

UNITED STATES DEPARTMENT OF COMMERCE • C. R. Smith, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Precision Measurement and Calibration

Selected NBS Papers on Temperature

J. F. Swindells, Editor

A compilation of previously published papers by the staff of the National Bureau of Standards, including selected abstracts by NBS and non-NBS authors. Issued in several volumes, *see page IV*.



Abstract

This volume is one of an extended series which brings together the previously published papers, monographs, abstracts, and bibliographies by NBS authors dealing with the precision measurement of specific physical quantities and the calibration of the related metrology equipment. The contents have been selected as being useful to the standards laboratories of the United States in tracing to NBS standards the accuracies of measurement needed for research work, factory production, or field evaluation.

Volume 2 contains reprints through June 1967 covering the general topics: Uncertainties, Temperature Scales, Resistance Thermometry, Thermoelectric Thermometry, Liquid-in-Glass Thermometry, Optical Pyrometry, and Spectroscopic Thermometry. A selected bibliography covering the period from January 1953 through December 1965 is included.

Key words: Acoustical thermometry, cerous magnesium nitrate thermometer, error analysis, liquid-in-glass thermometry, reprints, resistance thermometry, spectroscopic thermometry, standards, temperature scales, thermoelectric thermometry.

Foreword

In the 1950's the tremendous increase in industrial activity, particularly in the missile and satellite fields, led to an unprecedented demand for precision measurement, which, in turn, brought about the establishment of hundreds of new standards laboratories. To aid these laboratories in transmitting the accuracies of the national standards to the shops of industry, NBS in 1959 gathered together and reprinted a number of technical papers by members of its staff describing methods of precision measurements and the design and calibration of standards and instruments. These reprints, representing papers written over a period of several decades, were published as NBS Handbook 77, Precision Measurement and Calibration, in three volumes: Electricity and Electronics; Heat and Mechanics; Optics, Metrology, and Radiation.

Some of the papers in Handbook 77 are still useful, but new theoretical knowledge, improved materials, and increasingly complex experimental techniques have so advanced the art and science of measurement that a new compilation has become necessary. The present volume is part of a new reprint collection, designated NBS Special Publication 300, which has been planned to fill this need. Besides previously published papers by the NBS staff, the collection includes selected abstracts by both NBS and non-NBS authors. It is hoped that this new compilation of several volumes will serve both as a textbook and as a reference source for the many scientists and engineers who fill responsible positions in standards laboratories.

A. V. ASTIN, *Director.*

Preface

The general plan for this compilation has been reviewed by the Information Committee of the National Conference of Standards Laboratories. The plan calls for Special Publication 300 to be published in 12 volumes having the following titles and editors:

Statistical Concepts and Procedures, H. H. Ku
Frequency and Time, A. H. Morgan
Electricity—Low Frequency, F. L. Hermach and R. F. Dziuba
Electricity—Radio Frequency, A. J. Estlin
Heat, D. C. Ginnings
Temperature, J. F. Swindells
Mechanics, R. L. Bloss
Dimensional Metrology—Length and Angle, H. K. Hammond, III
Radiometry and Photometry, H. K. Hammond, III
Colorimetry and Image Optics, H. K. Hammond, III
Spectrochemical Analysis, B. F. Scribner
Ionizing Radiation, E. H. Eisenhower

This division of subject matter has been chosen to assure knowledgeable selection of content rather than to attain uniform size. However, the larger volumes, of approximately 600 pages, will still be small enough for convenient handling in the laboratory. The compilation consists primarily of original papers by NBS authors which have been reprinted by photoreproduction, with occasional updating of graphs or numerical data when this has appeared desirable. In addition, some important publications by non-NBS authors, as well as publications by NBS authors that are too long to be included, are represented by abstracts or references.

Each volume has a subject index and author index, and within each volume, contents are grouped by subtopics to facilitate browsing. Many entries follow the recent Bureau practice of assigning several key words to each document. Each paper reproduced for the compilation is essentially complete as originally published, retaining its original page numbers. In addition, all pages have been numbered in regular sequence throughout each volume. Thus, each page carries the volume page number and the original page number, for example, 201-32. In the index, an entry is referred to a volume number, boldface, and a volume page number, for example, 2-201. A convenient list of SI (Système International) physical units and conversion factors is to be found inside the back cover.

The publications listed herein for which a price is indicated are available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 (foreign postage, one-fourth additional). Many documents in the various NBS nonperiodical series are also available from the NBS Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151. Reprints from the NBS Journal of Research or from non-NBS journals may sometimes be obtained directly from an author.

Suggestions as to the selection of papers which should be included in future editions will be welcome. Current developments in measurement technology at NBS are covered in annual seminars held at either the Gaithersburg (Maryland) or the Boulder (Colorado) laboratories. These developments are summarized, along with a running list of publications by NBS authors, in the monthly NBS Technical News Bulletin.

H. L. MASON,
Coordinator for Measurement Services
NBS Institute for Basic Standards.

Editor's Note

With few exceptions, the papers are reprinted in this volume in unabridged form. Since the NBS Provisional Scale of 1955 has not been specifically described elsewhere in print, a paragraph explaining the Scale has been inserted preceding the Technical News Bulletin note on "Corrections for use in low-temperature platinum resistance thermometry".

Because the emphasis here is on measurement techniques, the actual tables have been deleted from the two papers, "Reference tables for the Pt-30 percent Rh versus Pt-6 percent Rh thermocouple", and "Reference tables for 40 percent iridium-60 percent rhodium versus iridium thermocouples". Reprints, complete with the tables, are available from the Heat Division, National Bureau of Standards.

It should be pointed out that in several of these papers "Certificates" are referred to, while under current NBS practice "Reports of Calibration" are issued rather than certificates. Also, in 1964 the NBS adopted the "International System of Units" for use by its staff, except where use of these units would obviously impair communication or would reduce the usefulness of a publication to the primary recipients. In this volume the units used by the authors have been left as originally published. The list of recommended units is given inside the back cover.

J. F. SWINDELLS, *Editor*.

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Expression of the Uncertainties of Calibration

Churchill Eisenhart

Senior Research Fellow, National Bureau of Standards

AND

A Tabular Guide to Commonly Used Terms and Expression

H. H. Ku

Institute for Basic Standards
National Bureau of Standards

Synopsis

Final results and their respective uncertainties should be reported in sentence form whenever possible. The short-hand form " $a \pm b$ " should be avoided in abstracts and summaries; and never used without explicit explanation of its connotation. If no explanation is given, many persons will take $\pm b$, to signify bounds to the inaccuracy of a . Others may assume that b is the "standard error," or the "probable error," of a , and hence the uncertainty of a is at least $\pm 3b$, or $\pm 4b$, respectively. Still others may take b to be an indication merely of the imprecision or dispersion of the individual measurements, that is, to be the "standard deviation," or the "average deviation," or the "probable error" of a SINGLE observation. Each of these interpretations reflects a practice of which instances can be found in current scientific literature.

The terms "standard deviation" and "standard error" should be reserved to denote the canonical values for the measurement process, based on considerable recent experience with the measurement process or processes involved. When there is insufficient recent experience, a value for the standard error (or standard deviation) must often of necessity be computed by recognized statistical procedures from the same measurements as the reported value itself. To avoid possible misunderstanding, in such cases, the term "computed standard error" ("computed standard deviation") should be used.

If the uncertainty in the accepted value of a national standard or of some fundamental constant of nature (e.g., in the volt as maintained at the National Bureau of Standards, or in the acceleration of gravity g on the Potsdam basis) is an important source of systematic error affecting the measurement of some other quantity of primary interest, the "accepted value" actually utilized should be given explicitly, and no allowance for possible systematic error from this source should be included ordinarily, in evaluating over-all bounds to the systematic error of the quantity of primary interest.

In quoting a reported value and its associated uncertainty from the literature, the interpretation of the uncertainty quoted should be stated if given by the author. If the interpretation is not known, a remark to this effect is in order.

No single form of expression for indicating the uncertainty of a reported value is universally satisfactory. Different forms of expression are called for,

depending on the relative magnitudes of the imprecision and likely bias, and their relative importance in relation to the intended use of the reported value, as well as to other possible uses to which it may be put.

Four distinct cases need to be recognized: (1) both systematic error and imprecision negligible in relation to the requirements of the intended and likely uses of the result; (2) systematic error not negligible, but imprecision negligible; (3) neither systematic error nor imprecision negligible; and (4) systematic error negligible, but imprecision not negligible.

Since imprecision and systematic error are distinctly different components of inaccuracy, and are subject to different treatments and interpretations in usage, two numerics, respectively, expressing the imprecision and bounds to the systematic error of the reported result, should be used whenever both of these errors are factors requiring consideration. Specific recommendations with respect to each of the foregoing cases are given.

The annotated guide gives a comprehensive listing of commonly used expressions of imprecision, systematic error, and uncertainty associated with a reported value.

The companion papers of which the preceding is a synopsis, have been submitted to technical journals for publication and are to be reprinted in full in NBS Special Publication 300, Volume 1, Precision Measurement and Calibration—Statistical Concepts and Procedures. (For an earlier version of the first paper, see Chapter 23 of NBS Handbook 91, Experimental Statistics).*

*Available for \$4.25 from the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.

Temperature Scales

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6. The Thermodynamic Temperature Scale, Its Definition and Realization

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REMARKS ON TEMPERATURE

Temperature is one of the primary quantities, along with length, time, and mass, but it is a different kind of concept than these. It is subtle, in some ways, and requires very precise definition. Several papers in this volume treat various aspects of the concept of temperature. Lindsay¹ treats the basic concept of temperature, as obtained in thermodynamics and statistical mechanics. The nature of non-equilibrium thermodynamics becomes important in non-equilibrium systems, and is discussed by Callen.² The approach to equilibrium can be worked out exactly in detail for certain simple systems, and Shuler³ shows how instructive results can be obtained. Certain general considerations about temperature are presented by McNish.⁴

Two basic points must be made concerning the general concept of temperature:

(1) The thermodynamic concept of temperature is an idealization. It is based on considerations of reversible processes, and of equilibrium. But no real measurement is reversible, and no real system is completely in equilibrium. (There is always a heat leak somewhere.) The problem is, therefore, to make the departures from equilibrium slight. If this can be achieved, then statistical mechanics indicates that the results of thermodynamics are correct in the limit of small disturbances.

(2) For systems which are not wholly in thermodynamic equilibrium, but where the departures from it are slight, it is possible to assume the existence of "local thermodynamic equilibrium," i.e., that the material in each small region of space is in thermodynamic equilibrium with itself, and in a steady state with respect to

changes involving neighboring regions of space. It is then possible to ascribe a temperature to this region, and the temperature will be a function of space and time.

These remarks may help to set this paper in a suitable context of general ideas. The aims of this paper are to give a general survey of the thermodynamic temperature scale and to discuss both its definition and its realization. The paper is not addressed to the specialist in temperature scales and is an elementary introduction to the more specialized papers which follow.

The matter of definition and realization of temperature scales is a matter wherein great care in analysis and experimentation is necessary. This review will attempt to deal with the principal ideas and methods and will omit discussions of experimental detail. For greater detail on a variety of matters the reader will be referred to other papers, some of them in these volumes.

Temperature scales can be devised in a variety of ways. In principle, nearly every property of a material which changes with temperature in a well defined way can serve as a thermometric substance, and the changes of this property could be used to define a temperature scale. Thus, for example, the expansion of mercury with temperature makes possible the mercury-in-glass thermometer, and has been the basis of a temperature scale. Let us denote temperature, as measured on such an arbitrary scale, by t . Some properties (and some materials) are better than others for the establishment of a scale. It is easy to see that the coefficient of thermal expansion of water would not provide a good thermometer around 4°C. Its temperature variation of density is such that answers obtained there would be quite confusing. The variety of thermo-

metric systems (material and property) which are of practical use is enormous. But it is obvious that a temperature scale which is easily or fundamentally defined is desirable. In fact two such scales exist. One is relatively easily defined, it is the so-called International Practical Temperature Scale. It is discussed by Stimson.⁵ The other scale is easily given a good theoretical foundation; it is the thermodynamic temperature scale. It is defined using the laws of thermodynamics and some additional arbitrary definitions (which should be held to the theoretical minimum of two definitions). It is a scale which is independent of the material used, or of the specific details of the experiment. In other words, it is a scale which is as near to a *true* scale as it is possible to come.

THE THERMODYNAMIC TEMPERATURE SCALE DEFINED

The basic definition of the Thermodynamic Temperature Scale is closely tied to the second law of thermodynamics. A simple, but rigorous definition can be given with the aid of the Carnot heat engine. While the use of Carnot cycles is perhaps never essential for thermodynamic derivations, it provides a good method for demonstration and explanation. For a discussion of the theory of Carnot cycles, see, for example, Zemansky.⁶

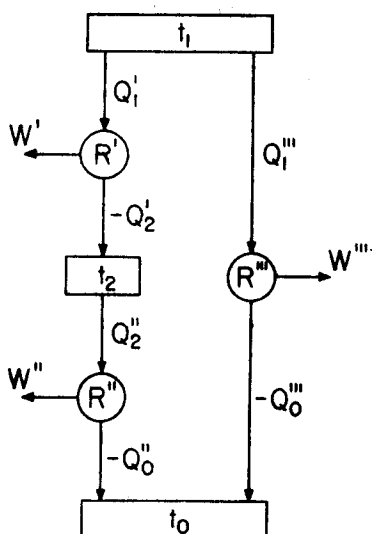


FIG. 1. Heat engines used for the classical definition of the thermodynamic temperature scale.

TABLE 1

Engine:	R'	R''	R'''
Work produced in surroundings:	W'	W''	W'''
Heat withdrawn from reservoir at t_1 :	Q_1'	—	Q_1'''
Heat withdrawn from reservoir at t_2 :	Q_2'	Q_2''	—
Heat withdrawn from reservoir at t_0 :	—	Q_0''	Q_0'''

Consider three Carnot heat engines R' , R'' , and R''' , which are connected to three heat reservoirs, at temperatures t_1 , t_2 , and t_0 . (These temperatures can be measured with any practical thermometer which has a monotonic behavior, i.e., one which does not produce the kind of ambiguity the water-in-glass thermometer does near 4°C .) Further, assume that $t_1 > t_2 > t_0$. Let the engines operate between the reservoirs as indicated in Fig. 1, and let the arrows give the directions of flow of heat. The relations of the various quantities are then given in Table 1. The Carnot engines can be run in a variety of ways. Let them operate in such a direction that Q_2' , Q_0'' , and Q_0''' are all negative. (This means that heat flows into the reservoirs at t_2 and t_0 .) All other heat flows and all work produced will therefore be positive. It is obviously possible to adjust the engines in such a way that

$$Q_1' = Q_1''' \quad (1)$$

and

$$Q_2' = -Q_2'' \quad (2)$$

that is, equal amounts of heat flow into engines R' and R''' from t_1 , and also, just as much heat is taken out of t_2 by R'' as is put into it by R' . Thus the reservoir t_2 does not change its state at all. The second law of thermodynamics requires that

$$W' + W'' = W''' \quad (3)$$

and

$$Q_0'' = Q_0''' \quad (4)$$

This is obvious if we consider R' and R'' as a single engine, operating between the same two reservoirs as R''' , and withdrawing the same amount of heat from t_1 .

The second law of thermodynamics tells us (among other things) that the efficiency of a Carnot heat engine is a function of the tempera-

6. THE THERMODYNAMIC TEMPERATURE SCALE

tures of the two heat reservoirs only. This also holds for the heats withdrawn from the reservoirs. Thus the following holds

$$\frac{Q_1'}{Q_2'} = f(t_1, t_2) \quad (5)$$

with similar equations for Q_2''/Q_0'' and Q_1'''/Q_0''' . We may obtain a relation between $f(t_1, t_2)$, $f(t_2, t_0)$ and $f(t_1, t_0)$ by using Eq. (1), (2) and (4) in Eq. (5). This gives

$$f(t_1, t_2) = -\frac{f(t_1, t_0)}{f(t_2, t_0)} \quad (6)$$

It is clear, however, that this last equation must be independent of t_0 , since $f(t_1, t_2)$ cannot depend on t_0 in any way. Hence we may rewrite Eq. (6) as follows:

$$\frac{Q_1'}{Q_2'} = f(t_1, t_2) = -\frac{g(t_1)}{g(t_2)} \quad (7)$$

Here the right equality expresses the fact that $f(t_1, t_2)$ does not depend on t_0 , and the left equality restates Eq. (5). The great importance of Eq. (7) is this: The heat absorbed from the reservoir at temperature t_1 depends in the same way on temperature t_1 , as the heat absorbed from the reservoir at temperature t_2 depends on t_2 . In other words, the function $g(t)$ is a function which holds for any temperature. (Note that the temperature t was defined in terms of any arbitrary, but well-behaved, thermometer.) The fact that $f(t)$ is a universal function of temperature allows one to use Eq. (7) as a definition of a temperature scale. There are a variety of ways in which this might be done. We will come back to an examination of the alternatives below. The modern definition of the Kelvin Thermodynamic Temperature Scale is obtained by letting $g(t) = T$. Then

$$\frac{T_1}{T_2} = -\frac{Q_1'}{Q_2'} \quad (8)$$

In other words, the ratio of the two temperatures of the heat reservoirs is defined as equal to the ratio of the heats absorbed from the two reservoirs. (The minus sign in Eq. (8) arises, of course, from the way the heats are defined, and from the fact that engine, R' , actually delivers heat to the reservoir at the lower temperature.)

There are a number of thermodynamic consequences of this definition: (a) the state with $T = 0$ cannot be reached in a finite number of

steps, (b) for reversible processes

$$\oint \frac{dQ}{T} = 0 \quad (9)$$

when integrated around a closed path, and (c) the temperature T is independent of the working substance used in the thermometer.

We return now to a more careful examination of the definition of T . Consider a Carnot engine operating between temperatures t and $t - dt$ (as measured by any well-behaved thermometer). The efficiency of the engine, η , is defined as follows:

$$\eta = \frac{Q(t - dt) + Q(t)}{Q(t)} = \frac{Q(t - dt)}{Q(t)} + 1 \quad (10)$$

and the Carnot function μ is defined as

$$\mu dt = \eta \quad (11)$$

Because of Eq. (7), this can be written as

$$\mu dt = -\frac{g(t - dt)}{g(t)} + 1 = \frac{g(t) - g(t - dt)}{g(t)} \quad (12)$$

But

$$\frac{dg(t)}{dt} = \frac{g(t) - g(t - dt)}{dt}$$

by definition of the derivative, and therefore,

$$\mu = \frac{dg(t)}{g(t) dt} = \frac{d \ln g(t)}{dt} \quad (13)$$

There are now a number of options available. Kelvin originally suggested that μ be set equal to 1, or

$$\frac{d \ln g}{d\theta} = 1$$

Therefore,

$$g(\theta) = ae^\theta \quad (14)$$

where θ is then on a thermodynamic scale. His later proposal, which is the basis of the Kelvin thermodynamic scale, was to set

$$\mu = \frac{1}{T} \quad (15)$$

and thus

$$\frac{d \ln g}{dT} = \frac{1}{T}$$

$$g(T) = bT \quad (16)$$

The scale defined by Eq. (16) is the same as that defined by Eq. (8). The point of the present discussion is twofold. One, the arbitrariness of the choice of the function f is exhibited here more clearly. Two, it is obvious from Eq. (16) that only *one* constant needs to be fixed arbitrarily, in order to fix the scale.⁸

The choice of the magnitude of b is arbitrary. In fact it was determined in 1954⁹ by *choosing* the temperature of the triple point of water to be 273.16 K exactly, on the thermodynamic scale of temperatures. It is obvious from the preceding, that this choice determines the scale completely, particularly by considering Eqs. (8) and (16). This point was made originally by Kelvin,¹⁰ later by Mendeleef,¹¹ and in recent times by Giauque.¹²

Prior to 1954, the thermodynamic scale was defined by assigning the temperatures of the ice point of water (equilibrium of air-saturated water with ice) and the steam point of water, the temperatures 0° Celsius (thermodynamic) and 100° Celsius (thermodynamic) respectively. The position of the zero of the scale was then a matter for experimentation. Prior to 1954 there were fairly good *practical* reasons for so defining the scale. Progress in thermometry has outgrown these practical reasons,¹³ and the new, more fundamental definition is clearly preferable on theoretical grounds. It is clear that in the new definition the interval between the ice and the steam point is a matter for experimental determination, and is almost certainly not exactly 100 degrees.

The definition of the thermodynamic temperature scale given in Eq. (8) lends itself particularly well to its realization by means of a gas thermometer. There is nothing unique or fundamental about this, however, and we shall see several examples of thermodynamic definitions and realizations of temperatures which have nothing to do with gas thermometry.

THE EQUALITY OF THE THERMODYNAMIC AND THE IDEAL GAS SCALES OF TEMPERATURES

The temperature scale based on an ideal (or perfect) gas is the same as that based on the considerations leading to Eq. (8), except for the arbitrary choice of the size of the degree, i.e., the choice of the single free constant in Eq. (16). It is this fact which makes gas thermometry so

important. Furthermore, while an ideal gas is an abstract concept (to be discussed below) it can be approximated experimentally as closely as one needs to for the present purpose.

An ideal gas is defined by two properties:

(1) Boyle's law:

$$PV = f(t) \text{ only} \quad (17)$$

where P is the pressure, V the volume, and t the temperature, as measured on any thermometer.

(2) Joule's law: The temperature of an ideal gas which expands into a vacuum, i.e., without doing work, does not change during the expansion.

It is important to note that this is a definition of an *ideal* gas. No real gas satisfies all these requirements exactly under all conditions, but the definitions give a useful model¹⁴ of an ideal gas.

In order to exhibit the identity of the thermodynamic and the ideal gas scale, we must digress briefly to consider thermometry in general. In all thermometry one has two systems to deal with, system A , the system whose temperature is required, and system B , the thermometer. One wishes to assign a numerical value t_A to the temperature of A , by measuring a property π of the system B . For example π may be a thermal emf of B , if B is a thermocouple, or π may be a pressure if B is a gas thermometer. The next step is this: A convention must be established which ascribes numerical values of temperature to two reference states of the thermometer B , say, t_1 , and t_2 . (In practice, these are fixed points on a temperature scale such as the triple point and the steam point of water. Then, when system B is in equilibrium with a system at either of these points, it has the temperatures t_1 , and t_2 respectively.) Next, the property π must be measured for these two temperatures. Let it be π_1 , and π_2 , respectively. When system B is in equilibrium with system A at temperature t_A , then t_A is determined from

$$\frac{(t_A - t_1)}{(\pi_A - \pi_1)} = \frac{(t_2 - t_1)}{(\pi_2 - \pi_1)} \quad (18)$$

which can be written as

$$t_A = t_1 + \frac{(\pi_A - \pi_1)}{(\pi_2 - \pi_1)} (t_2 - t_1) \quad (19)$$

Two different thermometers must agree in the way in which they *order* the temperatures of system A . This means that if thermometer B ascribes the temperatures t_{A1} and t_{A2} to two states