature and the condition (17) is then fulfilled at every instant; so that by taking as $t = 0$ the instant of the transfer to any medium at a different temperature (for immersion in which latter medium the equation is to be applied) both conditions outlined can be readily satisfied in practice.

A_1 and A_2 are given by the two equations

$$\theta_0 = u_0 + A_1 + A_2 - k\int^0 \epsilon^{\frac{1}{\lambda_C}t}\frac{\partial u}{\partial t}dt - (1-k)\int^0 \epsilon^{\frac{1}{\lambda_B}t}\frac{\partial u}{\partial t}dt \quad (18)$$

from the substitution of initial values in (16), and

$$\left(\frac{k}{\lambda_C} + \frac{(1-k)}{\lambda_B}\right)(\theta_0 - u_0) = \frac{A_1}{\lambda_B} + \frac{A_2}{\lambda_C} - \frac{k}{\lambda_C}\int^0 \epsilon^{\frac{1}{\lambda_C}t}\frac{\partial u}{\partial t}dt - \frac{1-k}{\lambda_B}\int^0 \epsilon^{\frac{1}{\lambda_B}t}\frac{\partial u}{\partial t}dt \quad (19)$$

from substitution in the first derivative of (16) of the first derivative of (14) and subsequent reduction of the result by the use of (12) and (13) to a form where the values at the time $t = O$ (relation 17) can be substituted to give the form as written.

Equations (18) and (19) are not worth solving explicitly for A_1, A_2 for substitution in (16), because the special cases arising in practice are more easily referred to these implicit forms. The cases arising more frequently in laboratory practice will be treated in a later section, but one of these must be developed at this point. By considering the behavior of a Beckmann thermometer plunged into a bath maintained at constant temperature, and the behavior predicted by the theory here developed, we shall find that an excellent test of the validity of the theory is afforded.

(a) **Constant Temperature.**—If $u = U_0$, $\frac{\partial u}{\partial t} = O$ and equation (16) becomes

$$\theta = U_0 + A_1 \epsilon^{-\frac{1}{\lambda_B}t} + A_2 \epsilon^{-\frac{1}{\lambda_C}t} \tag{20}$$

Equations (18) and (19) have the forms

$$\theta_0 = U_0 + A_1 + A_2$$

$$\left(\frac{k}{\lambda_C} + \frac{1-k}{\lambda_B}\right)(\theta_0 - U_0) = \frac{A_1}{\lambda_B} + \frac{A_2}{\lambda_C}$$

From which A_1 and A_2 may be readily obtained.

$$A_1 = (1-k)(\theta_0 - U_0) \tag{21}$$

$$A_2 = k\,(\theta_0 - U_0) \tag{22}$$

Equation (20) in its complete form is[19]

$$\frac{\theta - U_0}{\theta_0 - U_0} = (1-k)\epsilon^{-\frac{1}{\lambda_B}t} + k\epsilon^{-\frac{1}{\lambda_C}t} \tag{23}$$

under the conditions, at $t = o$, imposed above (p. 685).

When $k = 0$ or $k = 1$ or $\lambda_C = \lambda_B$, any one of which conditions corresponds to a single bulb instead of a compound one, this equation reduces to (4) of p. 664 as is necessary.

The properties of functions of ϵ^n depend so entirely on the numerical value of the exponent that it is rather difficult to generalize, but a few remarks may assist to a clearer picture of

---

[19] An equation of this general form was proposed by Thiesen (loc. cit.), with a bare statement that the idea had occurred to him of separate, independent lags for two parts of those thermometers which failed of expression by the more common single lag equations. No derivation of the equation is given, and it is left with undetermined coefficients in the form $\theta - U_0 = A\epsilon^{-\frac{1}{\lambda_1}t} + B\epsilon^{-\frac{1}{\lambda_2}t}$, with the suggestion that this form be tried in cases where $\theta - U_0 = A\epsilon^{-\frac{1}{\lambda_1}t}$ obviously fails to express the behavior of the instrument.

the curve theoretically representing the behavior of a thermometer of the usual Beckmann type plunged into a constant temperature bath. To illustrate the discussion, Fig. 9 is inserted, although it has been necessary to exaggerate greatly the value of k from the usual size, in order to separate sufficiently the curves, on the scale which must be here employed, to make clear which function is which.

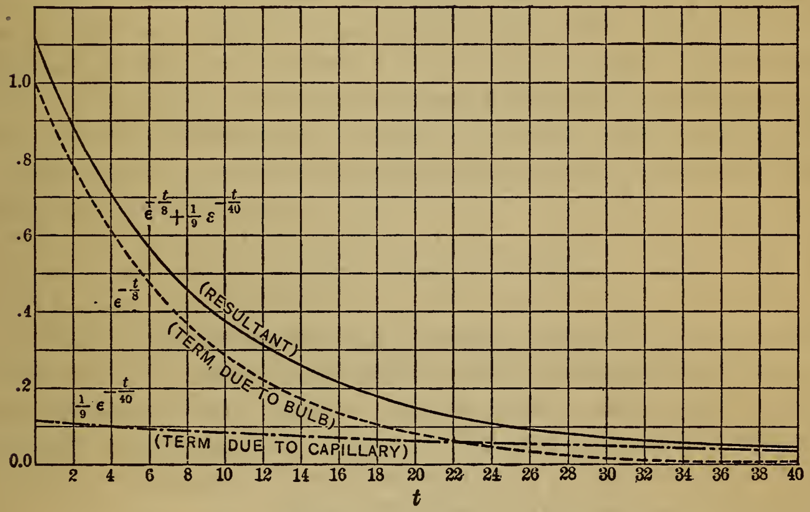

Fig. 9.—*Curves to explain theory of Beckmann lag (exaggerated value of k)*

$\lambda_B=8$ *sec.* $\lambda_c=40$ *sec.* $k=0.1$ $y=\epsilon^{-\frac{1}{\lambda_B}+}+\frac{1}{9}\epsilon^{-\frac{1}{\lambda_c}t}$

Let us confine our attention to the two terms separately, that due to the capillary, $\frac{k\epsilon^{-\frac{1}{\lambda_c}t}}{1-k}$, and then that due to the bulb, $\epsilon^{-\frac{1}{\lambda_B}t}$. K is small with respect to unity, and λ_c is generally several times λ_B. Fixing in mind λ_B as the interval of time for use as a convenient comparison unit, t must be large before $\epsilon^{-\frac{1}{\lambda_c}t}$ reduces very greatly from unity; whence for a considerable time the term $\frac{k}{1-k}\epsilon^{-\frac{1}{\lambda_c}t}$ is very little different from k. On Fig. 9, with the numbers employed, it starts at the value 1/9 and very gradually approaches the axis.

The term $\epsilon^{-\frac{1}{\lambda_B}t}$ decreases at a rate very much more rapid than that of $\epsilon^{-\frac{1}{\lambda_C}t}$, λ_B being but a fraction of λ_C, so that although its initial value unity is very large in comparison with k, it reduces to this value, k, before very long, and continuing to decrease disappears numerically while the other term is appreciable.

The sum of the terms in equation (23) is accordingly almost exactly the first for small values of t and the second after considerable time. This point is illustrated by Fig. 9, and the actual magnitudes which are involved in a practical case can be pictured by supposing k diminished perhaps as much as thirty times. At the one end the difference between the resultant and its first term would be reduced from 10 per cent of either, as there shown, to a very small fraction of it, or for most purposes the curves might be considered identical. At the other end the total magnitude of the resultant would of course be much smaller, but it would, at some time, bear exactly the same relation to the second term that it does on the plot, namely, become practically equal to it, because the first term is diminishing at all points at a rate much greater than that of the second. It may also be well to call attention to the fact that as k is smaller, the point where the first and second terms are the same size, about 22 seconds on Fig. 9, displaces more and more toward the right.

The conclusions that have been reached predict that if a thermometer of this type be plunged into a bath 10° warmer than it is, it will cover the first 9°, say, of its rise in almost the same way as would a thermometer with a single lag constant λ_B; and will cover (about) the last 0.°1 in nearly the same way as would a thermometer of single lag constant λ_C; the interval between corresponding to neither.

JUSTIFICATION OF ASSUMPTIONS MADE

The method of testing out the theory proposed is at once suggested. The value of k may be approximately determined for a thermometer with a "secondary" bulb, such as the large capillary below the scale in the usual type of Beckmann. Then λ_B and λ_C may be approximately found by using the two ends of the observed "lag curve" of that thermometer, obtained by the logarithmic method described on page 667. If, then, the middle of the curve computed from these values of λ_B, λ_C, and k in the equation (23) be the same as the middle of the curve obtained by direct observation, it is fair evidence that the function written is a proper one to represent the behavior of the thermometer. The test was made and the results with one thermometer are given in full to make clear the procedure.

Beckmann No. 5952 has, in its large capillary (Fig. 8) about 20° of mercury inclosed by the outer glass tube so as to have only poor thermal contact with the medium of immersion. 6300° being approximately the volume[20] of the mercury in a thermometer bulb, the value of k is $20/6300 = 0.003_2$; and $1-k$ is unity within the limits of accuracy of this computation. Substituting these numbers in equation (23),

$$\frac{\theta-U_0}{\theta_0-U_0}=\epsilon^{-\frac{1}{\lambda_B}t}+.003_2\epsilon^{-\frac{1}{\lambda_C}t}$$

should be the equation to give the reading (θ) of this thermometer, at any time (t) after immersion in a bath maintained at constant temperature (U_0), provided all parts of the thermometer were at the same temperature (θ_0) when the instrument was introduced into the bath. If θ_0 be below U_0 the first 0.9 of the rise must follow very closely the equation $\frac{\theta-U_0}{\theta_0-U_0}=1.00\epsilon^{-\frac{1}{\lambda_B}t}$, and applying the methods of page 667 to simultaneous readings of thermometer and time an approximate value of λ_B may be determined. A number of such experiments made with thermometer No. 5952 gave a mean value of 8.7 seconds for λ_B.

By the time the quantity $(U_0-\theta)$ is reduced to 1 per cent of $(U_0-\theta_0)$ the term $\epsilon^{-\frac{1}{\lambda_B}t}$ is smaller than 0.0032 $\epsilon^{-\frac{1}{\lambda_C}t}$ if λ_C be about five times λ_B, and a little later may, for first approximations be neglected. The equation

$$\frac{\theta-U_0}{\theta_0-U_0}=0.0032\epsilon^{-\frac{1}{\lambda_C}t}$$

---

[20] The unit of volume being the volume that forms one degree in the stem of the particular thermometer of which the bulb is a part. The number 6300 depends somewhat on the glass, but the relative expansion coefficient is seldom far from 0.00016=1/6300 (approximate).

applied for a number of readings after θ has almost reached U_0 gives λ_c. Since the temperature differences to be read are extremely small, little more than the order of magnitude of λ_c may be deduced. This however is all that is necessary, as an error of 20 to 30 per cent would not greatly influence numerical values in the complete equation. The mean of a number of experiments indicated 50 seconds to be the best value to use for λ_c.

In Table VIII is summarized the computation of

$$F \equiv (1-.0032)\,\epsilon^{-\frac{1}{\lambda_B}t} + .0032\,\epsilon^{-\frac{1}{\lambda_c}t}$$

for given values of t; λ_B taken as 8.70 seconds, λ_c, 50 seconds.

TABLE VIII

t	$(1-.0032)\,\epsilon^{-\frac{t}{8.70}}$	$.0032\,\epsilon^{-\frac{t}{50}}$	F	$\log_{10} F$	$\log_{10} \epsilon^{-\frac{t}{8.70}}$
10	0.3160	0.0026	0.3186	9.503	9.501
20	.1002	.0021	.1023	9.010	9.002
30	.0317	.0018	.0335	8.524	8.502
40	.0101	.0014	.0116	8.064	8.003
50	.0032	.0012	.0044	7.643	7.505
60	.0010	.0010	.0020	7.301	7.005
80	.00010	.00065	.00076	6.881	6.007
100	.00001	.00043	.00044	6.643	5.008
120	.00000	.00029	.00029	6.462	4.010

The second and fourth columns show at a glance the extent of the agreement of the function F with its first term, the fifth and sixth columns showing the same for the logarithms, which are more apt to be employed in computing a lag experiment. The sixth column is of course a straight line, when plotted against time; the fifth is so up to about 40 seconds, after which it rapidly assumes marked curvature. This length of time after immersion was accordingly the interval available for the determination of λ_B.

This curvature of the logarithmic plot, due to the term involving the lag of the capillary, distinguishes it sharply from the plot due to a single lag, which is linear. The functions themselves are of the same general shape as illustrated on Fig. 9, so that in comparing the function F to the corresponding curve obtained by experiment, it is better to compare logarithms than direct values. This is done in Fig. 10.

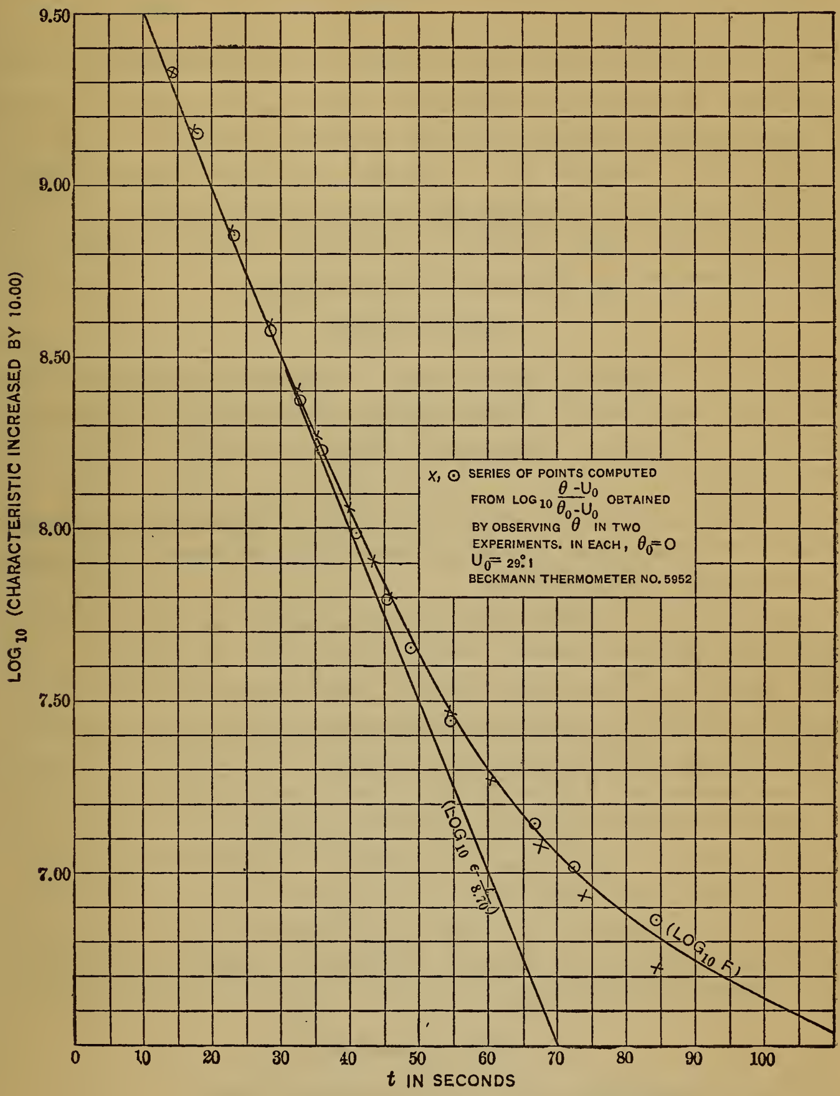

Fig. 10.—$Log_{10}\,F \quad F \equiv (1-0.0032)\epsilon^{-\frac{t}{8.70}} + 0.0032\epsilon^{-\frac{t}{50}}$

If equation (23) represents the facts, log F, of Table VIII, and $\log \frac{\theta - U_0}{\theta_0 - U_0}$, as obtained experimentally for this thermometer, must coincide. A number of experiments were made by cooling it to 0° throughout and plunging it into a bath maintained at 29°.10, reading as it warmed up. The data from two representative experiments gave the circles and crosses plotted on Fig. 10. The agreement with $\log_{10} F$ (the curve as shown) seems to justify the theory proposed for this type of thermometer.

SPECIAL CASES

The more important special cases for which the theory will be developed somewhat in detail are three, (a) constant temperature, (b) linear change, (c) exponential change, according to the law $u = A + B\epsilon^{-at}$.

The application of the equations to practical problems proceeds along the lines already given in the section devoted to common or "chemical" thermometers.

(a) Constant Temperature.—The equations for this condition have been derived above (p. 686) and need not be repeated. The only question of lag which arises is: How long after immersion of the thermometer in a constant temperature bath must an observer wait to secure a given accuracy in reading? The time is computed from equation (23), following the principle outlined for an ordinary thermometer in the discussion following equation (4). However, as the time for a Beckmann to attain an "equilibrium condition" when plunged into a liquid bath is greater than that for a common-type chemical thermometer, and it may be advisable to summarize the computations of an example to show the order of magnitude. The quantities involved are

$$(1-k)\epsilon^{-\frac{1}{\lambda_B}t} \text{ and } k\epsilon^{-\frac{1}{\lambda_C}t}$$

For the thermometer No. 5952 (in stirred water).

$$k = 0.0032 \qquad \lambda_B = 8.70 \text{ sec.} \qquad \lambda_C = 50 \text{ sec.}$$

The term $(1-k)\epsilon^{-\frac{1}{\lambda_B}t}$ becomes 10^{-4} after about $9\lambda_B$ seconds, or 78 seconds, but at that time $k\epsilon^{-\frac{1}{\lambda_C}t}$ is 0.0032×0.211, or 0.00067.

This term does not diminish to 10^{-4} until t reaches the value of 174 seconds. At this time the first term is so small that the sum is identical with the latter value. Accordingly, about three minutes is the time for a temperature difference of 10° to be reduced to 0°.001 when this Beckmann thermometer is plunged into a bath of water vigorously stirred.

(b) LINEAR RISE OF TEMPERATURE.—$u = U_0 + rt$, $\frac{\partial u}{\partial t} = r$. Substituting this value of $\frac{\partial u}{\partial t}$ in equation (16), (p. 685), and performing the integrations, the result is

$$\theta = u + A_1 \epsilon^{-\frac{1}{\lambda_B}t} + A_2 \epsilon^{-\frac{1}{\lambda_c}t} - rk\lambda_c - r(1-k)\lambda_B \tag{24}$$

A_1 and A_2 may be determined, under the conditions imposed (p. 685), by equations (18) and (19). Replacing $\frac{\partial u}{\partial t}$ of these equations by r and carrying out the solution for A_1, A_2,

$$A_1 = (1-k)(\theta_0 - U_0 + r\lambda_B) \tag{25}$$

$$A_2 = k\,(\theta_0 - U_0 + r\lambda_c) \tag{26}$$

These values may be put into equation (24) to give its complete form. A considerable time after immersion the terms containing them reduce to negligible size because of the factor $\epsilon^{-\frac{1}{\lambda}t}$, and the equation has the simple form.

$$\theta = u - r(1-k)\lambda_B - rk\lambda_c \tag{27}$$

whence the thermometer follows the bath in which it is immersed with a constant difference of temperature existing between them of

$$r[(1-k)\lambda_B + k\lambda_c] \tag{28}$$

Although λ_c is generally several times λ_B, k is usually so small a fraction of $1-k$ that the last term is quite small with respect to the first, being negligible more often than not.

For the thermometer previously discussed, $\lambda_B = 8.70$ seconds and $(1-k)\lambda_B + k\lambda_c = 8.83$ seconds, a difference less than 2 per cent and of the order of the uncertainty of λ_B as determined. The lag of this thermometer in the equilibrium condition when immersed in a medium whose temperature rises linearly is practically that of the bulb alone, the value of k and the lag of the capillary not entering the result to an appreciable extent. While the equilibrium condition is being established, however, their significance is not to be overlooked. From (24), (25), (26), neglecting small terms, it is seen that the ratio $\frac{\theta - u}{\theta_0 - U_0}$ is diminished with time at a rate dependent on $(1-k)\epsilon^{-\frac{1}{\lambda_B}t} + k\epsilon^{-\frac{1}{\lambda_C}t}$. This exact function was carefully examined for the case of a bath maintained at constant temperature, (p. 692), and the computations need not be repeated. About three minutes after immersion this thermometer would differ from the steady state by 10^{-4} times the initial temperature difference.

(c) LOGARITHMIC TEMPERATURE CHANGE, $u = A + B\epsilon^{-at}$.—The occurrence of this case has been explained in the footnote to p. 664, and the detailed development of pages 666–7 permits us to dismiss the form with a bare statement of the solution. Placing the value of $\frac{\partial u}{\partial t}$, namely $-\alpha B\epsilon^{-at}$ in equation (16), and dropping the terms containing an exponential, in accordance with the discussion following equation (7), we get for the solution in the steady state,

$$(\theta - u) = \alpha\left[k\frac{\lambda_C}{1-\alpha\lambda_C} + (1-k)\frac{\lambda_B}{1-\alpha\lambda_B}\right](u-A) \qquad (29)$$

III. LAG OF ELECTRICAL THERMOMETERS

Electrical thermometers in common use fall into one of two classes, thermoelectric or resistance. Some form of galvanometer is necessary as an indicator for either, and the lag of this galvanometer is to be added to the lag exhibited by the thermocouple or resistance coil in acquiring the temperature under measurement. It will often be found that the galvanometer lag is the greater portion of the whole; in fact, that frequently it is the only portion which need be considered at all.

GALVANOMETER LAG

An expression for the lag of a galvanometer is easily derived from the familiar equations governing the behavior of the instrument, whence it is quite unnecessary to treat the subject in detail, but the general method of deducing the required expression may well be summarized for the most common case, that of a D'Arsonval instrument, under the condition of critical damping. The fundamental equation for the motion of the coil

$$I\frac{d^2\theta}{dt^2}+K\frac{d\theta}{dt}+\tau\theta=N \tag{30}$$

N = applied moment (in general, a function of t)
θ = displacement
t = time
I = moment of inertia of moving system
K = damping coefficient
τ = elastic coefficient

has three different solutions according as K^2 is greater than, equal to, or less than $4I\tau$, leading respectively to the equation of motion if overdamped, critically damped, or underdamped. Critical damping occurs when $K^2=4I\tau$, and the solution [21] is

$$\theta=A\epsilon^{-\frac{K}{2I}t}+Bt\epsilon^{-\frac{K}{2I}t}+\epsilon^{-\frac{K}{2I}t}\left[t\int^t\frac{N}{I}\epsilon^{\frac{K}{2I}t}dt-\int^t\frac{N}{I}t\epsilon^{\frac{K}{2I}t}dt\right] \tag{31}$$

For nearly all thermometric work, the function N is linear. A Wheatstone bridge or potentiometer is approximately balanced, and the unbalanced emf causes a deflection of the galvanometer according to the equation just written. This unbalanced emf changes in direct ratio to the temperature change, and may be taken as linear over the range of any one reading.

Let the moment N_0 be impressed on the galvanometer coil by closing the circuit at time zero, and let this moment decrease at

---

[21] See, for instance, A. R. Forsyth: A Treatise on Differential Equations—"Linear equation with constant coefficients—Case of 'equal roots,'" p. 64 (3d ed., 1903). Notes on particular integral in the section on the General Linear Equation, p. 98, or "Method of variation of parameters," p. 110.

constant rate r (passing through nil and increasing in opposite direction). The function N will be

$$N = N_0 - rt \tag{32}$$

The moment is zero at the instant $t = \frac{N_0}{r}$, which is accordingly the time of the temperature corresponding to exact balance of the bridge or potentiometer. If the deflection, θ, of the galvanometer be not zero until λ seconds later, or at time $\frac{N_0}{r} + \lambda$, it is evident that an error, due to lag, is made in the usual manner of reading such instruments when measuring changing temperatures.

Omitting all the steps of substitution of $(N_0 - rt)$ for N in the equation (31) and of determination of A and B for the initial conditions, stated below,

$$\theta = \frac{4I}{K^2}\left\{N_0 - rt + \frac{4I}{K}r - \epsilon^{-\frac{K}{2I}t}\left[\left(\frac{K}{2I}N_0 + r\right)t + N_0 + \frac{4I}{K}r\right]\right\} \tag{33}$$

if, at time zero, moment N_0 be suddenly impressed on the coil by closing the circuit when the coil is at rest $\left(\frac{d\theta}{dt}\right]_0 = 0\Big)$ in its equilibrium position $(\theta]_0 = 0)$.

For most galvanometers the value of $\frac{K}{2I}$ when critically damped will be found to be such that in a few seconds the term $\epsilon^{-\frac{K}{2I}t}$ is very small with respect to the other terms, and the factor multiplying it is not large, so the equation simplifies to

$$\theta = \frac{4I}{K^2}\left\{N_0 - rt + \frac{4I}{K}r\right\} \tag{34}$$

When the deflection, θ, is zero,

$$t = \frac{N_0}{r} + \frac{4I}{K} \tag{35}$$

The lag, λ, of the galvanometer behind an emf changing linearly is accordingly, after a short time, $\frac{4I}{K}$ seconds (see eq. (32)). As an illustration of the magnitude of this quantity, a galvanometer much used by the author has the value $\frac{I}{\mathrm{K}}=0.4$ second, whence its lag is 1.6 seconds. The circuit must be closed at least 5 seconds before taking a reading, if an accuracy of 0.1 per cent of the deflection is desired, as shown by the following computation, which gives the time that must elapse before the term in $\epsilon^{-\frac{K}{2I}}$ becomes 0.001.

If $\frac{I}{K}=0.4$ second, $\epsilon^{-\frac{K}{2I}t}=\epsilon^{-1.25t}=$ (about) 0.001 for $t=5$ seconds.

For the determination of $\frac{K}{I}$ for any particular galvanometer, many methods might be divised from the common equations discussed in the numerous papers on galvanometers. One may be outlined here. The free period, T, of a system of moment of inertia I and elastic coefficient τ is $2\pi\sqrt{\frac{I}{\tau}}$, from which relation it follows that

$$\tau=\frac{4\pi^2 I}{T^2}$$

The condition imposed by critical damping is that

$$\mathrm{K}^2=4I\tau$$

from which

$$K^2=\frac{16\pi^2 I^2}{T^2}.$$

$$\frac{K}{I}=\frac{4\pi}{T}$$

The free period of a galvanometer system is very little different from that in which it vibrates under any conditions not closely those of critical damping, so that the period observed when swinging as little damped as possible, will usually suffice to give T with high accuracy. $\frac{K}{I}$ is thus given very directly; the lag of the galvanometer, being $\frac{4I}{K}$, is of the extremely simple form $\frac{T}{\pi}$ seconds.

RESISTANCE THERMOMETERS

The resistance thermometers studied were found to be either very fast or very slow in comparison with mercurial thermometers. The well-known type made after the design of Callendar, consisting of a platinum coil wound on a mica frame and inclosed in a glass, quartz, or porcelain tube, is quite slow. Immersed in well stirred water, the values of λ measured usually lay between 15 and 30 seconds, though even this value was exceeded. A departure from the straight-line plot by the logarithmic method described on page 667 was evident when the temperature difference was small, indicating that the equation $\frac{d\theta}{dt}=\frac{1}{\lambda}(u-\theta)$ is only a first approximation to the statement of the behavior of such thermometers. The deviation was quite marked in some instances and always in the direction and of the general curvature exhibited by the Beckmann thermometers discussed in an earlier section. It appears that the two-term formulæ there developed are better equations to apply empirically to a Callendar type resistance thermometer than the simpler equations. This may perhaps be explained by the fact that the temperature of the platinum coil is partly determined by that of the inner surface of the containing tube, for which the lag is relatively small, and partly by that of the support, for which the lag is relatively large. The conditions, therefore, resemble those considered in the section on Beckmann thermometers.

The very fast resistance thermometers were of the type in general use in this Bureau, in the range 0–100°C, an improved form of the instrument described in this Bulletin in 1907 by Dickinson and Mueller,[22] and will be more fully described in a future paper. The essential features respecting the lag of these instruments are the small heat capacity of the enveloping sheath and the intimate thermal contact between this and the resistance coil. Attempts to measure the lag (in liquids) gave no results, merely indicating it to be smaller than the method would admit of determining, namely, considerably smaller than the galvanometer lag which was about one and one-half seconds.

---

[22] Calorimetric Resistance Thermometers and Transition Temperature of Sodium Sulphate: This Bulletin, 3, p. 641, Reprint No. 68.

JAEGER-STEINWEHR METHOD OF COMPUTING THE LAG OF A RESISTANCE THERMOMETER

A method of computing the lag of such thermometers was proposed by Jaeger and Van Steinwehr, but in the form in which they published[23] it, only a lower limit is placed upon the value of the lag. The method depends upon measuring the heating of the coil by different intensities of current.

Writing the equation governing the transfer of heat between the coil and the medium in which the thermometer is immersed as

$$\frac{d\theta}{dt}=\frac{1}{\lambda}(u-\theta) \qquad (1)$$

θ = temperature of coil
u = temperature of medium
λ = lag (in seconds)

the rate at which heat is transferred will be

$$M\frac{d\theta}{dt}=\frac{M}{\lambda}(u-\theta)$$

M = heat capacity of the system cooling (or warming).

If θ be greater than u, the thermometer coil will lose heat and in time dt will lose a quantity dH

$$dH=\frac{M}{\lambda}(\theta-u)\,dt \qquad (36)$$

If there be any electric current, i, in the coil, heat will be generated at the rate Ri^2, where R is the resistance. This will tend to raise the temperature of the coil above that of the medium in which the thermometer is immersed. It will rise until the dissipation, which is proportional to $(\theta-u)$, equation (36), equals the generation. This heat generated in time dt, (J being number of joules in a calorie) is

$$\frac{Ri^2}{J}dt$$

---

[23] Jaeger and Von Steinwehr: Zeitschrift für Instrumentenkunde, **26**, p. 241; 1906.

and so in the equilibrium state of the thermometer

$$\frac{M}{\lambda}(\theta-u)dt=\frac{Ri^2dt}{J}$$

$$\frac{1}{\lambda}(\theta-u)=\frac{R}{MJ}i^2 \tag{37}$$

Direct measurement of $(\theta-u)$ is rather difficult, if at all possible, but indirect determination of the value by employing two or more values of i is quite easy. Applying (37) to such a series, u being kept constant

$$\frac{1}{\lambda}(\theta_1-u)=\frac{R_1}{MJ}i_1^2$$

$$\frac{1}{\lambda}(\theta_2-u)=\frac{R_2}{MJ}i_2^2$$

etc.

The difference in θ does not change R appreciably for the second members of the two equations, whence subtracting

$$\frac{1}{\lambda}(\theta_2-\theta_1)=\frac{R}{MJ}(i_2^2-i_1^2)$$

$$\lambda=M\frac{J}{R}\,\frac{\theta_2-\theta_1}{i_2^2-i_1^2} \tag{38}$$

The value of M proposed by Jaeger and Von Steinwehr is the water equivalent of the platinum resistance coil, computed from dimensions, density, and specific heat. Obviously, this gives merely a minimum value. The water equivalent of a portion of the silk and shellac wrapping about the wire of their thermometer should have been included. This being doubtless several times [24]

---

[24] When a cylindrical heat source is surrounded by an annular covering (inner radius a and outer radius b), whose outer surface is maintained at a definite constant temperature (0), the equilibrium distribution of temperatures is expressed by

$$U=C\frac{\log\frac{r}{b}}{\log\frac{a}{b}}$$

Integrating through the cylindrical shell, to determine the position of the boundary for considering the heat transfer as between two bodies, one the core and a portion of the annular covering, the other the that of the wire alone, the value of λ as 1/33 of a second, obtained in the computation, is many times too small. Nevertheless, the lag of such a form of thermometer is small compared with that of any ordinary galvanometer.

The thermometers of the Dickinson-Mueller type (improved form) possess the following constants: Heat capacity of platinum coil, 0.010 cal. per degree C. Heat capacity of mica in region of coil, 0.16 cal. per degree C.

The mica between the head of the thermometer and the resistance coil, supporting and insulating the leads (with a heat capacity of 0.30) and the platinum sheath (with a heat capacity of 0.60) can not be supposed to be heated by the coil appreciably above the temperature of any liquid in which the thermometer is immersed, and play no part in the computation under such a condition. This is equivalent to the statement that the whole temperature drop between the coil and the bath is to be found in the mica and air spaces separating these two. The value 0.17 for M places a safe upper limit, and the value 0.01 is the certain minimum for such a form of thermometer.

The factor

$$\frac{J}{R}.\frac{\theta_2-\theta_1}{i^2-i_1^2} \qquad \text{(see eq. 38)}$$

has been found, for the thermometer investigated when immersed in well-stirred water, to be 8.0 $\left(\frac{\text{sec.} \times \text{degrees}}{\text{calories}}\right)$, giving to λ, for the values of M just stated, the limits 1.4 seconds and 0.08 seconds. For a close winding, such that the middle mica plate is quite inclosed, the water equivalent should include all of this plate and one-half of each of the outer plates, separating coil from sheath. This is, in all, two-thirds of the mica; the corresponding value of

---

outside medium and remainder of covering, this boundary is located so that a fraction of the covering

$$\left[\frac{1}{\log\left(\frac{b}{a}\right)^2}-\frac{1}{\left(\frac{b}{a}\right)^2-1}\right]$$

belongs to the core.

If $b=10a$, as in the case of a 0.1 mm wire covered to a total diameter of 1 mm, the fraction evaluates to 0.20; and for $b=5a$, 0.27 of the total heat capacity of such a covering adds to that of the core. (In either case it should be borne in mind that the heat capacity of the whole covering is many times (99 or 24) that of the core if volume specific heats be the same, i. e., the total heat capacity is 20 times, or 7 times the heat capacity of the core.)

M is 0.11 and λ would be 0.9 second. However, the thermometers investigated were of very "open" winding (see Fig. 11), pitch 0.7 mm. and wire 0.1 mm. diameter. The mica to be included with the wire, roughly estimated, is that inclosed in the dotted circles, about one-third the total. The most probable value of λ in a well-stirred liquid is thus less than one-half second.

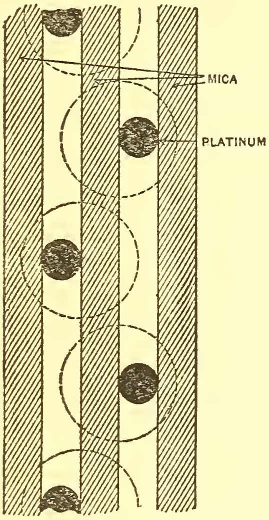

Fig. 11.—*Section through resistance thermometer of the Dickinson-Mueller type (greatly magnified)*

THERMOELECTRIC THERMOMETERS

The lag of a thermocouple in acquiring the temperature of a medium in which it is immersed is, like the lag of a resistance thermometer, principally a question of the form of mounting. Probably there are almost as many forms in use as there are makers of thermocouples, for there seems to be plenty of latitude for variation in this respect without impairing the usefulness of the finished instrument. Consequently it was deemed unimportant to test any particular forms of thermoelectric thermometer for lag. Dependent on the mounting of the junction one would no doubt find lags ranging from a small fraction of a second to perhaps 30 seconds for immersion in a well-stirred water bath. The important point is that for all work in that part of the temperature scale where high precision is attainable, so that lag corrections might be appreciable, it is possible to design a thermocouple with a lag as small or smaller than that of an ordinary galvanometer and generally, if not always, quite negligible.

IV. THERMOMETRIC LAG IN CALORIMETRY

In view of the different conclusions that have been reached by authors [25] who have considered the effect of thermometric lag on

---

[25] Jaeger and von Steinwehr: Verh. Deut. Phys. Gesells., 5, p. 353; 1903. Richards, Henderson, and Forbes: Proc. Amer. Acad., 41, p. 1; 1905; or Zs. für Phys. Chem., 52, p. 551; 1905. Jaeger and von Steinwehr: Zs. für Phys Chem., 54, p. 428; 1906. White: Physical Review, 27, p. 526; 1908.

calorimetric measurements, it was deemed of sufficient importance to consider the question in some detail. The conclusions reached have been arrived at, by a different analysis, by W. P. White.[26]

Classic procedure is to divide the ordinary calorimetric experiment into three parts, designated, respectively, as preperiod, middle period, and after period. A precise measurement of the calorimeter temperature, before adding the supply of heat whose determination constitutes the object of the experiment, defines the instant which separates the first two periods, and similarly a precise temperature measurement after the heat is added marks the dividing line between the second and third periods. Considerations of lag might therefore be said to pertain wholly to the middle period, but it is more convenient to treat the first temperature mentioned as the close of the preperiod rather than the beginning of the middle one, and to assign the second temperature similarly to the afterperiod. In this way the investigation is split up into three parts. Two of these concern the error, due to lag, in determining the temperatures mentioned, and are treated by investigating the conditions pertaining to the exchange of heat between the calorimeter, the thermometer, and the jacket, in the steady state, during preperiod and afterperiod. The third part involves the lag errors in the temperature readings used in the computation of the cooling correction, or is a middle-period function.

Numerous methods, differing radically in many ways, have been devised for performing calorimetric computations, but the fundamental relations underlying the "cooling correction" are the same, by whatever method the details be accomplished. It is generally assumed that the calorimetric aggregate exchanges heat with its envelope according to the law commonly called Newton's law of cooling:

$$-\frac{\partial u}{\partial t}=\alpha(u-U)$$

where u is the calorimeter temperature at the instant t and U the jacket temperature. In the simplest case the latter is constant throughout the three periods ($U=A$). α, the cooling constant,

---

[26] White: Physical Review, 31, p. 562; 1910.

and A are assumed possible of determination in the course of the run and will be discussed later.

After assembling the calorimeter any necessary time may be allowed to elapse for the effect of the initial conditions to be obliterated, so that during the preperiod the calorimeter temperature approaches that of the jacket according to a curve really logarithmic but of curvature so small it may frequently be considered linear. At a given instant, t, is commenced a supply of heat to the calorimeter and the middle period begins. If this supply could be distributed instantaneously, its measurement could be accomplished with no further process than the exact determination of the temperatures just before and just after the addition of the heat. No matter how long the middle period, the same result would ensue if the calorimeter could be perfectly insulated from external sources or sinks. In taking account of the loss or gain of heat in the middle period it is quite customary to compute, not a quantity of heat, but rather a temperature correction, to apply to the observed difference. The result is thereby stated in terms of the perfectly insulated calorimeter of the same heat capacity.

After the supply of heat to the calorimeter ceases, the temperature of the latter tends to a steady state of approaching that of the envelope at an almost constant rate. At any time after this state is attained, the precise measurement of the temperature is made, of which the time, t_2, marks the close of the middle period and beginning of the afterperiod.

After proper instrument corrections are applied, the thermometer readings give θ_1 and θ_2, which in turn, by appropriate lag corrections would give the observed rise of temperature, $u_2 - u_1$. The additional increment of temperature resulting from the "cooling correction" is given by applying

$$du = -\alpha(u-A)dt$$

to each instant of the middle period, t_1 to t_2; whence the total "correction" is

$$K = +\alpha \int_{t_1}^{t_2} (u-A)dt$$

The equivalent rise of temperature, as if there were no heat losses during the middle period, is accordingly

$$u_2 - u_1 + \alpha \int_{t_1}^{t_2} (u - A)\,dt$$

for which it is customary to substitute a similar formula containing thermometer readings (corrected for instrument errors) on the hypothesis that they represent actual temperatures without lag. If any error due to lag occur, let it be designated ε

$$\varepsilon = \left[\theta_2 - \theta_1 + \alpha' \int_{t_1}^{t_2} (\theta - A')\,dt\right] - \left[u_2 - u_1 + \alpha \int_{t_1}^{t_2} (u - A)\,dt\right] \quad (39)$$

and on the assumption that $\alpha' = \alpha$, $A' = A$. (See p. 706).

$$\varepsilon = (\theta_2 - u_2) - (\theta_1 - u_1) + \alpha \int_{t_1}^{t_2} (\theta - u)\,dt \quad (40)$$

If the thermometer used in the middle period obey the equation (1), $\frac{d\theta}{dt} = \frac{1}{\lambda}(u - \theta)$ (p. 661), equation (40) is very easily reduced. If it do not, as, for instance, when a Beckmann thermometer is employed, the mathematical manipulation is more complex. This case will be discussed after taking up the one first mentioned. From (1) we obtain directly.

$$\int_{t_1}^{t_2} (\theta - u)\,dt = \int_{t_1}^{t_2} - \lambda \frac{d\theta}{dt}\,dt = -\lambda(\theta_2 - \theta_1)$$

so that equation (40) has the form

$$\varepsilon = (\theta_2 - u_2) - (\theta_1 - u_1) - \alpha\lambda(\theta_2 - \theta_1) \quad (41)$$

The values θ_1 and θ_2 must be obtained in the preperiod and afterperiod in the steady state of heat exchange between the calorimeter, its surrounding jacket and the thermometer, for which condition the relations are given[27] by equation (8) as explained in the derivation of that equation, case (c) page 666.

---

[27] This relation is also derived by W. P. White, loc. cit.

Applying equation (8) to the conditions occurring at t_1 and t_2.

$$\theta_1 - u_1 = \frac{\alpha_1 \lambda_1}{1 - \alpha_1 \lambda_1}(u_1 - A)$$

$$\theta_2 - u_2 = \frac{\alpha_2 \lambda_2}{1 - \alpha_2 \lambda_2}(u_2 - A)$$

between which equations the jacket temperature A is to be eliminated. It is almost universal to employ the same thermometer in preperiod and afterperiod so that $\lambda_2 = \lambda_1$. Let us assume that the heat capacity of the calorimeter remains unaltered, as, for instance, by adding some substance in the course of a method of mixtures experiment; then $\alpha_2 = \alpha_1 = \alpha$. The elimination of A gives

$$(1 - \alpha\lambda_1)(\theta_2 - \theta_1) = (u_2 - u_1) \qquad (42)$$

But (41) is $$(1 - \alpha\lambda)(\theta_2 - \theta_1) = (u_2 - u_1) + \varepsilon$$

Therefore $$\alpha(\lambda_1 - \lambda)(\theta_2 - \theta_1) = \varepsilon \qquad (43)$$

The error due to thermometric lag is thus proportional to the difference of lag of the two thermometers used in the end periods and the middle period, vanishing if the same thermometer be employed in both.

The discussion is not quite complete without a consideration of the assumption $\alpha' = \alpha$ and $A' = A$ made at the time of defining ε and passed over almost without comment (p. 707). Examination of the magnitudes involved makes it quite evident that the assumption is always true to the extent that deviations from it are numerically insignificant for the highest precision work yet accomplished. For the Regnault-Pfaundler[28] and allied methods of computation it may be shown to hold to the extreme limit of being an exact statement of the relations involved. The proof follows:

From the primary equation

$$-\frac{du}{dt} = \alpha(u - A)$$

---

[28] Synopsis of this method may be found in Berthelot "Traite Pratique de Calorimetrie Chimique," 2d ed., p. 117.

applied to the instants t_1 and t_2, may be obtained two equations containing α and A, which may be solved for either. Solving,

$$\alpha = \frac{\left.\frac{du}{dt}\right]_1 - \left.\frac{du}{dt}\right]_2}{u_2 - u_1}$$

whereas we use a value computed from a similar expression connecting thermometer readings,

$$\alpha' = \frac{\left.\frac{d\theta}{dt}\right]_1 - \left.\frac{d\theta}{dt}\right]_2}{\theta_2 - \theta_1}$$

Now by equation (8)

$$\frac{d\theta}{dt} = \left(1 + \frac{\alpha\lambda}{1 - \alpha\lambda}\right)\frac{du}{dt} = \frac{1}{1 - \alpha\lambda}\,\frac{du}{dt} \tag{44}$$

$$\left.\frac{d\theta}{dt}\right]_1 - \left.\frac{d\theta}{dt}\right]_2 = \frac{1}{1 - \alpha\lambda}\left(\left.\frac{du}{dt}\right]_1 - \left.\frac{du}{dt}\right]_2\right)$$

and by equation (42)

$$\theta_2 - \theta_1 = \frac{1}{1 - \alpha\lambda}(u_2 - u_1)$$

from which it is evident that α' is identically α. Solving for A, for instance in the form,

$$A = u_1 + \frac{1}{\alpha}\left.\frac{du}{dt}\right]_1$$

an exactly similar process to the above shows that A' is identically A[29]

---

[29]
$$\begin{aligned} A' &= \theta_1 + \frac{1}{a}\left.\frac{d\theta}{dt}\right]_1 \\ &= u_1 - \lambda\left.\frac{d\theta}{dt}\right]_1 + \frac{1}{a}\left.\frac{d\theta}{dt}\right]_1 \quad \text{by equation (1)} \\ &= u_1 + \frac{1}{a}(1 - a\lambda)\left.\frac{d\theta}{dt}\right]_1 \\ &= u_1 + \frac{1}{a}\left.\frac{du}{dt}\right]_1 \quad \text{by equation (44)} \\ &\equiv A \qquad\qquad \text{Q. E. D.} \end{aligned}$$

When a thermometer obeying the law $\frac{d\theta}{dt}=\frac{1}{\lambda}(u-\theta)$ *is employed in a calorimetric experiment, no account is to be taken of lag, if the same thermometer be used for preperiod, middle period, and afterperiod.* The important restriction on the generality of this proposition that the upper temperature measurement be postponed until the steady state of heat exchanges is well established, need hardly be included in the italicized conclusion because no measurement taken before the restriction was complied with would satisfy the more fundamental requirements of the calorimetric determination.

A thermometer which does not obey the law above stated must be examined by a process similiar to that outlined in the preceding pages. The only type we will consider here is the Beckmann, general equations for which have been deduced in Section II. The conclusions of the investigation show also that not merely is any error due to lag quite inappreciable for ordinary conditions, but that it is mathematically zero as for the case above. The expression for the error is a little tedious of derivation, although not so very difficult.

Let us start from equation (40) which is an entirely general expression for ε, the total error due to thermometric lag, with no limitation as to the form of thermometer, except in so far as might be said to lie in the assumption that α' and A' computed from lagging thermometer readings may be used interchangeably with α (the real cooling constant of calorimeter) and A (real jacket or "convergence" temperature), the values which would be obtained with a lagless thermometer. This assumption, briefly discussed before, is quite evidently true for a Beckmann thermometer.

Equation (40) is $\varepsilon=(\theta_2-u_2)-(\theta_1-u_1)+\alpha\int_{t_1}^{t_2}(\theta-u)dt$, and the difficulty in reducing it, when a Beckmann thermometer is employed, is the determination of the value of the last term for a thermometer obeying the law expressed by the relation (15). (The explanation of which quite uninterpretable equation, and the notation employed for this type of instrument, are to be found in the paragraph on p. 683, containing equations (12) and (13).)

The expression for $(u-\theta)$ developed in the general treatment contained in Section II (equation (16)), unfortunately contains u under an integral sign, presupposing a knowledge of the function before further reduction of the relation. It is very desirable to make this investigation entirely independent of the form of the curve which the calorimeter temperature rise follows, so that this expression can not be employed as there written. Tracing it back to its genesis we are obliged to use equations (12), (13), and (14) as follows:

$$\theta = kC + (1-k)\ B \qquad (14)$$

$$u = ku + (1-k)\ u \qquad \text{(Identity)}$$

$$C - u = -\lambda_c \frac{dC}{dt} \qquad (13)$$

$$B - u = -\lambda_B \frac{dB}{dt} \qquad (12)$$

from which

$$\theta - u = k\left(-\lambda_c \frac{dC}{dt}\right) + (1-k)\left(-\lambda_B \frac{dB}{dt}\right)$$

and

$$\alpha \int_{t_1}^{t_2} (\theta - u)\,dt = -\alpha k \lambda_c \int_{t_1}^{t_2} \frac{dC}{dt} dt - \alpha(1-k)\lambda_B \int_{t_1}^{t_2} \frac{dB}{dt} dt$$
$$= -\alpha[k\lambda_c(C_2 - C_1) + (1-k)\lambda_B(B_2 - B_1)]$$

and equation (40), with the integration performed, becomes

$$\varepsilon = (\theta_2 - u_2) - (\theta_1 - u_1) - \alpha[k\lambda_c(C_2 - C_1) + (1-k)\lambda_B(B_2 - B_1)] \qquad (45)$$

The Bs and Cs can not be united to θs on account of the factors λ_c and λ_B multiplying them, so the θs must be split into parts to permit of collecting terms. This is accomplished by means of (14) and the identity just beneath it, a few lines above. Applying to the instants t_1 and t_2,

$$\theta_1 - u_1 = k(C_1 - u_1) + (1-k)(B_1 - u_1)$$
$$\theta_2 - u_2 = k(C_2 - u_2) + (1-k)(B_2 - u_2)$$

from which a value for $(\theta_2 - u_2) - (\theta_1 - u_1)$ may be substituted in equation (45) giving

$$\varepsilon = k[(C_2 - C_1)(1 - \alpha\lambda_c) - (u_2 - u_1)]$$
$$+ (1-k)[(B_2 - B_1)(1 - \alpha\lambda_B) - (u_2 - u_1)] \qquad (46)$$

We turn now to the equilibrium state in the preperiod and afterperiod and will pass by the case where thermometers of different lag are employed in these and the middle period. The relations of C and B to u are given by equations (12) and (13).

$$\frac{dB}{dt}=\frac{1}{\lambda_B}(u-B) \quad (12); \quad \frac{dC}{dt}=\frac{1}{\lambda_c}(u-C) \quad (13)$$

and u is determined by the relation

$$\frac{du}{dt}=-\alpha(u-A)$$

so that from the discussion of case (c) in Section I (p. 666) it may be seen that equation (8) states the relation of B or C to u when the steady state obtains.

$$B-u=\frac{\alpha\lambda_B}{1-\alpha\lambda_B}(u-A) \quad C-u=\frac{\alpha\lambda_c}{1-\alpha\lambda_c}(u-A) \tag{8}$$

from which, applied at instants t_1 and t_2 come the relations

$$(1-\alpha\lambda_B)(B_2-B_1)=u_2-u_1$$
$$(1-\alpha\lambda_c)(C_2-C_1)=u_2-u_1$$

and equation (46) is at once

$$\varepsilon=0$$

No error is therefore made by employing thermometer readings, uncorrected for lag, throughout the computation when a Beckmann instrument of the usual form is used. The restriction mentioned before that this conclusion is true only when both θ_1 and θ_2 are measured in the steady state of heat exchanges requires more emphasis than in the case of an ordinary thermometer, because the Beckmann type is so much slower to reach this state, as shown on pages 692–694.

When thermometers with different lag, whether Beckmann or "chemical" type or electrical, are employed for the middle period and the end periods, when the heat capacity of the calorimeter is greatly changed in the course of a run, or when the adiabatic method of calorimetry is used, with thermometers of different lag in the calorimeter and its jacket, the corrections because of lag may be appreciable and may be computed from the most convenient of the foregoing equations.

V. LAG CORRECTIONS IN APPLIED THERMOMETRY

Statements and conclusions relating to thermometric lag of importance in applied thermometry, are here summarized for convenience. As has been previously suggested, a determination of λ to an accuracy of only 50 or 100 per cent is quite often sufficient, as lag corrections are usually exceedingly small.

RÉSUMÉ OF PRACTICAL INSTRUCTIONS

1. **Constant Temperature.**—In a bath at constant temperature no correction for lag is to be made if the thermometer reading be taken a sufficient interval of time after introducing the instrument into the bath. A convenient interval to remember is 10λ seconds, in which time the initial difference of temperature is reduced to $\epsilon^{-10}(=0.00004)$ times itself. For all ordinary chemical thermometers in liquid baths stirred even slowly, 10λ will be rather less than a minute, and decrease from this value if the stirring be increased. In a gas where λ may have any value between 15 seconds and 10 minutes or more, depending upon conditions of stirring and form of thermometer, it may not be convenient to wait 10λ seconds for a reading. Computation on the basis of reduction every λ seconds of any temperature difference between bath and thermometer to a value ϵ^{-1} times that at the beginning of the period of λ seconds will show the interval which must elapse before the thermometer reading is correct within the allowable error.

2. **Linear Change of Temperature.**—In a bath whose temperature is rising at a uniform rate of r units per second, the correction to a thermometer reading at any time, to get the bath temperature at the same instant is $+r\lambda$ units. As a concrete example of the largest error likely to occur were lag neglected, may be reviewed the numbers in an intercomparison of a 3-second and a 15-second thermometer in a comparison bath rising at about the most rapid rate with which it would be practicable to obtain readings reliable to single thousandths, about 0°.03 per minute. One thermometer

would lag behind the bath by (0.0005 × 3) degrees, the other by (0°.0005 × 15), making a difference of 0°.006 in their indications due to lag. So rapid a rate of rise when reading single thousandths and so great a difference in the values of λ for two thermometers in the same bath is of quite infrequent occurrence, whence it is not often that a lag correction will be found necessary.

3. **General Case of Changing Temperature.**—In a bath whose temperature is changing according to any more complicated law, but so as to be a continuous single valued function of time, the lag correction to any reading of a thermometer immersed in it is found by reading temperatures at sufficiently short intervals to plot the function θ with time so as to have the value $\frac{\partial\theta}{\partial t}$ at any point. The fundamental equation (1) (p. 661) then gives $u=\theta+\lambda\frac{\partial\theta}{\partial t}$, the lag correction being $+\lambda\frac{\partial\theta}{\partial t}$.

4. **Calorimetry.**—No correction for thermometric lag is to be made if all of the following conditions hold:

(1) The thermometer be one whose behavior accords with

$$\frac{\partial\theta}{\partial t}=\frac{1}{\lambda}(u-\theta)$$

(Symbols explained on p. 661), or is a Beckmann instrument of the usual form with a large inclosed capillary just above the bulb.

(2) The same thermometer (or different ones with the same lag, λ) be employed for preperiod, after-period, and middle-period temperature readings.

(3) The lower and upper temperatures be read after the calorimeter, its jacket, and the thermometer have certainly "attained the steady state" of heat exchange (usually a close approximation to linear rise or fall of temperature of calorimetric aggregate). "Attaining steady state" must, of course, be interpreted in the sense used physically for any mathematically asymptotic relation. There is seldom any doubt about this respecting the lower temperature reading; it is only the upper one concerning which the observer must be cautioned.

(4) The heat capacity of the calorimeter be the same during the three periods of the experiment.

VI. SUMMARY

1. Thermometric lag is conveniently expressed by employing a quantity λ, whose significance may be stated as follows:

(1) If a thermometer has been immersed for a long time in a bath whose temperature is rising at a uniform rate, λ is the number of seconds between the time when the bath attains any given temperature and the time when the thermometer indicates this temperature. In other words, it is the number of seconds the thermometer "lags" behind the temperature; or [30]

(2) If a thermometer be plunged into a bath maintained at a constant temperature (the thermometer being initially at a different temperature), λ is the number of seconds in which a difference between the thermometer reading and bath temperature is reduced to $1/\epsilon$ of its initial value.

The fundamental equation of heat transfer, commonly referred to as Newton's law of cooling, is stated in terms of λ, for application to problems in thermometric lag, and the principal working equations derived therefrom are reviewed.

2. To express analytically the lag of the common form of Beckmann thermometer, the simpler theory was modified to take into account the fact that the lag of the bulb and that of the large capillary, between the bulb and the fine capillary, are different.

3. Methods of determining lag are discussed and experiments are cited to test the theories as applied to ordinary "chemical" thermometers and to Beckmann thermometers.

4. The large variation in the lag of a given thermometer with the nature of the medium in which it is immersed, and with the rate of stirring of this medium, is brought out by experiments in water, in a viscous kerosene, and in air, in which these media were forced past the bulb of the thermometer at different measured rates.

Values from the curves obtained are:

---

[30] These two interpretations of λ are mutually consistent. The *definition* of the quantity is most logically made by designating it as the "constant" of the fundamental equation, and then deducing the interpretations here given.

λ in seconds. Small-Bulb "Chemical" Thermometer

Vel. past bulb in cm/sec.	0	1	5	10	50	100	500	1000	∞
Water	10.0	5.1	3.3	2.9	2.4	2.3	......	......	2.2 sec. (any medium)
Oil	40 to 50	13.4	7.5	6.4	4.8	......	......	......	
Air	190	170	148	128	71	58	33	25	

5. Part, and frequently the largest part, of the lag of a thermoelectric or electrical resistance thermometer is the lag of the galvanometer. A d'Arsonval galvanometer, critically damped, is shown to lag $4\times\frac{\text{Moment of Inertia of Moving System}}{\text{Damping coefficient.}}$ seconds behind an emf changing linearly with time, after the steady state of motion is attained. A close approximation to this value is lag $= T/\pi$ seconds, where T is the complete period of the moving system, oscillating much underdamped.

6. Types of resistance thermometers were tested for lag. The Callendar type, in a liquid bath, was found to lag greatly in comparison with an ordinary "chemical" mercurial thermometer, and the empirical expression of the lag is of the same form as that developed for a Beckmann thermometer. The Dickinson-Mueller type of resistance thermometer bulb in a liquid bath was found to lag much less than the fastest of mercurial thermometers.

7. The Jaeger-Steinwehr method of computing the lag of a resistance thermometer, from the heating effect of the measuring current and the heat capacity of the thermometer, is critically discussed. The lag of a Dickinson-Mueller thermometer in a well-stirred liquid bath is shown to be about one-half second.

8. The necessary corrections that must be applied to the observed readings of a thermometer to correct for the effect of its lag under the usual conditions of use are discussed in some detail.

9. An analytic proof is given of the fact that in an ordinary calorimetric experiment, in which the same thermometer is used to determine temperatures in the "preperiod," the "middle period," and the "afterperiod," the correction for lag in the middle period neutralizes the corrections for lag in the preperiod and the afterperiod.

WASHINGTON, March 5, 1912.