THERMOMETRIC LAG AND A METHOD FOR ITS MEASUREMENT.

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INTRODUCTION.

The mercury-in-glass thermometer is the almost universal laboratory instrument for the measurement of temperature. Owing to the intimate relation between the properties of a substance and its temperature this instrument is surpassed in usefulness by very few if any other instrument found in physical and chemical laboratories. Its importance in the domain of science is attested by the voluminous literature relating to its development and accurate use. The training of a physicist or a chemist can scarcely be regarded as complete if it has not enabled him to use the Hg-in-glass thermometer with precision. The science of thermometry, therefore, has come to hold a position of fundamental importance.

This type of instrument depends, as is perfectly well known, upon observations of the relative expansion of mercury and glass. The properties of glass are such, however, that if the bulb of a thermometer having been exposed to a given temperature, either high or low, is transferred to an environment differing considerably in temperature it does not immediately undergo all the *possible change*—either expansion or contraction. It is true that the greater part of the possible change occurs very quickly but there are small *residual changes* which proceed very slowly over a period of hours, days or weeks. This “lagging” of the thermometer is known as “thermal hysteresis” and is not to be confused with “thermometric lag” the subject of discussion in this paper. The former manifests itself in the so-called “elevation,” “depression,” and “recovery” of the zero point. The magnitude of these phenomena depends mainly upon the nature of the glass and the differences in temperature to which the thermometer has been exposed.

It is obvious, therefore, that on account of these phenomena of thermal hysteresis that the observed “reading” of a thermometer depends not alone on its temperature, but also on its previous thermal history, and that procedures for the elimination of errors from this source should be formulated.

An examination of a treatise on thermometry will reveal to the student, of course, that the foregoing phenomena are not the only sources of error attendant upon the use of the thermometer and

that carefully defined procedures, tables of corrections and equations have been formulated to minimize errors from the sources indicated. As pointed out previously, it is essential that the student undertaking scientific work should be familiar with this data, and if his laboratory assignments have been sufficiently comprehensive he will have applied to his thermometric observations at some time or another all of the following corrections.

TABLE OF CORRECTIONS FOR HG-IN-GLASS THERMOMETERS.

(Primary Standards.)

1. Corrections for Irregularities in Graduation.
 - A. Correction of "fundamental interval."
 - a. Location of "ice-point" (O C). Changes of the ice-point. Temporary and permanent.
 - b. Location of "boiling-point."
 - B. Determination of the relation of the internal volume of the stem to the scale which has been provided.
 - a. By calibration of the stem between fixed points.
2. Correction for the effects of variation in the internal pressure. (Due to changes in the height of the mercury column, vapor pressure and capillarity.)
3. Correction for the effects of variation in the external pressure.
 - a. Determination of the effect of variation in the barometric pressure.
 - b. Determination of the effect of variation in depth to which thermometer may be immersed in a liquid.
4. Correction for emergent stem.
5. Correction for "thermometric lag."
6. Corrections for reduction to standard scales.
 - a. Corrections for "Hydrogen Scale" (100°C. to lowest attainable temperatures).
 - b. Corrections for "Nitrogen Scale" (100°C. to approximately 1600°C.).
 - c. Corrections for reduction of actual gas scales to "Thermodynamic Scale" (Ideal gas scale).

Of all the corrections listed in the foregoing table, the one designated as "thermometric lag" has been without doubt the most difficult of comprehension and application for the students doing work in thermometry and calorimetry in this laboratory. It was this experience which led the author originally to prepare the following "notes" for his students and it is at their suggestion that they are submitted for publication.

The discussion and determination of "thermometric lag" as outlined here do not possess the rigorous accuracy which is characteristic of the severely mathematical treatment accorded the subject by Thiesen¹, Guillaume², Harper³ and others; but it is believed that any departure is easily within the allowable limit of error and it is hoped that a treatment "put lightly like powder in jam" may eventually encourage the student to take more heroic doses.

¹Thiesen, *Metronomische Beiträge*, No. 3, page 13 (1881).²Guillaume, *Thermometrie de Precision*, page 184 (1889).³Harper, D. R., *Thermometric Lag*, Bur. of Standards, Rep. No. 185.

DETERMINATION OF THE LAG OF A THERMOMETER.

When a thermometer is immersed in a warmer or cooler medium, or in one of which the temperature is changing, for the purpose of ascertaining the temperature of said medium it does not immediately indicate the true temperature of the latter, but lags behind both in point of *time* and *degrees*.

For example, if a thermometer be plunged into a bath maintained at a constant temperature (it being assumed that the thermometer was initially at a different temperature) a certain time must elapse before the temperature indicated by the thermometer will agree with the temperature of the bath. The thermometer readings are thus said to "lag" behind the true temperature (of the bath) by an amount which depends upon the construction of the thermometer.⁴

The interval of time which must elapse between the time of a given "reading" and the time when the thermometer indicates the (true) temperature of the bath is known as the "time lag". or

The difference (expressed in degrees) between the temperature indicated by the thermometer at a given time and the final temperature when the thermometer is in thermal equilibrium with the bath is known as the "degree lag."

In the case of a thermometer immersed in a bath the temperature of which is changing uniformly the "degree lag" at any observation may be defined as the difference in degrees between the temperature indicated at the time of the observation and the true temperature of the bath. Such conditions are reproduced fairly well in ordinary calorimetric determinations.

In reply to the question, "How is the true temperature of the bath at time of any observation of the thermometer to be determined if the thermometer is 'lagging,'" it may be answered briefly here that *it is calculated from data* (previously secured by experimenting with the thermometer) *associated with the rate at which the thermometer is changing its temperature indications.*

Practically all theoretical treatment of the question of "thermometric lag" (i. e., the transfer of heat between a thermometer bulb and the medium in which it is immersed) is based on the assumption that "Newton's Law of Cooling"—namely, "the rate of heat transfer between two bodies is directly proportional to the difference of temperature between the two," holds for the thermometer.

⁴The magnitude of the "lag" is dependent not only upon the construction of the bulb, but also upon the medium in which it is immersed, the rate of stirring and the conditions of immersion. For example, it has been shown that the "lag" in the air of a room is 50 times that of the same thermometer immersed in a well-stirred water bath.—See Circ., B. of S., No. 8.

In other words, the rate of change in temperature indicated by a thermometer is proportional to the difference between the temperature of the thermometer and the temperature of the medium in which it is immersed.

From the foregoing it is at once concluded that the "lag" represents the difference between the temperature of the thermometer and the medium and that it is this difference in temperature (other conditions being kept constant) which determines the rate of change indicated by the thermometer. We would conclude also that there is a definite "lag" associated with each and every rate of change indicated by the thermometer, and that if these relationships had been established for a thermometer by experiment, we should be able at any future time when using this thermometer under the same conditions to calculate the "lag" by merely determining the rate at which the thermometer reading is changing. As a matter of fact, this represents the basis of theory underlying the method for correcting for thermometric lag.

We have now to consider the experimental method by which the relationship just pointed out, namely, between the "lag" and the rate of change in thermometer indications, may be established quantitatively. This is outlined in the following section of the paper.

EXPERIMENTAL PART.

The procedure for determining the "lag" of a thermometer under defined conditions is comparatively simple. The experimental study of "thermometric lags" of importance in applied thermometry and calorimetry involve the formulation of equations for but two sets of conditions: (1) The case of a medium at a constant temperature, and (2) The case of a medium with a uniformly changing temperature.

The Case of a Medium at a Constant Temperature.—In this case we have for our problem the investigation of the "lag" behavior of a certain thermometer, it being conditioned that the instrument is to be plunged into a bath maintained at a constant temperature, the thermometer being initially at a different temperature. Of course it is understood that if the thermometer reading be taken at a sufficient interval of time after introducing the instrument into the bath no correction for "lag" need be made but if this thermometer is to be used at any future time to determine the temperature of baths under similar conditions and the temperatures of these baths be required while the thermometer readings are changing, i. e., before it reaches the "equilibrium

state," it is obvious that the "degree lags" of the instrument at various rates of cooling must have been determined previously by experiments similar to those which have been outlined as follows in (a) and (b).

(A) THE DETERMINATION OF THE (DEGREE) LAG OF A THERMOMETER WHEN ITS TEMPERATURE IS FALLING.

Arrange a water-bath which can be well stirred and maintained at a constant temperature, for example, a calorimeter filled with water at the same temperature as the jacket and the room. Warm the thermometer until it indicates a temperature 2 or 3 degrees higher than that of the bath, then introduce it into the latter and quickly clamp it in position. Keep the water well stirred and take the reading of the thermometer every 10 or 15 seconds until the readings become constant. Be sure to keep the thermometer jarred by gently tapping it.

Plot the readings against the time and obtain the "cooling curve," such as ABC, Fig. 1. Then subtract each reading from the one preceding it. These values obtained (expressed in degrees) represent the rate of cooling for each succeeding interval of time. Now subtract from each reading of the thermometer the final temperature indicated by the instrument when it has reached its "equilibrium state." These differences (expressed in degrees) represent the "lags" exhibited by the thermometer at the given time intervals of the readings, or better, they represent the "lags" exhibited by the thermometer at its different rates of cooling.

The tabulation of this data will show at once that for each definite rate of cooling shown by the thermometer there is exhibited a definite "lag"—the theory being that whenever this thermometer is used under similar conditions and shows one of these definite rates of cooling, dr/dt , that its lag will be approximately the same as the one associated with that rate of cooling in the experiment just performed. Hence, if the observer knows the rate of cooling of the thermometer he can by referring to his table of data or diagram determine the lag of his thermometer at that time. By subtracting this "lag" from the last reading he noted when determining the rate of cooling he is able to compute the temperature of the bath without waiting for the thermometer to arrive at its "equilibrium state."

As an illustration of the method outlined, the following example has been added.

TABULATED DATA FROM EXPERIMENT.

(Bath has a constant T. of 20.000°C which corresponds to 1.020°C on Beckmann thermometer.)

No. of observation.	Time in secs.	Reading on Beckmann.	Rate of colling.	Lag in degrees.
1	0	2.850°C	?	?
2	15	1.145	1.705°C	.125°C
3	30	1.070	.075	.050
4	45	1.047	.023	.027
5	60	1.031	.016	.011
6	75	1.025	.006	.005*
7	90	1.022	.003	.002
8	105	1.021	.001	.001
9	120	1.020	.001	.000
10	135	1.020	.000	.000

*Lag when the rate of cooling is .006° per 15 sec.

Discussion of Figure: Tangents to the curve ABC show the rates at which the thermometer readings are changing and the angle θ determines the direction and, therefore, the point of contact of any tangent with the cooling curve ABC; for we have seen that the difference in thermometer readings (dr) divided by the corresponding difference in time (dt) of said readings, i. e., dr/dt , represents the rate at which the thermometer is

Fig. 1.

cooling, but this same value, dr/dt , is also equal to $\tan \theta$. Hence, if we draw a tangent to the curve ABC of thermometric readings at the point k , the rate at which the thermometer is cooling is equal to dr/dt and if θ is the angle the tangent makes with OX, the axis of time, then

$$\frac{dr}{dt} = \tan \theta$$

Therefore, if we draw a line, fk , from the point k to the axis of thermometer readings, parallel to the axis of time, it follows that the line fo (expressed in degrees) must represent how far the thermometer is from its "equilibrium state," i. e., its "lag" when the thermometer readings are changing at a rate represented by $\tan \theta$.

Problem.—Suppose it is required to find the lag when the readings on the thermometer is changing at the rate of $.020^\circ\text{C.}$ in 30 seconds ($.010^\circ\text{C.}$ in 15 sec.). Take a point m on OY, Fig. 1., equal to $.020^\circ\text{C.}$ and another point n on OX equal to 30 sec., then join the two points by the straight line mn . Now draw a tangent, to cooling curve ABC, parallel to mn . $\tan \theta$ is equal to the rate of cooling. From the point k where the tangent touches the curve ABC draw the line fk as directed above. Evaluate in degrees the line fo , and it will be found that the lag is approximately $.009^\circ\text{C.}$

(B) THE DETERMINATION OF THE LAG OF A THERMOMETER WHEN ITS TEMPERATURE IS RISING.

Arrange apparatus as outlined in (a). In this case, however, cool the thermometer until it indicates a temperature 2 or 3 degrees lower than that of the bath, then suspend it in the latter, make observations and record data as indicated in (a).

The graphic representation in this case (See Fig. 2.) will differ a little from that of (a) but the theory of it is identical.

⁵NOTE.—"Because of the sticking of the meniscus and possible separation of the Hg column, the readings of a Hg 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." B. of Standards, Reprint No. 185.

The Case of a Medium with a Uniformly Changing Temperature.

—Although this case requires for its comprehensive treatment the formulation of equations for the determination of lags of thermometers located in baths which do not attain to a constant temperature, as a rule, during the period of observation, it is restricted here to a consideration of calorimetric work in which the evaluation of the "lag" is of much importance.

In precise calorimetric measurements which are now very

Fig. 2.

generally conducted in "adiabatic" calorimeters in which case, of course, no correction need be made for loss of heat by radiation (and conduction), the procedure consists merely in determining the total change of temperature of the contents of the calorimeter by observing the initial temperature of the system and the final temperature of the same at which points the thermometer readings are practically constant. The method for correcting for the "lag" under these conditions has been considered and need not be applied again.

In the case of calorimetric measurements carried out in non-adiabatic calorimeters, however, the conditions under which the thermometer exhibits "lag" differ somewhat from those specified in the first case. This is due to the fact that a correction must be made for the loss of heat by radiation. The method employed in determining the magnitude of the correction to be applied for radiation effects determines the *modus operandi* in determining and applying the correction for "thermometric lag." Therefore, let us consider briefly this problem.

THERMOMETRIC LAG IN RELATION TO REGNAULT'S METHOD
FOR CORRECTING FOR RADIATION EFFECTS.

The two methods most frequently employed in correcting for radiation effects in calorimetric work are Rumford's Method and Regnault's Method. By the first method an effort is made to eliminate by experimental procedure the necessity for introducing a correction factor for radiation effects into the calculation of the final data. The method, however, is not entirely satisfactory and Regnault's method is to be regarded as the preferable one of the two methods.

Regnault's Method.—This method provides for the measurement of the loss of heat by radiation and the introduction of a "correction factor" for same. The evaluation of this "correction factor" is accomplished by the experimental determination of the "radiation factor" of the calorimeter at an observed temperature for definite period of time, from which may be calculated the "radiation quantities" for the successive periods of time during which the temperature of the calorimeter was rising. These quantities are then added to the maximum temperature recorded.

Regnault's method as originally formulated was unsatisfactory in that it assumed that the temperature of the thermometer followed exactly the temperature of the contents of the calorimeter. This we have seen is not the case and that a correction must be applied for the "lag." This may be done as follows: Having ascertained the "lag" behavior of the thermometer under conditions similar to those of the experiment contemplated proceed according to Regnault's method but note with care the final temperature (falling) observed. Obviously the last radiation quantity recorded represents the rate of cooling of the thermometer. Calculate the "lag" of the thermometer, subtract it from the final reading, then add all of the radiation quantities for the various periods of the experiment. The result thus obtained will represent the highest temperature which the thermometer would have recorded during the experiment had there been no loss of heat from the calorimeter by radiation and if the thermometer had not exhibited that which has been described in this paper as "thermometric lag."

SUMMARY.

"Thermometric lag" has been defined in terms of both "time" and "degrees."

It has been accorded a theoretical treatment from the standpoint of "Newton's Law of Cooling."

A comparatively simple method by which a severely mathematical treatment has been avoided, has been outlined for the determination of the "lag" of a thermometer under various conditions.

The method of combining the correction for "lag" with Regnault's method for correction for loss of heat by radiation in calorimetric measurements has been presented.

A LABORATORY EXERCISE ON HEAT CONDUCTIVITY.

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The conductivity of various substances plays a rather important part in the daily life of everyone, yet a simple and satisfactory laboratory experiment to measure it, does not seem to have been described.

The apparatus described here was developed for a course in physics given to students of home economics. It is so simple and the operations are so easy that there is no reason why girls in high schools should not be given such an exercise.

The conductivity of a substance is proportional to its area, to the difference in temperature between the two faces, to the time, and inversely proportional to the thickness of the substance. We may write

$$\text{Heat} = \frac{k \times \text{Area} \times (t-t') \times \text{time}}{\text{thickness}}$$

If H is to be expressed in calories, then the area must be given in square centimeters, $(t-t')$ in degrees Centigrade, time in seconds and thickness in centimeters.

Then

$$k = \frac{H \times \text{thickness}}{\text{Area} \times (t-t') \times \text{time}} = \text{coefficient of conductivity.}$$

The calorimeter, Fig. 1., consists of a double walled vessel A with a heavy copper bottom, 4 mm. thick, projecting 0.5 cm. beyond the walls. The diameter of the bottom is 16 cm. The areas of the two cylinders, B and C, are the same. A cover has openings for two stirrers, one in each compartment and for two thermometers.