

DEPARTMENT OF COMMERCE AND LABOR

CIRCULAR

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 8

TESTING OF THERMOMETERS

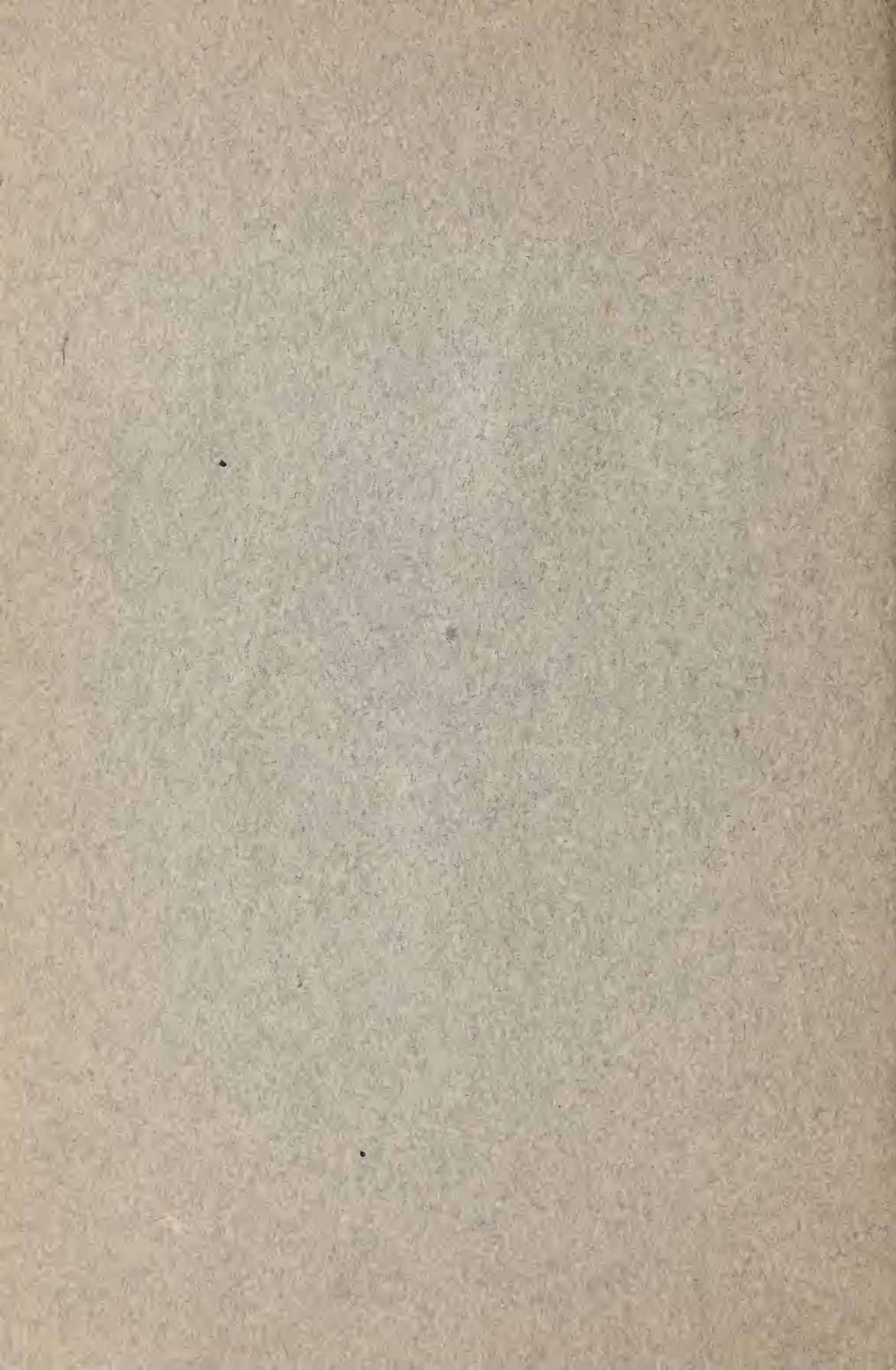
[2d Edition, Revised and Enlarged]

Issued June 30, 1911



WASHINGTON
GOVERNMENT PRINTING OFFICE

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1. INTRODUCTION

This circular ¹ has been enlarged beyond the scope of a table of fees in order to answer as far as possible the inquiries that are addressed to this Bureau from time to time concerning temperature measurements, methods

¹ Special circulars on Testing of Clinical Thermometers (No. 5), on Pyrometer Testing and Heat Measurements (No. 7), and on the Standardization of Bomb Calorimeters (No. 11) have been issued by this Bureau. Other circulars relating to Thermometer Specifications, the Specific Heat of Calcium Chloride Brines, etc., are in preparation.

of using thermometers, specifications for and construction of thermometers to meet the requirements of special problems, regulations governing their acceptance for test, etc. Some of the important thermometric properties of different kinds of glass, and their proper heat treatment, together with the essential requirements of a reliable thermometer, are emphasized in the hope of bringing about an improvement in the product, which is often not constructed according to the best practice of the present day.

Although many of the topics discussed in the previous edition of this circular have been enlarged and much new matter has been added, it is, of course, impossible to anticipate in a limited space the many questions that may arise in temperature measurement. The Bureau will always be pleased to furnish any information in its possession if the interested party will state clearly and in sufficient detail the problem at hand.

Thermometers of various types referred to under sections 11, 16, and 17 will be accepted for test in accordance with the schedules under section 20.

2. TEMPERATURE SCALE

It is well known that the scale of temperature defined by a mercurial thermometer is dependent upon the composition and treatment of the glass. Even samples of glass from the same pot show differences in this respect. Mercury in glass thermometers, although capable of very great precision when properly constructed and used with due precautions, are therefore not suited to establish the standard scale of temperature.

International Hydrogen Scale.—The temperature scale which has come into almost world-wide use in the interval -35° to $+100^{\circ}$ C is the hydrogen scale of the International Bureau of Weights and Measures, as defined by the following resolution of the International Committee on Weights and Measures, adopted October 15, 1887:

“The International Committee on Weights and Measures adopts as the standard thermometric scale for the international service of weights and measures the centigrade scale of the hydrogen thermometer, having as fixed points the temperature of melting ice (0°) and of the vapor of distilled water boiling (100°) at standard atmospheric pressure; the hydrogen being taken at an initial manometric pressure of 1 meter of mercury—that is to say, $\frac{1000}{760} = 1.3158$ times the standard atmospheric pressure.”

On this scale of temperature, therefore, 1° C is measured by $\frac{1}{100}$ of the change in pressure, between the two fixed temperatures, of the confined mass of hydrogen gas, whose volume is kept constant, and whose initial pressure (at 0° C) is equivalent to 1 meter of mercury (reduced to 0° C, lat. 45° , sea level).

For temperatures in the interval -35° to $+100^{\circ}$ C, the standard scale of temperature adopted by this Bureau is the international hydrogen scale,

defined by the mean indications of a number of primary standard mercurial thermometers, constructed by Tonnelot and by Baudin, which have been carefully studied and compared at various times with the standards of the International Bureau. The results of intercomparisons of these standards, based on many thousands of observations, the details of which will be found in B. S. Reprint No. 69, may be summarized in the statement that the mean scale defined by these thermometers is in agreement with the scale defined by the standards of the International Bureau and they serve to reproduce the international hydrogen scale to within the limits of accuracy (about 0.002°C) at present attainable in mercurial thermometry.

Hydrogen Scale.—The standard scale of temperature from -35°C down to the lowest attainable temperatures is also based on the hydrogen (or helium) gas thermometer, which has been used by various observers to determine a number of accurately reproducible temperatures or “fixed points,” such as the boiling points and freezing points of various gases. This temperature scale is then reproduced in the laboratory by means of resistance thermometers or thermocouples that have been standardized by observations of the resistances or electromotive forces, respectively, at these fixed points. The Bureau has available for this work a complete liquid air and liquid hydrogen plant. The theory of the Hampson liquefier is discussed in B. S. Reprint No. 123.

Nitrogen Scale.—As hydrogen is not well adapted for use at high temperatures, on account of its great chemical activity and the ease with which it diffuses through the walls of the containing envelope, the standard scale of temperature used in the interval from 100°C to the highest temperatures measurable with the gas thermometer is based on the constant volume nitrogen gas thermometer. A number of “fixed points,” such as the melting or freezing points of pure metals and the boiling points of suitable pure substances, on the temperature scale of the nitrogen thermometer, have been determined by a number of investigators, and these fixed points serve to reproduce the latter scale. The standard scale of temperature used by this Bureau in the interval 100° to 500°C is fixed and reproduced by means of a number of platinum resistance thermometers standardized by observations at these “fixed points.” Full details as to the temperature scale thus defined will be found in B. S. Reprints Nos. 124, 143, and 149, and in B. S. Circular No. 7.

Thermodynamic Scale.—From the foregoing it will be seen that the standard scale of temperature from 100°C down to the lowest attainable temperatures is based on the hydrogen (or helium) gas thermometer. Above 100°C , up to the highest temperatures at which the gas thermometer can be used at the present time (about 1600°C), the scale is based on the nitrogen gas thermometer. At still higher temperatures the scale is based on one or another of the radiation laws (see B. S. Circular No. 7 and B. S. reprints referred to under sec. 18). It is desirable for many purposes and essential to precise scientific work that ultimately measurements of temperature should be expressed in or be reducible to some one standard

scale. The thermodynamic scale, or scale of the *ideal gas* thermometer, is generally agreed on as best for this purpose. Practical gas thermometer scales differ from this by various small amounts. These differences, i. e., the corrections to be applied to the actual gas scales to reduce them to the thermodynamic scale, must be determined for the thermometric gases, since the ideal gas does not itself exist. The definition of an ideal gas is discussed in B. S. Reprint No. 136.

Those interested will find in B. S. Reprint No. 57 the recomputation of these corrections from the best available data. The departure of these various gas scales from the thermodynamic scale is, at all temperatures, within the limits of accuracy attained up to the present time with the gas thermometer. The scale defined by the radiation laws is the thermodynamic scale, provided that these laws (Stefan-Boltzmann, Planck, and Wien) have a sound theoretical basis and are real laws of nature and not merely empirical equations.

3. TEST REQUIREMENTS

In general, instruments showing defective construction will not be accepted for test, but if such instruments are tested attention will be called to the defects in the report on the test.

Attention is directed below to a few of the essential requirements for a reliable thermometer.

(a) The graduations must be ruled either directly on the stem, which is always preferable, or on a scale securely and firmly fastened to the stem. In the latter case a fiducial mark should be found on the stem coinciding with a mark on the scale, so that any relative displacement can be controlled.

(b) The divisions of the stem should be numbered at such frequent intervals and in such a way that the identification of any graduation mark is not unnecessarily difficult. The cross section of the capillary and the spacing of the graduations should be uniform and free from such irregularities as would produce uncertainties in the indications by amounts exceeding the limits otherwise set by the type of thermometer.

(c) The width of lines should in no case exceed 0.2 of the smallest scale interval, and should preferably be less than 0.1 where the corrections are desired to 0.1 of this interval. If the width or the form of the graduations introduces too great uncertainty in the scale readings, the corrections will be given only to the smallest scale interval.

(d) The thermometer should have a few graduations beyond the extreme points that are to be used.

(e) All hypsometric and calorimetric thermometers should have a pear-shaped reservoir at the upper extremity of the capillary tube. This auxiliary reservoir is also highly desirable in most of the other types of thermometers, as it makes possible a mercury thread calibration of the stem, the removal of gas from the mercury, and diminishes danger of breakage due to overheating.

(f) Every thermometer submitted for test must pass a preliminary examination for details of construction, such as, for example, fineness and uniformity of graduation and uniformity of caliber, purity of the mercury, and cleanness of capillary tube and freedom from moisture, gas bubbles, cracks in the glass, etc. Tests are also made on the change of the ice point after repeated heatings and on the amount of the ice point depression, as a check on the reliability of the indications and the properties of the glass of which the thermometer is constructed. If these experiments show that the thermometer has not been properly annealed, or that it is constructed of glass having an unduly large hysteresis effect, i. e., large ice point depression and slow recovery (see sec. 12), certification may be refused.

If in this preliminary test a thermometer shows evidence of insufficient annealing, it will, if accepted for test, be first thoroughly annealed, for which an additional charge will be made (schedule 32, sec. 20). The annealing of thermometers is discussed at length under section 13.

(g) It is highly desirable that all thermometers should have on their scales the ice point (0°C or 32°F) or the steam point (100°C or 212°F), preferably the former, so that the changes in the glass, referred to above, can be followed and the proper correction applied. This construction is essential in all precision and laboratory thermometers for use at ordinary temperatures when an accuracy of 0.1 , or better, is desired, in limited scale thermometers such as clinical standards, and in all high temperature thermometers, in which the changes may amount to many degrees.

(h) Thermometers showing careless workmanship or having any defects of construction that are likely to lead to significant uncertainties in the use of the instrument will not be certified. The Bureau of Standards reserves the right in every instance to decide as to the acceptance of the instrument for test.

4. GENERAL CONDITIONS OF TEST

The exact conditions prevailing during the test, for which the table of corrections applies, will be stated in the certificate. In general, however, the corrections will be given for the condition corresponding to what is termed "total immersion"—i. e., when the mercury in the bulb and in the stem are both at the temperature of the bath in which the thermometer is immersed. If a thermometer is used under any other conditions, the certificate issued with it will give the necessary data for applying the "stem correction."

The number of points at which tests will be made and the order of accuracy of the corrections will depend upon the intended use of the thermometer, its graduation, the fineness of the lines, the kind of glass of which it is made, etc. The order of accuracy of the corrections will, in general, be stated in the certificate.

It is always desirable that a statement should accompany the thermometer when it is sent in for test, giving the order of accuracy desired, the portion of the scale which it is desired to know with the greatest accuracy,

and the conditions under which the thermometer is to be used. If this information accompanies the transmitting letter, the necessary data will be at hand to determine the number and distribution of the points at which tests should be made.

If desired, the corrections will be given to one-tenth the smallest interval of graduation, provided that this interval is not too short (not less than 0.4 or 0.5 mm), and that the graduations are sufficiently fine and uniform and the construction and behavior of the thermometer warrant this order of accuracy.

In general, it may be stated that if the readings of a thermometer are to be trusted to one or two-tenths of the smallest scale division, the interval between test points should not exceed 50 divisions and need not be less than 20. For ordinary thermometers graduated in 1° or 2° intervals, when the corrections are given only to the nearest degree, test points 100° apart are often sufficiently near together. The Bureau can not undertake to test thermometers at too frequent points. The number and distribution of the test points can only be decided after a careful inspection of the thermometer, and often only after the test has been partly completed. Tests at intervals of less than 20 scale divisions will be made only by special arrangement.

5. METHODS OF TESTING THERMOMETERS

Primary standards will be tested, whenever possible, as follows: By mercury thread calibrations throughout the scale to determine caliber corrections, repeated determinations of ice and steam point to determine fundamental interval, determination of external and internal pressure coefficients, and by direct comparison with the standards of the Bureau at one or more points to determine the departure of the mercury-in-glass scale defined by the thermometer from the accepted gas scale.

Ordinary laboratory and working standard thermometers, in the interval 0° to 100° C, are usually tested by direct comparison with at least two standards of the Bureau at a number of selected temperatures throughout their scales. These intercomparisons are carried out in a specially designed thermometer comparator (fully described and illustrated in B. S. Reprint No. 69) consisting of a motor-stirred water bath whose temperature, within the interval 5° to 95° C, is very accurately controllable by electric heating and cold water circulation.

The methods of testing calorimetric and Beckmann thermometers are described under section 11, C.

Thermometers in the interval 100° to 300° C are tested by direct comparison with at least two standard mercurial thermometers or with platinum resistance thermometers that have been standardized as explained in section 16. These comparisons are carried out in a motor stirred and electrically heated oil bath of a high flash point oil. At temperatures above 300° C a bath of fused salts (about equal parts of sodium and potassium nitrates) is used instead of oil. For commercial testing above 300° C, where an accuracy of 1° is sufficient, a copper block comparator is frequently used, con-

sisting of a cylinder of copper about 6 cm diameter and 45 cm long, into which are drilled a number of holes in the direction of its axis for the insertion of the thermometers. This cylinder is heated by means of an electric heating coil of Advance or Nichrome ribbon wound with somewhat closer spacing at the ends to compensate for the greater heat losses at these points. Small independent heating coils are added at each end to further improve the uniformity of temperature throughout the cylinder. In this comparator the high conductivity of the copper is substituted for the stirring in the other comparators. With a view to further increasing the uniformity of temperature throughout the copper, a comparator has been constructed in which the copper cylinder is mounted within an electrically heated air bath, in which the air is rapidly circulated (in a closed circuit) past the copper block. Emergent thread (faden) thermometers are used to determine the stem corrections (see sec. 9) to the several thermometers under test.

So-called mechanical thermometers, which are usually mounted in a metal casing for protection and which can not be immersed in a liquid bath, are tested by comparison with standardized platinum resistance thermometers or thermocouples in an electrically or gas-heated air bath, in which the air is kept in rapid circulation to insure uniformity of temperature throughout.

For testing of low-temperature thermometers a well-stirred bath of pentane is used, which can be kept at any temperature down to -150°C by a circulation around it of the cold air evaporated from liquid air, the amount of the cold air and thus the regulation of the temperature being very exactly controllable by means of the heat supplied through an electric heating coil immersed in the liquid air. Another comparator is being designed for work in the interval 0° to -70°C , in which a well-stirred bath of some suitable liquid such as gasoline or alcohol is cooled by the expansion of carbon dioxide through a sensitive valve and copper coil.

6. THE CALIBRATION OF THERMOMETERS

The details of the various methods of determining the calibration corrections of mercurial thermometers by comparing the lengths of suitably chosen mercury threads in different parts of the scale, to correct for variations in the bore of the capillary and irregularities in graduation, can not be given within the limited compass of a circular of this kind. Those interested will find full details in the references cited below.²

² Guillaume: *Thermometrie de Precision*, p. 40, published by Gauthier-Villars et Fils; 1889. Report of Committee of the British Association for the Advancement of Science, B. A. Report, pp. 145-204; 1882.

Marek: *Carl's Repertorium*, 15, p. 300; 1879.

Thiesen: *Ibid.*, 15, pp. 285, 678; 1879.

Benoit: *Trav. et Mém. du Bur. Int. des Poids et Mesures*, 2, p. C35; 1883.

Broch: *Ibid.*, 5, 1886.

Guillaume: *Ibid.*, 5, 1886.

Pernet, Jaeger, und Gumlich: *Wissen. Abhandl. der Phys.-Tech. Reichsanstalt*, 1; 1894.

Pernet: *Viertel Jahrschrift der Naturforsch. Gesellschaft, Zurich*, 41, p. 128; Anm. 1.

Grützmaker: *Wissen. Abhandl. der Phys.-Tech. Reichsanstalt*, 3, p. 245; 1900.

7. ICE AND STEAM POINT DETERMINATIONS

Ice Point.—The ice point is determined by immersing the thermometer in a mixture of finely divided pure ice saturated with distilled water. The mixture should be thoroughly saturated, as otherwise very significant errors may arise entirely aside from the degree of purity of the ice used.³ For accurate determinations it is better to surround the vessel with a larger concentric one, also packed with ice, to prevent circulation of slightly warmed water from the sides of the vessel, which might otherwise reach the bulb of the thermometer. The entire apparatus should be inclosed in an opaque shield of some kind (e. g., a polished metal jacket) to shield the thermometer bulb from external radiation. A more convenient apparatus, and perhaps a better one, may be made by employing a cylindrical Dewar vessel as the container. If the walls are silvered, there is no necessity for any other radiation shield.

Precautions.—As the reading of the thermometer may be affected by the conduction of heat down the stem, the ice should be heaped up around the stem and a narrow deep channel made to permit of reading, with the meniscus well below the surface of the ice. This precaution is especially necessary if the ice point is near the top of the bulb, and more important with inclosed scale (einschluss) than with solid-stem thermometers. To avoid sticking of the meniscus, which is very likely to occur with a falling column (the usual condition in ice point determinations), it is necessary to shake down the mercury by suitable movement of the thermometer, as otherwise errors amounting to two or three hundredths of a degree may be introduced. The effect of sticking of the meniscus may be largely reduced by cooling the thermometer (e. g., in mercury) to -2° or -3° C just before plunging it into the ice bath, so that the reading is taken on a rising rather than on a falling meniscus.

In precision work, it is necessary to take into account also the recovery of the zero which begins as soon as the thermometer is placed in the ice bath and which is of the order of 0.001 per minute (for verre dur glass) during the first few minutes, so that the reading will depend on the length of time the thermometer has been in the ice bath. The error resulting from this cause may be diminished by transferring the thermometer quickly from the bath, the temperature of which has been under observation, to the ice bath, and then reducing all readings to correspond to a definite time (say three minutes) after removal from the temperature bath.

Purity of ice.—The ice-point reading will be largely influenced by the purity of the ice used, and too much care can not be exercised in precision work in securing pure material for the determinations. At the Bureau of Standards artificial ice made from twice distilled water (can ice) is used. The ice is tested for electrolytic impurities, which are the ones having the greatest effect on the melting point, by a conductivity test on water drawn

³ Pernet: Trav. et Mém. du Bur. Int., 1, p. B12; 1881.

from the ice bath, using a Kohlrausch bridge and Nernst cell with heavy platinum electrodes, and comparing the conductivity so found with that of distilled water. In some cases, an evaporation or other chemical test may serve as a check on the purity of the ice.

Most of the precautions enumerated above apply principally to work in which high accuracy is necessary. If an accuracy of 0.1° or less is sufficient, as in controlling zero changes of high-temperature thermometers, nearly any ice, if clear, can be used, and a little of it scraped into a clean vessel and saturated with the water obtained from the melted ice, will be sufficient for the determination of the ice point to the required accuracy.

Steam Point.—The most familiar type of steam-point apparatus is the Regnault form of laboratory hypsometer. This simple apparatus is not so well adapted to work of the highest accuracy, as is the Chappuis hypsometer used at the International Bureau. A careful comparison made at the Bureau of Standards by means of platinum resistance thermometers, has shown that for the same barometric pressure, temperatures in the Regnault hypsometer are from 0.003 to 0.006 higher than in the Chappuis form, the difference increasing with the rate of boiling and indicating a slight superheating of the steam in the Regnault apparatus.

Distilled water should be used in the steam-point apparatus, and it is advantageous to add some fragments of insoluble material, such as quartz crystals, to facilitate smooth boiling.

The top of the apparatus should be closed by a thin rubber disk, through a hole in which the thermometer is inserted, so that the whole of the mercury column with the exception of a few millimeters is immersed in the steam. If the thermometer is pushed through a cork, a certain part of the stem will not be exposed to the temperature of the steam and the resulting stem correction may in some cases be appreciable.

Barometer.—Observations in the steam point apparatus should be accompanied by simultaneous readings of the barometer from which the temperature of the steam can be computed, after reduction to standard conditions, by the use of steam tables. The pressure corresponding to a given height of mercury column depends both on the temperature of the mercury and on the acceleration of gravity at the point of observation. It is therefore necessary to reduce all observed barometric heights to accord with the accepted definition of "standard atmospheric pressure," which is that of a column of mercury 760 mm in height, at 0° C, and at latitude 45° , sea level. In correcting to 0° C, a correction is also made for the expansion of the scale on which the height is read. The tables for making the correction to 0° C usually include both the correction for density of mercury and expansion of the scale, either of brass or of glass.

If the observed pressure is quite near 760 mm, the use of steam tables may be dispensed with by using the relation, 1 mm pressure is equivalent to 0.0367° C. The error due to the use of this figure for a variation of 1° C from the 100° point is less than 0.02 . In a similar way, the correction to 0° C, allowing both for the expansion of the mercury and of the (brass)

scale, may be obtained by using the relation, 1° C is equivalent to 0.124 mm, the error due to the use of this relation not exceeding 0.1 mm under ordinary laboratory conditions. For temperatures above 0° the barometer reads too high, due to the combined effects of the expansion of mercury and of the scale. The correction for gravity may be taken from tables or computed for any latitude L and elevation A (in meters) above sea level by the formula ⁴

$$\frac{g_{LA}}{g_{45^{\circ}0}} = (1 - 0.00259 \cos 2 L) (1 - 0.000000196 A).$$

From the above it will be seen that in those cases in which an accuracy of 0.01 or 0.02 is desired in the determination of the steam point the ordinary type of Fortin barometer with which pressures can be determined to 0.1 or 0.2 mm may be used. For work of higher accuracy, however, it is necessary to use a barometer so constructed that the pressure of the residual gas in the closed limb can be determined. It must also be constructed so that the mean temperature of the mercury column can be determined within a few tenths of a degree.

The excess of pressure in the hypsometer over the atmospheric pressure, as shown by a water manometer, and usually equivalent to 0.1 or 0.2 mm of mercury, must be added to the reduced barometric pressure to obtain the pressure of the steam.

A more complete description of methods used in ice and steam point determinations will be found in B. S. Reprint No. 69.

8. METHODS OF USING PRECISION THERMOMETERS

Owing to the imperfect elastic properties of glass, which manifest themselves in the depression of the ice point, with its slow recovery, and which vary widely for different glasses, the indications of a thermometer will depend on its previous treatment; that is, if a given temperature were measured with the same thermometer, first, after it had been for a long time at room temperature, and, second, soon after it had been at 100° C, the indications would differ from one another by amounts depending on the quality of the glass, a half degree or more for some of the inferior glasses, and only a few hundredths for the better glasses (sec. 12). Pernet ⁵ has shown that these effects of imperfect elasticity can be eliminated and the indications of a thermometer rendered independent of its previous treatment by determining immediately after each temperature measurement, the ice point corresponding to that temperature, and using as the *fundamental interval* (sec. 11, A), the distance between the 100° C point and the ice point determined immediately after.

The method of Pernet is necessary in the use of primary standard thermometers, and of laboratory thermometers, where an accuracy better

⁴ Broch: Trav. et Mém. du Bur. Int., 1, p. A9; 1881.

⁵ Pernet: Trav. et Mém. du Bur. Int. des Poids et Mesures, 1; 1881.

than 0.02 is necessary, and with high-temperature thermometers in which large and irregular changes of zero may occur.

In other cases, a simpler method requiring fewer observations of the ice point is desirable. With laboratory thermometers in the range 0° to 100° C an accuracy of about 0.02 may be attained by a determination of the ice point corresponding to a given condition, the table of corrections being so computed that the depression is automatically included for a definite method of using the thermometer. Since the depression, when the thermometer is heated, takes place in a few minutes, while the recovery of the zero takes several days, it is evident that the thermometer will read lower, due to a previous heating to a higher temperature. The error due to this cause will be avoided if the thermometer is not used at the lower temperatures for several days after being heated to the higher ones. For example, if a thermometer be kept for several days at room temperature (20° C) and the ice point then observed, a certain reading called the *ice point after 20°* is obtained. If this reading is found to be higher (or lower) than the *ice point after 20°* , found when the thermometer was standardized, it is clear that all other readings will be too high (or low), by the same amount, and that a correction must be made to allow for the change.

If the thermometer is to be used at widely different temperatures within short intervals of time, and the condition just stated can not be observed, it is necessary to resort to the method of Pernet, taking ice-point observations after each temperature measurement, and applying a suitable correction, if the error due to depression is to be avoided.

Where the range of temperature is small and the time between observations is short, as in the use of calorimetric thermometers, it is more satisfactory, each time the thermometer is used, to first heat to the highest temperature to be measured, so that all the depression has taken place before the observations are begun. The condition to be observed is that the time required for observations is so short that no appreciable recovery shall have taken place during this time. As this condition is fairly well satisfied in calorimetric work, and is the only one for which consistent measurements of the same temperature interval can be made repeatedly, calorimetric thermometers should be used in this way.

Other cases occur in which simpler methods are permissible, as, for example, with thermometers for use at ordinary temperatures, where an accuracy of 1° or 2° is desired, the depression need not be considered at all and only an occasional ice-point determination, say once a year, will indicate whether any permanent changes have taken place. The same will apply to thermometers used at high temperatures, except that here permanent changes are very likely to occur and the ice-point determination must be much more frequent. In the latter case, also, the steam point may be used as the fixed point instead of the ice point if more convenient, or in case the ice point is not marked on the thermometer.

One of the principal limitations to increasing the accuracy of a mercurial thermometer by diminishing the capillary bore or increasing the volume of

the bulb, and thus increasing the length of a degree, arises from the variable capillary forces of the mercury meniscus and the resulting variations in pressure exerted on the bulb, which produce quite significant variations in the reading of the thermometer. The meniscus of the thermometer will be seen to advance or recede, not steadily, but in a series of nonuniform steps. These irregularities are much greater for a falling than for a rising meniscus. Often one thermometer will indicate an absolutely constant temperature, while another beside it may show that the temperature has fallen a hundredth of a degree or more. Higher accuracy is possible by taking all observations with a slowly rising meniscus. The errors due to this sticking of the meniscus are often very much reduced by imparting to the thermometer a series of mechanical vibrations; hence the general practice of using an electric tapper with calorimetric and Beckmann thermometers. A slowly varying (rising) temperature has the further advantage over a constant temperature, for the intercomparison of thermometers, since it requires readings in different positions relative to the scale, thus preventing the repetition of the same error of estimation.

Comparatively inexperienced observers can soon learn to estimate to within one-tenth of the smallest graduation interval. With some practice and the aid of a telescope magnifying about ten times an observer soon acquires the ability to estimate to hundredths of an interval (that is, to 0.001 for primary standards graduated to 0.1). While this does not mean that a single estimate can be depended on every time to this order of accuracy, it is surprisingly rare that two trained observers will differ by more than two or three hundredths of an interval. For this reason it is better to depend on eye estimates in reading thermometers than to resort to time-consuming micrometer measurements, as more observations can be taken in a given time thus more nearly eliminating errors due to the sticking of the meniscus.

Another important source of error in the use of thermometers arises from parallax. When a thermometer is made without an opaque backing this error may be eliminated by taking readings alternately with the divisions before and with the divisions behind the mercury without varying the line of sight, and taking the mean of the readings. For thermometers with opaque backs this result may be attained by taking care that the reflection of the scale can be seen in the mercury thread and so adjusting that the graduation of the scale nearest the meniscus exactly hides its own image. The line of sight will then be normal to the stem at this point.

For thermometers of the inclosed scale (*einschluss*) type parallax may be avoided by adjusting the line of sight so that the graduation lines nearest the meniscus appear straight as they pass behind the glass capillary.

The necessary precautions that must be observed in the determination of the ice and steam points, the methods of applying corrections for emergent stem, the change in fundamental interval due to annealing, etc., are discussed in other sections (7, 9, 11 (E), and 13) of this circular.

9. CORRECTIONS FOR EMERGENT STEM

In general, all corrections are determined for total immersion—i. e., for the condition where both bulb and stem of the thermometer are at the same temperature.⁶ If, however, the stem is emergent into space either hotter or colder than the temperature of the bulb, a *stem correction* must be applied to the observed reading of the thermometer.

This so-called stem correction is very large if the number of degrees emergent and the difference of temperature between the bath and the space above it are large. It may amount to more than 20° C for measurements made with a mercurial thermometer at 400° C (750° F).

The stem correction may be computed from the following formula:

Stem correction = $K \times n (T^\circ - t^\circ)$.

K = factor for relative expansion of mercury in glass;
 0.00015 to 0.00016 for centigrade thermometers,
 0.000083 to 0.000089 for fahrenheit thermometers,
 at ordinary temperatures, depending upon the glass
 of which the stem is made.

n = number of degrees emergent from the bath.

T = temperature of the bath.

t = mean temperature of the emergent stem.

Example: Suppose that the observed temperature was 100° C and the thermometer was immersed to the 20° mark on the scale, so that 80° of the mercury column projected out into the air, and the mean temperature of the emergent column was found to be 25° C, then—

$$\begin{aligned} \text{Stem correction} &= 0.00015 \times 80 \times (100 - 25^\circ) \\ &= 0.9^\circ \text{ C.} \end{aligned}$$

As the stem was at a lower temperature than the bulb the thermometer read too low, so that this correction must be added to the observed reading to find the reading corresponding to total immersion.

High Temperature Thermometers.—If a tested high temperature thermometer is used under conditions such that it has only a small stem correction, the reading of the thermometer, after applying the corrections given by the test, may be taken as the temperature of the bath for purposes of computing the stem correction, since an error in the temperature of the bath makes a much smaller error in the value of the stem correction. If, however, the number of degrees emergent and the difference of temperature between the bath and the space above it are large, it is necessary first to determine the stem correction approximately and apply this correction to the corrected reading of the thermometer in order to get the approximate

⁶ Thermometers are tested and corrections given for "total immersion," because this is a definite basis to which observations taken with any known distribution of temperature along the stem can be referred. If tests were made in a given type of comparison bath for a given depth of immersion and room temperature, the results would not be applicable when the thermometers were used in a different bath at a different room temperature, even though the depth of immersion remained the same.

temperature of the bath. This may be done by substituting the reading of the thermometer, after applying the corrections given by the test, for the temperature of the bath, T , in the above formula. This will determine the stem correction, and consequently the temperature of the bath, approximately. Then, using this corrected value of the temperature of the bath, the stem correction can be obtained as closely as required.

Example: Suppose that the observed reading corrected from the test was 500°C and the thermometer was immersed to the 100° mark, so that 400° of the mercury column projected out into the air; the mean temperature of the emergent column was found to be 150°C , then the approximate value of the stem correction $= 0.00016 \times 400 \times (500 - 150) = 22^{\circ}\text{C}$.

The approximate temperature of the bath is consequently $500^{\circ} + 22^{\circ} = 522^{\circ}$. Therefore, a closer approximation to the true value of the stem correction is given by substituting the corrected bath temperature, i. e., 522° , in the formula thus—

$$\text{Stem correction} = 0.00016 \times 400 \times (522 - 150) = 23.8$$

Calorimetric Thermometers.—The stem correction is often important in the case of thermometers used for differential temperature measurements, as in calorimetry.

In this case, provided the temperature of the stem remains constant, the correction may be computed from the following formula, involving the difference of the initial and final readings:

$$\text{Stem correction} = Kd(T_1 + T_2 - S - t).$$

K = factor for relative expansion of glass and mercury.

T_1 and T_2 = the initial and final readings.

$d = T_2 - T_1$.

S = scale reading to which the thermometer is immersed.

t = mean temperature of the emergent stem.

This correction must be applied (added if +, subtracted if -) to the difference of the readings to give the true difference of temperature.

Example: Suppose the thermometer was immersed to its 20° mark; its initial reading, T_1 , was 25°C ; its final reading, T_2 , was 30°C ; and the stem temperature was 20°C . Then the correction is $0.00015 \times 5(25 + 30 - 20 - 20) = 0.011\text{C}$. The difference between T_1 and T_2 is 5° . The true difference between the initial and final temperatures is $T_2 - T_1 + \text{correction} = 5.011\text{C}$.

Beckmann Thermometers.—For a Beckmann thermometer the correction may be readily computed from the following formula, differing slightly from the above, provided the thermometer is immersed to near its 0° mark and that the temperature of the stem remains constant:

$$\text{Stem correction} = Kd(S + T_1 + T_2 - t).$$

K = factor for relative expansion of glass and mercury.

S = setting of the thermometer (sec. 11, C).

T_1 and T_2 = initial and final readings.

$d = T_2 - T_1$

t = mean temperature of the emergent stem.

A Beckmann thermometer of the ordinary type should not be used with any part of the lower portion of the stem exposed, as this often contains

from five to ten times as much mercury per centimeter as the graduated portion, and if exposed introduces a large and uncertain error.

NOTE.—In case it is necessary to use such a thermometer with some of the lower enlarged portion of the stem emergent from the bath, the necessary correction may be computed from the above formula, provided S in the formula is replaced by $(S+n)$, where n is the number of degrees the temperature of the thermometer must be lowered below the temperature at which it reads 0° to bring the top of the mercury column to the point to which the thermometer was immersed; for instance, if a thermometer which has a setting of 20° C is immersed to a point 4 cm below the 0° mark and it is found that at a temperature of 12° C the top of the mercury thread stands at this point, the amount of mercury between this point and the 0° mark is $20^\circ - 12^\circ = 8^\circ$, and the value of " $S+n$ " is $20^\circ + 8^\circ = 28^\circ$.

STEM TEMPERATURES

The mean temperature, t , of the emergent stem may be approximately measured by means of a small auxiliary thermometer suspended near the emergent stem, or by surrounding the latter with a small water jacket and taking the temperature of the water with the auxiliary thermometer, or, more accurately, in the way suggested by Guillaume, by exposing an exactly similar stem and capillary mercury thread beside the emergent stem, and thus measuring its mean temperature. This is also conveniently carried out with the "thread thermometer" (Faden thermometer) of Mahlke,⁷ in which the expansion of the mercury in the capillary tube (bulb) is measured in a still finer capillary stem.

For high-temperature thermometers, when the stem correction is large, the stem temperatures and the value of K must be known with considerable accuracy. Stem temperatures may be measured with fair accuracy by means of either an auxiliary mercury thread or a "faden" thermometer.

If a thermometer stem is partly emergent from a heated comparison bath, assuming the temperature within the bath uniform, the mercury in the stem will be cooler than that in the bulb, and the thermometer will read too low. If, now, a capillary tube, somewhat longer than the exposed portion of the thermometer stem, and having a similar cross section and quality of glass, is nearly filled with mercury and immersed in the bath, beside the thermometer stem, to such a depth that the top of its mercury column is at the same level as that in the thermometer, the temperature distribution in the two capillaries will be nearly the same. If then this capillary can be first read totally immersed in the bath and then read when emergent, as above described (the bath temperature remaining constant), the difference in these two readings will give *in millimeters* the amount that the thermometer is in error due to the cooler exposed stem. This difference in millimeters can be reduced to degrees by measuring the length of a degree on the thermometer scale. Instead of observing the mercury capillary totally immersed for each observation, this can be done once for all, and a scale can be marked upon it as upon the stem of a thermometer.

This method, though probably more accurate, has not been so generally used as that based on the use of the so-called faden thermometer. In

⁷ Mahlke: *Zeitschrift für Instrumentenkunde*, 13, p. 58; 1893. *Wied. Ann.*, 53, p. 987; 1894.

practice the faden thermometer, which is essentially a thermometer with a very long bulb (from 10 to 20 cm), having a thickness of wall and size of bore nearly the same as the *stem* of an ordinary thermometer, may generally be treated simply as an ordinary thermometer calibrated to read approximately true temperatures when immersed to the top of the bulb. If such a thermometer with a bulb, say 10 cm long, is immersed beside a thermometer to be observed, to such a depth that the top of the faden thermometer bulb is at the same level as the top of the mercury column in the thermometer, the faden thermometer reading will give approximately the mean temperature of the portion of mercury thread beside it, i. e., a faden thermometer 10 cm long will give the mean temperature of 10 cm of the thermometer stem.

The number of degrees corresponding to 10 cm must be found by measurement of a portion of the thermometer scale. This measurement should be taken over the portion of the graduated scale which was opposite the faden thermometer bulb, because in high-temperature thermometers the length of a degree is not generally the same at all parts of the scale. This number of degrees is to be taken as n in the above formula. The thermometer reading, after applying any certificate corrections and an approximate stem correction as described above, is to be taken as T in the formula. The faden reading is taken as t . The value of K , which depends upon the temperature and the kind of glass of which the thermometer is made, may be found approximately from the following tables for Jena 16^{III} or "normal" glass and for Jena 59^{III} borosilicate glass.

In the following tables *temperature* is the mean between the temperatures T and t .

For Jena 16^{III} glass:

Temperature	K
0°	0.000158
100°	.000158
200°	.000159
300°	.000164

For Jena 59^{III} borosilicate glass:

0°	0.000164
100°	.000164
150°	.000165
200°	.000167
250°	.000170
300°	.000174
350°	.000178
400°	.000183
450°	.000188

Example: A thermometer indicates a temperature of 500° C (after applying the corrections given by a test) when immersed to the 375° mark in a bath at a constant temperature. A faden thermometer with a 10-cm bulb is immersed beside it so that the top of the bulb and of the mercury column in the thermometer are at the same level, and the faden thermometer indicates a temperature of 300° C.

The 10 cm of thermometer scale beside the faden includes 200°. These 200° (n degrees) of the thermometer stem are therefore at a mean temperature (t) of 300° C, while the bath temperature

is 500°C plus an *approximate* stem correction of 7° ($200 \times 0.00018 (500 - 300) = 7^{\circ}$) or 507°C . The factor K for the mean of bath and faden temperature (i. e., $\frac{500 + 300}{2} = 400^{\circ}$) is 0.000183 . The stem correction is therefore obtained from the formula for high-temperature thermometers as follows:

$$\text{Stem correction} = 0.000183 \times 200 (507 - 300) = 7.6$$

The corrected temperature is therefore 507.6 .

A more detailed treatment of the subject of stem corrections to mercurial thermometers will be found in B. S. Reprint No. 170.

10. THE LAG OF THERMOMETERS

Practically all theoretical treatment of the question of thermometer lag is based on the assumption that Newton's law of cooling (i. e., that the rate of change in the reading of the thermometer is proportional to the difference between thermometer temperature and bath temperature) holds for the thermometer. It is an immediate consequence of this law that when a thermometer is immersed in any medium it does not take up the temperature immediately, but approaches it asymptotically. A certain time must elapse before the thermometer reading agrees with the temperature of the medium to 0.01 , still longer to 0.001 , the temperature remaining constant. If the temperature is varying, the thermometer always indicates, not the true temperature, but what the temperature of the medium was at some previous time. The thermometer readings are thus said to "lag" behind the temperature by an amount which may or may not be negligible, depending upon the rapidity of temperature variation and the construction of the thermometer. A more complete treatment of this subject will be found in B. S. Reprint No. 171.

For a thermometer immersed in a bath, the temperature of which is changing uniformly, the lag may be defined as the interval in seconds between the time when the bath reaches a given temperature and the time when the thermometer indicates that temperature. This lag, λ , is dependent upon the dimensions and material of the thermometer bulb, the medium in which it is immersed, and the rate at which this medium is stirred. For instance, the lag when in the air of the room would be perhaps 50 times that of the same thermometer when immersed in a well-stirred water bath.

Since the value of λ for mercurial thermometers is not large, being from 2 to 10 seconds in a well-stirred water bath, it is not generally necessary to correct for it. For example, if two thermometers, one having a lag of 3 and another of 8 seconds, are read simultaneously in a bath whose temperature is rising at the rate of 0.001 in 5 seconds, the former will read 0.001 higher than the latter, due to the lag. In the intercomparison of thermometers the rate of temperature rise may nearly always be kept so small that this lag correction is negligible.

If a thermometer at a given initial temperature is plunged into a bath at a different temperature, the lag, λ , is the time required for the original

difference in temperature between thermometer and bath to be reduced to $\frac{1}{e}$; that is, $\frac{1}{2.8}$ of itself. In a length of time 4λ the difference will have become about 1.5 per cent and in a length of time 7λ about 0.1 per cent of the original difference.

This shows that it is necessary to wait for from 10 to 45 seconds after placing a thermometer in stirred water in order to get a reading correct to within 1 per cent of the original difference between bath and thermometer.

When a thermometer is used to measure changes of temperature, as in calorimetry, it has been shown by W. P. White that the lag enters into the observations in such a way as to be eliminated from the results in applying the usual radiation corrections and therefore need not be considered, provided only that the initial and final readings are made when the temperature is varying uniformly. This is not strictly true, however, in the case of some Beckmann thermometers which have no true value of λ , as has been explained in the paper referred to above. (See also sec. 11, C.)

An idea of the magnitude of the lag, λ , of thermometers of various types, when immersed in a well-stirred water bath, may be obtained from the following table:

Lag of Thermometers

Type of Thermometer	Lag, λ
Chabaud, small bulb, mercurial thermometer	2 secs.
Golaz, large bulb, calorimetric mercurial thermometer	5 "
Beckmann, large bulb, mercurial thermometer	9 "
Inclosed capillary portion of Beckmann thermometer	50+ "
Callendar type of platinum resistance thermometer, platinum coil on light mica frame, in glass or porcelain tube	15-35 "
Calorimetric platinum resistance thermometers in metal case, of the types used by Jaeger and by Dickinson and Mueller	Small fraction of sec.

11. TYPES OF THERMOMETERS

A. PRIMARY STANDARD THERMOMETERS

By the term "primary standard thermometer" is meant a thermometer that defines within itself a scale of temperature. Thermometers of this type must therefore have on their scales the two fixed points 0° and 100° C. Experience has shown that the length of 1 degree which best satisfies the requirements for primary standards in the interval 0° to 100° C is about 6 or 7 mm (not less than 5 mm); for higher temperatures, the length of the degree should be less. In order not to unduly increase the length of the thermometer, the scale of a primary standard need include only the region in which it is intended for use (e. g., 0° to 50° C, 100° to 200° C, etc.). It must, however, be so constructed, with suitable auxiliary reservoirs in

the stem, that it contains the two fixed points, and, further, that the volume of any part of the stem can be referred to the fundamental volume between the 0° and 100° C marks. Types of construction of primary standard thermometers are shown in the following illustration:

If a number of such thermometers were made of the same specimen of glass, and subjected to the same treatment, they should agree well among themselves, and they would serve to fix, within the limits of reproducibility of the glass, a definite scale of temperature for that particular kind of glass; and if the scale defined by thermometers of this glass had previously been compared with that defined by the gas thermometer, it would then be possible to express the indications of the mercury in glass thermometers as temperatures on the scale of the standard gas thermometer. The scales defined by a number of the best thermometric glasses (verre dur, Jena 16^{III}, Jena 59^{III}) have been compared, either directly or indirectly, with the hydrogen scale of the international bureau and with the nitrogen scale,

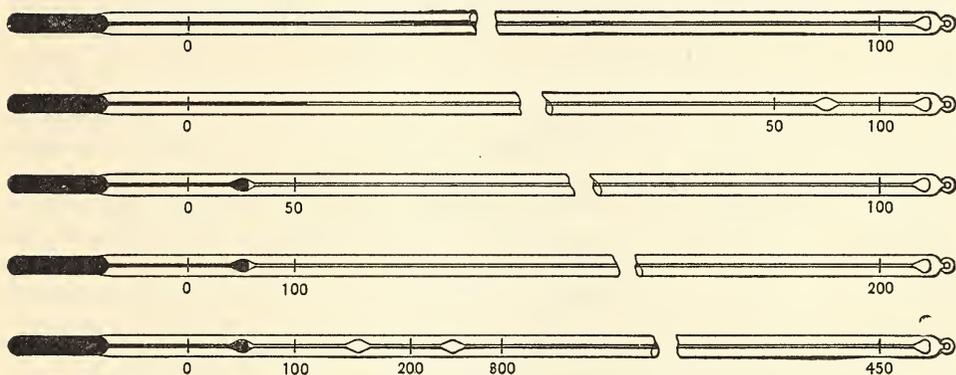


Fig. 1.—Primary Standard Thermometers.

so that the indications of primary standard thermometers made of these glasses can be used to measure temperatures on these scales (sec. 2).

As stated above, primary standards made from the same specimen of glass should be in agreement among themselves, but in order that this should be the case, it would be necessary that the thermometers be perfect in every respect, a condition that can not, of course, be realized in practice. They must, therefore, be constructed in such a way that the necessary corrections may be readily determined. One of the two fixed points (0° C) is determined in a mixture of pure ice and distilled water, and the other (100° C) in the vapor of pure water boiling under standard atmospheric pressure. In a perfect thermometer, the interval between these points would be divided into 100 parts of equal volume. In the practical construction of laboratory thermometers, this is approximately done by calibrating the tube by sliding mercury threads along the capillary and observing their lengths in various positions. By this method good laboratory and

commercial thermometers can be constructed reliable to a few hundredths of a degree, in the interval 0° to 100° C, and less accurate, of course, at higher temperatures.

For primary standards, however, this method of construction is not permissible, for here the correction for variation in caliber must be known to a far higher degree of accuracy and must be determined by the most careful calibration of the tube. The tube of which the thermometer is made must be carefully selected by a preliminary calibration and must be very uniform in cross section. The greatest difference in the calibration corrections must not exceed 0.2 (or 0.3 C at most). After the positions of the fixed points are determined, the space between must be divided into parts of equal length. For this purpose a dividing engine should be used whose screw has been very carefully studied for progressive and periodic errors. As the length of a degree is generally about 5 to 7 mm in primary standards in the interval 0° to 100° C, the accidental errors of ruling should be kept within a few thousandths of a millimeter. The graduation marks on the stem must be very fine and clear, and their width must not be greater than 0.1 of the smallest scale interval and should, preferably, be much less.

The indications of thermometers are also affected by variations of atmospheric pressure and of the pressure of the medium in which the bulb is immersed, and by the pressure from within, due to the mercury column of the thermometer itself and to capillary forces. For this reason it is necessary to determine the external and internal pressure coefficients so that the indications of the thermometer can be reduced to standard conditions, i. e., to an external pressure of 760 mm and an internal pressure of zero (really the somewhat variable pressure of the mercury meniscus) corresponding to the horizontal position of the thermometer.

Further, as it is not possible for the maker to locate without error the fixed points, these must be determined with the greatest care, in the manner already indicated, by observing the reading of the thermometer in steam, and the corresponding barometric pressure; and immediately after, before any recovery of the ice point shall have taken place, the reading in melting ice (secs. 7 and 8). This gives the number of scale-degrees corresponding to the interval between 0° and 100° C, called the *fundamental interval* of the thermometer. The fundamental interval should not differ from 100° by more than 0.1 .

The stem of the thermometer must be transparent, so that errors of parallax can be avoided by taking the mean of the readings with the scale before and the scale behind the mercury column, the line of sight remaining unchanged; for this reason the use of an enamel-back stem is not permissible in primary standard thermometers.

As the amount of work involved in the study of a primary standard thermometer is very great, and the order of accuracy aimed at is a few thousandths of a degree, the requirements that have been discussed, which are based on the elaborate and painstaking researches carried out at the

International Bureau of Weights and Measures and at the Physikalisch-Technische Reichsanstalt, are essential to the acceptance of such thermometers for test as primary standards.

As an illustration of the methods of reduction of the readings of a primary standard, the following example has been added:

Thermometers *Baudin 15555* and *Tonnelet 4334* were read in a vertical position in a well-stirred water bath. The bulbs were 60 cm below the surface, and the reduced barometric pressure was 768 mm. The ice points as given below were determined *immediately after* the temperature measurement.

Reduction of Readings and Determination of Ice Point of Primary Standard
Thermometers

Baudin 15555		Tonnelet 4334	
Observed reading.....	43.435°	Observed reading.....	43.491°
Calibration correction.....	+.021°	Calibration correction.....	-.081°
External pressure correction.....	-.006°	External pressure correction.....	-.005°
Internal pressure correction.....	+.069°	Internal pressure correction.....	+.048°
Ice point correction.....	-.069°	Ice point correction.....	+.025°
	43.450°		43.478°
Fundamental interval correction.....	-.009°	Fundamental interval correction.....	-.035°
Temperature on the scale of mercury thermometer.....	43.441°	Temperature on the scale of mercury thermometer.....	43.443°
Correction to hydrogen scale.....	-.107°	Correction to hydrogen scale.....	-.107°
Temperature on hydrogen scale.....	<u>43.334°</u>	Temperature on hydrogen scale.....	<u>43.336°</u>
Observed ice point.....	+.061°	Observed ice point.....	-.033°
Calibration correction.....	.000°	Calibration correction.....	.000°
External pressure correction.....	.000°	External pressure correction.....	.000°
Internal pressure correction.....	+.008°	Internal pressure correction.....	+.008°
Reduced ice point.....	+.069°	Reduced ice point.....	-.025°

Primary standard thermometers will be accepted for test in accordance with schedule 31, section 20.

B. LABORATORY AND SPECIAL THERMOMETERS

Under this head may be broadly grouped most thermometers of the usual types, including secondary and working standards for an accuracy of 0°.01, and ordinary thermometers for an accuracy of 1° or 2° at higher temperatures. Illustrations of special thermometers are maxima and minima, calorimetric, hypsometric, deep-sea, clinical, soil, flash-point, household, and other thermometers used for special purposes.

Thermometers of these types are usually pointed by the maker at a number of points along the scale by comparison with a standard thermometer the corrections for which are known, the thermometers being immersed in a stirred bath of some suitable liquid (sec. 5). When a thermometer is made of one of the standard thermometric glasses, of known coefficient of expansion, and if it has on its scale the ice and steam points, and the scale is continuous, it is possible to point the thermometer without resorting to a comparison with a standard thermometer in a stirred bath, by sliding along the scale a mercury thread the length of which is suitably chosen. (Sec. 11, D and E.)

In ordinary thermometers, intended to read directly true gas scale temperatures, as nearly as possible, the length of a graduation interval is different in different parts of the scale. This is necessary to allow for the relative expansion of mercury in the particular glass used, which varies with temperature, and for variations in the bore of the capillary tube, the correction for which has to be determined by a mercury thread calibration. Thermometers of this type with fitted graduation can, when extreme care is exercised, be made reliable to a few hundredths of a degree in the interval 0° to 100° C, and to within 1° at 400° C.

Laboratory and special thermometers, of the usual type of construction, and fulfilling the specifications set forth under section 3, will be accepted for test in accordance with schedule 32, section 20. For thermometers of special construction requiring other than the usual methods of testing, e. g., deep-sea, hypsometric, some maxima and minima thermometers, etc., a special fee will be charged.

Thermographs.—By special arrangement, thermographs may be accepted for test, the fee for which will depend on the nature of the test.

C. CALORIMETRIC AND METASTATIC (BECKMANN) THERMOMETERS

These thermometers have a limited portion of the scale covering the range of temperature in which they are to be used. Where an order of accuracy of 0.01 or 0.02 is sufficient, their corrections may be determined at a number of points of the scale by direct comparison with standard thermometers. This order of accuracy (equivalent to about 0.5 per cent in a calorimetric determination) will satisfy many of the requirements of commercial testing of the heating value of fuels and of other calorimetric measurements. For thermometers graduated to 0.01 or 0.02 , intended for measurements of the highest accuracy attainable with such thermometers, the scale corrections are determined by mercury thread calibrations. The value of the mean scale degree of the thermometer in terms of temperature on the international hydrogen scale is then determined by comparison, at the upper and lower points of the scale, with calorimetric platinum resistance thermometers (sec. 16 and B. S. Reprint No. 68)⁸ especially constructed for

⁸ Since the publication of this paper improved forms of these thermometers have been developed, full details of which will be furnished to those interested.

the measurement of small temperature differences with the highest attainable accuracy. As an additional check, two or three standard mercurial thermometers are included in this intercomparison. Finally, as a check on all the corrections, additional intercomparisons are made at one or two intermediate temperatures. The certificate will give the corrections at the points for which the calibration corrections have been determined and the necessary information to apply the corrections for setting and for emergent stem.

The highest accuracy attainable with mercurial thermometers of this type, of the best construction and after the most careful standardization, is of the order of 0.002 or 0.003 in the measurement of a small temperature interval of 2° or 3° , and, indeed, if this accuracy is to be attained, several thermometers should be used.

Experience has shown that capillaries smaller than 0.1 mm in diameter should not be used and the practicable limit in size of bulb is probably found in the Beckmann thermometers now in common use. These dimensions limit the length of 1 degree to about 5 cm. The use of elliptical or flattened capillaries to facilitate reading can not be recommended for these sensitive thermometers, as the noncircular section causes a great increase in the capillary forces.

The irregular action of these thermometers is especially noticeable on a falling temperature. The resulting error may be greatly diminished by tapping the thermometer just before taking the reading. This is most conveniently done by mounting a small electric buzzer on the top of the stem. Small buzzers weighing about 40 grams are readily obtainable and are quite suitable for the purpose.

In special investigations requiring the highest attainable accuracy, *platinum resistance thermometers* (sec. 16), or *thermocouples* (sec. 17), standardized by comparison with resistance thermometers, should be used. With these an accuracy of about 0.0002 may be attained in the measurement of small temperature intervals. The construction and calibration of thermoelements suitable for calorimetric work are described in the *Physical Review*, August, 1910.

Metastatic Thermometers.—Thermometers arranged so that part of the mercury may be removed from the bulb in order that a short scale may be utilized for differential work at various temperatures, are now made principally in the form developed by Beckmann. The details to be observed in the construction of these thermometers in order that the mercury may easily be removed from the bulb, or returned to it, have been fully described by Beckmann.⁹

The "setting" of such a thermometer may be defined as the temperature at which the reading on the scale of the instrument is zero. The manipula-

⁹ *Zeitschrift für Phys. Chemie*, 51, p. 329; 1905.

tion for changing the setting, as indicated by Beckmann, is substantially as follows:

(a) To "set" higher, the bulb is warmed until the mercury fills part of the upper reservoir. By inverting the thermometer in this condition, the mercury will usually continue to flow without further warming. The mercury in the upper reservoir may then be shaken off from the column, either by holding the thermometer in one hand near the bulb and striking the outer tube near the reservoir, lightly against the other hand, or by holding the thermometer vertically in one hand and striking this hand downward against the other. Sometimes the mercury is more easily shaken off by tapping the bulb vertically on a soft pad, such as a sheet of rubber or pad of paper.

(b) To "set" lower, the mercury in the upper reservoir is brought into the upper part of the reservoir and the mercury in the bulb is made to join this either by inverting the thermometer and tapping gently or by warming the bulb carefully. Then on righting the thermometer or cooling the bulb the desired amount of mercury may be drawn back and the rest shaken off as before. Warming should not be resorted to if the upper reservoir is entirely filled with mercury, as it would result in breaking the thermometer. The operation of tapping the thermometer is always attended with danger of breakage and especially so when the bulb is not completely filled with mercury. The manipulation of the mercury in a thermometer is further discussed under section 15.

Errors and corrections.—There are two corrections that must be considered particularly with metastatic thermometers. The first, applying principally in the Beckmann type, is a stem correction for the mercury contained in the stem between the bulb and the scale, when this portion of the stem is not immersed. This portion of the capillary contains in some cases five to ten times as much mercury per centimeter as the graduated part, and further enlargement where the two capillaries join increases the magnitude and uncertainty of this correction. Furthermore, the lag of this portion of the thermometer is much greater than that of the bulb alone. These corrections will become almost inappreciable if the small capillary is continued all the way down to the bulb or if the thermometer is immersed to the graduated portion of the scale. The second is a correction for the different amount of mercury when the thermometer is used with any other "setting" than that at which it was standardized. In computing this "setting" correction it is necessary to take into consideration two factors: (a) The change in the actual quantity of mercury which expands, and (b) the variation in the coefficient of expansion of mercury in glass with temperature, the latter including the linear expansion of the scale. The corrections for thermometers of Jena 16^m glass have been calculated by Grützmacher.¹⁰

¹⁰ *Zeitschrift für Instrumentenkunde*, 16, p. 176; 1896.

In standardizing Beckmann thermometers it is preferable to compare with standards at a setting of about 20° C. From the observations a table is computed, giving the corrections to be applied at various points on the scale when the setting is 20° . When another setting is used, the difference of temperatures, corrected by this table, must be multiplied by a factor depending on the setting. This factor will be unity for the setting 20° . For other settings and for thermometers of Jena 16^m glass, graduated from 0° to 5° (or 6°), the factors are given below:

Setting Factors

Setting	Factor	Setting	Factor
0° C	0.9934	55° C	1.0096
5°	0.9952	60°	1.0107
10°	0.9969	65°	1.0118
15°	0.9985	70°	1.0129
20°	1.0000	75°	1.0139
25°	1.0015	80°	1.0148
30°	1.0030	85°	1.0157
35°	1.0044	90°	1.0165
40°	1.0058	95°	1.0172
45°	1.0071	100°	1.0179
50°	1.0084		

A similar table may be computed for thermometers of Jena 59^m glass or verre dur, but not so accurately for other glasses, as the departure from the gas scale, of thermometers made of other glasses, has not been studied with sufficient care. Metastatic thermometers should, therefore, be made of one of the three glasses mentioned.

Stem Correction.—Grützmacher¹¹ includes a stem correction in the setting correction. For this purpose he assumes that if the thermometer is used with a given setting, the stem temperature will be sufficiently determined by this condition alone. If this were true, a modification of the factors given above could be made so as to take account of the stem correction. But on account of the difficulty of estimating the stem temperatures without knowing the conditions in which the thermometer is used, it would seem better for the user to determine and apply the stem correction separately. For calorimetric and Beckmann thermometers the stem correction may be computed as explained in section 9.

¹¹ Zeitschrift für Instrumentenkunde, 16, p. 200; 1896.

D. LOW-TEMPERATURE THERMOMETERS

For the measurement of temperatures below -35°C there are available alcohol, toluene, petroleum-ether, and pentane liquid in glass thermometers, copper-constantan and other thermocouples, and electric resistance thermometers.

The lower limit of alcohol thermometers is about -70°C , of toluene about -90°C , and of petroleum-ether and pentane thermometers about -200°C .

Alcohol and Toluene Thermometers.—Chappuis¹² has made a careful investigation of alcohol and toluene thermometers. The presence in the alcohol of impurities and of water, which can hardly be eliminated, produces a marked influence on its coefficient of expansion. Thus, Chappuis found that thermometers made up with different samples of alcohol, designated as chemically pure, differed among themselves¹³ by 1° at low temperature (-72°C), while thermometers obtained from different makers differed by 6°C or more. With thermometers filled with different samples of toluene, the greatest difference did not exceed 0.04°C .

The substitution of toluene or pentane for alcohol would, we believe, be a most desirable step in facilitating the introduction of satisfactory low temperature thermometers.

The coefficient of expansion of these liquids diminishes as the temperature is lowered. Hence, if the scale of a toluene or alcohol thermometer were continued down in degrees of equal volume, it would not read true gas scale temperatures, but would read too high by an increasing amount, the lower the temperature; in the actual construction of thermometers this is allowed for by making the degree intervals shorter in the lower parts of the scale. The thermometers can then be made to read true gas scale temperatures with great accuracy.

The necessary data for graduating toluene and alcohol thermometers, as given by Chappuis, will be found in the following table. Here the column headed "temperature" is the temperature on the scale of the hydrogen gas thermometer; the column headed "toluene" the corresponding temperatures that would be indicated by a toluene thermometer with a scale continued downward in degrees of uniform length and the volume of which per degree was one-hundredth of the volume between the 0° and 100°C marks; the column headed "alcohol" the corresponding temperatures that would be indicated by an alcohol thermometer with a scale continued downward in degrees of uniform length and the volume of which per degree was one-thirtieth of the volume between the 0° and 30° marks.

¹² Archives des Sciences Physiques et Naturelles, 28, p. 293; 1892.

¹³ After allowing for the effect of irregularities in the bore by means of a previous mercury thread calibration.

Temperature Scales of Toluene and Alcohol Thermometers

Temperature	Toluene	Alcohol purified by Jolly	Absolute alcohol from Billault
0° C	0°	0°	0°
-10°	- 8°54	- 9°31	- 9°44
-20°	-16°90	-18°45	-18°71
-30°	-25°10	-27°44	-27°84
-40°	-33°15	-36°30	-36°84
-50°	-41°08	-45°05	-45°74
-60°	-48°90	-53°71	-54°55
-70°	-56°63	-62°31	-63°31

Temperature of Solid CO₂ as Test Point.—A convenient fixed point for testing low-temperature thermometers is that of a mixture of solid CO₂ snow (in excess) and absolute alcohol (or gasoline). When this mixture, having a thick mushy consistency, is allowed to stand for a short time in a well-insulated vessel or Dewar beaker, it comes to an equilibrium temperature of $-78.3^{\circ}\text{C}^{15}$ at standard atmospheric pressure (760 mm). If the corrected pressure is greater or less than 760 mm, the corresponding correction to be applied is $+0.02$ or -0.02 C per mm variation from standard pressure. Solid CO₂ snow can be readily obtained from the ordinary iron bottles in which it is furnished commercially by holding a felt sack or several layers of towel over the mouth of the valve and allowing the gas to expand through the cloth.

Petroleum-Ether Thermometers.—Kohlrausch¹⁴ and Holborn¹⁵ have investigated the behavior of petroleum-ether thermometers at temperatures as low as -190°C . Complex mixtures of petroleum-ether distilled at temperatures between 20° and 33°C were used. The coefficients of expansion of these liquids and necessary details of construction of these thermometers will be found in the papers referred to. The coefficient of expansion varies with the temperature, the length of a degree at -150°C being only about 0.8 that at $+25^{\circ}\text{C}$. When these thermometers are used with the necessary precautions, their indications are consistent to 1°C or better at -190°C . Petroleum-ether has now been superseded as a thermometric liquid by commercial pentane, which is more satisfactory in every way at very low temperatures.

Pentane Thermometers.—The investigations of Rothe¹⁶ have shown that commercial pentane (furnished by Kahlbaum) is a very satisfactory

¹⁴ Wiedemann's *Annalen der Physik und Chemie*, **60**, p. 463; 1897.

¹⁵ *Annalen der Physik*, **6**, p. 242; 1901.

¹⁶ *Zeitschrift für Instrumentenkunde*, **22**, p. 192; 1902. Also, **24**, p. 47, 1904.

liquid for low-temperature thermometers, being still quite mobile at a temperature of -200°C and showing no cloudiness or heavy precipitates after long exposure to this temperature. Rothe concludes that such thermometers are consistent in their indications to 0.02 at the temperature of liquid air (-190°C). Pure pentane can not be used at such low temperatures, as it becomes very viscous and immobile. The papers referred to, from which the following data have been taken, contain all the information necessary for the construction of these thermometers. The data given below for pentane thermometers apply to thermometers of Jena 59^{III} borosilicate glass, but will hold approximately for other glasses.

The -100°C point may be located on the stem as follows: First locate the -78.2^{17} point in a mixture of absolute alcohol (or gasoline) and carbonic acid snow, as explained above. Increase this interval (0° to -78.2) by one-fourth of its length (if the bore is uniform) and the point thus located will correspond to -100°C . The -100° point being thus located, the remaining points of the scale may be found by the use of the following table:

Volume between	0° and $-10^{\circ} = 0.1097$ 0° " $-20^{\circ} = .2172$ 0° " $-30^{\circ} = .3226$ 0° " $-40^{\circ} = .4258$ 0° " $-50^{\circ} = .5269$ 0° " $-60^{\circ} = .6258$ 0° " $-70^{\circ} = .7226$ 0° " $-80^{\circ} = .8172$ 0° " $-90^{\circ} = .9097$ 0° " $-100^{\circ} = 1.0000$ 0° " $-120^{\circ} = 1.1742$ 0° " $-140^{\circ} = 1.3398$ 0° " $-160^{\circ} = 1.4967$ 0° " $-180^{\circ} = 1.6450$ 0° " $-200^{\circ} = 1.7847$) \times Volume between 0° and -100° .
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The test in CO_2 snow and alcohol may be avoided by making use of the following rules:

(a) The volume of the bulb and the stem up to the -200°C mark = 3.47 times the volume between the -200°C and the 0°C marks.

(b) The volume of the bulb and the stem up to the -100°C mark = 6.98 times the volume between the -100°C and the 0°C marks. These volumes can be found by weighing the mercury necessary to fill them.

The data for pointing low-temperature thermometers have been given at some length with the hope that they may be of use to thermometer makers and may contribute to the use of a thermometric liquid more satisfactory than alcohol for low-temperature thermometers.

Precautions in Use of Low-Temperature Thermometers.—Any liquid that wets the tube adheres to the walls and the reading of the thermometer will depend on the time given for the liquid to drain down the tube. It may take a very long time, an hour or more, before the effect of drainage is no longer noticeable. Hence, a most important precaution in the use

¹⁷ Rothe uses -78.2 for the temperature of solid CO_2 and alcohol (instead of -78.3°C) as found subsequently by Holborn.

of low-temperature thermometers, especially at the lower portions of their ranges, is very slow cooling. The bulb must be cooled down first, then the stem; otherwise the meniscus becomes stiff and tears off from the walls, becomes distorted, and leaves drops of liquid behind.

E. HIGH-TEMPERATURE THERMOMETERS

Construction.—Mercury boils at 357°C under atmospheric pressure and at lower temperatures if the pressure is lower. Hence, ordinary mercurial thermometers, with the space above the mercury free from gas, can not be used at high temperatures. Even at 100°C , if the top of the mercury column is heated and the stem above it is cool, drops of mercury collect slowly in the cooler parts of the stem. Keeping the top of the mercury column cool or the whole of the stem heated suffices to prevent this below 200°C ; but if the temperature is much above 200°C , the mercury will begin to boil in a thermometer sealed free from gas, even if the top of the column is cool. Boiling at any temperature can be prevented by filling the space above the mercury with a gas under sufficient pressure. The pressure required at 400°C is about four atmospheres and at 500°C about fifteen atmospheres.

For filling high-temperature thermometers an inert gas, such as nitrogen or carbon dioxide, free from moisture, should be used. If air is present, the mercury oxidizes and clings to the walls of the capillary. The use of pure dry mercury is also important.

To secure the necessary internal pressure, two types of construction are used, which may briefly be called the *small upper bulb* and the *large upper bulb* types. The former is used almost exclusively in this country and in England and France, while the latter is very generally used in Germany. In the former a very small bulb is blown at the upper end of the capillary, or a suitable length of the capillary is left above the highest graduation on the scale and the stem is sealed off with the inclosed gas at atmospheric pressure, or somewhat above, when the thermometer is at room temperature. Then, if the volume of the upper bulb or of the capillary extension is properly chosen, the mercury on rising will compress the contained gas and increase the pressure sufficiently to prevent boiling at all temperatures on the scale. It is not sufficient that the pressure be enough to prevent boiling at the highest points, but it must be sufficiently high to prevent boiling at all intermediate temperatures. Thus, it is readily seen that if the volume of the space above the highest graduation be too small, the pressure might be much greater than necessary at the highest temperature, but much too small at lower temperatures. In the *large upper bulb* type, there is at the upper end of the capillary an auxiliary bulb, the volume of which is large in comparison with the volume of the entire capillary (five to twenty times). This type of thermometer is sealed off with the gas under an initial pressure sufficiently high to prevent boiling

at the highest temperature on the scale. To seal off the thermometer under pressure, a little shellac or fusible metal, placed in a short glass tube joined to the stem above the auxiliary bulb and to the supply of gas under pressure, is heated so that it flows down and, on hardening, closes the upper short length of capillary just above the auxiliary bulb. The gas pressure is then removed and the capillary end is quickly sealed off just above the shellac or fusible metal seal before the latter has had time to soften.

Either the small or the large upper bulbs are entirely satisfactory types of construction for all ordinary high-temperature thermometers. There may be some little advantage in the large upper bulb type for the construction of primary standards for the reason that when the internal pressure is nearly the same at all temperatures the pressure correction is nearly constant and does not much affect the temperature scale defined by the thermometer. When the small upper bulb is used, the internal pressure increases rapidly as the temperature rises, lowering the readings of the thermometer. However, by carefully determining the total volume of the capillary above the graduations and of the small upper bulb in terms of scale degrees, before the thermometer is sealed off, the correction for this variable internal pressure can be made from the value of the pressure coefficient, which can be determined at any time.

Ice Point.—In view of the changes to which high-temperature thermometers are liable, it is highly desirable that the ice point be marked on the scale, as it enables the user to determine the reading in melting ice and to apply the proper correction for any change that may have taken place since the thermometer was last tested. If the thermometer has been thoroughly annealed, a small length of scale, say from -5° to $+10^{\circ}$, will be sufficient to take care of all subsequent changes. Such changes can also be checked by observations in steam from time to time, although less conveniently, as it requires simultaneous barometer readings, reductions to standard conditions, and the use of steam tables.

Annealing.—The importance of proper annealing of a mercurial thermometer intended for use at high temperatures can not be too strongly emphasized. This matter is treated briefly in section 13 and in detail in B. S. Reprint No. 32.

Pointing Thermometers.—Thermometers are usually pointed (i. e., a number of known temperatures marked on the stem) by comparison with a standard thermometer. The scale can also be laid out so that the thermometer will read true gas scale temperatures without resorting to such a comparison, provided the thermometer is made of one of the glasses the coefficient of expansion of which, relative to mercury at high temperatures, is known, and that the thermometer is so constructed, either with continuous scale or auxiliary reservoirs in the stem, that the volume of every part of the capillary can be expressed in terms of the fundamental volume between the 0° and 100° C marks.

The necessary data for pointing thermometers (made of Jena 59^m borosilicate and Jena 16^m normal glass) in this way are given in the follow-

ing tables (due to Mahlke and to Wiebe and Böttcher, respectively), where t represents temperature on the scale of the gas thermometer, and T the corresponding temperature on the mercury-in-glass scale.

TABLE I

Variation from the Gas Scale for a Thermometer of Jena 59^{III} Glass

t	T	t	T
0°	0	375°	385.4
100°	100	400°	412.3
200°	200.7	425°	440.7
300°	304.1	450°	469.1
325°	330.9	475°	498.0
350°	358.1	500°	527.8

TABLE II

Variation from the Gas Scale for a Thermometer of Jena 16^{III} Glass

t	T	t	T
0°	0	240°	240.46
100°	100	260°	260.83
150°	149.90	280°	281.33
200°	200.04	300°	301.96
220°	220.21		

On the mercury-in-glass scale, 1 degree is represented by one-hundredth of the volume of the capillary contained between the ice point and the steam point. The scale is then extended in degrees of the same volume. Hence, to point the scale, the 500° C mark should be placed at a point such that the *volume between the ice point and the graduation in question* is 5.278 times the "fundamental volume," i. e., between the ice and steam points, or between the 0° and 100° marks if these are exactly placed, the 450° mark such that this volume is 4.691 times the fundamental volume, the 400° mark such that this volume is 4.123 times the fundamental volume, etc. If the capillary is of uniform cross section, the marks will come at points distant from the 0° graduation by 5.278, 4.691, 4.123, etc., times the distance between the ice and the steam point readings. If the cross section is not uniform, it will be necessary to calibrate the tube by observing the length of suitable mercury threads in different positions in the tube.

Upper Temperature Limits.—Thermometers of Jena 16^{III} normal, Corning normal, or French hard glass, may be safely used at temperatures up to 450° C or somewhat higher. Some tests on well-annealed thermometers of Corning borosilicate glass have shown that at 505° C there was still a very slow rise of the ice point. At 510° C there was a slow lowering of about 0.5° C per day, indicating that the glass of the bulb was slowly yielding under the internal pressure. At 520° to 525° C this effect was increased to about 0.5° C per hour; 500° C should, therefore, be considered the upper safe limit for this glass for continued use, although a short exposure to 525° C would do no serious damage. Thermometers of Jena 59^{III} borosilicate glass are usually graduated to 550° C, but this is considerably above the safe upper limit, which may be put at 510°–520° C. Thermometers made of special grades of combustion tubing may be used at temperatures of about 560° C. Thermometers of fused quartz graduated to 750° C have recently been put on the market.

Care must be exercised that a thermometer is not overheated. If a long portion of the stem is cold, the stem correction may amount to 30° or 40° C, and in this case the reading might be 500° C when the temperature of the bulb was 540° C, and after a few minutes at that temperature the ice point might be lowered 20° C or more.

F. INDUSTRIAL THERMOMETERS

Under the head of industrial or so-called "mechanical thermometers" may be classed thermometers of special construction adapted to the requirements of the industries, such as flue gas, annealing oven, distilling, steam tank, brine circulation, and other thermometers. Those interested in the many forms of industrial thermometers should consult the trade catalogues. These thermometers are usually inclosed in a metal tube or case to protect them from damage in the ordinary usage for which they are intended. In some instances the bulb of the thermometer is surrounded by a metal casing which fits closely into a well permanently mounted in the pipe through which is flowing the liquid or gas the temperature of which is to be measured. To insure good contact between the bulb and the case, the former is frequently copper plated or the interspace is filled with a good conductor of heat. When the requirements of the work are such that the stem of the thermometer is very long and the graduated scale occupies only a short length of the stem near its upper end, the graduated portion of the capillary is generally connected to the bulb by a much finer capillary, to reduce the very large "stem correction" that might otherwise be introduced.

Industrial thermometers will be tested in accordance with schedule 33, section 20.

G. CLINICAL THERMOMETERS

Information will be found in B. S. Reprint No. 13 and Circular No. 5, relating to clinical thermometry, such as discussion of types in use, scale of

temperature on which thermometers are graduated, the construction of suitable standards for use in pointing clinical thermometers, defects to which clinical thermometers are liable, change in reading with time, difference in reading when warm and when cold, time of action, etc., together with a description of the apparatus and methods used in testing and the regulations that have been adopted by this Bureau governing the testing and certification of clinical thermometers.

Clinical thermometers will be tested in accordance with schedule 35, section 20.

12. THERMOMETRIC GLASSES

The satisfactory thermometric glasses now available and widely used are: Jena 16^m normal, Corning normal, French hard (verre dur), Jena 59^m borosilicate, Corning borosilicate, "Resistenzglas," and certain grades of combustion tubing for temperatures above the range of these glasses.

Ice-Point Depression.—The advantages of these glasses are that thermometers made of them have a small ice-point depression¹⁸ and quickly expand (in a few minutes) to their final equilibrium condition corresponding to any temperature. Moreover, the depression of the ice point will almost entirely disappear in a few days. With other glasses it may take 30 minutes or more for the thermometer to attain its final reading at any given temperature, for example, in steam, and the ice point may still be depressed by a quite noticeable amount for some weeks, and for some glasses even for some months, after the thermometer has been warmed much above room temperatures.

The magnitude of this "zero depression" for some of the most widely used thermometric glasses is given in the following table:

Zero depression in thermometers made of different kinds of glass

Jena 59 ^m borosilicate	0°02 to 0°04
Corning borosilicate	0°03 to 0°05
Jena 16 ^m normal	0°05 to 0°07
Corning normal	0°06 to 0°11
Verre dur	0°07 to 0°11
Greiner and Friederichs Resistenz	0°07 to 0°10
English crystal	0°15 to 0°20
Thüringer glasses	0°2 to 0°5

Wiebe¹⁹ has made a careful study of the so-called "compensated thermometer," first described by Schott, in which the "depression" is neutralized by mounting within the bulb a small rod of a glass having a relatively much larger "depression."

¹⁸ Difference in ice-point reading before and immediately after thermometer is heated to 100° C (212° F); or, more accurately, the difference in ice-point reading taken after the thermometer has been constantly at 0° for a long time (until the glass has reached an equilibrium condition at that temperature) and the ice-point reading taken immediately after the thermometer has been heated to 100° C.

¹⁹ Zeitschrift für Instrumentenkunde, 30, p. 245; 1910.

The slow secular rise of the ice point which goes on for years after the thermometer is made up is very small for thermometers made of the better glasses and used not much above room temperatures, being of the order of 0.1°C in many years, and more than one-half of this takes place within the first few months. With the inferior glasses, it is of the order of 0.5° to 1°C and extends over many years.

The safe upper limit of temperature at which thermometers of these glasses can be used is considered under section 11, E.

The bulbs of all thermometers should be made of one or the other of these glasses. For thermometers intended for use up to 420°C the stem may be made of a softer enamel back glass.

The investigations of Weber and of Wiebe have shown that thermometric glasses should contain only one of the oxides of sodium or potassium. If the oxides of both are present, the ice-point depression will be much larger than if only one is present and will be a maximum if both are present in nearly equal proportions, and it will take a longer exposure at any given temperature for the glass to expand to its final equilibrium condition corresponding to that temperature, and the recovery of the ice point will be slower. The satisfactory glasses enumerated above are lead free and practically contain only the oxide of sodium (Na_2O). The borosilicate glasses contain, in addition, 10 to 12 per cent of the oxide of boron (B_2O_3). English crystal glass, which was and probably still is used to a considerable extent for thermometers, contains about 12 per cent of K_2O and 1.5 per cent of Na_2O with a very large content of PbO (33 per cent).

Until quite recently it was the general practice to etch or sand blast the backs of thermometers made of the borosilicate glasses to furnish a diffuse background for reading. These glasses can now be obtained with white enamel back, which makes more sightly and satisfactory thermometers for general use.

The borosilicate glasses are the best glasses yet developed for thermometric purposes. One thing that has stood in the way of the adoption of these glasses for thermometers intended for high precision at ordinary temperatures (0° to 100°C) is the difficulty in obtaining tubes for the stem that have a sufficiently uniform bore. Improvements in drawing these tubes to overcome this defect would be of great service in the accurate measurement of temperature by means of mercurial thermometers.

Those interested will find full details relating to the physical and chemical properties of various glasses in Hovestadt's treatise entitled "Jenaer Glas," which contains numerous references to the publications of various investigators. (English translation by J. D. and A. Everett, published by Macmillan, 1902.)

13. THE ANNEALING OF THERMOMETERS

When the testing of high-temperature thermometers was taken up by the Bureau the fact soon developed that a large percentage of these thermometers were subject to very considerable changes, 30° to 40°C or more.

An investigation was accordingly undertaken to direct the attention of manufacturers to proper methods of annealing²⁰ such thermometers.

When a thermometer is heated, two kinds of changes may take place, (a) temporary, (b) permanent changes. The former, which manifest themselves in the "depression of the ice point" with its slow recovery, have already been discussed, together with the methods of eliminating their effect. When a thermometer which has not been properly annealed is exposed to high temperatures the strains present in the glass are relieved to some extent, the glass contracts, and on cooling the ice point will have been permanently raised. These latter changes of the ice point are much more rapid during the first few hours of heating, and become less as the time of heating is prolonged. The time required to reach an equilibrium condition is very long, as small changes of the ice-point reading may still be detected after many hundreds or even thousands of hours annealing.

The practice, once in vogue among thermometer makers, of annealing high temperature thermometers in an oil bath at about 315° C (600° F) is absolutely inadequate. Months or years of annealing at this temperature would not render the ice point constant for use at temperatures of 425° C or higher. The temperatures at which thermometers should be annealed will depend on the kind of glass of which they are made. Schott²¹ has shown that Jena 16^{III} normal glass begins to soften sufficiently at about 400° to 410° C and Jena 59^{III} borosilicate at about 430° to 440° C, so that the strains can be relieved by long annealing at these temperatures. The annealing temperatures of thermometers made of verre dur or the normal glasses should not therefore be below about 420° C, nor below about 450° C for the borosilicate glasses. The higher the annealing temperature the shorter the time required to produce the same degree of annealing (i. e., constancy of ice point). For example, for borosilicate glass annealing at 500° C would require only about half as long as at 450° C. It is therefore advantageous in practice to raise these annealing temperatures as much as possible.

If an electric furnace is used, the maximum safe annealing temperature will depend on the constancy of voltage on the line. It might not be safe to set the furnace at 500° C, as fluctuations in voltage might produce variations of some 25° C or more in temperature, and at 525° C the borosilicate glass might be sufficiently soft to yield under the high internal pressure and to permanently enlarge the bulb.

The permanent change (rise due to contraction of the bulb) of the ice point may amount to 30° or 40° C or even more. The capillary will also diminish in volume, which will result in an increase of the fundamental interval, i. e., the number of degrees of the scale comprised between the temperature of melting ice and that of steam at normal pressure. As the volume between the 0° and 100° C points is about one-sixtieth of the volume of the bulb, the change in the fundamental interval might be expected

²⁰ Sometimes erroneously called "artificial aging." Centuries of aging at ordinary temperatures would not insure a thermometer against large changes at high temperatures if it had not been properly annealed.

²¹ *Zeitschrift für Instrumentenkunde*, 11, p. 330; 1891.

to be about one-sixtieth of the change in the ice point; experiment shows that it is about one-thirtieth of the change in the ice point. This is undoubtedly explained by two facts, (a) the coefficient of expansion of annealed glass, free from strains, is known to be less than when in the strained condition, and (b) the strains present in thick glass such as is used for the stem may be somewhat greater than in the thin glass of the bulb, so that the volume changes when these strains are relieved may be relatively greater for the stem than for the bulb. If, then, the change in the ice point reading of a thermometer is 6°C , the change in the fundamental interval will be about 0.2°C . Since this is the additional correction to be applied at 100°C and must be added again for each 100° , the correction at 450°C will amount to 0.9° (i. e., if the ice point reading has been raised 6° , the reading at 450° will be raised to 6.9), a correction that can by no means be neglected. It is therefore necessary to determine the correction due to change in fundamental interval whenever the ice point has shown any very considerable change.

The conclusions regarding the annealing of thermometers may be thus briefly summarized:

Every thermometer, particularly if intended for use above 100°C , should undergo suitable annealing before it is used. The annealing can be done before the final filling of the thermometer, or an auxiliary bulb can be temporarily fused to the upper end of the capillary, into which the mercury from the main bulb is run during the annealing process. Thorough annealing requires from 4 to 10 days at a temperature of 450°C or as much higher as the glass will safely stand,²² according to the temperature at which the thermometer is to be used, and the annealing may well be followed by a period of slow cooling extending over several days. (The latter is, however, less important.)

Where results of high accuracy at high temperatures are required, the ice point of the thermometer must be determined from time to time and the changes allowed for, for no amount of annealing will insure an absolutely constant ice point where the thermometer is used at temperatures of 450° to 500°C . If changes have taken place in the ice point reading, the fundamental interval has also probably changed by about 3 per cent of this amount, and the resulting error at 500° due to this cause may be as much as one-fifth of the change of the ice point.

If a thermometer has not been properly annealed the changes in its indications due to long-continued exposure to relatively high temperatures may be very large, as much as 45°C .

In the process of annealing, thermometers should be mounted in the annealing oven in a vertical position in such a way as to avoid bending strains.

Further details relating to the experiments carried out by the Bureau and by others on the heat treatment of high temperature thermometers will be found in B. S. Reprint No. 32.

²² For thermometers having soft enamel back glass stems, and where a considerable portion of the stem is annealed, the safe upper limit for annealing is about 420°C . This limit seems to be fixed, not by the softening of the glass, but by the effects of differential expansion resulting in a permanent bending of the stem.

Annealing Oven.—The electric oven used in the annealing experiments carried out by the Bureau is fully described and illustrated in the reprint referred to. On an ordinary lighting circuit with moderate constancy of voltage, such an oven may be run for weeks with practically no attention. A number of ovens, similar in construction and of dimensions suited to the work, have been installed by thermometer manufacturers with excellent results.

The Bureau will be pleased to render any assistance it can to anyone contemplating such installations. Where electric power is not available, a gas-heated oven, automatically controlled by a thermostat, could also be used.

14. NOTES ON THERMOMETER SPECIFICATIONS

This topic will be treated in detail in a separate circular which, it is hoped, will be issued in the near future. The following notes may be of interest to those called on to prepare specifications for high-grade laboratory thermometers.

Bulb and Stem.—The bulb of the thermometer should be made of one of the approved thermometric glasses. (See sec. 12.) One or the other of the normal or borosilicate glasses is almost exclusively used in this country. For thermometers intended for temperatures up to about 450° C any of these glasses will be found satisfactory. For temperatures up to 500° C one of the borosilicate glasses should be used. For temperatures up to 560° C, or thereabouts, special grades of combustion tubing are available.

The maximum diameter of the bulb should preferably not exceed the diameter of the stem, except where necessary, as in calorimetric thermometers requiring a very open scale, in oil flash point thermometers, etc.

The stem should be made of enamel back tubing having a circular cross section. For a thermometer reading up to about 420° C the stem may be made of a softer glass. At temperatures much above this the stem is likely to bend if such glasses are used. The external diameter of the stem should not be less than 5 nor more than 7 mm.

The capillary should be circular in section and not less than 0.10 mm in diameter. The capillary tubes should be carefully examined for uniformity of cross section by a mercury thread calibration and only those tubes used in which the variation in cross section does not exceed 2 to 4 per cent, depending on the grade of thermometer. Where the highest grade of thermometer is required it is necessary to use short calibration threads and to reject all tubes showing sudden changes of cross section.

In all thermometers in which the space above the mercury is free from gas the capillary should terminate in a small pear-shaped reservoir having a volume at least equal to that of the entire capillary. This permits a mercury thread calibration of the capillary and the removal of gas bubbles from the mercury, and minimizes the danger of breakage due to accidental overheating of the thermometer.

It is sometimes convenient to have the stem terminate at the top in a small closed glass ring.

Graduations.—The graduation marks should be clear cut and fine and should be well and uniformly filled with coloring matter. For high-temperature thermometers it is an advantage to have the coloring matter burned into the graduations to insure its permanence. For thermometers intended for high precision in the interval 0° to 100° C, the width of the graduation marks should not exceed one-tenth of the interval between graduations. In thermometers graduated to $0^{\circ}1$, the 1° and the $0^{\circ}5$ graduations should be longer than the intermediate $0^{\circ}1$ graduations; for thermometers graduated to $0^{\circ}5$, the 1° graduations should be longer than the intermediate $0^{\circ}5$ graduations, etc., the longer graduations preferably extending equally on each side of the shorter ones.

Numbering.—The numbering of the graduations should be clear cut and distinct and free from ambiguity.

Length of Thermometer.—The scale need include only the interval within which the thermometer is to be used. To avoid making the thermometer unduly long auxiliary reservoirs in the stem may be used as shown in Fig. 1, page 21.

Ice Point on Scale.—It is highly desirable to have the ice point, and a short length of the scale above and below this point, on every thermometer for the reasons pointed out in preceding sections.

Length and Subdivision of a Degree.—No hard and fast rules can be laid down concerning the length and subdivision of a degree, as this will depend somewhat on the purposes to which the thermometer is to be adapted. In general, it may be stated that nothing is gained by having the interval between graduation marks less than 0.4 or 0.5 mm. Thermometers to be read with a lens should be so designed that the interval will be from 0.5 to 1.0 mm, while for reading without a lens this interval may be from about 0.8 to 2.0 mm.

Experience has shown that for thermometers intended for high precision ($0^{\circ}01$ or thereabouts) in the interval -35° to 100° C, a degree length of 6 to 8 mm and subdivision into $0^{\circ}1$ is very satisfactory.

For thermometers in the interval 100° to 200° C, nothing is gained by subdividing finer than $0^{\circ}2$, and for most purposes $0^{\circ}5$ is amply fine enough, as such a thermometer can be easily read to $0^{\circ}05$, which is generally beyond the accuracy to which temperature measurements can be depended upon, except under the most favorable conditions as to stirring, total immersion to eliminate all uncertain stem corrections, etc. For subdivision to $0^{\circ}2$, a convenient length is 1° C = 2.5 to 4 mm, and for subdivision to $0^{\circ}5$, 1° C = about 2 mm, and somewhat less if the scale is continuous from 0° up. For thermometers above 200° C, nothing is gained by subdividing finer than $0^{\circ}5$, a convenient length of degree being 1.5 to 2 mm. Subdivision to 1° will be sufficient in nearly every case, since the uncertainties, referred to above, at these temperatures, exceed the errors of reading.

For calorimetric and Beckmann thermometers including a short length of the scale and subdivided to $0^{\circ}.01$ or $0^{\circ}.02$, a length of $1^{\circ} \text{C} = 50\text{--}30 \text{ mm}$ is satisfactory.

In all cases care must be taken that the graduated part of the scale is not too near the bulb or too near an auxiliary reservoir in the capillary. The lowest graduation mark should not be less than 2 cm above the bulb, and the clear space allowed for an auxiliary reservoir should not be less than 3 cm. The highest graduation mark should not be less than 1 cm below the upper pear-shaped bulb.

Annealing.—Thorough annealing is highly desirable for thermometers intended for use at even ordinary temperatures, but is of the utmost importance for all high-temperature thermometers, which should be thoroughly annealed in accordance with the recommendations contained in section 13.

Workmanship.—A high-grade thermometer should conform also to the following requirements: The stem should be straight and the capillary in the center of the stem. The outside of the thermometer, where the bulb joins the stem, should be smooth, not showing any sharp indentation. The graduation marks should be straight, of uniform width, with clearly defined edges, and should be perpendicular to the axis of the thermometer. An imaginary line running through the middle points of the graduation marks should lie parallel to the axis of the stem. The marks made in pointing should not appear in the middle part of the graduation marks, as this makes the reading difficult at the most important points. The glass blowing should show first-class workmanship.

Carefully distilled mercury should be used, and it and the interior of the thermometer should be thoroughly clean and dry.

Failure to meet the above requirements is principally an indication of careless workmanship, but is very common in thermometers now on the market.

The maker's name and an identification number should appear on the thermometer.

15. REMOVAL OF MERCURY FROM THE UPPER RESERVOIR AND OF GAS BUBBLES FROM THE MERCURY

In the handling of thermometers it is often found necessary to manipulate the mercury within the capillary, in order to reunite with the main column a part of the mercury which has become separated, to remove gas bubbles from the mercury in the bulb or stem, or to separate a mercury thread for use in calibrating. There are four operations usually resorted to in manipulating the mercury, viz, (a) warming, (b) cooling, (c) tapping on the end, and (d) tapping on the side of the thermometer.

(a) Warming the bulb of a thermometer may be done in water or oil or in the air high above a gas or alcohol flame, but great care must be taken, especially with high-temperature thermometers, not to heat the bulb to a

temperature higher than the thermometer is intended to measure. The upper end of a thermometer stem may be warmed over a Bunsen burner if this is done very gradually. When the thermometer is warmed over a flame, it should be rotated about its axis.

(b) Cooling may be accomplished in cold water, ice, a freezing mixture, or CO₂ snow, but such cooling should not be attempted while the thermometer bulb is still hot to the touch.

(c) Tapping or striking a thermometer on the end must be done carefully at all times and much more so when the bulb is only partly filled with mercury and the thermometer is inverted. This tapping may be "soft," as when the thermometer is held vertically in the hand and the hand (not the thermometer) is struck on the table, or it may be "sharp," as when the thermometer is held vertically and struck downward on a pad of paper.

(d) Tapping on the side of a thermometer may be done "softly" with the hand or "sharply" with a pencil. Either must be done with care, as there is danger of breaking the stem. Different thermometers require different treatment, but the following procedure may serve as a guide in the manipulation of thermometers not filled with gas under pressure.

To remove mercury from upper bulb when it is partly full.

Hold thermometer vertically, bulb down.

Tap "softly" on side near the top and "softly" on end, to bring mercury to lower part of upper reservoir.

Then try both tapping "softly" and "sharply" on end, and if this fails to bring the mercury down the stem—

Warm the bulb until mercury rises and unites with that in the reservoir.

Cool very slowly and probably the mercury will all come down.

If not, try again, cooling more slowly.

To remove mercury from upper reservoir when this is completely full or when mercury persistently stays at the top of reservoir.

Warm the upper end carefully over a Bunsen flame beginning at the extreme tip. Mercury will be driven down the capillary by its own vapor pressure.

If small mercury globules are left, warm a little more and they will condense farther down.

Wait until the upper end cools to a temperature comfortable to the hand.

Warm the lower bulb until mercury rises and collects the small globules.

To find whether there is any residual gas in the thermometer bulb.

Warm the bulb until at least a few centimeters of mercury appear in the capillary; if mercury is already there, do not warm.

Invert the thermometer and see whether mercury runs down.

If not, there is probably no gas in the bulb.

If mercury runs down, let it run a few centimeters and look for a bubble in the bulb.

Right the thermometer and see whether this bubble *entirely* disappears when the mercury returns to the bulb. If this bubble disappears, no significant amount of gas is present.

To remove gas when found.

Invert thermometer and run some mercury into the capillary.

Right thermometer and tap "sharply" on side and on end to bring gas to the top of bulb *before* mercury all returns.

Cool bulb as much as possible, tapping sharply on end when cold.

Invert thermometer and tap very "softly" on end to bring down mercury, which is still separated by the air bubble from that in the bulb.

When this has come down, either tap "sharply" or warm to bring down the mercury from the bulb, but do not let the separated thread get into the upper bulb until the main mercury column is ready to join it.

Get the two separated parts to join in any convenient enlargement or in the upper reservoir.

Right the thermometer or hold it at an angle, with the top higher, and let the mercury run *slowly* into the bulb, watching carefully the point where the bubble is left, to be sure that the column does not separate.

If the bubble begins to enlarge, run the mercury more slowly.

To remove bubbles from high-temperature thermometers.

Bubbles can often be removed, even from high-temperature thermometers, which are filled under pressure, provided there is an enlargement in the stem (e. g., between the 0° and the 300° C mark).

If there is no such enlargement, the gas can sometimes be removed by long continued sharp tapping on the end, or sometimes by freezing the mercury by means of CO₂ snow, then warming the bulb (from the bottom) rapidly against the hand. Mercury will not break the bulb on freezing, as it does not expand.

16. ELECTRIC RESISTANCE THERMOMETERS.

Resistance thermometry is based on the variation of the electric resistance of a metal wire with temperature. Various pure metals may be used at low and at ordinary temperatures. Nickel is frequently used up to about 300° C, above which point there is an irregularity in the resistance-temperature curve due to a "critical point." When properly constructed and used, the platinum resistance thermometer is an instrument of great accuracy for the measurement of temperatures from -200°, or lower, up to about 1000° C, or even higher for limited periods.

Full details relating to the construction of platinum-resistance thermometers of the Callendar and the Siemens compensated lead types and the

potential terminal type, their standardization and method of use, the changes which they undergo at high temperatures, the effect of variations in purity of the platinum wire, and the temperature scale which they define when calibrated in ice, steam, and sulphur vapor (444.97°C at standard atmospheric pressure) will be found in B. S. Reprints Nos. 124, 143, and 149. These reprints also contain data on the reproducibility of "fixed points" of the temperature scale, by means of the melting and freezing points of metals and the boiling points of substances obtained from different sources, on the value of the sulphur boiling point and its use as a calibration temperature, on the comparison of the temperature scales defined by the platinum thermometer with the scales defined by Pt, Pt-Rh and Pt, Pt-Ir thermocouples, and a fairly complete bibliography of papers relating to resistance thermometry.

The resistance thermometer is especially adapted to the measurement of small temperature changes with the highest accuracy, as is required in calorimetry, in freezing and boiling point work, and in special physical and thermochemical investigations. For example, in calorimetric work, where a temperature change of a few degrees is to be measured, the highest accuracy attainable with mercurial thermometers of the calorimetric or Beckmann type, after most careful standardization, is hardly better than 1 or 2 parts in 1000 of the measured interval, while with a suitable resistance thermometer an accuracy of about 1 or 2 in 10 000 may be attained, although the apparatus required is somewhat elaborate and expensive. The construction and use of resistance thermometers that have satisfactorily fulfilled every requirement of calorimetric work of high accuracy are fully described in B. S. Reprint No. 68. (See also footnote No. 8.)

Calibration.—The investigations of Callendar,²³ Callendar and Griffiths,²⁴ Heycock and Neville,²⁵ Harker and Chappuis,²⁶ Harker,²⁷ Holborn,²⁸ and a number of others have shown that a platinum-resistance thermometer calibrated at the temperatures of melting pure ice, of the vapor of boiling pure water, and of the vapor of boiling pure sulphur, may be used to reproduce gas-scale temperatures throughout the range -100° to $+500^{\circ}\text{C}$ with a degree of accuracy equal to that attained up to the present time in gas thermometry, and when this calibration is extrapolated to the melting points of silver, gold, and copper, it gives values which are in agreement with the best gas-scale determinations of these melting (or freezing) points. Such extrapolation does not hold, however, for impure platinum. (See B. S. Reprint No. 124.)

²³ Phil. Trans. Royal Soc., A, 178, p. 160; 1887.

²⁴ Phil. Trans. Royal Soc., A, 182, p. 110; 1891.

²⁵ Jl. Chem. Soc., London, 67, p. 160; 1895.

²⁶ Phil. Trans. Roy. Soc., A, 194, p. 37; 1900. Phil. Mag. (VI.) 3, p. 343; 1902.

²⁷ Phil. Trans. Roy. Soc., A, 203, p. 343; 1904.

²⁸ Ann. d. Phys., 6, p. 242; 1901.

Callendar has shown that if the *platinum temperature*, pt , is defined by the equation

$$(1) \quad pt = \frac{R - R_0}{R_{100} - R_0} \times 100$$

where R = the observed resistance at the temperature to be measured.

R_0 = the observed resistance at 0°C .

R_{100} = the observed resistance at 100°C .

then the relation between the *platinum temperature*, pt , and the corresponding *gas scale temperature*, t , is defined by the equation

$$(2) \quad t - pt = \delta \left(\frac{t}{100} - 1 \right) \frac{t}{100}$$

where δ is a constant depending on the purity of the platinum wire. It has been found that, in general, the purer the platinum, the smaller is the value of δ . For platinum of the highest purity, this value, determined as below, is about 1.5; for platinum of ordinary commercial purity it may be 2 or even higher.

As the above equation (2) is that of a parabola, the constants of the thermometer can be determined by measurements at three known temperatures.

The three calibration temperatures usually employed are, as already indicated, the two fixed points (ice and steam) of the thermometric scale, and the boiling point of sulphur at known pressure and in a definite form of boiling point apparatus, the latter point being used because it is the most accurately known fixed point in the lower range of the high temperature scale. The accepted value of the sulphur boiling point, now generally used, is 444.7°C (at standard atmospheric pressure) on the scale of the constant volume nitrogen (or air) thermometer. The results of the determinations of this point by different investigators and the necessary precautions that must be observed in the use of this point as a calibration temperature are considered in B. S. Reprint No. 124.

For the standardization of resistance thermometers for calorimetric work requiring the measurement of small temperature intervals with the highest accuracy and for the reproduction of the international hydrogen scale by means of platinum resistance thermometers, the transition temperature²⁹ of pure sodium sulphate (32.384°C) should be used.

For temperatures down to about -100°C the temperature of a mixture of solid CO_2 with alcohol, ether, or gasoline (-78.3°C), as described in section 11 D, may be used as a calibration point.

If temperatures below about -100°C are to be measured, the boiling point of liquid oxygen (-182.5°C) should be chosen as a calibration point,

²⁹ Richards and Wells: Proc. Am. Acad. of Arts and Sciences, 38, p. 431, 1902. B. S. Bulletin, 3, p. 641; 1907. B. S. Reprint No. 68.

and for temperatures much below -200° C the boiling point of liquid hydrogen as well. The work of Kammerlingh Onnes³⁰ and his collaborators indicates that if the highest accuracy, at very low temperatures, is desired, a number of such low temperature fixed points must be used in the calibration of a resistance thermometer.

17. THERMOELECTRIC THERMOMETERS

In thermometers of this type temperatures are measured by the magnitude of the electromotive forces set up between wires of different materials, when one junction is exposed to the temperature to be measured and the other junction (or junctions) is kept at some known temperature. In what follows only such combinations as are suitable for use in the lower range of temperature, say below 600° C, will be considered. Thermocouples for use at higher temperatures are considered in Circular No. 7.

Although a very large number of combination of metals and alloys have been examined as to their thermoelectric properties and the results tabulated,³¹ the number that have been used and recommended for temperature measurement is limited. Those in common use³² are iron, copper, or silver vs. constantan, and for very low temperatures, gold vs. silver and german-silver vs. platinum.

Recently other couples have come into quite extended use, such as nickel against an alloy of nickel with chromium, nickel against steel, etc. Couples of platinum against its alloys with rhodium or iridium, such as are used at high temperatures, have also been used in the range of temperatures here considered. The electromotive force of the platinum couples is much less than that of the base metal couples referred to above. For temperatures above 300° C, however, the accuracy attainable with these couples is probably greater than with the base metal couples, on account of the greater homogeneity of the wires. Rothe³³ has shown that the platinum, platinum-rhodium couple has an inversion point in its emf-temperature relation at -142° C.

Compound Couples.—The largest thermoelectric power of any of the combinations in common use, that of iron vs. constantan, about 50 microvolts per degree, is still so small as to require rather sensitive measuring instruments. In many cases the sensibility can be greatly increased, without corresponding disadvantages in other directions, by connecting a number of couples in series to make a compound couple. As many as 100 have

³⁰ Communications from the Physical Laboratory of the University of Leiden, No. 93, 1904; No. 95 c, 1906; No. 101 a, 1908.

³¹ Dewar and Fleming: *Phil. Mag.*, (V), **40**, p. 95; 1895. Jaeger and Disselhorst: *Wiss. Abhandl. d. Phys.-Tech. Reichsanstalt*, **3**, p. 394; 1900.

³² Holborn and Wein: *Wied. Ann.*, **59**, p. 213; 1896. Palmer: *Phys. Rev.*, **21**, p. 65; 1905. Dewar: *Proc. Roy. Soc.*, **76**, p. 317; 1905. White: *Phys. Rev.*, **23**, p. 468; 1906; and **31**, p. 135; 1910. Kammerlingh Onnes and C. A. Crommelin: *Comm. from Phys. Lab. of Univ. of Leyden*, No. 95 a; 1906. Kammerlingh Onnes and J. Clay: *ibid.*, No. 107 b and d; 1908.

³³ *Zeitschrift für Instrumentenkunde*, **22**, p. 40; 1902.

been successfully used in this way.³⁴ Further, the wires may be combined, as explained below, so as to neutralize, to a large extent, the effects of inhomogeneity. Compound couples made in this way, however, must be rigidly inclosed, as otherwise the inhomogeneities produced by bending or twisting will render the care used in selecting the wire of no avail.

Homogeneity.—If the wires of a thermocouple are perfectly homogeneous throughout their length, the electromotive force produced will depend only upon the temperatures of the junctions, but if the wires are not homogeneous the electromotive force will depend also upon the temperature distribution along the wire. This source of error is probably one of the most serious encountered in the use of thermocouples. It is usually small in such metals as platinum, gold, silver, and copper, but may be of considerable magnitude in such metals as iron and nickel, and still greater in alloys. The effects of inhomogeneity³⁵ in German silver and in constantan have been studied with considerable care and the magnitude of the error estimated. Several methods of testing a wire for inhomogeneity have been used, all of which consist essentially in heating or cooling successive portions of the wire, and observing, on a galvanometer in circuit with it, the electromotive forces produced. In this way wires may be found in which inhomogeneities have a small effect, and by combining several wires the effects of inhomogeneity in one may be neutralized by those in another.

Compound couples may thus be made, the indications of which are but little affected by the temperature distribution along the wires. In addition to the effects of inhomogeneity, thermoelectric measurements are liable to error from parasitic electromotive forces due to chemical action (as from adhering soldering paste or from oxidation) and from those due to switches, contacts, etc. Most of those which are external to the thermocouple proper can be eliminated by proper methods of measurement. The couple itself may be tested by observing (*a*) whether the same indication is obtained when the junctions, in baths at different temperatures, are interchanged, (*b*) whether the electromotive force is zero when both junctions are at the same temperature, and (*c*) whether the emf changes with depth of immersion in the bath.

Instruments.—For a great deal of work the thermocouple, when used with a direct reading deflection instrument, is a very convenient indicator. For more precise work a potentiometer, preferably of low resistance, is a necessary adjunct. There are several types on the market which are suitable for this class of work. Some of the newer designs provide for constant resistance in the galvanometer circuit and also for the elimination of electromotive forces due to sliding contacts.

Formulas.—For the iron vs. constantan couple Holborn and Wein found that where t is temperature of one junction, the other junction being

³⁴ Magnus: *Ann. d. Phys.*, **31**, p. 597; 1910.

³⁵ Hall, Campbell, and Serviss: *Proc. Am. Acad.*, **41**, p. 559; 1906. White: *Phys. Rev.*, **23**, p. 454; 1906.

at 0°C , and e is the electromotive force, a formula

$$t = ae + be^2$$

held to within 1° from 0° to -190°C . For precision work in the range 0° to 100°C a formula

$$e = at + bt^2 + ct^3$$

has been found to represent a series of observations to about 0.004° .³⁶ The same type of formula is necessary to represent observations from 0° to 200°C (Palmer, loc. cit.). For accurate work at low temperatures, Kammerlingh Onnes (loc. cit.) found that a formula of four and even five terms is necessary.

Applications.—As a thermometer for use in the interval -200° to $+600^{\circ}\text{C}$, the thermocouple may compete with the various expansion thermometers and with the resistance thermometer, the accuracy attainable being, however, less than with the latter instrument. From comparisons with the gas thermometer at temperatures below the boiling point of liquid hydrogen, it has been established that the resistance-temperature relation, found by direct observation at temperatures as low as the boiling point of liquid oxygen (-182.5°C), or even lower, fails to hold if extrapolated to lower temperatures. With the exception of the gas thermometer, the thermocouple is almost the sole means of measuring these extremely low temperatures. Where a small difference in the temperatures at two points is to be measured, the thermoelectric method is often the most convenient one. The use of the thermocouple as a precision thermometer for the measurement of small temperature changes such as are met with in calorimetric work, etc., has recently been shown to be very satisfactory, and its usefulness in this field is increasing.

18. PUBLICATIONS IN THERMOMETRY, PYROMETRY, AND HEAT MEASUREMENTS

The following papers, embodying the investigations in thermometry, pyrometry, and heat measurements carried out at the Bureau have been published. They are issued in pamphlet form and will be sent upon request. They may be designated by the numbers which precede the titles in the list. A complete list of the technical publications of the Bureau, with brief abstracts of contents, will also be sent upon application.

TECHNICAL PAPERS.

8. On the Temperature of the Arc (Sept. 1, 1904), 16 pp. *C. W. Waidner* and *G. K. Burgess*.
11. Optical Pyrometry (Sept. 15, 1904), 61 pp. *C. W. Waidner* and *G. K. Burgess*.
13. The Testing of Clinical Thermometers (Nov. 1, 1905), 15 pp. *C. W. Waidner* and *L. A. Fischer*.
24. Radiation from Platinum at High Temperatures (Aug. 15, 1905), 3 pp. *G. K. Burgess*.
32. Heat Treatment of High-Temperature Mercurial Thermometers (Apr. 15, 1906), 36 pp.
H. C. Dickinson.

³⁶ White, Dickinson, and Mueller: *Phys. Rev.*, **31**, p. 159; 1910.

40. Preliminary Measurements on Temperature and Selective Radiation of Incandescent Lamps (Sept. 30, 1906), 11 pp. *C. W. Waidner and G. K. Burgess.*
55. Radiation from and Melting Points of Palladium and Platinum (Mar. 4, 1907), 46 pp. *C. W. Waidner and G. K. Burgess.*
57. On the Establishment of the Thermodynamic Scale of Temperature by Means of the Constant-Pressure Gas Thermometer (Feb. 4, 1907), 57 pp. *E. Buckingham.*
62. Melting Points of the Iron-Group Elements by a New Radiation Method (Apr. 5, 1907), 11 pp. *G. K. Burgess.*
68. Calorimetric Resistance Thermometers and the Transition Temperature of Sodium Sulphate (June 21, 1907), 21 pp. *H. C. Dickinson and E. F. Mueller.*
69. On the Standard Scale of Temperature in the Interval 0° to 100° C (May 3, 1907), 66 pp. *C. W. Waidner and H. C. Dickinson.*
99. On Methods of Obtaining Cooling Curves (Aug. 3, 1908), 26 pp. *G. K. Burgess.*
121. The Estimation of the Temperature of Copper by Means of Optical Pyrometers (June 17, 1909), 9 pp. *G. K. Burgess.*
123. The Theory of the Hampson Liquefier (May 15, 1909), 22 pp. *E. Buckingham.*
124. Platinum Resistance Thermometry at High Temperatures (June 26, 1909), 80 pp. *C. W. Waidner and G. K. Burgess.*
135. Specific Heat of Some Calcium Chloride Solutions between -35° C and $+20^{\circ}$ C (Nov. 4, 1909), 29 pp. *H. C. Dickinson, E. F. Mueller, and E. B. George.*
136. On the Definition of the Ideal Gas (Nov. 13, 1909), 20 pp. *E. Buckingham.*
143. Note on the Temperature Scale in the Interval 100° to 500° C (May 27, 1910), 6 pp. *C. W. Waidner and G. K. Burgess.*
149. On the Constancy of the Sulphur Boiling Point (Dec. 6, 1910), 4 pp. *C. W. Waidner and G. K. Burgess.*
163. On the Computation of the Constant C_2 of Planck's Equation by an Extension of Paschen's Method of Equal Ordinates *E. Buckingham and J. H. Dellinger.*
167. The Steam-Turbine Expansion Line on the Mollier Diagram, and a Short Method of Finding the Reheat Factor. *E. Buckingham.*
170. The "Correction for Emergent Stem" of a Mercurial Thermometer. *E. Buckingham.*
171. Thermometric Lag. *D. R. Harper 3d.*
- Calorimetric Resistance Thermometers. *H. C. Dickinson and E. F. Mueller.*

BUREAU CIRCULARS.

- Circular No. 5. Testing of Clinical Thermometers.
- Circular No. 7. Pyrometer Testing and Heat Measurements.
- Circular No. 8. Testing of Thermometers.
- Circular No. 11. Standardization of Bomb Calorimeters.

19. GENERAL INSTRUCTIONS TO APPLICANTS FOR TESTS

Application for Test.—The request for test should be made in writing, addressed to "Bureau of Standards, Washington, D. C.," and should enumerate the articles submitted for test, giving sufficient information to identify each article or group of similar articles, and should state the nature of the test desired.

Nature of Test.—When apparatus is sent simply for test, without definite instructions, the Bureau will, if practicable, decide upon the nature of the test. Any special requirements or conditions to be observed, such as particular temperatures at which thermometers are to be tested, order of accuracy desired, etc., should be clearly stated in the request for test.

Identification Marks.—All packages should bear the shipper's name and address and, when convenient, a list of the contents. Each separate article should be plainly marked to facilitate identification.

Packing.—Thermometers are liable to be broken in packing and shipment in three ways:

(a) Thermometers often break from sliding or shaking in their individual cases. This can be avoided by wrapping each thermometer carefully in soft paper before placing it in its case, and having sufficient soft packing, as paper or cotton wool, at each end of the case so that the thermometer can not slip endwise.

(b) Thermometers are sometimes broken by the bending of the individual cases due to uneven packing outside of them. This can be avoided by using metal or wooden cases in place of paper cases, and even with paper cases, by care in distributing the packing material.

(c) Thermometers are often broken by jars and blows on the outside of the packing case, due to careless handling. The danger of such breakage can be minimized by surrounding the individual thermometer case or cases with a sufficient amount, say 3 or 4 inches, of excelsior or similar elastic material on all sides and at the ends, within a strong but light wooden box. The marking on the outside of this box should call attention to the necessity for careful handling.

Proper packing is emphasized because an unduly large percentage of the thermometers shipped to the Bureau for test are broken when received.

Shipping Directions.—Apparatus should be securely packed in cases or packages which will not be broken in transportation. The shipment in both directions is at the applicant's risk. To facilitate packing and shipping, the tops of the cases should have the return or forwarding address on the under side and should be put on with screws. Transportation charges are payable by the party desiring the test and must be prepaid. Unless otherwise arranged articles will be returned or forwarded by express "collect."

Return of Apparatus.—Regular tests will be made in the order in which the applications are received, except as this practice may be varied by grouping similar tests together. It is therefore suggested that the applicant make request for a test from two weeks to a month preceding the shipment of the apparatus. This facilitates the work of the Bureau, as well as the prompt return of the apparatus.

Address.—Apparatus submitted for test, as well as all correspondence, should be addressed simply "Bureau of Standards, Washington, D. C." Apparatus delivered in person or by messenger must be accompanied by a written request for the test.

Remittances.—Fees should be sent with the request for test, in accordance with the following schedules, or promptly upon receipt of bill. Certificates are not given nor is apparatus returned until the fees due thereon have been received. Remittances may be made by money order or check drawn to the order of the "Bureau of Standards."

20. SCHEDULES OF FEES

These schedules will go into effect October 1, 1911, and on and after that date supersede previous schedules.

Schedule 31.—Primary Standard Thermometers

- (a) Calibration with single mercury thread..... \$3. 00 to \$5. 00
- (b) Calibration of five to ten principal points by the Neumann-Thiesen or abridged calibration methods, and subcalibration of each interval..... 12. 00 to 20. 00
- (c) Determination of the internal and external pressure coefficients..... 2. 50
- (d) Determination of the fundamental interval..... 7. 50

Schedule 32.—Laboratory and Special Thermometers

(For types of thermometers included under this head, see section 11 B.)

- (a) Determination of corrections in the interval 0° to 100° C to an order of accuracy of 0.01 or 0.02, or as accurately as the construction of the thermometer warrants, for each point tested on a single thermometer..... \$0. 30
For the same points tested on additional similar thermometers, per point..... .20
- (b) Determination of corrections in the interval 0° to 100° C to the nearest 0.1 or 0.2, for each point tested on a single thermometer..... .20
For the same points tested on additional similar thermometers, per point..... .10
- (c) Determination of corrections in the interval 100° to 500° C with the highest accuracy warranted by the construction of the thermometer (0.05 to 0.2 up to 300° C, and somewhat less accurately at higher temperatures), for each point tested on a single thermometer..... .75
For the same points tested on additional similar thermometers, per point..... .50
- (d) Determination of corrections in the interval 100° to 300° C to an accuracy of 0.1 to 0.5 and less accurately at higher temperatures, for each point tested on a single thermometer..... .40
For the same points tested on additional similar thermometers, per point..... .30
- (e) Determination of corrections in the interval 0° to -60° C, for each point tested on a single thermometer..... .50
For the same points tested on additional thermometers, per point..... .30
- (f) Determination of corrections for alcohol, toluene, petroleum-ether, or pentane thermometers, below -60° C, for each point tested on a single thermometer..... 1. 00
For the same points tested on additional thermometers, per point..... .60
- (g) *Annealing*.—Preliminary annealing of high-temperature thermometers to determine whether they have been satisfactorily annealed, so that subsequent changes of the ice point will be small, single thermometer..... .50
Additional thermometers, each..... .30
Complete annealing of high-temperature thermometers for a period of at least six days, single thermometer..... 1. 00
Additional thermometers, each..... .60

NOTE.—When the preliminary annealing shows that a thermometer requires complete annealing, a fee is charged only for the complete annealing.

Schedule 33.—Industrial Thermometers

(For types of thermometers included under this head, see section 11 F.)

- (a) The fees for testing thermometers of this class will depend on the range and construction of the instrument. If the thermometer is adapted to the comparators of the Bureau, for each point tested..... \$1. 50 to \$2. 50
- (b) Where a thermometer is accepted for test that requires the construction of special apparatus, a special fee will be arranged for the particular test.

Schedule 34.—Calorimetric and Beckmann Thermometers

- (a) For the testing of ordinary calorimetric thermometers by comparison with standard thermometers, to an accuracy of 0.01, the fees are the same as Schedule 32 (a).
- (b) For the complete standardization of a calorimetric or Beckmann thermometer with the highest accuracy warranted by the construction and action of the thermometer, including determination of the calibration corrections at every 0.5 of the scale (provided the length of scale does not exceed 10°), and determination of the value of the scale degree by comparison with calorimetric platinum resistance thermometers and with standard mercurial thermometers, for a single thermometer. \$10.00
For each additional thermometer. 8.00
- (c) Same as above, (b), only with somewhat less accuracy, giving corrections at 1° (or 2°) intervals, for a single thermometer. 6.00
For each additional thermometer. 5.00
- (d) Calorimetric platinum-resistance thermometers will be standardized as explained in section 16, and in accordance with the following schedule:
Test of a calorimetric platinum-resistance thermometer. 10.00
- NOTE.—Thermocouples and resistance thermometers are tested in accordance with Schedules 36 and 37 (Circular No. 7).

Schedule 35.—Clinical Thermometers

(For the usual test of clinical thermometers at four test points, with a certification of corrections.)

- (a) In lots up to 8, each. \$0.25
(b) Any number between 8 and 12, total fee. 2.00
(c) In lots of 1 dozen or over, and less than 4½ dozen, per dozen. 2.00
(d) Any number between 4½ and 6 dozen, total fee. 9.00
(e) In lots of 6 dozen or over, per dozen. 1.50

S. W. STRATTON,
Director.

Approved:

BENJ. S. CABLE,
Acting Secretary.