Traceable Temperatures

An Introduction to Temperature Measurement and Calibration

SECOND EDITION

J. V. Nicholas | D. R. White

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Second Edition

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Contents

Preface to First Edition

We expect this book to shake your faith in temperature measurement because, unlike most other books on measurement, it emphasises the things that go wrong. We have done this because we believe that only by knowing what can go wrong can you be confident that your measurement is sound. This book then provides you with the means to develop your measurement expertise and increase your confidence in your temperature measurements.

Traceable Temperatures is an introduction to temperature measurement and calibration. We have put an emphasis on calibration not because we want to train everybody to do calibrations, but because calibration is a simple example of sound measurement design. We have tried to cater particularly for the beginner with modest experience who wishes to acquire expertise or knowledge quickly. It is therefore more of a self-teaching text rather than a handbook, although we have included some reference material. We have, however, written it for a wide readership, ranging from the beginner seeking help to experienced scientists and engineers; in particular readers who find that temperature is only one of their measurement responsibilities. We do not expect the book to be read and digested at one sitting; we hope you will grow into it as you become more proficient.

This book began in 1981 as a set of notes for a series of one-day workshops on temperature measurement, designed primarily to assist those seeking laboratory accreditation. The notes formed the basis for a bulletin, also entitled *Traceable Temperatures*, which was published in 1982 by the New Zealand Department of Scientific and Industrial Research (DSIR). We used the bulletin as the text for ongoing workshops over the next ten years.

Over that period the concept of traceability has gained almost overwhelming importance, with many nations investing heavily in systems to ensure that traceability can be readily achieved. Traceability now clearly links all the people, organisations, documents, techniques, and measurements within a large and diverse measurement community. If we are to communicate and interact easily and constructively with each other and our clients, we must also be systematic and talk the same 'language'. Unfortunately there are still too many areas where this ideal has yet to be achieved.

In preparing this edition of Traceable Temperatures we have completely rewritten the text and restricted some of the scope. This was necessary to present a systematic approach and include our approach to calibration. We have also attempted to capture the trends of recent developments in international standards relating to measurement. The most important trends relate to the harmonisation of treatments of uncertainty in measurement and an emphasis on quality assurance (QA) systems and procedures. The

simple procedures that we outline should simplify the task of those having to prepare detailed procedures of their own. In many cases the information can be used directly.

The approach should also assist in the interpretation and implementation of documentary standards — as much as is practicable.

We have tried to make the book, and each chapter to a lesser extent, as self-contained as possible. For this reason we have not provided extensive references. Those who require more information are reaching beyond the scope of the book or asking difficult questions. If you require more information, the references at the end of each chapter are a good point to start. We have also listed some good general references below, which complement the treatment of thermometry given here. Your National Standards Laboratory is also a good source of advice.

We recommend that you read all of the book to gain a broad view of thermometry practice. If you require a rapid introduction we recommend as a minimum the first half of each of Chapters 2 and 3, all of Chapter 4, and all of the chapter covering the thermometer of your choice. If you are involved in QA systems or have an interest in how the measurement system works you will also find Chapter 1 useful. If some of the terms are new to you, you will note that we have *italicised* terms which have a specific meaning to thermometrists and metrologists when they are first defined or encountered. The corresponding entry is placed in **bold** type in the index.

If there is a single message that we wish to convey it is this:

> For a measurement to be successful, traceability must be addressed at the planning stage.

That is, measurement and calibration are not separable and traceability is not something we can sort out after the measurement.

Preface to Second Edition

Almost before the first edition was published, we were dissatisfied with some parts of the text. In an attempt to assemble a systematic treatment of temperature measurement, we had exposed a number of gaps that we did not know how to fill. While some of this was undoubtedly due to our ignorance, we could not help but feel that some of the gaps in measurement theory and philosophy were the consequence of a lack of well-seasoned pedagogy. What is a measurement? why do we measure? and similar basic questions appeared not to have satisfactory answers. During the last eight years, we have thought and read hard in an effort to fill the gaps. Chapter 1 on measurement and traceability now offers answers to some of these questions and a view of measurement that we have found useful and discerning.

A number of the changes in the text also reflect changes in the measurement community that have taken place since the first edition was prepared. Chapter 2 has been updated to present a description of uncertainty consistent with the ISO *Guide to the expression of uncertainty in measurement*. Chapter 5 on calibration reflects the more recently published ISO 17025 *General requirements for the competence of testing and calibration laboratories*. The remaining chapters all have smaller changes, many in response to welcomed feedback from readers of the first edition or to technical advances that have occurred in the last eight years.

John Nicholas, respected colleague, mentor, and always the master of the well-timed disappearance, passed away very shortly after we agreed to prepare this second edition. However, much of the text embodies John's perspective of measurement and ideas that we developed together. I am also indebted to my colleague Peter Saunders for significant contributions to the text, the figures, and critical reading of the manuscript. Other helpers include Hamish Edgar who prepared many of the line drawings, and Mark Clarkson and Emile Bax who kindly reviewed the new chapters.

Rod White
February 2001

General Reading for First Edition

Temperature (2nd edition), T. J. Quinn, Academic Press, London (1990).

Thermometry, J. F. Schooley, Chemical Rubber Press, Boca Raton, Florida (1986).

Temperature Measurement, L. Michalski, K. Eckersdorf and J. McGhee. Wiley, Chichester (1991).

Principles and Methods of Temperature Measurement, T. D. McGee. Wiley, New York (1988).

Industrial Temperature Measurement, T. W. Kerlin and R. L. Shepard. Instrument Society of America (1982).

The first two books concentrate on the science behind temperature measurement and are recommended reading for researchers and those establishing the ITS-90 scale directly. The third and fourth provide a very broad outline of the theory and operation of almost all types of thermometers and are suited for readers requiring more general information. The last book is one of the few texts that treats thermocouples correctly. It has a strong industrial flavour with information on response times of thermometers.

Proceedings of Symposia on Temperature

Six symposia have been held under the general title of *Temperature Measurement and Control in Science and Industry*. The proceedings of the first held in 1919 were not published; those of the second were published in 1941 and are now known as *Temperature, its Measurement and Control in Science and Industry, Volume 1, 1941* (Reinhold Publishing Co.).

The third symposium was held in 1954 and its proceedings were published as *Temperature, its Measurement and Control in Science and Industry, Volume 2, 1955*, published by Reinhold (New York) and Chapman and Hall (London), edited by H. C. Wolfe.

The fourth symposium was held in 1961 and its proceedings were published as *Temperature, its Measurement and Control in Science and Industry, Volume 3, Parts 1, 2 and 3, 1962*, published by Reinhold (New York) and Chapman and Hall (London), edited by C. M. Herzfeld.

The fifth symposium was held in 1972 and its proceedings were published as: *Temperature, its Measurement and Control in Science and Industry, Volume 4, Parts 1, 2 and 3, 1972*, published by the Instrument Society of America, edited by H. H. Plumb.

The sixth symposium was held in 1982 and its proceedings were published as *Temperature, its Measurement and Control in Science and Industry, Volume 5, Parts 1 and 2, 1982*, published by the American Institute of Physics, edited by J. F. Schooley.

The seventh symposium was held in 1992 and its proceedings published as *Temperature, its Measurement and Control in Science and Industry, Volume 6, Parts 1 and 2, 1992*, published by the American Institute of Physics, edited by J. F. Schooley.

Most of the symposia have been sponsored by the American Institute of Physics, the Instrument Society of America, and the National Institute of Standards and Technology. They have brought together many scientists and engineers involved in all aspects of temperature. The resulting volumes form a most important reference for thermometry as they cover all its aspects from theory to everyday industrial practice.

Acknowledgements for First Edition

Acknowledgements for Figures and Tables

With the exception of some of the photographs, all of the figures have been prepared by the authors (and helpers). However, we acknowledge with thanks the following people and organisations for providing photographs or information on which some of the figures and tables are based.

Figure 2.16
Data provided by Dr K. D. Hill, NRC, Canada.
Figures 3.6, 3.9, 8.15
Photographs and drawings supplied by Isothermal Technology Ltd, United Kingdom.
Figures 3.10, 3.11, 3.12, 6.19
From the BIPM booklets: *Techniques for approximating the international temperature scale and Supplementary information for the international temperature scale of 1990.*
Figure 3.14
Based on drawing by Dr T. P. Jones, CSIRO Division of Applied Physics, Australia.
Figure 4.1, and Tables 4.1 and 4.2
F. P. Incropera and D. P. DeWitt, *Fundamentals of Heat and Mass Transfer*, 4th Edn. John Wiley & Sons, New York (1996). Copyright © 1996 John Wiley & Sons Inc. Reprinted by permission.
Figure 4.5
NBS monograph 126, *Platinum resistance thermometry*, US Department of Commerce, 1973.
Figure 6.2(a)
Based on drawing from information bulletin: Minco Products Ltd, United States.
Figure 6.2(b)
Based on drawing from information bulletin: Sensing Devices Ltd, United Kingdom.
Figure 6.14
D. J. Curtis, *Temperature, Its Measurement and Control in Science and Industry*, Vol. 5, pp. 803–12 (1982).

1

Measurement and Traceability

1.1 Introduction

Let's start with a thought experiment.

You've just bought this book, but you're concerned about the growing piles of unread books lying around the house. Impulsively you decide that it's time to build a bookshelf, and telephone the local timber merchants and ask them to deliver some suitable timber.

'How much?', they say.

'Eight metres ought to be enough', you reply.

'What's a metre?'

After some discussion and free exchange of ideas, you find that you and the timber merchants do not use the same measures of length. How can you communicate your needs?

Over the millennia, we have tended to use assorted body parts (feet, nails, inches, cubits, hands, palms, yards, etc.) to communicate measures of length. This might work well enough with the timber merchants but there are occasions when something more rigid and precise is required. The time also comes when we must interact with people other than the timber merchants, and eventually with the rest of the world. Then the only practical solution is for us all to share a single standard for each measure.

The concept of traceability has evolved to describe measurements that can be related to a common standard. To make traceability practical on a worldwide scale a huge number of people have to be involved defining the units, disseminating the units through calibration laboratories, manufacturing instruments, setting specifications for the manufacturers, and, finally, using the instruments and measurement results. Consequently, complex and extensive systems have evolved to provide for physical measurement standards, assessments of technical competence and the development of measurement protocols. For those of you whose business is measurement, achieving traceability and working with the measurement community will have a greater impact on your business than any technological advance in measurement technique.

This chapter is primarily background material answering some of the 'what' and 'why' questions of measurement, and describing how to interact with the rest of the measurement community. We begin by delving into measurement theory: what is a measurement, and why do we measure? This is followed by a short history of the evolution of temperature as a physical concept and the primary methods for measuring temperature. The last sections provide an overview of the systems that have evolved nationally and internationally to make traceability practical: the international system

of units, accreditation systems and documentary standards systems. We describe what they do and why they are there.

1.2 Measurement

1.2.1   What is a measurement?

Measurement is one of the most fundamental tasks carried out by humans, or any other species. All knowledge of the world is gained through the senses, and our ability to survive comes from our reactions to that knowledge. Our curiosity, intelligence and self-awareness are adaptations that allow us to prepare for the unexperienced, and our sensors and measuring instruments extend our knowledge of the universe beyond that acquirable from our senses alone.

For those of us working inside corporate organisations survival and risk have slightly different meanings from the biological sense, but whether we or our organisations make measurements for commerce, control or curiosity the ultimate motivation is the same: improving survival and minimising risk.

One way of identifying the reason for making a measurement is to determine how it affects our actions. For commercial measurements, the answer is simple because measurements are the basis of contracts. A buyer agrees to pay for a certain quantity of goods and his or her decision on whether to buy or not depends on the quantity and price. In commerce, measurements affect decisions about sale and purchase.

Measurements are often associated with control or regulatory mechanisms. In air-conditioning systems, temperature measurements determine whether heat flows are increased or decreased. Measurements of rust in cars control their roadworthiness, and measurements of toxicity control the quality of the environment. In each case the measurements precede decisions to increase or decrease, reject or accept, or to prosecute or not prosecute.

With curiosity-driven measurements the decisions are less obvious. In science, experiments are used as the basis for developing and testing theory or models of phenomena, and at each stage of the development a scientist makes a decision: does this work, does that work, what if we do this, etc.? Eighty years after Einstein published his general theory of relativity researchers are still making measurements to test the validity of the theory. Again measurements are made to aid in the making of decisions.

The accepted metrological definition of a measurement is in two parts:

> **Measurement:**
> The set of operations having the object of determining a value of a quantity.

> **Result of a measurement:**
> The value attributed to a measurand obtained by measurement.

While these two definitions are technically correct, they are so because of a tautology. The dictionary definition of a quantity is something that has a value, and a measurand is the thing being measured. Consequently, these are self-evident statements rather than definitions. More importantly, they are not especially helpful in distinguishing

a measurement from a meaningless assignment of numbers. We offer an alternative definition that applies to both the process and the result:

> **Measurement (alternative definition):**
> The symbolic representation of a state, event or attribute to aid in the making of a decision.

This definition highlights three important aspects of measurement not apparent from the first two definitions:

(1) The results of measurement need not be numeric: grade A, red and sodium are all legitimate measurement results in the appropriate context. One of the most valuable aspects of symbolic representation is that we use the symbols in our models to make predictions. Mathematical models and numeric symbols particularly help to quantify predictions that might otherwise be qualitative or subjective.

(2) Every measurement has a purpose. This is the distinction we seek between a meaningful measurement and meaningless assignment of numbers. In a great many measurements, especially outside the calibration laboratory, the purpose influences the design and outcome of the measurement. Consequently, measurement results may have meaning only within the context of that purpose. Results used for other purposes or gathered without purpose are potentially dangerous.

(3) Decisions are associated with risks and rewards. This highlights the need to know the uncertainty in a measurement in order to assess the risk or optimise the measurement.

These three points are the main themes of Sections 1.2.2 to 1.2.4.

Exercise 1.1

Consider some of the measurements you make. What decisions do they influence? What are some of the risks and rewards associated with those decisions?

1.2.2 Measurement scales

In this section, we look at some of the basic systems for the symbolic representation of measurement results: our measurement scales. Table 1.1 provides a coarse summary of the various types of measurement scale that we use. The classification given in the table is based on the algebraic properties underlying the measurement scales. While there are other systems of classification we have chosen this one in order to highlight the fundamental limitations associated with the different systems of representation.

Nominal scales

Measurements on nominal scales are essentially a naming, and often the results do not look like measurements at all. An example familiar to most is the number on a football player's shirt. In many sports, the number on a player's shirt indicates the position the

Table 1.1   A classification of measurement scales based on possible mathematical operations

Scale type	Description	Operations	Examples
Nominal	A renaming; can establish equivalence	$=$	Colours (red, blue) Team numbers (e.g. football) Stellar spectral types (O,B,A,F,G,...)
Ordinal	Can establish order	$= < >$	Moh hardness Rockwell hardness Beaufort wind scale Fahrenheit and Celsius scales
Interval	Can establish meaningful differences	$= < > + -$	Date, Time of day Year Latitude and longitude Centigrade temperature scale
Metric or ratio	Can establish meaningful ratios	$= < > + - \times \div$	All SI scales, e.g. Length Mass Frequency Thermodynamic temperature
Counting or natural	Counts of objects or events, an integer metric scale	$= < > + - \times \div$	Apples, Buses Birthdays

sports person plays on the field. In Rugby Union, for example, the numbers 11 and 14 refer to the left and right wings. But the numbers carry no numeric meaning: it is meaningless to say that a number 14 player is any better than a number 11, or that the number 14 is twice as good as the number 7. However, it is possible to establish equivalence: a number 14 in one team plays in the same position and requires the same skills as the number 14 in another team. In this case, the measurement is performed when a coach determines the player's position.

Other examples of nominal scales include colours, the names of plants, and the classification of chemicals such as alcohols and acids. Indeed most of our language is based on nominal assignments. All of our verbs, nouns and adjectives are verbal and written symbols for actions, objects and attributes. One of the key aspects of nominal scales is that each classification or naming must have its own standard or definition. Thus, for example, each of us has to learn what red and blue or apples and pears are before we can make use of the symbols.

Ordinal scales

As its name implies, results on ordinal scales convey some sense of order. As with nominal scales, ordinal results need not be numerical. Perhaps one of the most famous ordinal scales, amongst English-speaking parents and children at least, is the one used by Goldilocks at the house of the three bears: too little, just right, and too much. This is the very same scale underlying many commercial transactions. A more typical example is the Moh hardness scale (Table 1.2), a scale once used by mineralogists to help identify minerals on the basis of hardness. The scale is constructed so that each mineral listed is harder than those below it. In this way the mineralogist can determine

Table 1.2 Moh's scale of hardness

Hardness	Mineral standard
10	Diamond
9	Sapphire
8	Topaz
7	Quartz
6	Feldspar
5	Apatite
4	Flourspar
3	Calcite
2	Gypsum
1	Talc

the hardness of an unknown mineral by determining which minerals scratch it. Strictly speaking, the scale measures resistance to scratching rather than hardness.

Other examples include the Beaufort wind strength scale, the Mercalli earthquake intensity scale, examination grades, credit ratings, library codes, and most of the early temperature scales. As can be seen from the examples, ordinal scales are characterised by several standards or definitions, one for each of the defined points on the scale.

In many cases ordinal scales also have a specified interpolating instrument that makes it possible to assign values in between the defined points. A very large number of chemical measurement scales are constructed this way, for example using standard solutions and a spectrometer to interpolate between the standards. The International Temperature Scale of 1990 (ITS-90) is also an ordinal scale, where the defined points are the various melting, freezing and triple points of pure substances, and the interpolating instruments include platinum resistance thermometers, vapour-pressure thermometers and radiation thermometers. With many ordinal measurements, the response of the interpolating instrument is known to be non-linear but it is still possible to tell when one sample has a greater concentration of a particular compound than another, or higher temperature than another.

Interval scales

Interval scales are those that are known to be linear in some fundamental sense, and are the simplest scale type to allow meaningful comparison of differences. Interval scales typically have an arbitrary zero. Familiar examples include the latitude and longitude scales, which are used to determine position on the surface of the earth. The longitude scale requires two standards to define it: the position of the zero, which is arbitrarily chosen to be Greenwich, and the number of degrees in a full revolution of the earth, which is arbitrarily chosen to be 360. It is possible to compare changes in longitude meaningfully, or to add and subtract intervals of longitude, but it is still not meaningful to talk about ratios. Statements such as 'a country at 40 degrees of longitude is twice the country at 20 degrees of longitude' are nonsense.

Other examples of interval scales include all of the time scales that we use to tell the time of day, date and year, and the 4 mA to 20 mA current loop representation used by many industrial instruments (a symbol need not be a squiggle on paper). One of the earliest thermodynamic temperature scales, the centigrade scale, was an interval scale based on the definition of the melting and boiling points of water at 0 °C and 100 °C

respectively. Because interval scales are the first that enable us to talk meaningfully about intervals, these are the first scales that allow us to do normal statistics, that is to calculate means and standard deviations. On more primitive scales, we have to adopt different statistical techniques that do not require the concept of meaningful intervals.

Metric scales

Metric scales are those that have a natural zero. On such scales, we can usefully talk about ratios and fractions. Metric scales include all of the familiar SI scales of length, mass, thermodynamic temperature, etc. On the mass scale, for example, we know exactly what zero mass means, we can add and subtract mass, and we can talk meaningfully about dividing a mass into fractions or doubling and tripling a mass. The key attribute of metric scales that distinguishes them from other scales is that only one standard is required to define each completely. The mass scale is defined in terms of the prototype kilogram stored in a safe in a basement of the Bureau International des Poids et Mesures (BIPM) in Paris. All other measurements reported on the mass scale are expressed as ratios with respect to the kilogram. The standard used to define the scale is known as the metric or the unit of the scale. Metric scales are also known as ratio scales, and the literal translation of the word metrology, from the Greek *metrologia*, is the study of ratios.

Perhaps the most important of our metric scales is also one of the earliest: the natural or counting scale. Early in our cultural development we learned to count apples, oranges, etc. However, it was apparently not until the time of the Greek mathematicians that it was recognised that numbers had properties independent of the objects. That is, the problem of '2 apples plus 3 apples' is fundamentally the same as '2 oranges plus 3 oranges', and can be generalised without reference to any object. However, we must remember that the measurement scales for counting oranges and apples are different because they have different metrics, one orange and one apple respectively, and one cannot take one apple from two oranges and obtain a meaningful result.

The log-ratio scales form a special class of interval scales that are actually based on metric quantities. Because of the very large range of values encountered, it is often convenient to transform metric measurements to a logarithmic scale. These scales are typically constructed as

$$\text{value on log scale} = \text{constant} \times \log (\text{value/reference value}).$$

There are two definitions required to define a log-ratio scale: the multiplying constant and the reference value. Examples of such scales include the various decibel scales, the visual magnitude of stars, and the Richter scale for the energy dissipated in earthquakes. On these scales equal intervals correspond to constant multiplying factors of the underlying metric quantity. An interval of 10 dB corresponds to a 10 times increase in power, five steps of visual magnitude correspond to 100 times decrease in the brightness of stars, and two steps on the Richter scale correspond to a 1000 times increase in the energy dissipated in an earthquake.

The progression of scales given above suggests that as the nature of quantities and measurements becomes well understood, the associated scales evolve towards metric scales. Science begins with classification — stamp collecting as Lord Rutherford called it. This evolutionary trend is common, but it is not universal. Some scales can never be

metric: colour will always be a three-dimensional scale based on two interval quantities and one metric quantity, and the Rockwell hardness scales will always be ordinal scales. Also, not all nominal scales are primitive. The models and mathematics underlying the current descriptions of fundamental particles, with demonstrably nominal attributes like beauty, charm, top and bottom, are amongst the most sophisticated that we have developed. Similarly the models and mathematics underlying chemical reactions, which are described by symbols like NaCl and H_2O, are also sophisticated.

The influence of scale type on traceability

In order to communicate results unambiguously it is necessary for each of us to share the same scale for a quantity and to have access to the standards that define the scale. For metric scales the traceability problem is relatively simple: all measurements have to be related to a single standard. For the other scale types, the traceability problem can be more complicated because more standards are required.

Many interval scales can be expressed in terms of metric quantities, so the traceability problem is not too difficult. The log-ratio scale, for example, requires a definition of the multiplying constant, which can be defined without error, and a reference value, which in most cases takes the place of the unit on metric scales. All of the time scales (time of day, year, etc.) rely on measurements of time interval (a metric quantity) and an arbitrarily defined zero. Angle scales, such as latitude and longitude, also rely on angle interval and an arbitrary zero.

Ordinal scales are the most problematic in respect of traceability. They require a minimum of two standards, and in many cases require an approved or specified interpolating instrument. To realise the Moh hardness scale the mineralogist has to carry samples of the 10 minerals that define the scale. A large number of measurements based on calibrated scales are in fact carried out on ordinal scales, and in particular many chemical measurements fall into this category.

Nominal scales typically have the greatest number of standards associated with them, usually one for each possible category on the scale. The standards may be descriptive or based on artefacts such as standard reference materials. At one time, for example, there was a descriptive definition for each of the elements in the periodic table, based on the distinguishing chemical and physical properties. Nowadays the definitions of the elements are based on the number of protons in the nucleus of an atom, which is derived from the natural scale.

The influence of scale type on treatment of uncertainty

According to the ISO *Guide for the expression of uncertainty in measurement* (ISO Guide), an uncertainty is the range of values that may reasonably be attributed to a measurand. Just how one goes about characterising a range depends on the scale type. The fewer mathematical operations that are permitted on a scale the fewer options there are available for statistical analysis. Table 1.3 summarises the various statistical operations available on the different measurement scales.

To clarify the meaning of uncertainty on nominal scales we have to remember that results are used to make decisions, and when we characterise uncertainties we are in fact concerned about the likelihood of making wrong decisions. The problem

Table 1.3 The options available for characterising the dispersion of results (uncertainties) depend on the mathematical options available. Each scale has available the measures of average and dispersion as indicated and those of the scales above it

Scale type	Allowable operations	Statistical Average	Statistical measure of dispersion
Nominal	$=$	Mode	Non-parametric
Ordinal	$= < >$	Median	Percentiles
Interval	$= < > + -$	Arithmetic mean	Standard deviation
Metric	$= < > + - \times \div$	Geometric or harmonic mean	Per cent deviation

with nominal scales is that there are many ways of being wrong. Chemical tests for lead, for example, may confuse lead with other heavy metals: mercury, tin, cadmium, antimony and other neighbours of lead in the periodic table. The consequences of failing to identify each of the other metals correctly may all be different, depending of course on the purpose of the measurements. With measurements on nominal scales it is usually necessary to consider every possible outcome of the measurements, so risk and uncertainty analyses can become complex.

With ordinal scales, the problem becomes much simpler because measurements can be wrong in only one of two ways, too big or too small (this is the Goldilocks scale), and sometimes only in one way (pass–fail). Risk is then evaluated strictly in terms of the distribution of probabilities for particular outcomes, which can usually be characterised simply in terms of percentiles.

With metric and interval scales, the distributions of possible results can often be expressed in terms of a model based on metric parameters. Thus all of the classical distributions, such as the normal, geometric, chi-square, Poisson, binomial, etc., can be used to characterise uncertainty. In this way, the description of the distributions can be rendered in terms of one or two numbers. This greatly simplifies risk and uncertainty analysis.

With metric scales, an additional possibility is available, namely geometric or harmonic analysis, which is based on distributions measured in terms of ratio rather than interval. An analysis of quantities measured on log-ratio scales using interval statistics is effectively a ratio analysis of the underlying metric quantity. Note that the ISO Guide strictly applies only to interval and metric scales, since the concepts of an arithmetic mean and standard deviation depend on meaningful measures of difference. However, many ordinal scales approximate metric scales or are sufficiently linear over small ranges to be treated as interval scales for the purposes of statistical analysis. Chapter 2 gives a detailed treatment of uncertainty in measurement as it is applied to metric and interval scales.

Exercise 1.2

Consider the following examples where numbers are assigned to objects or states. In what context could they be interpreted as measurements? Consider the numbers on a roulette wheel, street numbers, the 'seed' used to start a random number generator, a car numberplate, and a musical note indicated on a musical manuscript. To what type of measurement scale to they belong?

1.2.3   The problem of definition and the importance of purpose

Consider the statement

$$\text{water temperature} = 20\,^{\circ}\text{C} \pm 1\,^{\circ}\text{C}.$$

The description 'water temperature' is a shorthand statement for something like 'the temperature of the chilled water on the outlet side of heat exchanger no. 2 on the Upside Downs site of the Moojoose Dairy Company'. The problem of clearly defining the measurand is called the *problem of definition*, and has two parts, one simple and one rather subtle and complex.

The first and simplest part of the problem of definition relates to the identification of the quantity measured. In principle, as given in the example above, all that is required is to provide sufficient information to allow the measurement to be repeated. Influences may also have to be specified, for example the operating conditions of the plant and the time of day that the measurement was made.

The second and most difficult part of the problem of definition relates to the technical definition of the attribute that is being measured. In this case, what do we mean by temperature? As we shall see in Chapter 4, the temperature of a system is strictly defined only in conditions of *thermal equilibrium*, that is no net flow of heat between any of the components of the system. The catch in the tail of this definition is that normally we are only interested in temperature because we want to understand something about the flow of heat from the system.

In the calibration laboratory our calibration baths and furnaces are designed to have a controlled volume that is in thermal equilibrium. A measure of the temperature has only one possible meaning and there can be no confusion. In contrast, in some industrial situations the system is so far from thermal equilibrium that different thermometers read different temperatures. A fluorescent tube is a good example. The electron temperature may be $30\,000\,^{\circ}\text{C}$, and the colour temperature of the radiation from the tube is about $5600\,^{\circ}\text{C}$. Yet the tube is cool enough to touch. In cases where there is no thermal equilibrium the concept of temperature is at the very least ambiguous, at worst meaningless. Yet any thermometer immersed into a non-equilibrium system will indicate a temperature. In order to make a meaningful measurement we have to understand the purpose of the measurement.

Heat is transported by conduction, convection and radiation. The thermal interaction of any system with a second system depends on the relative contributions of the different modes of heat flow. (This topic is covered in detail in Chapter 4.) If we are interested in a temperature that describes the thermal conditions experienced by the second system then the only meaningful way to define a temperature is to use a thermometer that duplicates the thermal conditions obtained when the second system is placed in thermal contact with the first. The definition of temperature is then determined as much by the thermometer as the system of interest. That is, the meaning of temperature is determined by the purpose of the measurements. With the fluorescent tube, the design of the thermometer and the results of the measurement depend on whether we are interested in the current density at the electrodes, the colour rendering properties of the lamp, or whether there is a burn risk to human fingers.

In the most precise temperature measurements, the insertion of a thermometer usually causes a measurable disturbance. Examples include the heat dissipated by resistance thermometers, the loss of radiation through apertures in blackbody cavities, and heat losses along the stems of all insertion thermometers. In most of these cases the system remains very close to equilibrium and the physics of the measurement process is well enough known to allow us to model the effects and apply corrections, or to enable the measurement to be designed so the effects are negligible. This topic is covered in detail in Chapter 4.

Even in large industrial plants modelling can be an effective solution to the problem. For example, sections of the wall of a large chemical reactor could be considered to have zero net heat flow; for example, a 100 kW flux into the reactor wall is balanced by a 100 kW flux out of the wall. So long as the thermometer is smaller than the volume over which the temperature can be said to be constant we can measure a meaningful temperature.

Where measurements take on high monetary value or are associated with high risks, it is important that the technique employed be acceptable to all parties. This is the rationale for many documentary standards, not just in temperature measurement but measurement in general. A particular example might be a safety standard where the temperature of a surface is measured using a thermocouple mounted in a 'standard finger', which duplicates the thermal properties of the human finger. In this way, the 'temperature measurement' has little utility as a measure of temperature but significant utility as an assessment of burn risk.

Measurements with definition problems are often the source of great argument. Unfortunately most scientists are passively taught to ignore the possibility of definition problems. Physicists in particular are taught that the aim of their science is to eliminate human subjectivity from their models of the universe. This is an admirable aim but there follow the inevitable problems of making conceptual definitions and models useful. To a theoretical physicist a length is the distance between two points. To a metrologist the most accurate measure of the length of a gauge block is the mean distance at 20 °C between the two end-planes, which are ideally parallel, with one plane defined optically and the other defined by a monolayer of oil and mechanical interference with a flat surface of the same mechanical finish. The first definition is conceptual, the second is practical and driven by a purpose: the need to disseminate practical standards of length at the least uncertainty. Thus for all of our measurements the quantities we measure are to a degree approximations to some conceptual ideal, with the non-ideal aspects of the measurement managed or controlled according to a purpose. Usually the further we get from the calibration laboratory the less control we have over the non-idealities or influence variables, and the more difficult our definition problems become.

The telltale sign of a definition problem is a measurement where the result seems to vary with the measurement technique. Such measurements tend to be subjective and a source of argument until the purpose has been properly identified. In thermometry, surfaces, gases and flames are particular problems.

Note that measurements made for one purpose may not be useful for another purpose. While documentary standards can be useful guides for factors affecting a particular measurement, blindly applying standards to measurements for which they

were not designed can lead to misleading or valueless results. Similarly, taking measurements of some handy attribute 'just in case' can also be risky if the measurement is later found to be ill suited to the required purpose.

Exercise 1.3

Think about alternative definitions of length and how they might depend on purpose. For example, the length of a pendulum, the length of an athlete's jump in the long jump pit, the distance between Paris and Beijing by air or road. How do they compare to the theoretical physicist's definition?

1.2.4 Decision, risk and uncertainty

All measurements eventually contribute to a decision, and associated with each decision are risk and reward. In this section we take a very brief look at the evaluation of risk, as this can affect the design and interpretation of measurements. The simplest cases occur when a single measurement leads to a pass or fail decision. In complex cases, multiple measurements contribute to a figure of merit that is the basis of decisions. In every case, the quality of the decision is affected by the uncertainty in the measurement. Figure 1.1 shows one example and Table 1.4 shows the possible outcomes of decisions based on the measurement.

Once the consequences of a decision have been identified, the decision process and measurement can be modified to maximise the rewards and minimise the risks. In order to avoid the high costs associated with the 'incorrect-pass' risks (Table 1.4) the usual strategy is to increase the pass–fail criterion, as in Figure 1.1. For this reason, industries supplying goods on the basis of net weight usually overfill their containers.

The required increase in the pass–fail criterion is determined by the uncertainty in the measurements. Thus by reducing the uncertainty one can also reduce risk or increase
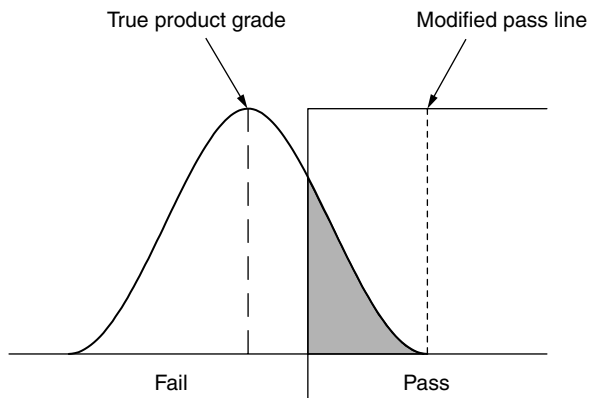
Figure 1.1   A simple decision made on the basis of a single measurement. If the true value is as indicated then, because of the uncertainty in the measurement, the result of the measurement may be anywhere under the curve. The shaded area indicates the probability of making a wrong decision

Table 1.4   The possible outcomes of decisions based on uncertain measurements

	Pass	**Fail**
Correct	Correct identification of satisfactory product or plant operation. This is where the company makes most of its profit	Correct identification of poor-quality product or sub-optimal operation. This eliminates risk of prosecution, plant failure or customer dissatisfaction
Incorrect	These decisions carry a high external risk or cost, possible plant failure, prosecution for substandard goods, or consumer dissatisfaction	These decisions carry an internal cost, often associated with unused plant capacity, wasted product, unnecessary reprocessing, or low prices for second-grade product

the rewards. In some cases the benefits of improved measurements can vastly outweigh the costs. Examples of this are found in the petroleum industry where measurements are made to 0.01 °C to enable thousands of tonnes of aviation fuel to be classified at the highest grade. This phenomenon is common where pass–fail criteria are defined or regulated, and large quantities of product are involved.

Commonly the most costly wrong decisions are associated with catastrophe: plant failure or huge costs from which there is no recovery. In these cases, the optimisation is straightforward: keep well away from the catastrophe. It is also common for industries to forget the internal costs associated with 'incorrect–fail', a reason for the emphasis on this quarter in quality management systems. From the measurement perspective the key factor that makes any optimisation possible is knowledge of the uncertainty in the measurement. In Chapter 2 we give a guide to expression of uncertainty in measurement. Readers interested in the optimisation of decision making should consult books on game theory, and may find risk analysis software available for spreadsheets useful.

Exercise 1.4

Do a risk benefit analysis on a temperature measurement system used for the temperature control of a baking oven. The decision table for this example is more complex than Table 1.4 since the measurement has three outcomes too high, just right and too low instead of the two-outcome pass–fail example of Table 1.4.

1.3 Temperature

In this section, we describe the evolution of temperature measurement from the perspectives of a classical historian, a physicist and a meteorologist. The main purpose is to provide a historical background for subsequent chapters and to illustrate the principles outlined in previous sections. The history of temperature measurement is a good example of the evolution of the measurement of a poorly understood ordinal quantity to a metric quantity founded on sound physical principles. The differences between the physicist's and the meteorologist's approaches also highlight differences between

scientific and applied measurements, and in particular the importance of purpose and accepted measurement protocol in the design of applied measurements.

1.3.1   The evolution of the temperature scale

The very first record of a temperature scale belongs to the Greek Galen (AD 130–200) who identified eight degrees of *temperamentum*, which he used to characterise the temperament of his patients and the effects of his medicines. He also defined a neutral temperature based on equal mixtures of boiling water and ice. However, he did not have a thermometer so the temperature was presumably assessed with the physician's hand. A more sophisticated version of Galen's scale of temperament surfaced again to help physicians in the sixteenth century.

In the late sixteenth century the first thermoscopes appeared (see Figure 1.2). These consisted of a glass bulb attached to a thin tube immersed in water. It is not certain who the inventor was, perhaps Galileo, but it seems likely that he was inspired by the pneumatic experiments of the Greeks Philo and Hero that were carried out in the first and second centuries BC. Thermoscopes were used for 50 years or so for both medical and meteorological experiments.

Figure 1.2   An early air thermometer or thermoscope. The thermoscope consists of a glass bulb with a long capillary attached immersed in water or oil. With an increase in the temperature, the air in the bulb expands lowering the fluid level. The scale was marked using two fixed points as indicated by the pieces of string, and interpolated using a pair of dividers to measure intermediate steps or degrees

Ferdinand II of Tuscany made the first sealed thermometer using wine spirit in 1641. This was the first device that we would recognise as a thermometer and was a major advance: a liquid sensor sealed against atmospheric pressure variations and evaporation, and degrees of temperature permanently marked on the stem. Subsequent developments of thermometers focused on improved methods of manufacture, especially on the choice of thermometric fluid and glass, and the method of fixing the scale.

By the early eighteenth century most liquid-in-glass thermometers were stable and had a reproducible scale. Typically the scales were marked using the temperatures of fixed points, such as melting snow, body temperature and boiling water (see Figure 1.3). The scale was then divided into a convenient number of steps or degrees. These scales are clearly ordinal scales with fixed points, and with the temperatures in between determined by interpolation using the expansion of the thermometric fluid, usually mercury. The familiar scales of Fahrenheit and Celsius are good examples of these types of scales. Elegant experiments involving the mixing of known volumes of hot and cold mercury, or hot and cold wine spirit, enabled experimenters to establish that mercury is a more linear thermometric fluid than spirit, but that both are non-linear to some extent.

In the late eighteenth century Gay-Lussac and Charles, building on the ingenious work of Amontons 100 years earlier, were both able to demonstrate that the thermal expansion coefficients of different gases were almost identical. Although Amontons had suggested that the linear expansion of gases with temperature implied that only one fixed point was required to calibrate a thermometer (i.e. to establish a metric scale), and a number of experiments determined values for absolute zero ($-273.15\,°C$), the suggestion was not adopted. Chappuis, working at the BIPM, refined gas thermometry further. He had been charged with the responsibility of calibrating a set of mercury-in-glass thermometers by gas thermometry. During a series of remarkable studies comparing temperatures determined using different gases he showed that the gas thermometer did in fact have a small gas species dependence, and that a scale based on hydrogen, although not ideal, was probably accurate to better than $0.01\,°C$. In 1889 the Conférence Générale des Poids et Mesures (CGPM), at its first meeting, adopted the first official temperature scale, the 'normal hydrogen' scale. Because of the known dependence of the scale on the non-ideal properties of hydrogen the initial filling pressure of the thermometer was also specified. This scale was still not a metric scale; instead the scale was defined by fixing the interval between the ice point and steam point to be $100\,°C$. The scale was an ordinal approximation to an interval scale based on two fixed points and an almost linear interpolating instrument.

The first proposals to use the variation of electrical resistance to measure temperature came from Davy in 1821 and later Siemens in 1861. However, it took the elaborate experiments and refinements in the construction of platinum resistance thermometers by Callendar to get the resistance thermometer accepted. By comparing the platinum resistance thermometer with the gas thermometer, Callendar and others were able to show that platinum has a parabolic or quadratic characteristic. In 1899 Callendar proposed a temperature scale that would be more practical than the 'normal hydrogen' scale, based on three fixed points: the ice point, the steam point and the melting point of sulphur. The scale was defined by fixing the interval between the ice point and steam point to be $100\,°C$, with the sulphur point defined to be $444.5\,°C$ as determined by a gas thermometer calibrated at the other two points. Callendar's proposal, again an ordinal
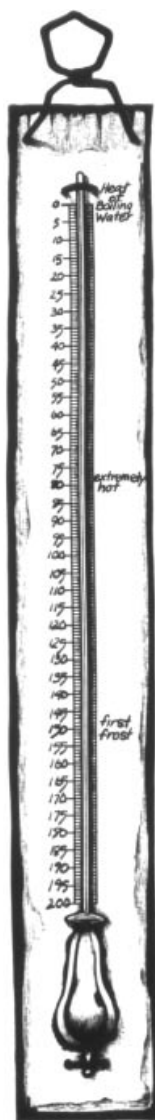
Figure 1.3   A thermometer from the mid-eighteenth century. It has a large bulb because of the large capillary. Note too the inverted scale, which was common in cooler countries where there was more interest in the number of degrees of cold than in the number of degrees of heat

approximation to an interval scale, was extended to a wider range of temperatures using more fixed points and was adopted in 1927.

The latter half of the nineteenth century saw the beginning of the golden age of physics and with it the development of the sciences of thermodynamics and statistical mechanics. Despite these theoretical developments giving meaning to temperature and suggesting a metric temperature scale, it took approximately 100 years before a metric scale was formally adopted. In 1960 the unit of temperature, the kelvin, was defined
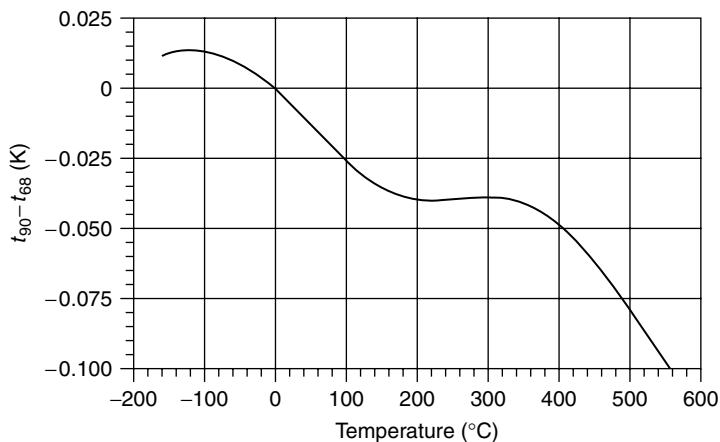
Figure 1.4 The differences between ITS-90 and the earlier scale IPTS-68

as 1/273.16 of the temperature of the triple point of water. There was also a change in the way temperatures were reported. Prior to 1960, measurements on the temperature scale were reported as degrees Kelvin (°K), meaning 'steps' on Kelvin's scale. Since 1960 measurements have been reported as numbers of kelvin, kelvin being the unit for the metric scale.

The advantage of Callendar's platinum resistance scale was that it was more highly reproducible, simpler and more practical to realise than a thermodynamic scale based purely on a gas thermometer. Even today, thermodynamic measurements prove to be extraordinarily difficult, and may cost as much as 20 person-years of effort to achieve accuracies an order of magnitude short of that necessary to support scientific research and commerce. The most practical solution is to adopt a 'wire scale', a scale based on highly reproducible thermometers, calibrated at fixed points, for which the temperatures have been determined by thermodynamic means.

As we have already noted the first wire scale was adopted in 1927 and covered the range from −190 °C upwards. Since then there have been revisions in the international temperature scale occurring in 1948, 1968 and 1990. These revisions have provided improvements in respect of closer approximation of the thermodynamic temperature, improved interpolating equations, extensions to lower temperatures, and greater accessibility for users. Figure 1.4 shows the differences between ITS-90 and the International Practical Temperature Scale of 1968 (IPTS-68), and equations and a table of difference are given in Appendix B. Chapter 3 discusses ITS-90 in detail.

1.3.2 Thermodynamic temperature

For most materials temperature can be considered to be a measure of the density of heat in a body. While this interpretation appeals to intuition and is useful in many situations, it is not especially helpful when comparing different materials or materials near boiling points or other phase transitions. A better model is required. A thermodynamic analysis of Carnot engines (a particular form of ideal heat engine) shows that the efficiency of

reversible heat engines depends only on temperature. In particular the ratio of heat Q_1 taken in at a high temperature θ_1 to the heat Q_2 given out at a lower temperature θ_2 depends purely on the ratio of a function of the temperatures:

$$\frac{Q_1}{Q_2} = \frac{f(\theta_1)}{f(\theta_2)}, \tag{1.1}$$

where θ is any empirical measure of temperature. Kelvin's breakthrough was to recognise that the relationship could be used to define the temperature T:

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \tag{1.2}$$

Kelvin was also able to show that this definition leads to an equation for ideal gases of the form

$$PV = \text{constant} \times T, \tag{1.3}$$

so that Kelvin's definition of temperature is equivalent to the gas scale originally proposed by Amontons, and implemented by Chappuis in 1889. While Kelvin's approach provides a definition of temperature, it does not provide much insight into the nature of the temperature. A diagram of a gas thermometer designed by Kelvin is shown is Figure 1.5.

It took the combined work of Maxwell, Boltzmann and Gibb, using what is now known as statistical mechanics, to solve the problem. By considering the movement
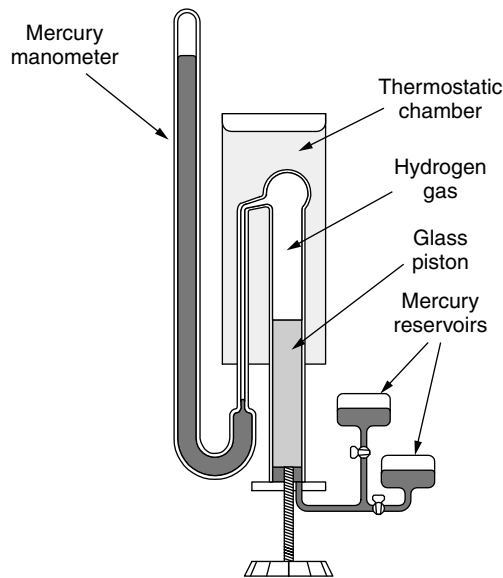
Figure 1.5 A constant-pressure hydrogen-gas thermometer designed by Kelvin. The glass piston is adjusted so that the pressure from the mercury manometer is constant. Under these conditions the volume of gas in the thermostatic chamber is proportional to temperature. The volume of the chamber is indicated by the displacement of the piston. The other mercury containers provide seals for the piston

Table 1.5   Some of the thermodynamic relations that have been used as the basis for thermometers to measure the thermodynamic temperature

Thermometer	Thermodynamic relation
Gas thermometer: pressure, P, and volume, V, of gas versus number of molecules, n, and temperature	$PV = nkT = NRT$
Total radiation thermometer: total radiance, L, versus temperature	$L = \dfrac{2\pi^5 k^4}{15c^2 h^3} T^4$
Spectral band radiation thermometer: spectral radiance, L_λ, versus wavelength, λ, and temperature	$L_\lambda = \dfrac{2hc^2}{\lambda^5}\left[\exp\left(\dfrac{hc}{\lambda kT}\right) - 1\right]^{-1}$
Acoustic thermometer: speed of sound, c_s, versus specific heat ratio, γ, molecular mass, m, and temperature	$c_s^2 = \dfrac{\gamma kT}{m} = \dfrac{\gamma RT}{M}$
Noise thermometer: mean square noise voltage $\overline{V_T^2}$ versus real part of impedance, Z, bandwidth, Δf, and temperature	$\overline{V_T^2} = 4kT\,\mathrm{Re}(Z)\Delta f$

molar gas constant, $R = 8.314\,447\,2\,\mathrm{J\,mol^{-1}\,K^{-1}}$	speed of light, $c = 299\,792\,458\,\mathrm{m\,s^{-1}}$
Planck's constant, $h = 6.626\,068\,76 \times 10^{-34}\,\mathrm{J\,s}$	Boltzmann's constant, $k = 1.380\,650\,3 \times 10^{-23}\,\mathrm{J\,K^{-1}}$

and collisions of individual atoms in a closed box they were able to show that thermal equilibrium requires the mean kinetic energy of all the atoms to be the same. When applied to an ideal gas they obtained the result

$$PV = \text{constant} \times <mv^2/2>, \tag{1.4}$$

where $\langle mv^2/2 \rangle$ is the average kinetic energy of each atom in the gas. Comparison of this equation with Equation (1.3) shows that the *temperature* is proportional to the average kinetic energy of each atom, which finally gives a meaning to temperature that we can comprehend relatively easily. Note that the total kinetic energy of molecular gases is higher than that for monatomic gases because they can rotate and vibrate; in that case the temperature is proportional to the mean translational kinetic energy.

When the principles of thermodynamics and statistical mechanics are applied to other idealised systems we obtain relations that may be exploited in thermodynamic thermometers. A few of the equations and the corresponding thermometers are described in Table 1.5. All of these thermometers have been, and continue to be, used to measure temperature on the thermodynamic scale. Unfortunately the accuracy of thermodynamic thermometers falls well short of the repeatability and ease of use required for both research and commerce. Figure 1.6 summarises the latest measurements of the differences between the thermodynamic scale and ITS-90. The distributions of results presented are indicative of the accuracy of the thermodynamic thermometers. By comparison the ITS-90 scale achieves a repeatability of about 1 mK over the same temperature range.

1.3.3   Meteorological temperatures

In contrast with thermodynamic measurements, which represent the best efforts to measure temperature in accordance with the theoretical concepts, meteorological
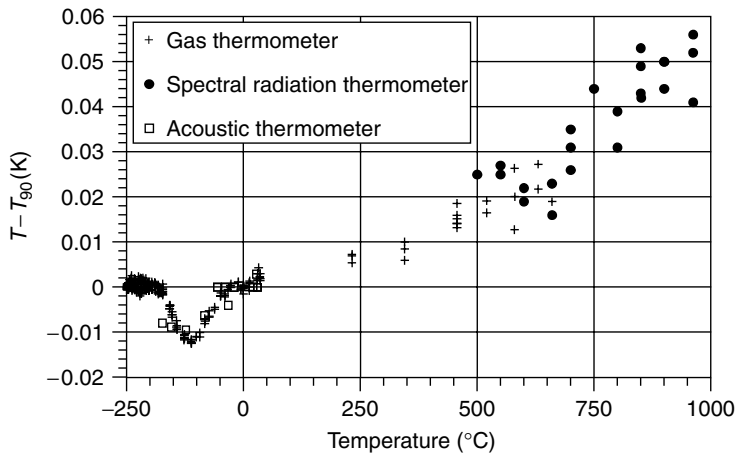
Figure 1.6 The latest measurements of the differences between ITS-90 and the thermodynamic temperature scale

temperature measurements are amongst the most empirical. In this section we discuss meteorological temperature in more detail to highlight some of the difficulties of giving meaning to temperature measurements when the system of interest is not in thermal equilibrium.

Some of the earliest thermometry observations recorded the change in temperature during the day. It was hoped that the measurements would correspond to how hot or cold a person felt, but this was not always the case. Lakes felt warm in winter and cool in summer, but the thermometers indicated otherwise. Problems also arose when people compared observations. An observer at one site, where the thermometer was kept in a living room heated by a fire, would find that the temperature variation was less than that of an observer who kept the thermometer in a spare room. Another observer, who thought that thermometers should be located outside the window on the sunny side of the house, found an even wider temperature variation.

It took some time before everybody was convinced that meteorological readings should be taken outdoors, even though temperature variations could be greater than for measurements made indoors. Debate continued as measurement techniques became more refined: should the thermometer be near a building, shaded from the sun, protected from the wind, and how large should the thermometer be?

Finally, after about 150 years, meteorologists settled on the Stevenson screen, as shown in Figure 1.7, to protect and mount the thermometer. The screen has double-louvred walls with the louvres sloping in opposite directions to allow the air to circulate yet block all radiation from direct access to the chamber. The screen must be mounted at a fixed height above the ground, a minimum distance from buildings and trees, and the paint used on the screens is specified. The thermometer is also specified and must be calibrated to 0.1 °C. Despite the tight specification based on 250 years of development the screens are only expected to be reproducible to about 1.5 °C!

So what then is the correct meteorological temperature? Ideally, we want to measure the air temperature, but this is not possible with a contact or immersion-type ther-mometer. In an ideal situation, such as a stirred liquid, the thermometer is in very

Figure 1.7   A large double-louvred thermometer screen of the Stevenson type. The screen contains a thermograph, wet bulb and dry bulb thermometers, and maximum and minimum thermometers. Note that the screen is located clear of buildings and well off the ground

good thermal contact with the liquid and very poor thermal contact with everything else around it. Therefore, it reads a temperature very close to that of the liquid. Air on the other hand has a very poor thermal conductivity, a very low thermal mass, is transparent to most infrared radiation and is extremely viscous (its kinematic viscosity is similar to that of treacle!). In air, a thermometer is in poor contact with everything. The still air that could be said to be in immediate contact with the thermometer may have a mass much less than a gram, far less than the mass of the thermometer. If the conditions become windy, effectively increasing the mass of air in contact with the thermometer, then thermal contact with the air can improve by more than 100 times. At room temperature, everything radiates infrared radiation totalling about $500\,\mathrm{W\,m^{-2}}$, so the thermometer is in radiative contact with literally everything around it. This radiative contact is not trivial and is very difficult to control. The relative effect of conduction and radiation also depends on the size of the thermometer.

In the final analysis the thermometer measures a very complex weighted average of the temperature of the air and all of the other objects around it, and it proves to be practically impossible to eliminate the effects of the other objects. However, with the use of screens and the other constraints it is practical to establish a measurement protocol that controls the most significant influence effects and delivers a result close to the physical definition. This ensures that results in different parts of the world are comparable. Thus with meteorological measurements the temperature has an uncertain physical meaning but does provide an internationally accepted basis for comparing meteorological conditions related to human comfort.

The use of the Stevenson screen highlights a traceability issue common to all measurements, which is essentially a problem of giving meaning to the measured quantity. Whereas a physicist (or any other theoretical scientist) may have a concise conceptual definition of the quantity measured, in almost every practical measurement there are problems leading to ambiguities or uncertainty. Therefore, if the measurement is to have meaning or be comparable with similar measurements made elsewhere we must follow accepted measurement protocols. In this example, the 'meteorological temperature' is defined by international standards for the screens and thermometers, and anyone who wants to claim to have measured the meteorological temperature must conform to those standards.

1.4 Traceability

1.4.1 Defining traceability

The ISO definition of traceability is:

> **Traceability:**
> The property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.

There is considerable scope for variation in the interpretation of this definition. In order to clarify the meaning let us consider a few of the possible interpretations and investigate their limitations. While we discuss these options, we should keep in mind that the purpose of traceability is to enable different users, potentially on opposite sides of the world, to compare measurement results meaningfully.

Case 1: The dictionary interpretation

The word traceable has a wide range of colloquial meanings, the most appropriate being 'able to be followed to the source'. This adds nothing to the ISO definition, but does highlight two important points. The ISO definition tells us where the chain begins and ends. Specifically, it begins with the measurement result, not with the instrument. Secondly the uncertainty provides a measure of the proximity to the source of traceability.

Case 2: The measurement scale interpretation

Following our exposition in Section 1.2.2 on measurement scales we could argue that traceability simply requires all measuring instruments to use the same measurement scale. However, this is not a very discerning interpretation. If we look around us we find that almost all of our measuring instruments indicate results in terms of the SI scales, so we must conclude that almost every measurement is already traceable. It has also happened on occasions that very good thermometers, such as standard platinum resistance thermometers, have been 'calibrated' using very poor thermometers such as thermocouples. In such cases the scale on the calibrated thermometer is not as good as it could or should be. Thus it is useful to have a measure of the quality of the scale and, as we noted in Section 1.2.4, it is necessary to know the uncertainty to make sensible decisions. Both arguments provide the rationale for the requirement in the ISO definition for stating the uncertainties.

Case 3: The filing cabinet interpretation

Let us suppose that for each measuring instrument used to make traceable measurements there is a calibration certificate kept in a filing cabinet, which allows the location of another filing cabinet to be traced, and so on, until a filing cabinet containing a certificate for the primary standard is found in a national measurement institute. Let us further suppose that each of these certificates appears to be a good and useful certificate; that is, each reports the uncertainties in measurements obtained with the instrument, under the appropriate specified conditions. The problem here is that possession of a certificate is no assurance that the final measurement, or indeed any of the measurements, have been carried out competently.

Case 4: The laboratory accreditation interpretation

In this case each of the laboratories involved in the calibration of the instruments and the final measurements is required to have the filing cabinets and certificates, but is additionally subject to an independent and expert audit of the entire measurement process. In this scenario, there is no real opportunity for measurement results to become corrupted in any sense (unless we question the competence of the accrediting body, and there are accreditation processes for them too). This requirement for an assessment of technical competence is not stated in the ISO definition of traceability, but accreditation to ISO 17025 *General requirements for the competence of testing and calibration laboratories* has become the practical working definition of traceability.

To summarise, we can interpret the ISO definition to mean:

> **Traceability (alternative definition):**
> The ability to demonstrate the accuracy of a measurement result in terms of appropriate national or international standards.

For thermometry, the appropriate standard is the SI kelvin.

1.4.2   Achieving traceability

So how is traceability achieved in practice? Clearly a substantial community effort is required. In general there are three main requirements for an international measurement system, as follows.

A source of primary physical standards

Primary physical standards are required to provide a unique definition of the measurement scales. Easily the most important source is the SI, Système International d'unités, which defines a system of seven base measurement scales, and primary physical standards for the unit for each of those scales. The scales for a large number of other metric quantities are also derived from the seven base scales. The SI is managed and maintained under a diplomatic treaty originally signed in 1875.

A large number of measurements are also made on non-SI scales, especially nominal, ordinal and interval scales, and these scales also require standards. These include for example: proprietary colour scales owned by the manufacturers of printing inks; scales based on tightly specified testing machines such as for Rockwell hardness, engine octane rating for fuel, and viscosity; and chemical scales for complex mixtures that are based on certified reference materials.

A source of documentary standards

With difficult measurements, as we found with meteorological temperatures, it is sometimes necessary to agree on a measurement protocol in order to be able to make comparable measurements. This is true also for measurements of viscosity, thermal resistance and electrical resistance; indeed almost all temperature-related product tests. Test methods for these quantities are usually standardised and published as documentary standards.

Documentary standards are also used to define other protocols, some of which have a direct effect on measurements. These include standardised responses for platinum resistance thermometers and thermocouples, mechanical specifications for electrical instruments and parts, software specifications and interfaces, and quality assurance systems. While such standards may not have a direct impact on traceability they do benefit the measurement community by ensuring that sensors, instrumentation and systems made by different manufacturers are equivalent or compatible.

The documentary standards system is a rather mixed group of national and international organisations, and some centred on professional societies or particular industries.

A source of independent third-party assessors

Measurements are quite unlike many of the products that we buy. When we buy a television set or a banana we can see something of the quality of the product that we are buying. With a measurement there is generally no way to tell from the result we receive whether the measurement is of good or bad quality. Measurements are also different in another way. Whereas a television manufacturer might like to change the

model each year or provide additional marketing gimmicks, a measurement sold on the basis of being made in terms of the ITS-90 temperature scale should mean no more and no less. In a sense the terms 'kelvin', the other SI units and other primary standards have accepted meanings, and the measurement community cannot afford to allow those meanings to become corrupted. If changes in meaning were allowed a supplier of measurements would be able to tender on the basis of the largest kelvin or the shortest metre. Chaos would soon result.

Given that a calibration or testing laboratory has followed documentary standards and calibrated its equipment, it must demonstrate that it has conformed to the community expectation in respect of measurement standards and technical procedures. The most important accreditation bodies are those accrediting to ISO 17025 *General requirements for the competence of testing and calibration laboratories*. Most countries now have organisations that offer accreditation and are recognised through mutual recognition agreements and the International Laboratory Accreditation Co-operation (ILAC). This ensures that the results from laboratories endorsed by these organisations are accepted in other countries. Because of the importance of measurement in the development and utilisation of technology, and the technological standing of countries as perceived by their trading partners, accrediting organisations are usually established under government regulations.

There are also other third-party assessment schemes. These are often associated with specific industries such as the military or aviation industry. Increasingly, however, these schemes are evolving towards and merging with the ISO 17025 system.

In the following sections we investigate these three components in more detail.

1.5 The SI

1.5.1   The Metre Convention

In a museum in Utrecht lies a thermometer with 18 different scales marked on a wide board behind the thermometer tube. The early 1700s were a time when each thermometer manufacturer had its own proprietary scale and natural philosophers were only beginning to appreciate the value of meteorological observations that could be compared with those made at other places. This was a lesson that traders have known since at least the time of the pharaohs. Nowadays temperature is one of the most measured quantities and is associated with commerce and technology reaching across every continent. Were we still to have 18 scales, disasters like the recent NASA Mars Climate Orbiter fiasco, which was caused by the confusion of SI and Imperial units for the small translational forces imparted by the jets that rotated the satellite, would be commonplace. The only way to be sure of the clear communication of measurement results is for all users of the measurements to share a common system of measurement.

The seeds of the SI system were planted by King Louis XVI at the time of the French Revolution; he wanted a decimal system of measurement. The metre was defined to be 1/10 000 000 of the distance between the Equator and the North Pole as measured along the quadrant that passes through Paris. (That the earth has a circumference that is almost exactly 40 000 km is no coincidence.) After the definition of the metre, the kilogram was defined to be the weight of 1 cubic decimetre of water. Platinum

artefact standards representing these two quantities were deposited in the Archives de la République in Paris. All measures of length and weight were derived from these standards, and hence these scales were amongst the first to be implemented as truly metric scales.

By the middle of the nineteenth century international trade was on the increase and a number of eminent scientists and industrialists of the time foresaw the value of a universal system of measurement and lobbied their governments intensively. The metric system was the obvious choice since it was well established in several European countries. Seventy-five years after King Louis XVI founded the metric system, on 20 May 1875, 17 nations signed a diplomatic treaty, the *Convention du Mètre*. This established an international organisation, and a laboratory, the Bureau International des Poids et Mesures (BIPM), on land set aside by the French government, with the responsibility of maintaining standards of measurement for the metre, the kilogram and the second. Over the years the responsibility has been extended to cover the ampere, the kelvin, the candela and the mole. Approximately 50 countries are now signatories to the Metre Convention and almost all of the world's 190+ independent states use the SI. However, the importance of the treaty is not so much that it establishes a metric system of units but rather that nations agree on the meaning of the units.

Figure 1.8 shows the various organs of the Convention du Mètre. Delegates from member countries meet at the Conférence Générale des Poids et Mesures (CGPM) at four-yearly intervals to approve the latest recommendations on improvements to the SI and the operation of the organisation. Nearly all of the recommendations come from the other parts of the organisational structure to which member nations have the opportunity to contribute. The consultative committees in particular are made up from experts in each measurement discipline, usually from the world's national measurement standards laboratories, and have the responsibility for overseeing and encouraging appropriate research into the various units. This ensures that the units have sufficient accuracy to meet the ever-increasing needs of commerce and technology, and can be made readily available to those who need them.

When the Metre Convention was signed it was envisaged that the BIPM would maintain the primary standards for all of the various scales. However, scales based on a single artefact are troublesome. As the number of measurements traceable to that artefact increases so too does the value of the artefact. The need to protect it from damage becomes paramount and it becomes very difficult to disseminate many measurements at the highest accuracy. The alternative, which has been pursued vigorously, is to base the standards on fundamental physical constants, in the same way that temperature is defined in terms of the triple point of water. This ensures that the standards can be rebuilt easily if damaged and in principle copied by every national standards laboratory. Nowadays only one artefact standard is maintained at the BIPM, namely the kilogram. It is hoped that in the near future, the kilogram will join the other units and be defined in terms of fundamental physical constants.

1.5.2   The SI units and conventions

The SI units are divided into two classes: base units and derived units. In principle, some of the base units are unnecessary since they can be related to each other through
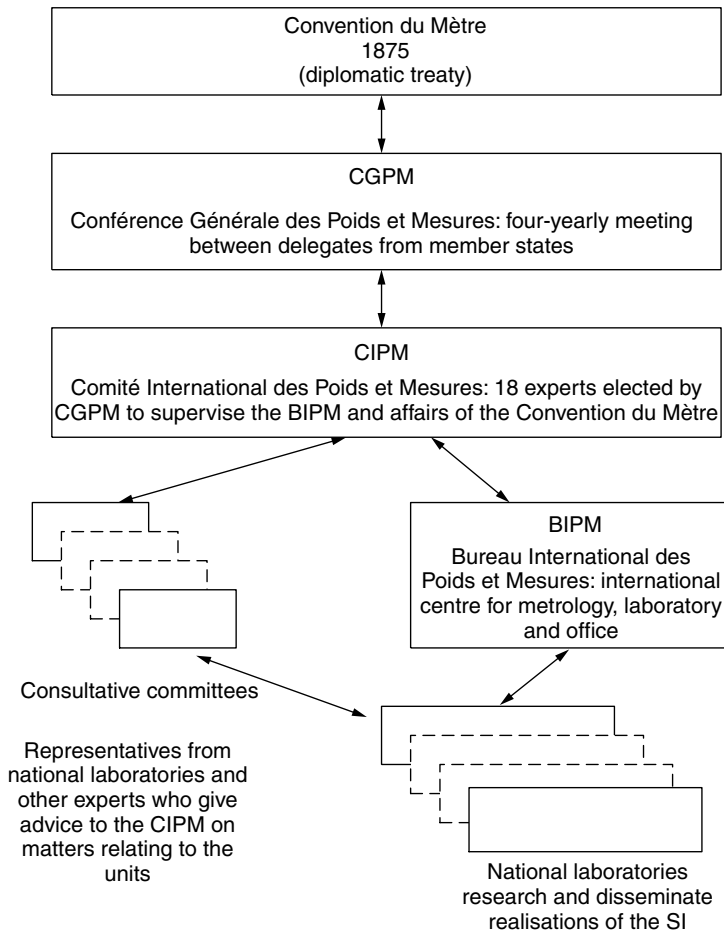
Figure 1.8 The structure and responsibilities of the various organs of the Metre Convention

measurements of the fundamental physical constants; however, they are necessary for the most accurate measurements and are regarded as dimensionally independent. The current SI definitions for the base units are as follows:

The second (s), the unit of time interval: The second is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium atom.

The metre (m), the unit of length: The metre is the length of the path travelled by light in a vacuum during a time interval of 1/299 792 458 of a second.

The kilogram (kg), the unit of mass: The kilogram is the unit of mass, equal to the mass of the international prototype kilogram.

The ampere (A), the unit of electric current: The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of circular

cross-section and placed 1 metre apart in a vacuum, would produce between these conductors a force equal to $2\pi \times 10^{-7}$ newton, per metre of length.

The kelvin (K), the unit of thermodynamic temperature: The kelvin is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

The candela (cd), the unit of luminous intensity: The luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and has a radiant intensity in that direction of 1/683 of a watt per steradian.

The mole (mol), the unit of amount of substance: The amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kilograms of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

The derived units are formed from products and powers of the base units according to the algebraic formulae linking the quantities involved. Thus, for example, velocity is measured as metres per second, the ratio of two of the base units. A few of the derived units prove to be so useful that they are given special names and symbols; these are given in Table 1.6.

In order to avoid confusion in the presentation of results the SI conventions should be adhered to.

Table 1.6 The SI derived units with special names and symbols

Derived quantity	SI derived unit	
	Special name	Symbol
Plane angle	radian	$\text{rad} = \text{m} \cdot \text{m}^{-1}$
Solid angle	steradian	$\text{sr} = \text{m}^2 \cdot \text{m}^{-2}$
Frequency	hertz	$\text{Hz} = \text{s}^{-1}$
Force	newton	$\text{N} = \text{kg} \cdot \text{m} \cdot \text{s}^{-2}$
Pressure	pascal	$\text{Pa} = \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$
Energy	joule	$\text{J} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$
Power, radiant flux	watt	$\text{W} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-3}$
Electric charge	coulomb	$\text{C} = \text{A} \cdot \text{s}$
Electric potential difference	volt	$\text{V} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-3} \cdot \text{A}^{-1}$
Capacitance	farad	$\text{F} = \text{kg}^{-1} \cdot \text{m}^{-2} \cdot \text{s}^4 \cdot \text{A}^2$
Electric resistance	ohm	$\Omega = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-3} \cdot \text{A}^{-2}$
Electric conductance	siemens	$\text{S} = \Omega^{-1}$
Magnetic flux	weber	$\text{Wb} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{A}^{-1}$
Magnetic flux density	tesla	$\text{T} = \text{kg} \cdot \text{s}^{-2} \cdot \text{A}^{-1}$
Inductance	henry	$\text{H} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{A}^{-2}$
Celsius temperature	degree Celsius	$°\text{C} = \text{K}$
Luminous flux	lumen	$\text{lm} = \text{cd} \cdot \text{sr}$
Illuminance	lux	$\text{lx} = \text{cd} \cdot \text{m}^{-2}$
Activity	becquerel	$\text{Bq} = \text{s}^{-1}$
Absorbed dose	gray	$\text{Gy} = \text{m}^2 \cdot \text{s}^{-2}$
Dose equivalent	sievert	$\text{SV} = \text{m}^2 \cdot \text{s}^{-2}$

Use of names for units

- When written in full, the names of all SI units start with a lower-case letter, except at the beginning of a sentence; for example, kelvin not Kelvin or degrees kelvin, degrees Celsius not Degrees Celsius.
- The symbols are lower case except when named after a person. Hence K is the symbol for kelvin. When written in full, the names of the units may be made plural according to the rules of English grammar; for example, 'temperature difference in kelvins'.

Use of the symbols for units

- Symbols should be used to denote the units when reporting numerical results, and the full name when referring to units in written text. The symbol should be separated from the last digit by a single space, e.g. 273.15 K not 273.15K.
- When reporting quantities with compound units formed by the product of two or more units, the unit symbols should be separated by a half-high dot, dot or a space; for example, for metre-kelvin: m·K or m.K or m K, but not mK, which implies millikelvin.
- When reporting quantities with compound units formed by ratios of two or more units, exponentiation or a single solidus may be used. Parentheses should be used to prevent ambiguities: for example, W/m^2 or $W.m^{-2}$; $J/(kg.°C)$ or $J.kg^{-1}°C^{-1}$ not $J/kg/°C$.

Decimal points and commas

- Numbers less than one should have a single zero before the decimal point. A comma should be used as the decimal point. In English-speaking countries a dot on the line is more commonly used, e.g. 0.1 °C or 0,1 °C, but not .1 °C.

Table 1.7   The most commonly used SI prefixes

Factor	Prefix	Symbol
10^{12}	tera	T
10^9	giga	G
10^6	mega	M
10^3	kilo	k
10^2	hecto	h
10	deca	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f

- To facilitate the reading of numbers with many digits, the digits may be separated into groups of three counting from the decimal point. The groups should be separated by a space, never a comma, which may be confused for a decimal point.

Use of prefixes for symbols

- The most commonly used prefixes are given in Table 1.7.
- When joining a prefix and SI unit symbol, there is no space between the prefix symbol and the unit symbol, e.g. 10 mK or 10 m °C, not 10 m K.

1.6 Documentary Standards

From a traceability perspective the most important contribution of documentary standards to thermometry is in the area of test methods. There are very few properties of materials that do not change with temperature, and consequently a very high percentage of test methods involve the measurement of temperature.

Documentary standards also cover a number of aspects of interest to thermometrists, including:

- Specifications for the response of platinum resistance thermometers and thermocouples, and the dimensions and scales for liquid-in-glass thermometers.
- Colour codes for thermocouple lead wires, and colours and dimensions of thermocouple plugs and sockets.
- The materials and dimensions for sheathing materials and thermowells (the protective pockets used for mounting thermocouples in industrial plants).
- Dimensional and electrical specifications for industrial instrumentation such as temperature controllers.
- Specifications for furnaces and ovens, especially those used for heat treatment and sterilisation.
- Electrical and communication standards for instrument interfaces.
- Quality assurance and laboratory accreditation systems.

A short summary of major standards organisations relevant to thermometry is given in Table 1.8.

It is notable that only a few of the standards organisations are truly international. Consequently, there may be differences between standards from different organisations, apparently for the same device or protocol. Particular examples include the standards for platinum resistance thermometers and thermocouples, where there are small differences. As the standards have been revised following the change from the IPTS-68 to the ITS-90 temperature scale, many of the standards have become harmonised.

It is beyond the scope of this book to catalogue all of the temperature-related standards available from these organisations. Your local standards organisations will have catalogues available and may be able to advise which standards are relevant. In addition, most of the organisations now have Internet sites, with good search engines and on-line shops. Many of the organisations also have application guides and manuals

Table 1.8 Some of the larger standards organisations that produce thermometry-related documentary standards

Acronym	Title	Internet address
ANSI	American National Standards Institute	www.ansi.org
ASTM	American Society for Testing and Materials	www.astm.org
BSI	British Standards Institution	www.bsi-global.com
DIN	Deutsches Institut für Normung	www.din.de
IEC	International Electrotechnical Commission	www.iec.ch
IP	Institute of Petroleum	www.petroleum.co.uk
ISO	International Organisation for Standardisation	www.iso.ch
JIS	Japanese Industrial Standards	www.tokyo.jsa.or.jp
OIML	International Organisation for Legal Metrology	www.oiml.org

for particular measurement disciplines, and booklets giving detailed information on the SI.

> *Exercise 1.5*
>
> Spend an hour or so visiting some of the Internet sites given in Table 1.8 and search for standards and documents relating to temperature. If you have responsibilities for product testing you should try searching on a few relevant keywords.

1.7 Laboratory Accreditation to ISO/IEC 17025

The standard, ISO/IEC 17025:1999 *General requirements for the competence of testing and calibration laboratories*, has evolved from the ISO Guide 25 of the same name. The standard applies to all calibration and testing laboratories whether using standard, non-standard or laboratory-developed methods. The standard has two groups of requirements: managerial and technical.

The managerial requirements are equivalent to those required under the ISO 9001 and ISO 9002 quality systems, and include the following:

- The laboratory's management must be committed to a quality scheme by ensuring that policies and objectives are communicated to, and understood and implemented by, all laboratory personnel.

- Independence and financial stability of the laboratory are desirable. Where the laboratory is part of a larger organisation it is particularly important for the laboratory to act independently. There should be no conflicts of interest.

- Quality systems must be properly documented. Procedures must be written to cover the responsibilities of the staff. Documentation control is needed to ensure that the staff use the latest procedures.

- New work must be reviewed to understand its requirements and determine whether the laboratory can carry it out.

- Records should be made and kept for all work. Regulatory or contractual requirements may determine the length of time to hold records.

- Complaints and corrective action procedures are essential, especially for the control of sub-standard testing work.

- Control over procurement of equipment, consumables and services requires procedures to see that they are of appropriate quality; for example, calibration certificates supplied with test equipment.

The technical requirements include the following:

- Staff should be properly qualified and a regular training programme should be in place.

- Accommodation and environment provisions must be adequate for staff, test equipment and test samples.

- There must be adequate management and control of test equipment. This is an essential feature for traceability, which translates into the whole life of a piece of test equipment being properly documented.

- Calibration of test equipment must be carried out in a timely and proficient manner.

- Test methods, whether in-house or standard methods, must be validated.

- If sampling is involved in any of the work then the laboratory should have a sampling plan and procedures.

- There must be procedures for the identification of items for test, and for safe handling and storage, to ensure the integrity of the item.

- Test reports and certificates must be well specified in terms of content and format.

- The laboratory should participate in proficiency testing programmes or employ other statistical techniques, where appropriate, to enhance the confidence in procedures.

Because calibration laboratories provide an important link in the traceability chain to the SI, and may affect many clients downstream from the laboratory, the accreditation process for calibration laboratories tends to be more stringent than that for testing laboratories, especially in respect of the care of instruments and in the assessment of uncertainty. This is recognised in the ISO 17025 standard. In some countries, separate accreditation bodies deal with testing and calibration.

If you or your laboratory is considering accreditation you should remember that the accreditation authority is not a customer but a supplier of a service. You are paying the authority to represent your clients' interests, and you should be treated as their client. It is not a regulatory authority, although it may request conformance to documentary standards if that is what your clients expect, and will judge whether you are conforming to any documentary standards that you nominate. Remember too that when it assesses your laboratory it acts on behalf of its other clients who expect it to help maintain the integrity of the various parts of the measurement system. The service it provides is the acceptance of your test and measurement results by a wide range of international customers.

Users of measurement results should be careful to distinguish between accreditation and certification. In the quality industry, accreditation is a jargon term applied strictly

to companies assessed for competence according to the ISO 17025 standard. When applied to organisations, certification simply means that the company has implemented an ISO 9000 management system, which has no explicit requirement for technical competence.

1.8 National Measurement System

Having knowledge of what is necessary for good measurements (i.e. to achieve traceability) is of no use unless the theory can be put into practice. Much of what is required is beyond the direct influence of any individual. Fortunately most governments have taken an interest in their country's ability to measure because it affects the country's wealth and welfare, and standing with trading partners. Planning of the national measurement system (NMS) by government also ensures that the necessary services are available to enable regulatory and contractual requirements to be met by industry. The total of the measurement services inside a country can be considered together as the NMS, a concept that has grown in importance over the last few decades.

Good measurement practice requires several services to be readily available:

- calibration of instruments;
- training of staff in measurement techniques;
- regulation of trade measurement;
- endorsement of results by accreditation;
- specifications and procedures for measurements;
- supply of measuring instruments; and
- repair and servicing of instruments.

In this section we consider the first three of these topics. Accreditation and documentary standards have been covered already in sufficient detail, and repair and supply of servicing is normally provided by non-government organisations.

Figure 1.9 outlines the formal components of a national measurement system that are external to its users, that is calibration, specification and accreditation. The figure gives an outline only; in a well-organised NMS there are many components, including second- and third-tier calibration laboratories and standards committees, and many more interactions.

For measurements to have legal standing countries must have laws providing for measurement units, and for the laws to be effective a national measurement institute (NMI) is required to hold primary measurement standards. Such laws provide a basis for national and international trade, consumer protection, and environmental and health management. Where the best accuracies are required the NMI will realise the physical definitions of the units in accordance with the SI definitions and BIPM guidelines, and maintain these as the primary standards. International obligations can also be met by using reference standards calibrated by the BIPM or other NMIs.

The infrastructure requirement of maintaining uniform measures is the most important of the NMI's responsibilities and is met most simply by providing calibration services. While this satisfies the prime function in support of legislation and trade,
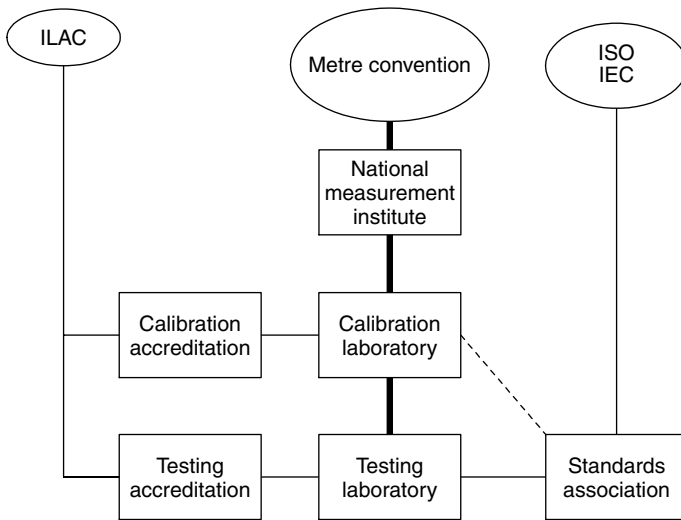
Figure 1.9   Traceability links in a national measurement system. The main traceability path is shown by the heavy line. Documentary input that affects the path is shown by the other lines. Accreditation bodies for testing and calibration may be separate from each other

the end-users of the NMI's 'product' are generally distributed wherever the country's products are exported. In order to satisfy all clients the NMI must not only ensure that the country's measures are uniform but also establish the credibility of its standards on the international stage. To this end the BIPM has extended its responsibilities to the maintenance of a mutual recognition arrangement (MRA) that enables one country to recognise another's measurement standards. To participate in the MRA the NMI must be an associate signatory to the Metre Convention, participate in international comparisons of measurement standards, have a quality system equivalent to ISO 17025, and publish relevant contributions to metrological science. The MRA, which laid the 'ground rules' for recognition, was signed in October 1999, and will gradually take effect over the next five years or so.

The NMIs also provide a pool of expertise that makes a valuable contribution to a country. The links with other NMIs and familiarity with new measurement techniques often mean that the NMIs provide a way of introducing new measurement technology to a country, and of keeping up with international trends. To this end most NMIs offer training courses and participate in accreditation assessments, as well as carrying out consultancy for specific clients.

Generally the NMI has no powers of enforcement, and experience shows that within a country some enforcement is required to protect consumers and the general public. To this end most countries have a legal metrology organisation. Its responsibility is to ensure that traders' weights and measures are correct and that the public is not being defrauded in any transactions. Again there is an international connection through the Organisation Internationale de Metrologie Légale (OIML). It provides experience and resources to aid countries in the establishment and enforcement of appropriate law.

Training is essential throughout the whole NMS to ensure that those involved are technically competent to make measurements. Unlike the other three components, there

is no recognised organisational structure to achieve this, and it is rare to find tertiary education institutes providing formal measurement training. Usually measurement expertise is absorbed by osmosis as a part of other technical training courses, or passed on as lore from other staff. Indeed much of the subject matter lacks a formal basis for an educational curriculum. In many countries, most of the government-operated bodies in the NMS offer short training courses in their respective disciplines.

> *Exercise 1.6*
>
> Draw a diagram similar to Figure 1.9 for your temperature measurements. Then note how the procedures differ for any other measurements you make. If possible obtain the names and addresses of the organisations involved in these procedures and the name of a contact person. Include any linkages to organisations outside your NMS.
>
> Indicate in the diagram if you are subject to more than one accreditation body or standards association and show their international linkages. Scientific users can give the relevant scientific references instead of the organisations. Are your measurements traceable according to the definitions given in this chapter?

Further Reading

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2

Uncertainty in Measurement

2.1 Introduction

When we base decisions on measurements, there is a chance that errors in the measurement influence the decision. The primary purpose of uncertainty analysis is to provide a measure of that influence and the likelihood of making a wrong decision. While risk assessment is often not important in calibration and research situations, it is vitally important for measurements affecting trade, health and the natural environment.

Uncertainty analyses are often difficult. For most of us they stretch our understanding of the measurement to the limit, and the lower the uncertainty required in a measurement the greater the understanding required. For this reason detailed and reasoned uncertainty analyses have a second purpose: they provide a measure of our competence. This is one of the reasons for emphasising uncertainty analyses in the calibration and test environments, especially where laboratory accreditation is sought.

In this chapter, we introduce the mathematical tools used in uncertainty analysis. The first few sections concentrate on the basic techniques that are applicable to most measurements. We begin by developing the concept of a distribution and the statistical tools for describing distributions. We then progress through techniques for assessing, propagating and combining uncertainties. More advanced sections follow on correlation, interpolation and least-squares fitting. The guidelines given here are based on the ISO *Guide to the Expression of Uncertainty in Measurement*. The final sections give guidelines for interpretation of uncertainties, limitations of the ISO Guide, and presentation of uncertainties.

In addition to the statistical tools described in this chapter, uncertainty analysis also requires understanding of the measurement, usually in terms of mathematical models of the various influence effects that cause errors. Throughout the chapter, we provide examples of the application of the tools to simple, usually temperature-related, problems. Other temperature examples may be found throughout the book. Exercises are also provided to aid students and to catalogue useful results not given in the main text. The uncertainty equations are quite general and applicable to measurements reported on any interval scale or metric scale.

Necessarily, uncertainty analysis involves mathematics. For those who are beginners or who find the mathematics intimidating, we suggest reading the chapter through to the end of Section 2.7, omitting Sections 2.3.1, 2.3.2 and 2.6.3, and focusing on the discussion rather than the equations. Uncertainty analysis is an extensive subject, and cannot be absorbed at one sitting. We expect that you will gradually become

familiar with the relevant parts of the chapter as the need arises and confidence allows.

2.2 Risk, Uncertainty and Error

Figure 2.1 shows a set of temperature measurements made to assess the operating conditions of a large petrochemical reactor. Also shown in Figure 2.1 is a line representing the maximum specified operating temperature. Measurements to the right of the line indicate that the reactor is too hot and may fail resulting in huge costs associated with repair and lost production. Measurements to the left indicate that the reactor is safe, but those to the far left indicate that the process temperature, and hence the productivity, are too low. Now, based on these measurements, should we increase or decrease the temperature, or leave the operating conditions as they are? Clearly a difficult compromise must be reached: the reactor must be as hot as practical while keeping the risk of reactor failure acceptably low. Although the nature of the risks and rewards may be very different such decisions are the natural endpoint for all measurements.

As Figure 2.1 shows, multiple measurements of quantities tend to be distributed over a range of values. Some of those measurements may be in error by an amount sufficient to induce an incorrect decision; other measurements may make the decision more conservative. To increase confidence in decisions we usually take several measurements and account for the errors as best we can. However, even with the best planning and analysis we cannot always know for sure that the decision will be right; there is always risk, a finite chance of being wrong. For this reason risk and uncertainty are characterised in terms of probability. By measuring the dispersion of the measurements in Figure 2.1, we can estimate the probability of a wrong decision based on any one or all of the measurements. This principle underlies all uncertainty analysis:
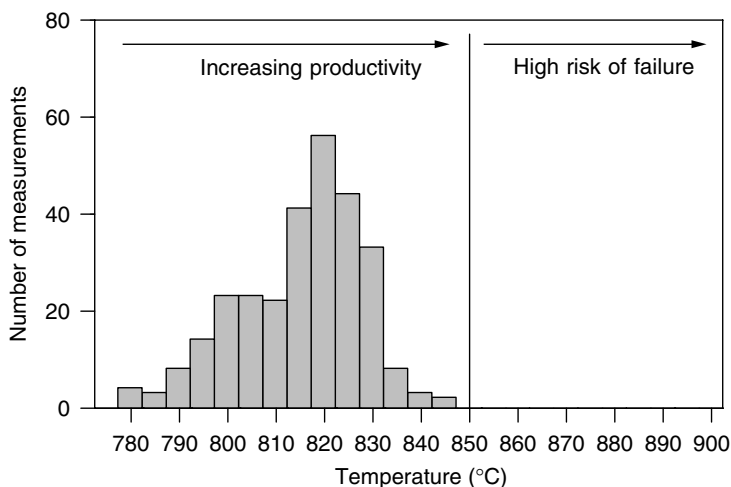
Figure 2.1   The distribution of measurements of temperature in a petrochemical reactor

Uncertainty of measurement:
The parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand.

The simplest way of assessing uncertainty is to make many measurements, as in Figure 2.1, and to use these results to estimate the range of possible values. Uncertainties calculated this way, using actual measurements and statistical analysis, are called *Type A uncertainties*.

An alternative method of assessing uncertainty, often used when statistical sampling is impractical, is to bring other information to bear on the problem. Such information may include physical theory, information from handbooks, or varying degrees of experience of similar situations. These uncertainties are called *Type B uncertainties*. They may be subjective, and usually involve a number of assumptions, some of which may be untestable. Methods for assessing Type A and Type B uncertainties are given in detail in Sections 2.6 and 2.7 respectively.

One of the factors contributing to the dispersion of measurements is measurement error. However, one must be careful not to confuse error with uncertainty. Error affects every measurement while uncertainty characterises the dispersion of many measurements, some of which may be caused by error. For example, the measurements presented in Figure 2.1 may be completely free of error so that the histogram reflects the true distribution of temperatures in the petrochemical reactor. Indeed, it is very common in thermometry that the quantity of interest is not single valued, but distributed over a range of values. We will return to this issue several times as it has an impact on the interpretation of uncertainties and the design of calibrations.

When carrying out a measurement we generally recognise two types of error. The most obvious is the *random error*, which causes a sequence of readings to be scattered unpredictably. The second type of error, the *systematic error*, causes all the readings on average to be biased away from the true value of the measurand.

Systematic errors are usually associated with uncalibrated equipment or imperfect realisation of calibration conditions, imperfect definitions and realisation of the measurand, errors in theory or interpretation of theory, non-representative sampling, and environmental influences. While the term systematic has a strong intuitive implication suggesting that the error is in some sense predictable, this meaning is highly subjective and cannot be translated into an unambiguous technical definition. Indeed, traditional treatments of errors that have attempted such a definition have resulted in controversy. Instead, the modern definitions of random and systematic error are based only on the premise that a systematic error causes bias in the results whereas a random error does not.

Systematic error:
The mean of a large number of repeated measurements of the same measurand minus the true value of the measurand.

Random error:
The result of a measurement minus the mean of a large number of repeated measurements.

It is assumed that corrections are applied to reduce significant systematic errors wherever practical.

> **Correction:**
> The value added algebraically to the uncorrected result of a measurement to compensate for systematic error.

The error arising from incomplete correction of a systematic effect cannot be exactly known so it is treated as a random error. In this way the uncertainty in the correction contributes to the 'dispersion of values that could reasonably be attributed to the measurand'.

It is tempting to associate the Type A and Type B assessments of uncertainty with random and systematic errors respectively; however, no such association exists. The terms Type A and Type B characterise methods for assessing uncertainty, while random and systematic refer to types of error. When random and systematic errors contribute to uncertainty both may be assessed by either Type A or Type B methods, as will be shown by example.

Exercise 2.1

Think about some of the measurements you make. What decisions depend on these measurements? What are the risks associated with wrong decisions and the rewards associated with correct decisions? [Hint: How do the measurements affect your actions? Remember that a decision has at least two possible outcomes, and both might be wrong.]

2.3 Distributions, Mean and Variance

By repeating measurements we build up a picture of the *distribution* of the measurements. In the mathematical context, a distribution describes the range of possible results and the likelihood of obtaining specific results. Figure 2.2 shows a histogram of 20 measurements. The vertical axis on the left-hand side is the sample *frequency*, namely the number of times results occur within the ranges indicated by the vertical bars, while the right-hand axis is an estimate of the *probability* of obtaining a result within each range. The probability is calculated as the frequency divided by the total number of measurements. For example, we can expect about 3 out of every 10 measurements to yield a result in the range 6.45 to 6.55. Note that the probability of obtaining a particular result within a given interval is proportional to the area enclosed within that interval.

As the number of measurements is increased the shape of the distribution becomes better determined and, in some cases, smoother. The distribution obtained for an infinite number of measurements and an infinite number of sections is known as the *limiting distribution* for the measurements. Usually we can only take a small number of measurements, so any histogram, like that in Figure 2.2, can only approximate the limiting distribution.
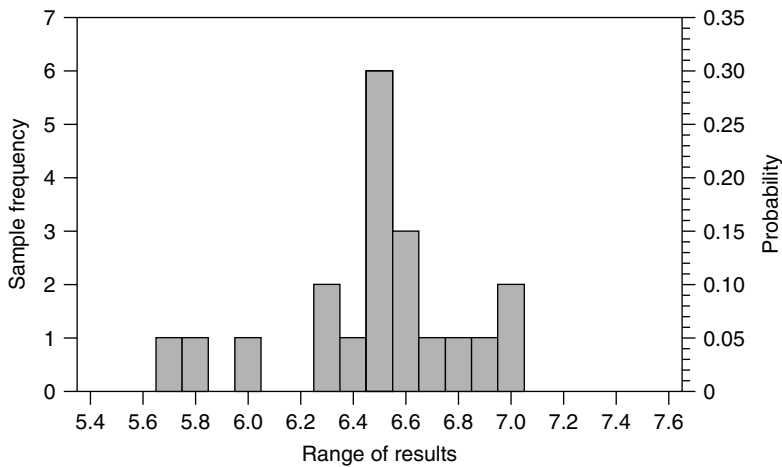
Figure 2.2   A histogram of 20 measurements

There are a number of different ways of representing distributions, but for the purposes of calculating uncertainties distributions need only be characterised in terms of two parameters: the centre and the width of the distribution.

2.3.1   Discrete distributions

For discrete distributions, the number of possible outcomes for a measurement is finite and each outcome is distinct. Figure 2.3 shows, for example, the probabilities expected from the throw of a die (note, die is the singular of dice, but according to Ambrose Bierce you don't hear it often because of the prohibitory proverb, 'never say die'). In this case there are only six possible outcomes, the numbers 1 through 6, and the total probability is 100%.
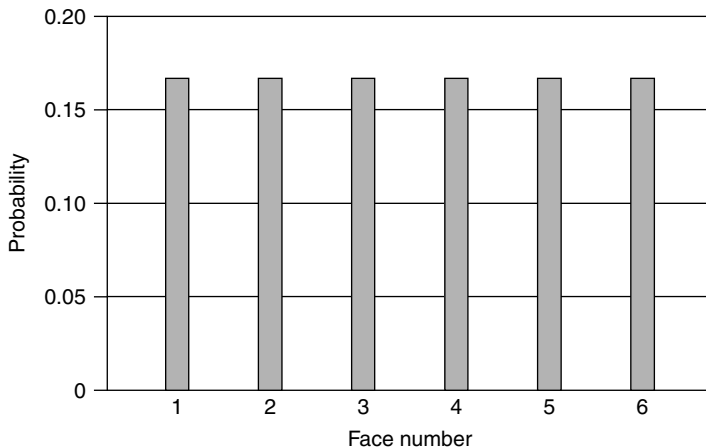
Figure 2.3   The possible outcomes from the throw of a die, an example of a discrete distribution

The centre of the distribution is calculated as the *mean* and is given the Greek symbol μ (mu):

$$\mu = \sum_{i=1}^{N} X_i P(X_i), \tag{2.1}$$

where $P(X_i)$ is the probability of obtaining the result X_i and N is the number of measurements.

The width of the distribution is characterised by the *variance* and is calculated as

$$\sigma^2 = \sum_{i=1}^{N} (X_i - \mu)^2 P(X_i). \tag{2.2}$$

The Greek symbol σ (sigma) is called the *standard deviation* of the distribution and is usually directly proportional to the width. The variance, as defined by Equation (2.2), may seem a little complicated but it has some useful properties that will be exploited later.

Example 2.1

Calculate the mean, variance and standard deviation of the distribution of results from throws of a die.

On numbered dice there are six possible outcomes, each of the numbers 1 through 6. If we assume that each number is equally likely then the probability of each result, $P(X_i)$, is one-sixth. Therefore the mean is given by Equation (2.1) as

$$\mu = \sum_{i=1}^{6} \frac{X_i}{6} = \frac{1}{6} + \frac{2}{6} + \frac{3}{6} + \frac{4}{6} + \frac{5}{6} + \frac{6}{6} = 3.5,$$

and the variance is given by Equation (2.2) as

$$\sigma^2 = \sum_{i=1}^{6} \frac{(X_i - 3.5)^2}{6} = \frac{(-2.5)^2}{6} + \frac{(-1.5)^2}{6} + \frac{(-0.5)^2}{6} + \frac{(0.5)^2}{6}$$

$$+ \frac{(1.5)^2}{6} + \frac{(2.5)^2}{6}$$

$$= 2.9166'.$$

Therefore, the standard deviation, σ, is $\sqrt{2.9166'} = 1.7078$.

Exercise 2.2 Mean and variance for a discrete distribution

The sum of the numbers obtained from two dice thrown together forms a discrete triangular distribution, $P(2) = P(12) = 1/36$, $P(3) = P(11) = 2/36$, ..., $P(7) = 6/36$. Calculate the mean and variance for the distribution. Compare these values to those for a single die in Example 2.1.

2.3.2   Continuous distributions

Because most of our measurements are made on metric scales, the quantities we measure are not discrete but continuous. For example, the heights of different people vary continuously rather than taking on a finite number of fixed values. An example of a continuous distribution is shown in Figure 2.4. Because there are an infinite number of possible results the probability of any particular result is zero. Therefore we must think in terms of the probability of finding results within a range of values. Just as the total probability for the discrete distribution is 100%, the total area under the curve describing a continuous distribution is also equal to 1.0 or 100%. The curve is called the probability density function, $p(x)$. The probability of finding a result within an interval between X_1 and X_2 is given by the area under $p(x)$ between X_1 and X_2:

$$P(X_1 < x < X_2) = \int_{X_1}^{X_2} p(x)\mathrm{d}x. \tag{2.3}$$

For the *rectangular distribution* shown in Figure 2.4 the probability of finding a result x between X_1 and X_2 is

$$P(X_1 < x < X_2) = \frac{X_2 - X_1}{X_\mathrm{H} - X_\mathrm{L}}, \tag{2.4}$$

which is the ratio of the area in the interval to the total area.

For continuous distributions the mean is calculated as

$$\mu = \int_{-\infty}^{+\infty} xp(x)\mathrm{d}x, \tag{2.5}$$

and the variance is

$$\sigma^2 = \int_{-\infty}^{+\infty} (x - \mu)^2\, p(x)\mathrm{d}x. \tag{2.6}$$
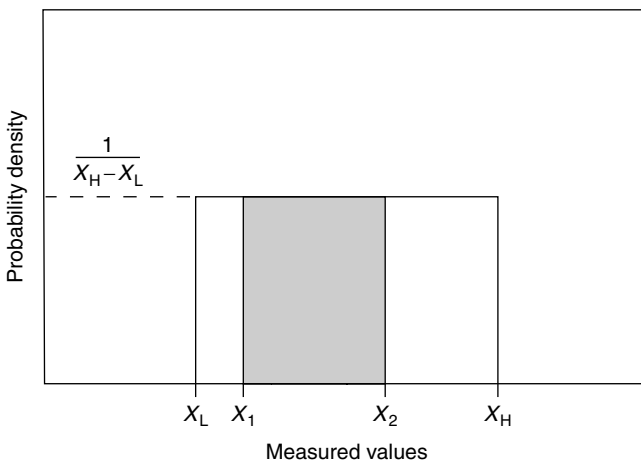
Figure 2.4   The rectangular distribution, an example of a continuous distribution

Example 2.2

Calculate the mean, variance and standard deviation of the rectangular distribution.

The probability density for the rectangular distribution is

$$
p(x) = \begin{cases} 0 & x < X_L \\ \dfrac{1}{X_H - X_L} & X_L < x < X_H \\ 0 & x > X_H. \end{cases} \tag{2.7}
$$

Hence, the mean is

$$
\mu = \frac{1}{X_H - X_L} \int_{X_L}^{X_H} x \, dx = \frac{X_H + X_L}{2}. \tag{2.8}
$$

As might be expected the mean is midway between the two extremes of the distribution.

The variance is

$$
\sigma^2 = \frac{1}{X_H - X_L} \int_{X_L}^{X_H} \left(x - \frac{X_H + X_L}{2} \right)^2 dx = \frac{(X_H - X_L)^2}{12}, \tag{2.9}
$$

and hence the standard deviation is

$$
\sigma = \frac{1}{\sqrt{3}} \frac{(X_H - X_L)}{2} \approx 0.29(X_H - X_L), \tag{2.10}
$$

from which it can be seen that the standard deviation is proportional to the width of the distribution.

The most common example of the rectangular distribution occurs with rounding or quantisation. Quantisation is the term describing the process of converting any continuous reading into a discrete number. For example, a digital thermometer with a resolution of $1\,°C$ has residual errors in the range $\pm 0.5\,°C$, with any error in the range being equally likely. If we use Δ to represent the resolution of a digital instrument ($\Delta = X_H - X_L$), then the variance of the quantisation or rounding error is, from Equation (2.9),

$$
\sigma^2 = \frac{\Delta^2}{12}. \tag{2.11}
$$

Since the mean error is zero the range of the error can be expressed as

$$
\text{range} = \pm \Delta/2 \text{ or } \pm \sqrt{3}\sigma. \tag{2.12}
$$

Quantisation occurs with both analogue and digital instruments because results are always reported to a finite number of decimal places. Although quantisation error is

introduced at least twice into most measurements, measurements are usually taken with sufficient resolution to ensure that the effects are not significant.

The rectangular distribution is a useful tool for characterising some uncertainties. Simply by assigning upper and lower limits to a quantity, we obtain a value for the mean, which may be applied as a correction, and a variance that characterises the uncertainty. This is demonstrated in Section 2.7.

2.4 The Normal Distribution

In addition to the rectangular distribution, there are a number of other continuous distributions that are useful in uncertainty analyses. The most important is called the *normal* or *Gaussian distribution* and has a probability density function given by

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right], \tag{2.13}$$

where μ and σ are the mean and standard deviation of the distribution. Figure 2.5 shows a plot of the normal probability density function. It has a bell shape indicating that results close to the mean are more likely than results further away from the mean.

As with the rectangular distribution, the probability of finding a result within an interval is proportional to the area under the curve. Unfortunately the integral in Equation (2.3) for calculating probability is rather difficult when applied to the normal distribution, so the probabilities for different intervals are commonly presented as tables like Table 2.1.

The normal distribution is useful because the distribution of many random effects added together tends to become normal. This means that many natural processes involving large numbers of effects, such as road noise in cars and temperature fluctuations due to turbulence in calibration baths, tend to have a normal distribution.

Figure 2.5   The normal or Gaussian probability distribution

Table 2.1   Area under the normal probability distribution

The percentage probability of finding
x within $\mu \pm k\sigma$

$\mu-k\sigma$ μ $\mu+k\sigma$

k	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.00	0.80	1.60	2.39	3.19	3.99	4.78	5.58	6.38	7.17
0.1	7.97	8.76	9.55	10.34	11.13	11.92	12.71	13.50	14.28	15.07
0.2	15.85	16.63	17.41	18.19	18.97	19.74	20.51	21.28	22.05	22.82
0.3	23.58	24.34	25.10	25.86	26.61	27.37	28.12	28.86	29.61	30.35
0.4	31.08	31.82	32.55	33.28	34.01	34.73	35.45	36.16	36.88	37.59
0.5	38.29	38.99	39.69	40.39	41.08	41.77	42.45	43.13	43.81	44.48
0.6	45.15	45.81	46.47	47.13	47.78	48.43	49.07	49.71	50.35	50.98
0.7	51.61	52.23	52.85	53.46	54.07	54.67	55.27	55.87	56.46	57.05
0.8	57.63	58.21	58.78	59.35	59.91	60.47	61.02	61.57	62.11	62.65
0.9	63.19	63.72	64.24	64.76	65.28	65.79	66.29	66.80	67.29	67.78
1.0	68.27	68.75	69.23	69.70	70.17	70.63	71.09	71.54	71.99	72.43
1.1	72.87	73.30	73.73	74.15	74.57	74.99	75.40	75.80	76.20	76.60
1.2	76.99	77.37	77.75	78.13	78.50	78.87	79.23	79.59	79.95	80.29
1.3	80.64	80.98	81.32	81.65	81.98	82.30	82.62	82.93	83.24	83.55
1.4	83.85	84.15	84.44	84.73	85.01	85.29	85.57	85.84	86.11	86.38
1.5	86.64	86.90	87.15	87.40	87.64	87.89	88.12	88.36	88.59	88.82
1.6	89.04	89.26	89.48	89.69	89.90	90.11	90.31	90.51	90.70	90.90
1.7	91.09	91.27	91.46	91.64	91.81	91.99	92.16	92.33	92.49	92.65
1.8	92.81	92.97	93.12	93.28	93.42	93.57	93.71	93.85	93.99	94.12
1.9	94.26	94.39	94.51	94.64	94.76	94.88	95.00	95.12	95.23	95.34
2.0	95.45	95.56	95.66	95.76	95.86	95.96	96.06	96.15	96.25	96.34
2.1	96.43	96.51	96.60	96.68	96.76	96.84	96.92	97.00	97.07	97.15
2.2	97.22	97.29	97.36	97.43	97.49	97.56	97.62	97.68	97.74	97.80
2.3	97.86	97.91	97.97	98.02	98.07	98.12	98.17	98.22	98.27	98.32
2.4	98.36	98.40	98.45	98.49	98.53	98.57	98.61	98.65	98.69	98.72
2.5	98.76	98.79	98.83	98.86	98.89	98.92	98.95	98.98	99.01	99.04
2.6	99.07	99.09	99.12	99.15	99.17	99.20	99.22	99.24	99.26	99.29
2.7	99.31	99.33	99.35	99.37	99.39	99.40	99.42	99.44	99.46	99.47
2.8	99.49	99.50	99.52	99.53	99.55	99.56	99.58	99.59	99.60	99.61
2.9	99.63	99.64	99.65	99.66	99.67	99.68	99.69	99.70	99.71	99.72
3.0	99.73	—	—	—	—	—	—	—	—	—
3.5	99.95	—	—	—	—	—	—	—	—	—
4.0	99.994	—	—	—	—	—	—	—	—	—
4.5	99.9993	—	—	—	—	—	—	—	—	—
5.0	99.99994	—	—	—	—	—	—	—	—	—

Similarly, whenever we calculate averages or collect and sum uncertainties we can, with some justification, assume that the resulting distribution is normal.

Example 2.3

Using Table 2.1, which tabulates the area under the normal distribution, determine the percentage of measurements that fall within $\pm 1\sigma$, $\pm 2\sigma$ and $\pm 3\sigma$ of the mean.

Table 2.1 lists the probability that the result lies within k standard deviations of the mean. Using the values for $k = 1$, 2, and 3 we find that

> 68.27% of measurements lie within $\pm 1\sigma$ of the mean,
> 95.45% of measurements lie within $\pm 2\sigma$ of the mean,
> 99.73% of measurements lie within $\pm 3\sigma$ of the mean.

With a little approximation and rewording these rules are easy to remember and provide useful rules of thumb that help develop an intuitive sense of the shape of the distribution:

> 1 in 3 measurements lie outside $\mu \pm 1\sigma$,
> 1 in 20 measurements lie outside $\mu \pm 2\sigma$,
> almost no measurements lie outside $\mu \pm 3\sigma$.

Exercise 2.3

Using the normal probability table (Table 2.1), characterise the ranges containing 50%, 95% and 99% of measurements.

2.5 Experimental Measurements of Mean and Variance

In most practical cases it is not possible to know the limiting distribution of measurements, so it is not possible to calculate exact values of the mean μ and variance σ^2. The alternative is to estimate them from a set of measurements. The best estimate of the mean of the distribution is the arithmetic mean, m:

$$m = \frac{1}{N} \sum_{i=1}^{N} X_i, \tag{2.14}$$

where X_i are the N measurements of x. The best estimate of the variance is called the experimental or sample variance, s^2:

$$s^2 = \frac{1}{N-1} \sum_{i=1}^{N} (X_i - m)^2, \tag{2.15}$$

where s is the experimental standard deviation. Equations (2.14) and (2.15) apply to both discrete and continuous distributions. The Latin symbols m and s^2 are used to distinguish the experimental values from those based on theory and given by the Greek symbols μ and σ^2.

Example 2.4

Calculate the mean and variance of the 20 measurements compiled in Figure 2.2. These are 6.6, 6.5, 7.0, 6.4, 6.5, 6.3, 6.6, 7.0, 6.5, 6.5, 6.3, 6.0, 6.8, 6.5, 5.7, 5.8, 6.6, 6.5, 6.7, 6.9.

The measurements constitute the readings X_i. We note first that many of the measurements are the same so that many terms of Equations (2.14) and (2.15) are the same. To simplify the calculations the readings are arranged in ascending order and tabulated using f, the frequency of occurrence for a given reading, as seen in the first three columns of the table below. As a check, the sum of the frequencies should equal the number of measurements.

Results X_i	Frequency f_i	$f_i X_i$	Deviation $(X_i - m)$	$(X_i - m)^2$	$f_i(X_i - m)^2$
5.7	1	5.7	−0.785	0.616	0.616
5.8	1	5.8	−0.685	0.469	0.469
5.9	0				
6.0	1	6.0	−0.485	0.235	0.235
6.1	0				
6.2	0				
6.3	2	12.6	−0.185	0.034	0.068
6.4	1	6.4	−0.085	0.007	0.007
6.5	6	39.0	+0.015	0.000	0.000
6.6	3	19.8	+0.115	0.013	0.039
6.7	1	6.7	+0.215	0.046	0.046
6.8	1	6.8	+0.315	0.099	0.099
6.9	1	6.9	+0.415	0.172	0.172
7.0	2	14.0	+0.515	0.265	0.530
Totals	**20**	**129.7**			**2.281**

The mean m is then determined:

$$m = \frac{1}{N} \sum f_i X_i = \frac{129.7}{20} = 6.485.$$

Note that the mean is written here with three decimal places while the original readings have only one decimal place. Guidelines on rounding and presentation of results are described in Section 2.14.

Once the mean has been calculated, the last three columns of the table can be filled in and the variance calculated as

$$s^2 = \frac{1}{N-1} \sum f_i(X_i - m)^2 = \frac{2.281}{19} = 0.120.$$

Hence the standard deviation, the square root of the variance, is $s = 0.346$.

Because m and s are experimental estimates of the true mean and variance, repeat measurements yield slightly different values each time. The distributions of the values for the mean and variance depend purely on the variance of the parent distribution and the number of measurements used in the calculation. The experimental mean of a set of N independent measurements is distributed with a variance

$$\sigma_m^2 = \frac{\sigma^2}{N}. \tag{2.16}$$

Similarly, the sample variance is distributed with a variance of

$$\sigma_{s^2}^2 = \frac{2\sigma^4}{N-1}, \tag{2.17}$$

where σ^2 is the variance of the parent distribution. Equation (2.16) shows that the experimental mean of two or more measurements is a better estimate of μ than a single measurement, and the more measurements used in the calculation of the mean the better. Since we don't know the actual value for the true variance, we can estimate the variance in the experimental mean by substituting s^2 for σ^2:

$$s_m^2 = \frac{s^2}{N} = \frac{1}{N(N-1)} \sum_{i=1}^{N} (X_i - m)^2. \tag{2.18}$$

Example 2.5

Calculate the distribution of the mean for 10 throws of a die.

Figure 2.6 shows the distribution of the mean for 10 throws of a die. Two histograms are shown, one for a numerical simulation of 300 measurements of the mean, and one for the theoretical distribution. The figure highlights several interesting points. Both distributions have an overall appearance almost indistinguishable from the normal distribution, and much different from the parent distribution for a single die (Figure 2.3). This illustrates the tendency for sums of random measurements to approach the normal distribution. Secondly, the variance is one-tenth of the variance for a single throw, as expected from Equation (2.16), so the distribution is narrower than the parent distribution. Finally, the distribution is still a discrete distribution, the possible outcomes
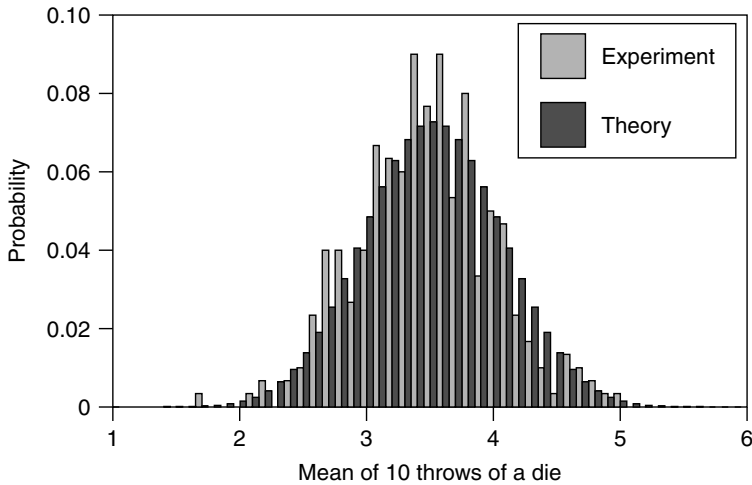
Figure 2.6   The distribution of the mean of 10 throws of a die

of the experiment are 0.1 apart (since we are averaging the results from 10 dice), and the total probability (area under the curve) is 100%.

Exercise 2.4

Calculate the mean and standard deviation for the following 12 measurements in degrees Celsius of the freezing point of indium:

156.5994	156.5988	156.5989	156.5991	156.5995	156.5990
156.5989	156.5989	156.5986	156.5987	156.5989	156.5984

[Hint: To simplify the averaging calculation, consider only the last two digits of each number: 94, 88, etc. The final mean is calculated as the mean plus 156.590, while the standard deviation and variance are unchanged.]

2.6 Evaluating Type A Uncertainties

Figure 2.7 shows the histogram of Figure 2.2 overlaid with a normal distribution with the same mean and variance. Although the histogram is very different from the normal distribution in appearance, it obeys rather closely the three distribution rules that we gave with Example 2.3.

Since the standard deviation is proportional to the width this suggests that we should use it to characterise the dispersion of the measurements. There are two cases to consider.
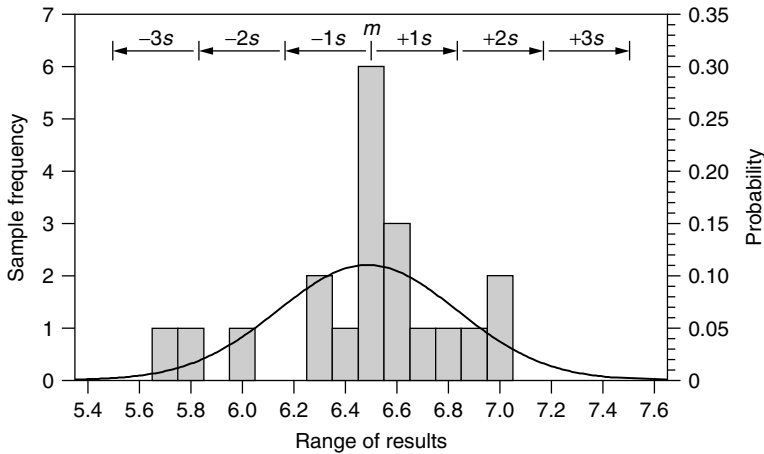
Figure 2.7   Histogram of Figure 2.2 with corresponding normal distribution overlaid

2.6.1   Evaluating uncertainties of single-valued quantities

Often the value we seek is affected by purely random fluctuations such as electrical or mechanical noise. The conventional method of reducing noise is to apply a filter or some sort of damping to reduce the fluctuations. The process of calculating a mean has the same effect on the noise as a filter does, and Equation (2.16) for the variance in the mean shows that the uncertainty due to the noise is reduced by the factor $1/\sqrt{N}$, where N is the number of measurements contributing to the mean. An advantage of using a mean value rather than a filter is that we can estimate the uncertainty due to the remaining noise in the average value. Accordingly, the measurement can be reported as the mean with an uncertainty given by

$$\text{uncertainty} = s_m \qquad (2.19)$$

An uncertainty expressed using the standard deviation in this way is known as the *standard uncertainty*. Uncertainties in the scientific literature are very commonly reported as the standard uncertainty and may be referred to as the *one-sigma* uncertainty. However, the range characterised by the standard deviation typically includes only 68% of all measurements, and there are many measurements in the test and calibration environment requiring uncertainties that include a higher percentage of measurements.

Where higher confidence is required results are reported with an *expanded uncertainty*:

$$\text{uncertainty} = k \times s_m, \qquad (2.20)$$

where k is a multiplying factor that increases the range to include a greater proportion of the measurements. The k factor, known as the *coverage factor*, is chosen so that the range or *confidence interval* includes a prescribed percentage of the measurements.

Approximate values for the coverage factor can be determined from the normal probability table (Table 2.1). For example, a value of $k = 1.96$ would characterise the

uncertainty by a confidence interval that is expected to include 95% of all results. The statement 'expected to include 95% of the measurements' states the *level of confidence* for the uncertainty. Note that k has to be large to include all measurements. In practice, there is a compromise, and $k = 2$ (∼95%) and $k = 3$ (∼99%) are common choices.

However, coverage factors derived from the normal distribution are approximate and usually underestimate the uncertainty. When we use the normal probability tables, we assume that we know the mean and variance exactly. Equations (2.16) and (2.17), for the variance in the experimental mean and variance, show that the picture of the distribution derived from measurements is itself uncertain. This means that we cannot be as confident as the normal probability tables imply. The way to remedy this loss of confidence is to increase the coverage factor to account for the higher uncertainty. But by how much must the coverage factor be increased?

2.6.2   The Student's *t*-distribution

To account for the uncertainty in the experimental mean and variance, coverage factors should be found from a special distribution known as the *Student's t-distribution*. The tables for this distribution are similar to normal probability tables except that they depend also on the number of measurements. Actually the third parameter is ν (Greek symbol nu), the *number of degrees of freedom*. This can be thought of as the number of pieces of information used to calculate the variance. Where N measurements are used to calculate a mean there are $N - 1$ degrees of freedom. Effectively, one piece of information is used to calculate the mean, so there are $N - 1$ pieces left. This explains the $N - 1$ in the denominator of Equation (2.15).

Figure 2.8 illustrates the Student's *t*-distribution for several values of ν. The most important feature of the curves is the very long tails on the distributions for low values of ν (few measurements). In order to establish a given level of confidence, the coverage factors for the longer-tailed distributions must be larger in order to enclose the same area, or equivalently to have the same level of confidence. The distribution
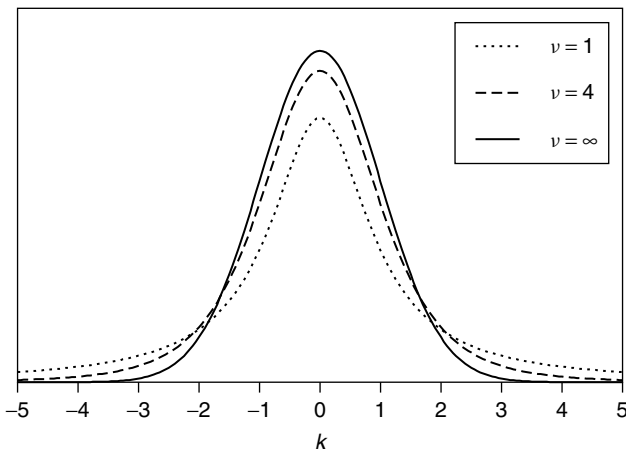
Figure 2.8   The Student's *t*-distribution for different values of ν, the number of degrees of freedom. Note the long tails on the distributions for small values of ν

becomes more and more like the normal distribution as the number of degrees of freedom increases. For an infinite number of degrees of freedom the normal distribution and Student's t-distribution are identical.

Example 2.6

Determining confidence intervals with Student's t-tables.

Using Table 2.2, which tabulates the area under the Student's t-distribution, calculate the coverage factor for a 95% confidence interval for a mean result determined from six measurements.

By looking up the entry for $P = 95.0\%$ and $N = 6$ ($v = 5$) we find that $k = 2.57$. That is, we expect 95% of measurements to lie within $m \pm 2.57 s_m$.

Close inspection of Table 2.2 shows that the largest values of k occur at the top right-hand corner of the table; that is, the uncertainty is largest for small numbers of measurements and high confidence. These are situations to be avoided in practice if

Table 2.2   The Student's t-distribution: values of k for specified level of confidence, P, as a function of the number of degrees of freedom, v. Where N measurements are used to determine ρ parameters, the number of degrees of freedom is $v = N - \rho$

P is the percentage probability of finding μ within $m \pm k s_m$
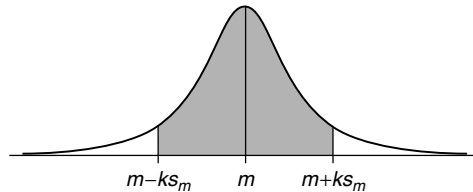
v\\P	50%	68.3%	95.0%	95.5%	99.0%	99.7%
1	1.000	1.84	12.7	14.0	63.7	236
2	0.817	1.32	4.30	4.53	9.92	19.2
3	0.765	1.20	3.18	3.31	5.84	9.22
4	0.741	1.14	2.78	2.87	4.60	6.62
5	0.727	1.11	2.57	2.65	4.03	5.51
6	0.718	1.09	2.45	2.52	3.71	4.90
7	0.711	1.08	2.36	2.43	3.50	4.53
8	0.706	1.07	2.31	2.37	3.36	4.28
9	0.703	1.06	2.26	2.32	3.25	4.09
10	0.700	1.05	2.23	2.28	3.17	3.96
11	0.697	1.05	2.20	2.25	3.11	3.85
12	0.695	1.04	2.18	2.23	3.05	3.76
13	0.694	1.04	2.16	2.21	3.01	3.69
14	0.692	1.04	2.14	2.20	2.98	3.64
15	0.691	1.03	2.13	2.18	2.95	3.59
16	0.690	1.03	2.12	2.17	2.92	3.54
17	0.689	1.03	2.11	2.16	2.90	3.51
18	0.688	1.03	2.10	2.15	2.88	3.48
19	0.688	1.03	2.09	2.14	2.86	3.45
∞	0.675	1.00	1.96	2.00	2.58	3.00

relatively small uncertainties (low risk) are required. A reasonable compromise must be reached between the desire for higher confidence and the need for the number of measurements to be practical, and for many cases a 95% level of confidence is considered acceptable. The 95% confidence level requires five or more measurements to keep k to values less than 3.0, and the typical coverage factor is commonly in the range 2.2 to 2.5. The 95% level of confidence is becoming the preferred option for characterising uncertainties in a lot of non-scientific reporting.

2.6.3   Evaluating uncertainties for distributed quantities

When we use the standard deviation of the mean, s_m, to characterise uncertainty, we are assuming that the quantity of interest has a single well-defined value. For measurements made in the calibration laboratory, this is often a good approximation, especially for artefact standards like standard resistors, standard weights and gauge blocks. However, when measuring the performance of measuring instruments and objects outside the calibration laboratory the quantities of interest are often not single valued but distributed.

    Let us consider two examples in order to highlight the distinction. We will use the same data for both.

Case 1

Suppose the hypothetical data of Figure 2.9 shows the measured value of temperature error of a liquid-in-glass thermometer versus time as measured at one temperature in an unstable calibration bath. The temperature fluctuations in the bath are responsible for the dispersion of the measurements. If we assume that the fluctuations are purely random and on average do not bias the measured temperature error, we can average the results to improve the estimate of the correction. The uncertainty in the correction
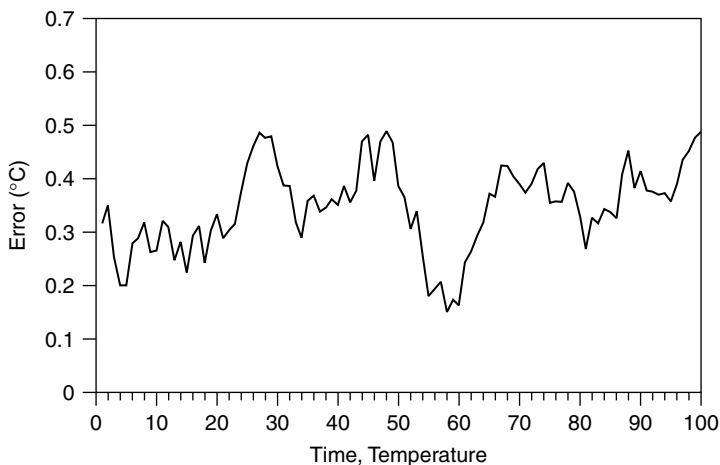
Figure 2.9   Random variations in temperature error

is related to the standard deviation of the mean, s_m, and is calculated following the procedure given in Sections 2.6.1 and 2.6.2 above.

Case 2

Suppose now that Figure 2.9 shows the measured value of the temperature error of a liquid-in-glass thermometer versus temperature reading. The dispersion in the temperature error is due to unpredictable variations in the diameter of the capillary and small misplacements of the scale markings. In this case the correction has many different values depending on the thermometer reading, and over a range of temperatures no single value of the correction will completely eliminate the systematic error. However, we can choose a mean value for the correction that will substantially reduce the error over a range of temperatures. In this case the uncertainty in the correction is better characterised by the experimental standard deviation, s. Actually, the uncertainty in this case, where the quantity of interest is distributed, depends on two factors: the uncertainty in the estimate of the mean correction, and the dispersion of the remaining systematic error. The sum of these two uncertainties leads to a standard uncertainty $(1 + N)^{1/2}$ times larger than for a single valued quantity (see Exercise 2.8 for an explanation). Accordingly, the results would be expressed as

$$\text{result} = m \pm \left(1 + \frac{1}{N}\right)^{1/2} s. \tag{2.21}$$

The same measurement with an expanded uncertainty would be reported as

$$\text{result} = m \pm k \left(1 + \frac{1}{N}\right)^{1/2} s, \tag{2.22}$$

where the coverage factor k is determined from the Student's t-distribution.

The measurements of the temperature of the petrochemical reactor in Figure 2.1 are another example of a distributed quantity because the temperature is not single valued but different at different points within the reactor. In this case, as with many examples of distributed quantities, the reactor can be modelled by many small subsections each at a temperature that may be considered to be single valued. However, measuring every temperature and modelling the behaviour of a large collection of subsections may not be practical. Very often, as with the thermometer calibration considered above, most of the benefits of the measurement can be gained by treating the quantity as distributed.

Exercise 2.5

A client asks you to measure the mean value of a quantity and asks for a 99% confidence interval with a coverage factor of no more than 3.0. How many measurements must you make?

2.7 Evaluating Type B Uncertainties

Type B uncertainties are those determined by other than statistical means. Evaluations can be based on theoretical models of the measurement, information from handbooks and data sheets, the work of other experimenters, calibration certificates, even intuition and experience. The need to estimate Type B uncertainties arises when single measurements are made, and commonly when corrections are applied to eliminate known errors.

As with Type A uncertainties the key is to build up a picture of the appropriate distribution. The assessment process has five main stages:

(1)   Identify the influence effect.
(2)   Collect information on the effect.
(3)   Describe the effect in terms of a distribution.
(4)   Determine a mean and variance for the distribution.
(5)   Calculate the confidence interval.

The first stage, identifying the effect that biases or causes dispersion of the readings, is often the most difficult. For the thermometers discussed in this book we have catalogued the most significant effects, so for much of your work this should not be too difficult. In the next section we give some specific guidelines that may help to identify effects for other measurement problems.

Once the influences have been identified collect as much information and advice as is available. This may involve information in data sheets, manufacturers' specifications, physical models of the effect, results from related measurements, or simply experience. Subsidiary measurements that vary the experimental conditions can be useful. This stage is analogous to the collection of measurements in the Type A evaluation.

Based on this information, develop a picture of the distribution. If the effect causes a random error then the distribution characterises the range of the error. If the error is systematic then the distribution characterises our ignorance: the range that we believe the error is likely to lie within. Approximate the distribution by one of the known distributions, such as the normal or rectangular distributions. In some cases there may be sufficient information to identify the real distribution, which may be of another kind, such as Poisson, binomial or chi-square (see the references at the end of the chapter). The use of a Student's t-distribution can be useful to characterise the uncertainty in the description of the distribution. If we are prepared to estimate an uncertainty in the uncertainty for a Type B assessment we can use the *effective number of degrees of freedom*:

$$\nu_{\text{eff}} = \frac{1}{2} \left[\frac{U}{U_{\text{U}}} \right]^2 , \tag{2.23}$$

where U is the uncertainty derived from the Type B assessment and U_{U} is an estimate of the uncertainty in the uncertainty. Equation (2.23) is a rearrangement and approximation of Equation (2.17) for the Type A uncertainties.

Once the distribution is described, the mean and standard deviation for the distribution are calculated. The mean may be used to make a correction and the standard deviation to characterise the uncertainty in the corrected measurements.

Finally, and most importantly, record all of the assumptions and the reasoning leading to the estimates so that the rationale is clear and unambiguous. This is compulsory in some QA systems. The record ensures that the evaluation can be audited if necessary (i.e. it is traceable), and can be improved at a later date as new information or expertise becomes available.

When you finish your assessment you should be comfortable with the result. To quote one metrologist, 'The experimenter must recognise that he is quoting betting odds . . . . If he has formed his uncertainty estimate honestly, avoiding both undue optimism and undue conservatism, he should be willing to take both sides of the bet.'

In Sections 2.7.2 to 2.7.5 we provide specific guidelines and examples of Type B assessments, but first we give guidelines on how to identify influences.

2.7.1   Identification and recording of influences

Identification of the influence effects is difficult but is often made easier with a model of the measurement. Figure 2.10 shows a very general model of a temperature measurement. Before measurements are made, time should be spent assembling a detailed model for your particular measurement and thinking about the physical processes occurring in and between each block of the model. Imperfections in a process, or external influences on a process, usually give rise to errors and, in turn, to uncertainty. Clues to the nature of influence effects can often be obtained from manufacturers' specifications, handbooks, application notes, related documentary standards, textbooks and local experts. However, there is no guaranteed method for identifying all sources of error. At best, one can explore various models of the measurement and research other workers' approaches to the measurement.

In addition to the identification of the influence effects we must also ascertain the reliability of the information we have. Manufacturers' specifications are a good case in point. While the specifications are amongst the most useful tools for identifying influence effects, we have to remember that manufacturers tailor the specifications to present their instruments in the best light. There are occasions when manufacturers hide weaknesses by specifying under tight conditions or simply omitting the relevant
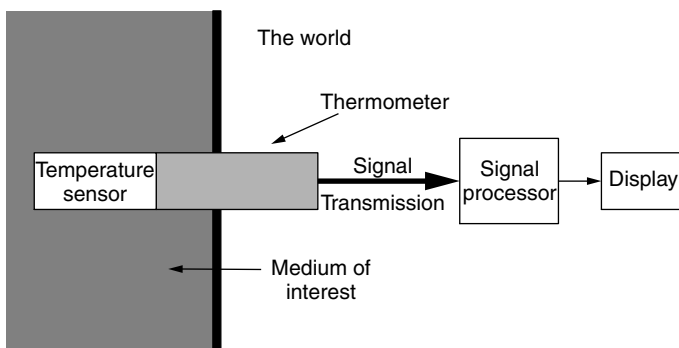
Figure 2.10   A general model of a temperature measurement. Consideration of the processes in and between the various blocks of the model often exposes potential for errors
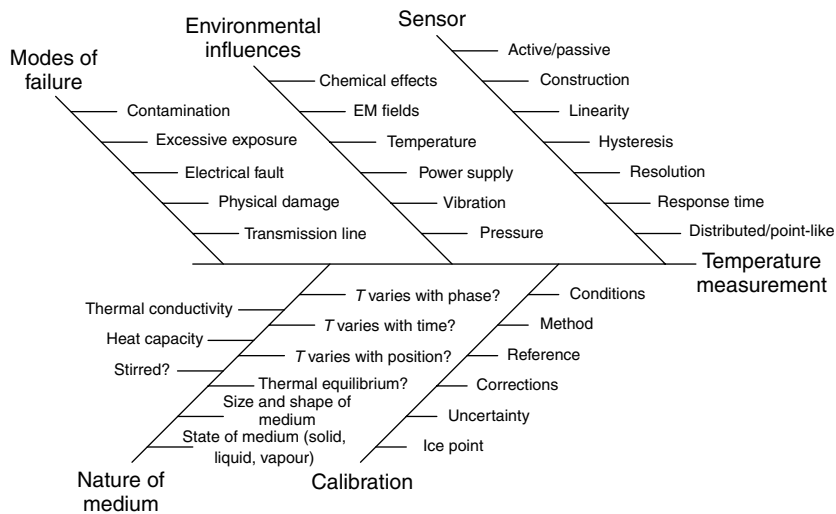
Figure 2.11   A general cause and effect diagram for temperature measurement. Cause and effect diagrams are a convenient way of recording and summarising influence effects

specification. For this reason always look at the specifications of competing instruments from different manufacturers. Finally, remember that the experience of most calibration laboratories is that about one in six of all instruments performs outside the manufacturer's specification, and complex or multi-range instruments are nearly always outside the specification at some point in their range.

Once influence variables have been identified they should be recorded. Figure 2.11 shows an example of a cause and effect diagram, a very convenient way of recording influence factors. The label on the trunk of the diagram should address the purpose of the measurement, and the main branches should group all similar influences and effects together. The sub-branches list each of the influence variables, and in some cases may have twigs listing influences on the influences. Although not shown on the diagrams presented here, it is also usual to indicate (often with dotted lines) the links between causes and effects. Examples might include vibration and physical damage, temperature variations with time constant effects, and size of the medium with immersion effects.

2.7.2   Theoretical evaluations

The most reliable assessments of uncertainty are based on models that are well established and understood. There are two broad classes of theoretical assessment. The most common class includes systematic effects where the underlying theory is well known: for example, pressure effects on the boiling and freezing points of substances, reflection errors in radiation thermometry, and stem corrections for liquid-in-glass thermometers. These often involve very simple models with accurate values for parameters obtained from other sources.

The second class is less common and involves effects that contribute purely random error to a measurement. Examples include phenomena involving counting of discrete

events such as blood counts, the throw of dice, political polls, radioactivity, and a number of thermal noise phenomena associated with dissipation, for example electrical resistance, viscosity and friction. In thermometry the effects are generally small and so only affect the most precise measurements such as those employing radiation thermometers and resistance thermometers.

Example 2.7

Investigate the variation in the boiling point of water with atmospheric pressure and altitude.

Many people who marvel at the simplicity and accuracy of the ice point as a temperature reference expect the boiling point of water to be as good. Unfortunately the boiling point of water makes a better altimeter than a fixed point (see also Section 3.2.2).

The vapour pressure of a fluid depends on temperature according to

$$p = p_0 \exp\left(\frac{L_0}{RT_0} - \frac{L_0}{RT}\right), \tag{2.24}$$

where L_0 is the latent heat of vaporisation for the liquid, p_0 is standard atmospheric pressure (101.325 kPa), T_0 is the normal boiling point of the liquid, and R is the gas constant ($\sim 8.3143\,\mathrm{J\,mol^{-1}\,K^{-1}}$). The atmospheric pressure varies with altitude x, approximately, according to a similar equation

$$p = p_0 \exp\left(\frac{-Mgx}{RT_a}\right), \tag{2.25}$$

where M is the molar mass of the atmosphere ($\sim 29\,\mathrm{g}$), g is the gravitational acceleration, and T_a is the temperature of the atmosphere. Since boiling occurs when the two pressures are equal we can combine the equations to yield an expression for the boiling point as a function of altitude:

$$T = T_0 \left[1 + x\frac{Mg}{L_0}\frac{T_0}{T_a}\right]^{-1}. \tag{2.26}$$

For water the sensitivity of the boiling point to altitude is very high, about $-2.8\,\mathrm{mK\,m^{-1}}$ or about $-1\,^\circ\mathrm{C}$ for each 355 m. Indeed a boiling point apparatus, or hypsometer (Greek for height measurer), was carried by many early explorers and surveyors to help them determine altitude.

Fluctuations of atmospheric pressure with changes in the weather also affect the boiling point. The pressure fluctuations represent a random error with a standard deviation of about 1.4 kPa. Since, at sea level, the sensitivity of the boiling point to pressure changes is about $0.28\,^\circ\mathrm{C\,kPa^{-1}}$, the uncertainty in the boiling point due to the fluctuations is about $\pm 0.8\,^\circ\mathrm{C}$.

As a temperature standard, a hypsometer is not very useful. A correction must be made for altitude, and the combination of the uncertainty in the altitude effect and daily pressure fluctuations due to the weather make for a total uncertainty typically greater than $\pm 1\,°\mathrm{C}$.

Example 2.8

Investigate the effects of Johnson noise on a resistance measurement.

Every resistor generates a random noise voltage, called Johnson noise, that is proportional to the resistor temperature T, resistance R and the bandwidth of the voltage measuring system Δf. The variance of the noise voltage is

$$\sigma_\mathrm{v}^2 = 4kTR\Delta f, \tag{2.27}$$

where k is Boltzmann's constant ($\sim 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$). For a resistance of $100\,\Omega$, at a temperature of $300\,\mathrm{K}$ and a voltage measuring system with a bandwidth of $1\,\mathrm{kHz}$, the noise contributes a standard deviation of about $40\,\mathrm{nV}$ to the measurement. The maximum sensitivity for a platinum resistance measurement is about $0.4\,\mathrm{mV\,°C^{-1}}$, so the noise from the resistor gives rise to a temperature uncertainty of about $100\,\mu\mathrm{K}$ (1σ). Johnson noise is one of the factors limiting the resolution of all resistance measurements. In practice there are usually several terms of this form due to other components in the bridge, including the reference resistor and amplifiers. This is an example of a Type B evaluation of a purely random effect.

2.7.3 Evaluations based on single subsidiary measurements

In many cases theory alone is not sufficient, often because some of the constants in the equations are not well known, or perhaps the theory is only very approximate. In these cases a single simple measurement can provide a good indicator of the magnitude of the effect. Single-measurement experiments are particularly useful for exposing and evaluating sensitivities to influences such as pressure, temperature and line voltage.

Example 2.9

Assess the self-heating in a platinum resistance thermometer.

When resistance thermometers are used a sensing current is passed through the resistor. The resulting power dissipation in the sensing element causes it to be at a slightly higher temperature than its surrounds. This effect is known as self-heating (see Section 6.5.4). It is assumed that the magnitude of the

temperature rise is proportional to the power dissipated:

$$\Delta T_{\mathrm{m}} = R(t)I^2/h,$$

where h is the thermal resistance between the sensing element and its surrounds. Experience tells us that this equation is quite good, but the thermal resistance depends on both the construction of the probe and the immediate environment around the probe. Consequently we cannot use the equation to correct the measurement unless we have a realistic value for h.

A single measurement of the effect at each of two currents provides the means to measure h and to extrapolate to zero current to correct for the systematic effect (see Section 6.5.4). This is a Type B assessment of a systematic error. A common assumption is that simple evaluations of corrections are only accurate to about 10%; therefore we could assume that the uncertainty in the correction is at most 10% and distributed according to a rectangular distribution. Equation (2.12) then provides us with a measure of the uncertainty.

If several measurements of the effect were made then the mean value could be used as the correction and the standard deviation of the mean as the uncertainty in the correction. This would be a Type A assessment of a systematic error. Note that whether one or several measurements are made, assumptions are also made that lead to the model of the self-heating effect. For the Type B evaluation we also make an assumption about the accuracy of the correction.

Resistance thermometers are usually calibrated in a well-stirred bath which keeps the thermal resistance low, so that the self-heating is typically only a few millikelvins. Also in most applications the self-heating is similar to that in calibration so that negligible error occurs. However, for some measurements, notably air-temperature measurements, the self-heating effect can be as high as several tenths of a degree. The effect is therefore an important source of error in an air-temperature measurement.

Example 2.10

Describe a method for evaluating the uncertainty due to hysteresis.

Hysteresis is a phenomenon that causes the readings of an instrument to depend on previous exposure or use, as shown Figure 2.12. The main feature of the graph is the loop in the thermometer characteristic as it is cycled with temperature. This means, for example, that any given thermometer reading (R in Figure 2.12) can be associated with a range of temperatures. With no information on the previous history of the use of the thermometer the best representation of the temperature is a rectangular distribution covering the range T_1 to T_2.
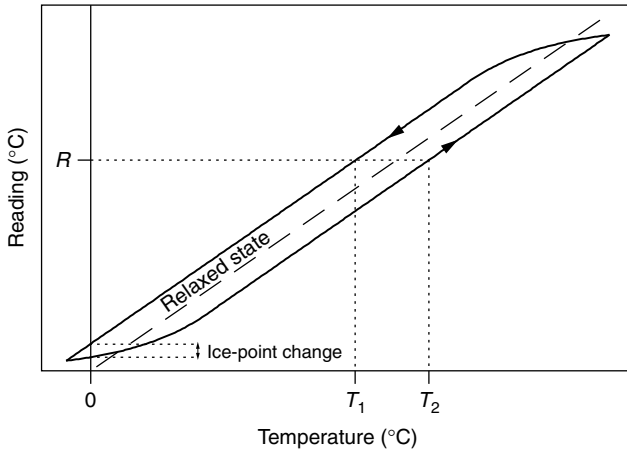
Figure 2.12   Hysteresis errors in thermometry. For most thermometers the reading depends on the previous exposure of the thermometer to different temperatures. The 'relaxed state' is the curve the thermometer will return to if it is maintained at a stable temperature for a period of time

The evaluation of the hysteresis error is complicated by relaxation. If the thermometer is left at a particular temperature for long enough it will relax towards the line labelled 'Relaxed state' in Figure 2.12; that is, it will gradually 'forget' the previous exposure. To measure temperatures reliably with a smaller uncertainty than is indicated by the rectangular distribution, the measurement and calibration procedures must control the range, the history and the duration of the measurements. These procedures are generally impractical, but for some instruments, such as load cells, the procedures are necessary to obtain useful accuracy.

Calibrating the thermometer in both directions and directly measuring the width of the hysteresis loop would provide an assessment of the uncertainty associated with any reading. This would be a Type A assessment, but involves measuring every calibration point twice, once with rising temperature and once with falling temperature. A less expensive procedure that also affords some reduction in the uncertainty is to use the thermometer only to measure temperatures in ascending order for temperatures above room temperature and in descending order for temperatures below room temperature. This ensures that only the portion of the hysteresis on one side of the relaxed-state line is relevant, thereby halving the uncertainty. In this case, as shown in Figure 2.12, the uncertainty can be assessed from the change in the ice-point reading before and after exposure to higher temperatures.

The simplest approach is to make two assumptions and design the calibration accordingly. Firstly, the calibration is carried out slowly so the thermometer

is partially relaxed and therefore the reading corresponds to the mean of the distribution (so no correction need be applied). Secondly, assume that the rectangular distribution is an appropriate description of the likely difference between hysteresis under the calibration conditions and the conditions in use. Therefore, for a change in ice-point reading of $0.3\,°C$, we apply Equation (2.10) for the standard deviation of the rectangular distribution, and infer that the standard uncertainty in the reading is estimated as $0.087\,°C$.

The ice point may not be the best temperature at which to sample the width of the hysteresis loop, since it is often at the end of a thermometer's range. A separate measurement midway through the thermometer's range may be better.

2.7.4 Evaluations based on data provided from other sources

In many cases the influences are known but not well enough for a model, and the effort involved in subsidiary experiments may be prohibitive. In these cases we commonly have to rely on information or advice from others. Such information may come from manufacturers' data sheets, handbooks and application notes, reference data, textbooks, and reports from other workers. The main difficulty in these cases is the reliability of the data.

Example 2.11

Describe an assessment of self-heating based on manufacturers' specifications.

Example 2.9 suggested a way of measuring the self-heating of resistance thermometers in use. However, if the measuring instrument does not have the facility to change the sensing current, the measurement is not possible. One option is to use manufacturers' data sheets. Based on a couple of manufacturers' data sheets it is found that the self-heating varies between $50\,mK$ and at most $500\,mK$, so that it positively biases the measurement. The distribution of the likely error can then be approximated by a rectangular distribution with upper and lower limits of $0.50\,°C$ and $0.05\,°C$. The correction is therefore estimated to be $-0.27\,°C$ (Equation (2.8)), and the standard uncertainty (Equation (2.10)) is $0.13\,°C$.

Example 2.12

Estimate the standard uncertainty using a calibration certificate giving only the expanded uncertainty.

A calibration certificate states that the uncertainty in a thermometer correction is $0.15\,°C$ at a 95% level of confidence. What is the standard uncertainty? Contrary

to the guidelines given in Section 5.4.5, many calibration certificates do not supply enough information to determine the standard uncertainty, thus making some uncertainty calculations a little difficult. In this case we must estimate a value for the coverage factor, and therefore make some assumptions about the uncertainty evaluation. In many European countries the coverage factor is dictated by the accreditation organisations to be 2.0. In that case the standard uncertainty is 0.075 °C. In many other countries (but not all) the accreditation organisations require a true estimate of the 95% confidence interval. In these cases the coverage factor is likely to be between 2.2 and 2.5, and for thermometers is most likely to be nearer the higher value. Thus we could assume a coverage factor of 2.5 and determine that the standard uncertainty is 0.06 °C.

Example 2.13   Assessment of uncertainty due to drift with time

Figure 2.13 shows the change in corrections for an electronic reference thermometer at 0 °C and 160 °C recorded from eight calibrations over a period of 12 years. Estimate the corrections and extra uncertainty due to drift in the thermometer readings for measurements made 4 years after the last calibration.

Platinum resistance thermometers (see Chapter 6) tend to exhibit a steady temperature-independent increase in resistance with time, with the rate of increase depending on the vibration and mechanical shock incurred during use. With the exception of the first 3 years the thermometer in this example also
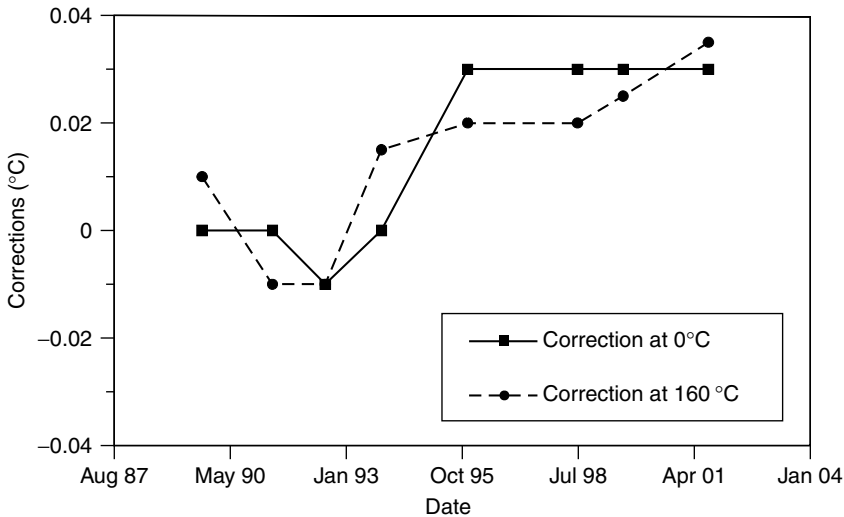
Figure 2.13   A control chart for an electronic reference thermometer. Corrections at 0 °C and 160 °C are plotted versus calibration date. The instrument has a resolution of 0.01 °C and the uncertainty (95%) in the corrections is typically 0.02 °C

seems to exhibit this behaviour. Since this instrument is an instrument employing a d.c. (direct current) sensing current for the thermometer, it is affected by offset voltages in the internal circuitry which may have stabilised after a few years. This highlights the need for frequent calibrations early in the working life of an instrument.

Over the last 8 years the corrections have increased at approximately $0.005\,°C$ per year. Departures from this rate have not exceeded $±0.01\,°C$ over that period. If we treat this level of uncertainty as a 95% confidence interval then we estimate the additional correction and uncertainty after 4 years to be $+0.02 ± 0.01\,°C$.

2.7.5   Evaluations based on intuition and experience

The most difficult and subjective Type B evaluations are those based purely on experience or intuition. Generally one should do all that is practical to avoid purely subjective evaluations. The best approach is to focus attention on work done in the past that is the foundation for the intuition. Are there experiments we could perform, notebooks with numerical information, perhaps colleagues that have a better understanding? These are usually clues to the whereabouts of information that enables a firmer and less subjective evaluation. It is also useful to use effective degrees of freedom (Equation (2.23)) to include the uncertainty in the uncertainty in the assessment.

   If we are forced into an entirely subjective assessment then we must remember that we are characterising risk. Richard Feynman, one of the commissioners investigating the *Challenger* Space Shuttle disaster, which was caused in part by an excessively optimistic estimate of the reliability of the booster rockets, captured the principle nicely: 'For a successful technology, reality should take precedence over public relations, for Nature cannot be fooled.'

Example 2.14
Describe an assessment of self-heating based on experience.

Examples 2.9 and 2.11 provide two variations on the evaluation of the self-heating effect for a resistance thermometer. A more experienced thermometrist might have experience of an air-temperature measurement where the self-heating was measured. The thermometrist estimates that the error is probably between $0.1\,°C$ and $0.2\,°C$, but is not absolutely sure. The thermometrist chooses to characterise the range of values by a normal distribution with a mean of $0.15\,°C$ and a standard deviation of $0.05\,°C$. Being unsure of the estimate of the standard deviation the thermometrist assigns an uncertainty of 30% to the estimate. From Equation (2.23) the thermometrist concludes that this is the same uncertainty that would be obtained with a Type A assessment with approximately five degrees of freedom. The 95% confidence interval is then computed, using a k factor of 2.65, to be $0.13\,°C$.

Exercise 2.6

Without reference to any other clock, make a Type B assessment of the accuracy of your watch or a familiar clock. Base your assessment on your knowledge of its past behaviour — is it normally slow or fast, how often do you reset it, etc.? If you can check the watch afterwards, how good was your assessment?

2.8 Combining Uncertainties

In most measurements there is more than one source of uncertainty. In a calibration, for example, there are uncertainties arising in the reference thermometer readings, the non-uniformity of the calibration bath, as well as in the readings of the thermometer under test. In order to determine the overall uncertainty we need to know how to combine all the contributing uncertainties.

Firstly, we assume that the uncertainties are uncorrelated. The case where uncertainties are correlated is more difficult and will be discussed in Section 2.10. Suppose we have measurements u, v, w, x, ..., which we add together to form z:

$$z = u + v + w + x + \cdots.$$

Given that we know the mean and variance for each of the distributions, what is the distribution of z? The mean of z is straightforward and is the linear sum of the contributing means:

$$\mu_z = \mu_u + \mu_v + \mu_w + \mu_x + \cdots. \tag{2.28}$$

For the variances we use a powerful result from distribution theory, which tells us that the variances also add linearly:

$$\sigma_z^2 = \sigma_u^2 + \sigma_v^2 + \sigma_w^2 + \sigma_x^2 + \cdots \tag{2.29}$$

(or equivalently the standard deviations add in *quadrature*). This is true for all types of distributions for which the variance exists, and is the reason why we relate all uncertainties to the variance or standard deviation.

By replacing the theoretical standard deviations σ by experimental standard deviations, s, Equation (2.29) solves the problem of how to combine standard uncertainties. However, determining the 95% confidence interval from the total variance is not so easy; indeed there is no exact formula for the general case. There are, however, a couple of useful approximations.

The simplest approximation is to evaluate the coverage factor for each contributing uncertainty and sum the expanded uncertainties in quadrature:

$$U_z = \left(k_u^2 s_u^2 + k_v^2 s_v^2 + k_w^2 s_w^2 + k_x^2 s_x^2 + \cdots \right)^{1/2}, \tag{2.30}$$

where k_u, k_v, ... all correspond to the same level of confidence. For the case when the number of degrees of freedom is the same for all variables this simplifies to

$$U_z = k s_z, \tag{2.31}$$

where $k = k_u = k_v = \ldots$. In most cases, but not all, Equation (2.30) tends to over-estimate the uncertainty slightly.

A better approximation is to recognise that each of our estimates of the variances in Equation (2.29) are themselves uncertain, with the uncertainty depending on the number of degrees of freedom according to Equation (2.17). This leads to an equation for the effective number of degrees of freedom for the total variance, which is known as the *Welch–Satterthwaite formula*:

$$\nu_{\text{eff}} = s_z^4 \left[\frac{s_u^4}{\nu_u} + \frac{s_v^4}{\nu_v} + \frac{s_w^4}{\nu_w} + \frac{s_x^4}{\nu_x} + \ldots \right]^{-1}. \tag{2.32}$$

This allows a calculation of the confidence interval using a coverage factor derived from the Student's t-distribution. The Welch–Satterthwaite formula is usually more accurate and results in smaller confidence intervals when summing uncertainties of similar magnitude. The equation does, however, have some limitations. One is that it requires an estimate of the number of degrees of freedom for each variance, and this may not be available for some Type B estimates. A second limitation is that Equation (2.32) requires all of the uncertainties to be uncorrelated. If the total variance includes correlation effects then the effective number of degrees of freedom can be in error by a factor of 4 or more.

Example 2.15

Calculate the total uncertainty for a measurement with a liquid-in-glass thermometer used in partial immersion.

A total-immersion mercury-in-glass thermometer is used in partial immersion to determine the temperature of an oil bath. The average and standard deviation of the mean of nine temperature measurements are:

$$\text{measured temperature} = 120.68\,^\circ\text{C}$$

$$\text{standard uncertainty} = 0.04\,^\circ\text{C}.$$

The calibration certificate for the thermometer shows that a correction of $-0.07\,^\circ\text{C}$ should be applied at $120\,^\circ\text{C}$, and the 95% confidence interval reported on the certificate is $\pm 0.02\,^\circ\text{C}$ ($\nu = 6$). To correct for the use of the thermometer in partial immersion, a stem correction of $+0.42\,^\circ\text{C}$ is also applied. The standard uncertainty in the stem correction is estimated using a normal distribution as 0.03 (1σ), with the effective number of degrees of freedom of 50. Calculate the corrected bath temperature and the uncertainty.

The three contributing measurements and their uncertainties can be summarised in the table that follows. All measurements are in degrees Celsius, and the entries in bold are calculated from the information given.

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The corrected bath temperature is given by the measured temperature plus the two corrections:

$$t = t_\mathrm{m} + \Delta t_\mathrm{cert} + \Delta t_\mathrm{stem},$$

and hence the corrected bath temperature is $121.03\,°\mathrm{C}$. The uncertainty can be calculated by either of the two methods.

Term	Value	Standard uncertainty	Confidence interval (95%)	Type
Temperature reading	120.68	0.04	**0.09**	Type A, $\nu = 8$
Certificate correction	−0.07	**0.008**	0.02	Type A, $\nu = 6$
Stem correction	+0.42	0.03	**0.06**	Type B, $\nu = 50$
Totals	**121.03**	**0.051**	**0.11**	$\nu_\mathrm{eff} = \mathbf{20.1}$

In the first method, calculate the 95% confidence intervals for each contributing uncertainty and then sum them in quadrature. The total uncertainty is then given by

$$U_\mathrm{t}^2 = U_\mathrm{t,meas}^2 + U_{\Delta t,\mathrm{cert}}^2 + U_{\Delta t,\mathrm{stem}}^2$$
$$U_\mathrm{t} = 0.11\,°\mathrm{C}\,(95\%)$$

In the second method, calculate the total standard uncertainty (sum the standard deviations in quadrature), calculate the effective number of degrees of freedom from Equation (2.32) for the total standard uncertainty, then calculate the 95% confidence interval using the coverage factor from the Student's t-distribution. The effective number of degrees of freedom is found to be 20.1, which corresponds to a coverage factor of 2.09; hence the 95% confidence interval is $0.051 \times 2.09 = 0.107\,°\mathrm{C}$. Note that this is slightly smaller than the uncertainty obtained by the first method.

Example 2.16

Calculate the uncertainty in a temperature difference.

Consider the uncertainty in the measurement of a temperature difference

$$\Delta T = T_1 - T_2,$$

where the measured uncertainties in T_1 and T_2 are s_{T_1} and s_{T_2} respectively. As a first approximation it may be assumed that the errors in the measurement of the two temperatures are independent, although the errors are likely to be highly dependent if the same thermometer was used for both measurements. We investigate this example with correlated measurements later (see Exercise 2.13).

By applying Equation (2.29) directly the standard uncertainty in the difference is found to be

$$s_{\Delta T} = \left(s_{T_1}^2 + s_{T_2}^2\right)^{1/2} . \tag{2.33}$$

Exercise 2.7

A variable w is given by $x + y + z$. The standard uncertainties in x, y and z are 1.1, 1.2 and 1.5 with 4, 4 and 50 degrees of freedom respectively. Calculate the 95% confidence interval for w by both of the methods given above.

Exercise 2.8

Derive Equation (2.21) for the standard uncertainty in a distributed quantity. [Hint: It helps to consider a specific case, e.g. the dispersion of residual error in readings corrected for a distributed systematic error; that is, residual error = error + correction.]

2.9 Propagation of Uncertainty

With many measurements, the quantity of interest is inferred from other measurements. Similarly, the uncertainty in the quantity of interest must also be inferred from the uncertainties in the measured quantities. To do so we need to know how the uncertainties in the measured quantities propagate to the quantity of interest. Unlike in previous sections, where we have been able to treat uncertainties in isolation from the physics of the measurement, propagation of uncertainty requires some extra knowledge, usually a model, of the measurement process.

Example 2.17

Estimate the uncertainty in a temperature measurement due to an uncertainty in the resistance measurement made by using a platinum resistance thermometer.

A platinum resistance thermometer is used to measure a temperature near $100\,°C$. The standard uncertainty in the resistance measurement is $0.1\,\Omega$. In this measurement the temperature is related to the resistance of the thermometer by the simple equation (the model)

$$R(t) = R_0\left(1 + \alpha t\right),$$

where R_0 is the resistance at $0\,°C$ and α is the temperature coefficient. This can be rearranged to calculate the temperature:

$$t = \frac{R(t) - R_0}{R_0 \alpha}.$$

Now suppose there is a small error ΔR in the measurement $R(t)$. This will give rise to a temperature measurement that is in error by the amount

$$\Delta t = t_{\text{meas}} - t_{\text{true}} = \frac{R(t) + \Delta R - R_0}{R_0 \alpha} - \frac{R(t) - R_0}{R_0 \alpha} = \frac{1}{R_0 \alpha} \Delta R.$$

This equation tells us the scaling factor between the errors in the resistance measurements and the errors in the temperature measurements. The propagation of uncertainty follows a similar equation

$$\sigma_t = \left(\frac{1}{R_0 \alpha} \right) \sigma_R.$$

The term in parentheses is called the *sensitivity coefficient*. For a $100\,\Omega$ platinum resistance thermometer the sensitivity coefficient has the value of approximately $2.6\,°\text{C}\,\Omega^{-1}$. Hence an uncertainty of $0.1\,\Omega$ in the resistance measurement propagates to $0.26\,°\text{C}$ uncertainty in the temperature measurement.

The key aspect of Example 2.17 is the determination of the sensitivity coefficient. Readers with knowledge of calculus will recognise that the sensitivity coefficient is the derivative dt/dR of the resistance–temperature relationship for the platinum thermometer. The general result for any function of independent random variables (the model),

$$z = f(x, y, \ldots), \tag{2.34}$$

is that the uncertainty propagates according to

$$\sigma_z^2 = \left(\frac{\partial f}{\partial x} \right)^2 \sigma_x^2 + \left(\frac{\partial f}{\partial y} \right)^2 \sigma_y^2 \ldots \ . \tag{2.35}$$

This equation is known as the *propagation-of-uncertainty* formula, where the terms in parentheses are the various sensitivity coefficients. The variables $x, y, \ldots$ are called the input quantities, and z is called the output quantity. While Equation (2.35) implies that a model (Equation (2.34)) must be known in order to calculate the uncertainty, this is not necessarily so; the sensitivity coefficients can be determined experimentally. In Example 2.17 the sensitivity coefficient could have been determined by changing the temperature by a fixed amount and measuring the resistance change, or by replacing the thermometer by a decade resistance box, changing the resistance by a known amount, and observing the change in the reading.

Table 2.3 shows the propagation of uncertainty formulae for common mathematical relationships. Note that for forms involving products and ratios of quantities, expressing the uncertainties in terms of relative uncertainties is often simpler.

Table 2.3   Propagation of uncertainty laws for some simple functional forms

Functional form	Propagation of uncertainty	Propagation of relative uncertainty
$z = x + y$	$\sigma_z^2 = \sigma_x^2 + \sigma_y^2$	–
$z = x - y$	$\sigma_z^2 = \sigma_x^2 + \sigma_y^2$	–
$z = xy$	$\sigma_z^2 = y^2\sigma_x^2 + x^2\sigma_y^2$	$\dfrac{\sigma_z^2}{z^2} = \dfrac{\sigma_x^2}{x^2} + \dfrac{\sigma_y^2}{y^2}$
$z = x/y$	$\sigma_z^2 = \left(\dfrac{1}{y}\right)^2\sigma_x^2 + \left(\dfrac{x}{y^2}\right)^2\sigma_y^2$	$\dfrac{\sigma_z^2}{z^2} = \dfrac{\sigma_x^2}{x^2} + \dfrac{\sigma_y^2}{y^2}$
$z = x^n$	$\sigma_z = nx^{n-1}\sigma_x$	$\dfrac{\sigma_z}{z} = n\dfrac{\sigma_x}{x}$
$z = \exp(ky)$	$\sigma_z = \exp(ky)k\sigma_y$	$\dfrac{\sigma_z}{z} = k\sigma_y$

Example 2.18

Estimate the uncertainty in stem corrections applied to liquid-in-glass thermometers.

The stem-correction formula enables the reading on a liquid-in-glass thermometer to be corrected for the error that occurs because some of the mercury in the column is not fully immersed (see Section 7.3.9 for details). The temperature correction is given by

$$\Delta T = L\,(t_2 - t_1)\,\kappa, \tag{2.36}$$

where:

L is the length of the emergent column in degrees Celsius;

t_1 is the mean temperature of the emergent column in use;

t_2 is the mean temperature of the emergent column during calibration;

κ is the expansion coefficient of mercury ($0.000\,16\,°\mathrm{C}^{-1}$).

Now, given the uncertainties in L, $t_1 - t_2$ and κ what is the uncertainty in ΔT?

By applying Equation (2.35) directly we get

$$\sigma_{\Delta T}^2 = (t_1 - t_2)^2\kappa^2\sigma_L^2 + L^2\kappa^2\sigma_{t_1-t_2}^2 + L^2(t_1 - t_2)^2\sigma_\kappa^2. \tag{2.37}$$

By inserting the values for the known uncertainties we can now determine the uncertainty in the correction. But this is a cumbersome form of the formula. By dividing through by $(N(t_1 - t_2)\kappa)^2$ we get a simpler equation

$$\frac{\sigma_{\Delta T}^2}{(\Delta T)^2} = \frac{\sigma_L^2}{L^2} + \frac{\sigma_{t_1-t_2}^2}{(t_1-t_2)^2} + \frac{\sigma_\kappa^2}{\kappa^2}, \tag{2.38}$$

or

$$\rho_{\Delta T}^2 = \rho_L^2 + \rho_{t_1-t_2}^2 + \rho_\kappa^2, \tag{2.39}$$

where the ρ are the relative uncertainties, which may be expressed in per cent. Where products of variables occur in equations, such as Equation (2.36), it is often simpler to express the uncertainties as relative uncertainties.

Typically the relative uncertainty in L, the length of the emergent column, is of the order of 1 or 2%, as is the uncertainty in κ (which is not truly constant). The greatest source of uncertainty is in the temperature difference of the exposed column, $t_1 - t_2$. Typically the relative uncertainty may be 5% or more. Substituting these values into Equation (2.39) we find that the total relative variance is

$$\rho_{\Delta T}^2 = 4 + 4 + 25,$$

so that the relative standard uncertainty in the correction is about 6%.

Exercise 2.9

Derive the entries in the third to the sixth rows of Table 2.3.

Exercise 2.10

Show that σ_m^2, the variance in the mean of a series of N measurements, is σ^2/N, where σ^2 is the variance of a single measurement of X. [Hint: The mean, m, can be expressed as $m = X_1/N + X_2/N + \ldots + X_N/N$.]

Exercise 2.11   *The uncertainty in the readings of a total radiation thermometer*

A total radiation thermometer uses the Stefan–Boltzmann law,

$$L = \varepsilon \frac{\sigma}{\pi} T^4.$$

Show that the uncertainty in the temperature inferred from a measurement of total radiance, L, and an estimate of the emissivity, ε, is

$$\sigma_T = \frac{T}{4} \left[\left(\frac{\sigma_\varepsilon}{\varepsilon}\right)^2 + \left(\frac{\sigma_L}{L}\right)^2 \right]^{1/2}. \tag{2.40}$$

Exercise 2.12   The uncertainty in the readings of a spectral band radiation
thermometer

A spectral band radiation thermometer approximately obeys Wien's law:

$$L_\lambda = \varepsilon \frac{c_1}{\lambda^5} \exp\left(\frac{-c_2}{\lambda T}\right),$$

where c_1 and c_2 are constants. Show that the uncertainty in measured temperature inferred from measurements of spectral radiance, L_λ, and emissivity, ε, is

$$\sigma_T = \frac{\lambda T^2}{c_2} \left(\frac{\sigma_{L_\lambda}^2}{L_\lambda^2} + \frac{\sigma_\varepsilon^2}{\varepsilon^2}\right)^{1/2}. \tag{2.41}$$

2.10 Correlated Uncertainties

In previous sections of this chapter it was assumed that all contributing uncertainties are independent. What does independent mean and how might a lack of independence affect calculations of uncertainty?

Example 2.19

Calculate the effect on a resistance ratio measurement of an error in the value of the reference resistor.

A resistance bridge measures resistance as a ratio with respect to an internal reference resistor. That is, the measured resistance is

$$R_{\text{meas}} = n R_{\text{S}},$$

with the ratio n displayed as the reading on the bridge. Investigate how errors in the value of R_{S} affect measurements of resistance ratio, $W = R(t)/R(0\,^\circ\text{C})$.

Suppose that there is a small error ΔR_{S} in our knowledge of the value of the reference resistor. First we would measure the ratio

$$n = R(t)/R_{\text{S}}$$

and infer that the measured resistance is

$$R(t)_{\text{meas}} = (R_{\text{S}} + \Delta R_{\text{S}})\, n = R(t)\frac{(R_{\text{S}} + \Delta R_{\text{S}})}{R_{\text{S}}}.$$

Similarly, the measurement of the ice-point resistance would also be in error. However, the ratio of the two resistances would be

$$
\begin{aligned}
W_{\text{meas}} &= \frac{R(t)_{\text{meas}}}{R(0\,^\circ\text{C})_{\text{meas}}} = \left[R(t)\frac{(R_{\text{S}} + \Delta R_{\text{S}})}{R_{\text{S}}} \right] \left[R(0\,^\circ\text{C})\frac{(R_{\text{S}} + \Delta R_{\text{S}})}{R_{\text{S}}} \right]^{-1} \\
&= \frac{R(t)}{R(0\,^\circ\text{C})} = W.
\end{aligned}
$$

That is, the error in the value of R_S has no effect on the measurement of resistance ratio.

In this case we have assumed that there is a systematic error in our knowledge of the value of R_{S}; however, it is also possible to have the same result with random errors. Suppose, for example, that the reason the value of the standard resistor is in error is because its resistance is fluctuating owing to random variations in its temperature. So long as the two measurements used to calculate W are made very close in time the same cancellation effects work in our favour. This is an example where a correlation between uncertainties in two measurements results in a lower uncertainty than might be expected. Correlation can also result in increased uncertainties.

This example also illustrates why platinum resistance thermometers are calibrated in terms of resistance ratio W; so long as the measurements are always compared to the ice-point resistance (or water triple-point resistance) and measured by the same instrument there is less need to use highly accurate reference resistors.

As might be expected, the mathematics for treating correlated uncertainties is not as simple as that for independent uncertainties. For any function of the form

$$
z = f\,(x_1, x_2, \ldots, x_N)\,, \tag{2.42}
$$

the uncertainties in x_1, x_2, ... are propagated as

$$
\sigma_z^2 = \sum_{i=1}^{N} \left(\frac{\partial z}{\partial x_i} \right)^2 \sigma_{x_i}^2 + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \left(\frac{\partial z}{\partial x_i} \right) \left(\frac{\partial z}{\partial x_j} \right) \sigma_{x_i, x_j}\,, \tag{2.43}
$$

where $\sigma_{x,y}$ is known as the *covariance*. This is the most general form of the propagation-of-uncertainty formula. When two random variables are independent the covariance is zero. (The converse is true only for variables with a normal distribution.) With a covariance of zero, Equation (2.43) reduces to the propagation-of-uncertainty formula, Equation (2.35), given in Section 2.9.

The covariance can be estimated from measurements as

$$
s_{y,x} = s_{x,y} = \frac{1}{N-1} \sum_{i=1}^{N} (X_i - m_x)\,(Y_i - m_y)\,. \tag{2.44}
$$

Covariances are often expressed in terms of the *correlation coefficient*, r, which is defined as

$$r = \frac{\sigma_{x,y}}{\sigma_x \sigma_y} \quad \text{or} \quad r = \frac{s_{x,y}}{s_x s_y}. \tag{2.45}$$

Depending on the degree of correlation, r varies between $+1$ and -1, with $r = 1$ for highly correlated variables and $r = 0$ for independent variables. Anticorrelation, which occurs quite rarely, results in negative values for r.

Example 2.20

Calculate the propagation-of-uncertainty formula for a measurement of resistance ratio. (Example 2.19 revisited.)

By applying Equation (2.43) to the definition of resistance ratio, $W = R(t)/R(0^{\circ}C)$, the total uncertainty is found to be

$$\sigma_W^2 = \left(\frac{1}{R_0}\right)^2 \sigma_{R(t)}^2 + \left(\frac{R(t)}{R_0^2}\right)^2 \sigma_{R_0}^2 - 2\left(\frac{R(t)}{R_0^2}\right)\sigma_{R(t),R_0}. \tag{2.46}$$

This can be rearranged using the definition of W and the correlation coefficient, Equation (2.45), to be

$$\sigma_W^2 = \left(\frac{1}{R_0}\right)^2 \left[(1-r)\left(\sigma_{R(t)}^2 + W^2\sigma_{R_0}^2\right) + r\left(\sigma_{R(t)} - W\sigma_{R_0}\right)^2\right]. \tag{2.47}$$

There are two interesting cases of this equation. Firstly, if the uncertainties are uncorrelated ($r = 0$), then the uncertainties add entirely in quadrature, with the uncertainty for the R_0 measurement weighted by W. Secondly, if the correlation is complete ($r = 1$) and $\sigma_{R(t)} = W\sigma_{R_0}$ then the total uncertainty is zero. It happens that the particular error we chose in Example 2.19 gave rise to uncertainties that satisfied both criteria.

Example 2.21

Calculate the propagation of uncertainty for the mean when the uncertainties in each measurement are correlated.

The arithmetic mean is defined by Equation (2.14),

$$m = \frac{1}{N}\sum_{i=1}^{N} X_i.$$

Direct application of the law of propagation of uncertainty yields

$$\sigma_m^2 = \left(\frac{1}{N}\right)^2 \left(\sum_{i=1}^{N} \sigma_{X_i}^2 + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j\neq i}}^{N} \sigma_{X_i, X_j}\right). \tag{2.48}$$

If this equation is rearranged using the definition of the correlation coefficient, Equation (2.45), and assuming that the correlation coefficient is the same for all pairs of measurements and that $\sigma_{X_i}^2 = \sigma_X^2$ for all measurements, we obtain

$$\sigma_m^2 = \left(\frac{1}{N}\right)^2 \left[(1-r)\sum_{i=1}^{N} \sigma_{X_i}^2 + r\left(\sum_{i=1}^{N} \sigma_{X_i}\right)^2\right] = \sigma_X^2 \left(\frac{1-r}{N} + r\right). \tag{2.49}$$

This example also has two interesting cases. Firstly, for independent measurements ($r = 0$) the uncertainty in the mean is given by the $1/N$ rule for the variance in the mean (Equation (2.16) in Section 2.5). Secondly, if the measurements are totally correlated ($r = 1$) then averaging has no effect at all; that is, Equation (2.49) is independent of N. Unfortunately, correlation occurs quite frequently in averaged measurements because measuring instruments use filters to reduce noise, and the same filters cause successive measurements to be correlated (see Exercise 2.14).

These two examples show that correlated uncertainties tend to add linearly, while uncorrelated uncertainties add in quadrature. Recalling that the definition of systematic error is the mean error, it is tempting to conclude (incorrectly) that all systematic errors add linearly. However, no such distinction is possible. Consider the case of the random fluctuations in the resistance of the standard resistor of Example 2.19. Over short time scales repeated measurements will be correlated and any departure of the resistance from its nominal value behaves like a systematic error. But over long time scales the fluctuations will be uncorrelated and on average the resistance will be close to its calibrated value. There are also numerous examples of systematic errors that do not lead to correlated uncertainties. The presence or absence of correlation is not sufficient to distinguish random and systematic effects.

In cases where there is correlation, the mathematics is often either trivial or very difficult. When reporting uncertainties in the difficult cases it may be sufficient to indicate that there is correlation between those correlated uncertainties and simply to add the variances as though they were independent. Alternatively, where correlations are suspected, such as with time averages, variances should be determined experimentally by repeating the measurements, rather than by relying on the one-upon-N rule for determining the variance in the mean.

Exercise 2.13

Show that the uncertainty in a temperature difference is

$$\sigma_{\Delta T}^2 = 2\sigma_T^2 (1 - r),\qquad(2.50)$$

where r is the correlation coefficient for the uncertainties in each of the two readings.

Exercise 2.14   *Uncertainty in a time average (a difficult problem)*

For many measuring instruments the resolution is limited by random electrical *noise* originating in electrical components such as transistors, resistors, etc. Usually a simple low-pass filter that removes high-frequency noise limits the contribution of noise to the reading. Because the filter resists rapid changes it 'remembers' previous signals. The correlation coefficient of the random noise component of two successive measurements is

$$r = \exp(-\tau/\tau_F),\qquad(2.51)$$

where τ and τ_F are the time between measurements and the time constant of the filter respectively. Show that when a large number of measurements, N, are taken the variance in the mean of the measurements is

$$\sigma_m^2 = \frac{\sigma^2}{N} \coth\left(\frac{\tau}{2\tau_F}\right).\qquad(2.52)$$

Note that the coth function is always greater than 1.0, so the variance in the mean is always larger than expected from the one-upon-N rule, Equation (2.16).

2.11. Interpolation

In principle a calibration should provide sufficient information to interpret or correct all readings on an instrument's scale. However, it is impractical to compare every point against a reference instrument, so usually only a small number of points are compared. The problem then is how to interpret the readings at intermediate points. One approach is to find an equation that passes through each of the measured points and use it to correct or interpret all other measurements. This is called interpolation.

The simplest form of interpolation is based on polynomials and is called Lagrange interpolation after the French mathematician who developed the mathematics. Lagrange interpolation is used in parts of ITS-90, is now commonly implemented in the linearisation software of many bench-top instruments, and provides a good approximation for the propagation of uncertainty for other forms of interpolation.

2.11.1   Lagrange interpolation

Consider the specific case of a quadratic polynomial (the analysis for interpolations of other orders is very similar). A quadratic equation has three coefficients and we determine the values for the coefficients by requiring the polynomial to pass through three measured points (x_1, y_1), (x_2, y_2) and (x_3, y_3). Conventionally the polynomial equation is found by substituting the co-ordinates for the three points into the interpolating equation

$$\hat{y}(x) = ax^2 + bx + c \tag{2.53}$$

and solving the resulting set of linear equations for the coefficients a, b and c. Note that the caret $\wedge$ in Equation (2.53) indicates that the interpolation may be an approximation to the true behaviour $y(x)$ (we will return to this later). In principle the set of equations derived from Equation (2.53) is easily solved both numerically and algebraically. However, Lagrange found an alternative representation of the polynomial that allows the solution to be obtained by inspection, even for higher-order polynomials. Specifically, for the quadratic case,

$$\hat{y}(x) = \sum_{i=1}^{3} y_i L_i(x) = y_1 L_1(x) + y_2 L_2(x) + y_3 L_3(x), \tag{2.54}$$

where the $L_i(x)$, in this case, are the second-order Lagrange polynomials

$$L_1(x) = \frac{(x - x_2)(x - x_3)}{(x_1 - x_2)(x_1 - x_3)}, \quad L_2(x) = \frac{(x - x_1)(x - x_3)}{(x_2 - x_1)(x_2 - x_3)},$$

$$L_3(x) = \frac{(x - x_1)(x - x_2)}{(x_3 - x_1)(x_3 - x_2)}. \tag{2.55}$$

While this rearrangement might seem unnecessarily complicated, Lagrange polynomials have special properties that make the uncertainty analysis very simple. An example of a set of three second-order Lagrange polynomials is shown in Figure 2.14. Note that each one takes the value 1.0 at one calibration point and is zero at all others. This can also been seen from Equations (2.55) by successively substituting $x = x_1$, x_2 and x_3 into each of the equations (do this, it helps to see the pattern). It is this property that makes it possible simply to write down the equations without having to solve the original set of equations generated by Equation (2.53). In general Lagrange polynomials of all orders satisfy the relations

$$L_i(x_j) = \begin{cases} 1, & \text{for } i = j \\ 0, & \text{for } i \neq j. \end{cases} \tag{2.56}$$

If we differentiate Equation (2.54) with respect to any of the y_i values we find that

$$\frac{\partial \hat{y}}{\partial y_i} = L_i(x). \tag{2.57}$$
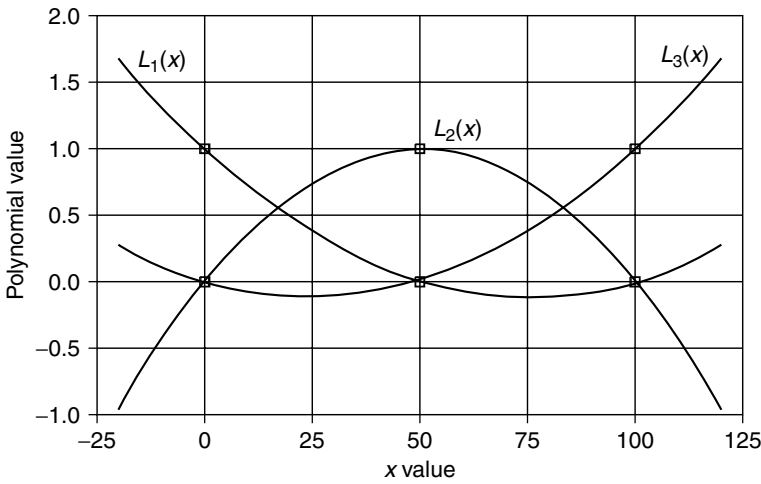
Figure 2.14 The three second-order Lagrange polynomials for calibration points at 0, 50 and 100. Note that the values of the polynomials are generally less than 1.0 within the interpolation range, but increase rapidly with extrapolation

That is, the Lagrange polynomials are the sensitivity coefficients for uncertainties in the y_i values. The uncertainties in the x_i values propagate similarly:

$$\frac{\partial \hat{y}}{\partial x_i} = -L_i(x) \left. \frac{d\hat{y}}{dx} \right|_{x=x_i}. \tag{2.58}$$

Close inspection of Figure 2.14 shows that the sum of the three Lagrange polynomials is equal to 1.0 for all values of x. This can also be seen by substituting $\hat{y}(x) = y_1 = y_2 = y_3 = 1$ in Equation (2.54). In fact the polynomials satisfy a complete set of such identities:

$$\sum_{i=1}^{N} x_i^n L_i(x) = x^n, \quad n = 0 \ldots N - 1, \tag{2.59}$$

and these can be useful when simplifying some uncertainty expressions.

2.11.2 Propagation of uncertainty

In Equation (2.54) there are $2N + 1$ measurements, comprising the N pairs of calibration points (x_i, y_i) and the measured variable x, which is the subject of the interpolation. Full differentiation of the general form of Equation (2.54) with respect to each measured variable yields

$$d\hat{y} = \sum_{i=1}^{N} L_i(x) dy_i - \sum_{i=1}^{N} L_i(x) \left(\left. \frac{d\hat{y}}{dx} \right|_{x=x_i} \right) dx_i + \frac{d\hat{y}}{dx} dx, \tag{2.60}$$

which enumerates all of the sensitivity coefficients required to calculate the uncertainty. If all of the contributing uncertainties are uncorrelated then the total uncertainty in the interpolated value, $\hat{y}$, is

$$\sigma_{\hat{y}}^2 = \sum_{i=1}^{N} L_i^2(x) \left[\sigma_{y_i}^2 + \left(\frac{\mathrm{d}\hat{y}}{\mathrm{d}x} \bigg|_{x=x_i} \right)^2 \sigma_{x_i}^2 \right] + \left(\frac{\mathrm{d}\hat{y}}{\mathrm{d}x} \right)^2 \sigma_x^2. \tag{2.61}$$

Note that the N pairs of terms in the square brackets are the uncertainties in the interpolation equation itself, while the last term is the additional uncertainty arising from the use of the equation to correct or interpret the reading x.

Figure 2.15 shows an example of the calibration uncertainty (last term of Equation (2.61) omitted) for a platinum resistance thermometer calibrated at three points using a quadratic equation. A useful feature of the graph is that the total uncertainty within the interpolation range is almost constant and equal to the uncertainty at any of the calibration points. This is typical when calibration points are evenly spaced and have similar uncertainties. If these conditions are not satisfied then the uncertainties can be amplified considerably and Equation (2.61) has to be evaluated in full.

The second feature of Figure 2.15 is the rapid increase in uncertainty outside the interpolation range, that is when extrapolating. In this case, because a quadratic equation is used, the uncertainty with extrapolation increases as the square of the temperature difference from the mean calibration temperature. Amplification of uncertainty with extrapolation occurs for all interpolation equations; it does not matter how the calibration equation is written or how the coefficients are calculated, it is a fundamental property of the mathematics of extrapolation.
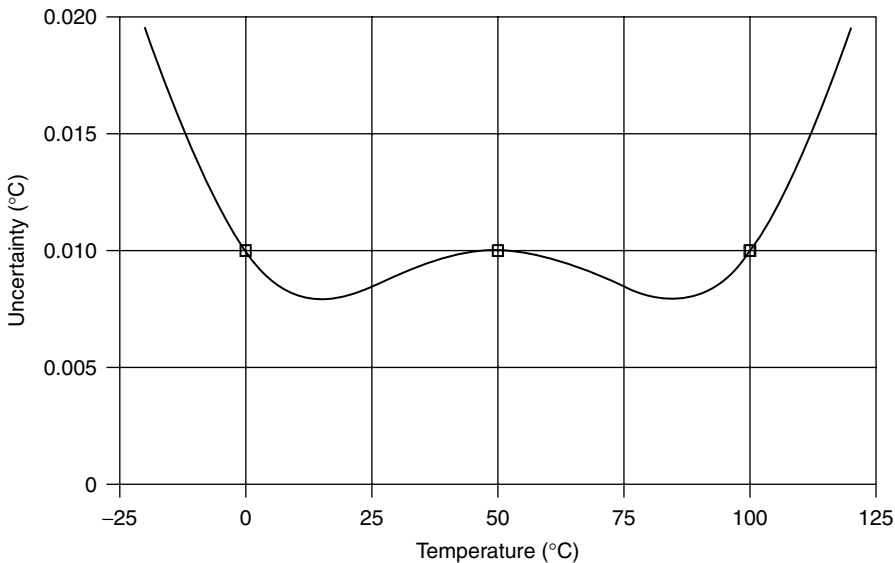
Figure 2.15 The propagated uncertainty in the calibration of a platinum resistance thermometer calibrated at $0\,°C$, $50\,°C$ and $100\,°C$ using a quadratic calibration equation. It is assumed that the uncertainty at each of the calibration points (marked) is $0.01\,°C$

2.11.3 Interpolation error

Most interpolation equations are an approximation to the true behaviour of an instrument. As a result, for those readings away from the calibration points there is an additional uncertainty due to the interpolation error. There are two ways to assess the error. In the simplest cases it may be possible to calculate the interpolation error. This requires a good model of the true behaviour of the instrument or sensor.

Example 2.22

Calculate the interpolation error for a linear platinum resistance thermometer.

The thermometer is made to read correctly by adjusting the zero and range at two temperatures t_1 and t_2. The Lagrange interpolation corresponding to the operation of the thermometer is then

$$\hat{t} = t_1 \frac{R(t) - R(t_2)}{R(t_1) - R(t_2)} + t_2 \frac{R(t) - R(t_1)}{R(t_2) - R(t_1)}, \tag{2.62}$$

where $R(t_1)$ and $R(t_2)$ are the measured resistances at the two temperatures. However, the platinum resistance thermometer has a response that is approximately quadratic:

$$R(t) = R_0 \left(1 + At + Bt^2\right).$$

If this is substituted into Equation (2.62) we obtain

$$\hat{t} = t + \frac{B\,(t - t_1)\,(t - t_2)}{A + B\,(t_1 + t_2)}, \tag{2.63}$$

which shows the form of the interpolation error. Note that the interpolation error is zero at the two defining points for the interpolation and that the interpolation error is quadratic, one order higher than the linear interpolation. With all interpolations, the interpolation error is always one order higher than the interpolation itself. Therefore, if the interpolation is not a good model of the behaviour of the instrument, the errors arising from the interpolation error with extrapolation may be much greater than the propagated uncertainty in the defining points. Both features are characteristic of all interpolations.

In many cases, unfortunately, interpolation is used because the exact form of the instrument response is unknown or too complicated to be modelled by a simple expression. In these cases the interpolation error must be determined experimentally. An indication of the error can be gained by comparing interpolations of different orders, and by comparing similar instruments. However, the best method is to compare the instrument with a better instrument, that is a calibration. Figure 2.16 shows the variation in the interpolation error associated with a standard platinum resistance thermometer (SPRT) used to realise the ITS-90 scale. Note the knots (zero error) in the curves at the defining points for the interpolation, as expected from Equation (2.63).
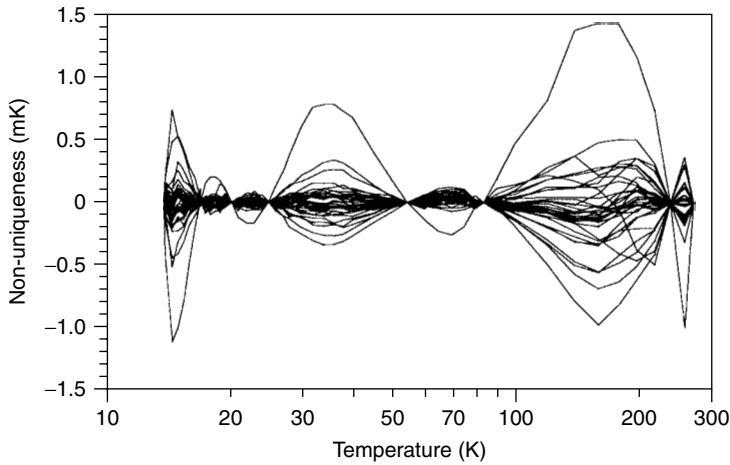
Figure 2.16   The non-uniqueness of the ITS-90 scale in the range 14 K to 273 K due to varia-
tions in the interpolation error of different standard platinum resistance thermometers. Note the
'knots' in the curves, which occur at the defining points for the interpolation

2.11.4   Other interpolations

Quite a number of the calibration equations used in thermometry can be written in
the form

$$\hat{y} = \sum_{i=1}^{N} y_i F_i(x). \tag{2.64}$$

That is, the interpolated variable can be expressed as a linear combination of a set of
functions $F_i(x)$. The calibration equations for thermistors, some radiation thermome-
ters, and the non-Lagrangian SPRT equations of ITS-90 can all be written in this form.
As with the Lagrange interpolation, the $F_i(x)$ functions are the sensitivity coefficients
for uncertainties in the y_i values, so all of the uncertainties propagate according to
Equation (2.61) with $L_i(x)$ replaced by $F_i(x)$. The sensitivity coefficients are, however,
often difficult to calculate. In these cases, because both the $F_i(x)$ and $L_i(x)$ pass
through the same points as required by Equation (2.56), the Lagrange polynomials
provide a good enough approximation for the purposes of uncertainty assessment.
They should not, however, be used to assess the uncertainty with extrapolation.

A few of the calibration equations used in radiation thermometry are also non-
linear; that is, the y_i values used in the calculation of the calibration constants cannot
be separated as multipliers for functions of x only as in Equations (2.54) and (2.64).
To find the exact form for the sensitivity coefficients the interpolation equation can be
expanded as a multivariate first-order Taylor series:

$$\hat{y} = F(x)|_{x_i, y_i \text{constant}} + \sum_{i=1}^{N} \Delta y_i \left. \frac{\partial F(x)}{\partial y} \right|_{y=y_i}. \tag{2.65}$$

A full evaluation of Equation (2.65) is necessary when evaluating uncertainties for extrapolation. When interpolating, this is usually not necessary because the Lagrange polynomials provide a good enough approximation for uncertainty analysis.

Exercise 2.15

Find, in terms of Lagrange polynomials, the equation of the quadratic equation that passes through the points (0, 100), (50, 119.4) and (100, 138.5). [Figure 2.14 plots the three Lagrange polynomials for this example.]

Exercise 2.16

Investigate the effects of correlation on the uncertainty propagated with Lagrange interpolation. Assume that the uncertainty is in the y_i values only and show that if the correlation coefficients are all 1.0 then

$$\sigma_{\hat{y}} = \sum L_i(x)\sigma_{y_i}. \tag{2.66}$$

That is, the uncertainty in the interpolation is found by interpolating between the uncertainties using an interpolation of the same order.

2.12 Least-squares Fitting

Interpolation, as described in the previous section, is the simplest way of determining the coefficients in calibration equations. However, calibration equations determined by the method of least squares have a number of advantages:

- With interpolation we need exactly the same number of measurements as there are coefficients in the equation. Just as a mean is a better estimate than a single measurement, least squares uses more calibration points than necessary, so the values of the coefficients are, in a sense, average values. This results in lower uncertainties for the calibration equation.

- With least squares there are enough redundant points to assess how well the instrument follows the expected form of the equation. In effect the extra points provide a measure of the uncertainty due to interpolation error.

- In order to propagate the calibration uncertainty using Equation (2.61) for interpolation we must already have estimates of the various contributing uncertainties. This normally requires subsidiary experiments or assessments. With least squares an experimental measure of the uncertainty is obtained at the same time.

- With interpolation there is no protection against 'rogue points' (calibration points where something has gone wrong and we've not noticed). The redundant points used in least squares provide that protection.

This section gives an introduction to the method of least squares. It should be sufficient for most temperature calibrations. Readers requiring more information are

referred to the books listed at the end of the chapter, which are reasonably tutorial and include examples. We begin first with an outline of the technique as applied to quadratic equations, and then follow with an example. Extension to other calibrations should be straightforward.

Assume that we wish to determine the coefficients a_0, a_1 and a_2 in a quadratic calibration equation of the form

$$\hat{y}(x) = a_0 + a_1 x + a_2 x^2, \tag{2.67}$$

and that we have made N measurements (x_i, y_i) of the relationship between x and $y(x)$. The values for the coefficients are found by minimising the function χ^2:

$$\chi^2 = \sum_{i=1}^{N} \left[y_i - \left(a_0 + a_1 x_i + a_2 x_i^2 \right) \right]^2. \tag{2.68}$$

That is, we minimise the sum of the squares of the deviations of the measured values from the fitted values of $y(x)$ — hence the name of the method. The minimum is found by setting to zero the derivatives of χ^2 with respect to each of the coefficients. This yields one equation for each coefficient. For a fit to a quadratic equation there are three equations:

$$\frac{\partial \chi^2}{\partial a_0} = -2 \sum_{i=1}^{N} \left(y_i - a_0 - a_1 x_i - a_2 x_i^2 \right) = 0,$$

$$\frac{\partial \chi^2}{\partial a_1} = -2 \sum_{i=1}^{N} \left(y_i - a_0 - a_1 x_i - a_2 x_i^2 \right) x_i = 0, \tag{2.69}$$

$$\frac{\partial \chi^2}{\partial a_2} = -2 \sum_{i=1}^{N} \left(y_i - a_0 - a_1 x_i - a_2 x_i^2 \right) x_i^2 = 0$$

These are known as the *normal equations* of the method of least squares. They are most succinctly written in matrix notation, which also shows the pattern of the equations more clearly. Appendix A lists all of the calibration equations recommended in this book and the corresponding normal equations. For a second-order fit the equations are

$$\begin{pmatrix} N & \sum x_i & \sum x_i^2 \\ \sum x_i & \sum x_i^2 & \sum x_i^3 \\ \sum x_i^2 & \sum x_i^3 & \sum x_i^4 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} \sum y_i \\ \sum y_i x_i \\ \sum y_i x_i^2 \end{pmatrix}, \tag{2.70}$$

or symbolically,

$$\mathbf{Aa} = \mathbf{b}, \tag{2.71}$$

where $\mathbf{A}$ is a matrix and $\mathbf{a}$ and $\mathbf{b}$ are vectors. The unknown coefficients are then found by inverting the matrix $\mathbf{A}$:

$$\mathbf{a} = \mathbf{A}^{-1}\mathbf{b}. \tag{2.72}$$

The matrix inversion is easily accomplished using the matrix inversion function found in most spreadsheet applications.

2.12.1   Propagation of uncertainty

Once the coefficients have been determined they can be substituted into Equation (2.68) to find the value for χ^2, and the variance of the residual errors in the fit,

$$s^2 = \frac{\chi^2}{N - \rho},\tag{2.73}$$

where ρ is the number of coefficients. That is, the least-squares technique finds values of the coefficients that minimise the variance of the residual errors. The standard deviation of the fit s is sometimes called the standard error of fit. Note also the division by $N - \rho$. This is the number of degrees of freedom in the calculation of the variance s^2, or the number of spare pieces of information we have (N measurements with ρ of them used to determine the coefficients; $\rho = 3$ for a quadratic equation).

The equivalent variances in a_0, a_1, a_2 propagated from the standard deviation of the fit are estimated by

$$s_{a_{i-1}}^2 = \mathbf{A}_{ii}^{-1} s^2.\tag{2.74}$$

As with the variance in the mean, Equation (2.16), these uncertainties decrease as the number of measurements is increased. The off-diagonal elements of $\mathbf{A}^{-1}s^2$ are the covariances of the coefficients (see Section 2.10). With these determined, the uncertainty in the calculated value of $\hat{y}(x)$ can be calculated:

$$\sigma_{\hat{y}}^2 = \sum_{i=0}^{N-1} \left(\frac{\mathrm{d}\hat{y}}{\mathrm{d}a_i}\right)^2 \sigma_{a_i}^2 + \sum_{i=0}^{N-1} \sum_{\substack{j=0, \\ i \neq j}}^{N-1} \left(\frac{\mathrm{d}\hat{y}}{\mathrm{d}a_i}\right)\left(\frac{\mathrm{d}\hat{y}}{\mathrm{d}a_j}\right)\sigma_{a_i a_j} + \left(\frac{\mathrm{d}\hat{y}}{\mathrm{d}x}\right)^2 \sigma_x^2.\tag{2.75}$$

This equation is the analogue of Equation (2.61) for Lagrange interpolation. The terms within the summations give the uncertainty due to the uncertainty in the calibration equation. The last term is the additional uncertainty arising from the uncertainty in the measured value of x. As with Lagrange interpolation, if the uncertainties in the calibration points are all similar and the points are evenly distributed then the calibration uncertainty is almost constant within the interpolation range. In this case Equation (2.75) can be approximated by

$$\sigma_{\hat{y}}^2 \approx \frac{\rho}{N}s^2 + \left(\frac{\mathrm{d}\hat{y}}{\mathrm{d}x}\right)^2 \sigma_x^2,\tag{2.76}$$

where s^2 is the measured variance (Equation (2.73)). Figure 2.17 shows the calibration uncertainty (omitting the last term of Equation (2.75)) for a platinum resistance thermometer calibrated using a quadratic equation at different numbers of points. Both the graph and Equation (2.76) show the benefit of using an excess of measurements ($N > \rho$); that is, the uncertainty in the calibration equation is reduced. In Figure 2.17, the curve for $N = 3$ is identical to that in Figure 2.15 for Lagrange interpolation.
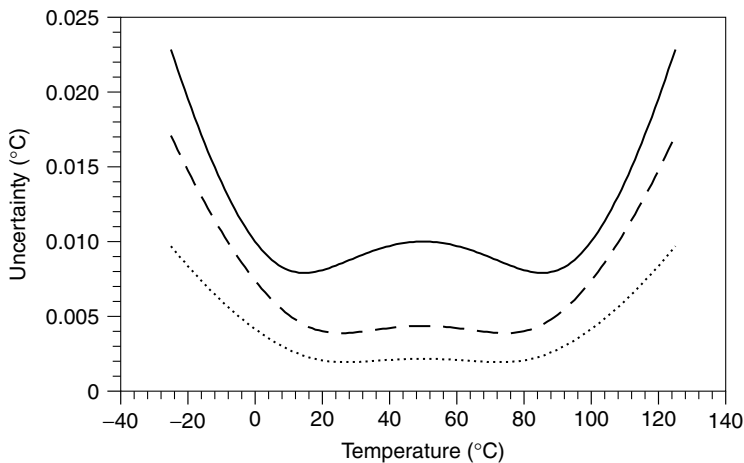
Figure 2.17   The propagation of uncertainty for a least-squares fit to a quadratic equation over the range 0 °C to 100 °C. It is assumed that the calibration points are evenly distributed over the calibration range. The top curve corresponds to three calibration points (i.e. Lagrange interpolation), while the next two curves correspond to 12 and 48 points respectively

Indeed for a polynomial fit and $N = \rho$ the least-squares fitting is always identical to Lagrange interpolation. The remaining curves in Figure 2.17 have the same general shape but are reduced by the factor $(\rho/N)^{1/2}$.

Note that the reduction of uncertainty with averaging that occurs with least-squares fitting is subject to the same conditions as the uncertainty in the mean. That is, the uncertainty associated with each measurement must be uncorrelated with the uncertainties in any of the other measurements, and the residual errors should be purely random rather than distributed over temperature.

To make the best use of least squares the calibration equation should be a good model of the behaviour of the instrument. A simple equation for a highly non-linear thermometer, for example, would introduce extra and unnecessary interpolation error. For all the thermometers discussed in this book we describe calibration equations that have been proved experimentally or theoretically to be good interpolators.

Figure 2.17 shows that any excess of measurement points is beneficial compared to pure interpolation in the sense of reducing uncertainty. It is also desirable in a calibration to demonstrate that the thermometer under test behaves as expected. This is accomplished by using a relatively large number of calibration points and checking that the measurements consistently follow the fitted calibration equation. From a purely statistical point of view the number of measurements should be such that the number of degrees of freedom is no less than five. This ensures that the coverage factors from the Student's t-distribution (Table 2.2) are reasonably small. However, a satisfactory demonstration of the validity of a calibration equation requires a few more measurements. We recommend a minimum of three or four data points per unknown coefficient. Thus, when fitting a quadratic equation for a resistance thermometer about 9 to 12 points are sufficient. Figure 2.17 also shows that the increase in uncertainty with extrapolation is as much a problem with least squares as it is for Lagrange interpolation.

Example 2.23

Use the DIN 43 760 tables for a platinum resistance thermometer to test a quadratic least-squares fit implemented in a spreadsheet.

The most general form of the resistance–temperature relationship (see Section 6.3.1) for a platinum resistance thermometer above $0\,°C$ is

$$R(t) = R(0)(1 + At + Bt^2). \qquad (2.77)$$

The equation can be expanded to a form suitable for least-squares fitting:

$$R(t) = R_0 + R_0 At + R_0 Bt^2.$$

By comparing this equation with Equation (2.67) we can identify

$$\hat{y} = R(t), \quad x = t, \quad a_0 = R_0, \quad a_1 = R_0 A, \quad a_2 = R_0 B.$$

The equations we must solve, from Equation (2.70), are

$$\begin{pmatrix} N & \sum t_i & \sum t_i^2 \\ \sum t_i & \sum t_i^2 & \sum t_i^3 \\ \sum t_i^2 & \sum t_i^3 & \sum t_i^4 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} \sum R_i \\ \sum R_i^2 \\ \sum R_i^3 \end{pmatrix}, \qquad (2.78)$$

where R_i are the values of the resistance measured at temperatures t_i.

Figure 2.18 shows a least-squares analysis carried out using a spreadsheet with a SUM function to calculate the elements of **A** and **b**, and a matrix inverse function. The data is taken from the DIN 43 760 standard for platinum resistance thermometers. Such tables are very useful for proving and debugging fitting programs. Most of Figure 2.18 is self-explanatory. The least-squares problem set by Equation (2.68) minimises the variance of the differences between the measured and fitted resistances, and consequently the standard deviation (from Equation (2.73)) has the dimensions of ohms. To calculate the equivalent variance in the temperature measurements the quadratic Equation (2.77) must be solved for t for each value of R_i. This is done using the iterative technique described in Section 6.7.1, which is also implemented in the spreadsheet using the iteration feature. The variance of the temperature deviations is then computed as

$$\sigma_t^2 = \frac{1}{N-3} \sum_{i=1}^{N} [t_i - t(R_i)]^2, \qquad (2.79)$$

where $t(R_i)$ is the inverse of the quadratic relationship. This is not the variance minimised by the least-squares fit; however, for equations where the relationship is close to a straight line the variance of the temperature errors is very nearly minimal and the results are the same. In principle the problem could be rewritten in terms of temperature but this would yield a more difficult least-squares

Summary for Platinum Resistance Thermometer						
Reading Number	Measured resistance	Measured temperature	Predicted resistance	Predicted temperature	Residual error (°C)	Residual error (Ω)
1	100.00	0.00	100.00	0.0045	−0.0045	0.002
2	103.90	10.00	103.90	9.9971	0.0029	−0.001
3	107.79	20.00	107.79	19.9942	0.0058	−0.002
4	111.67	30.00	111.67	29.9958	0.0042	−0.002
5	115.54	40.00	115.54	40.0020	−0.0020	0.001
6	119.40	50.00	119.40	50.0127	−0.0127	0.005
7	123.24	60.00	123.24	60.0020	−0.0020	0.001
8	127.07	70.00	127.07	69.9958	0.0042	−0.002
9	130.89	80.00	130.89	79.9941	0.0059	−0.002
10	134.70	90.00	134.70	89.9971	0.0029	−0.001
11	138.50	100.00	138.50	100.0046	−0.0046	0.002
Normal equation matrix			Inverse matrix			**b**
11	550	38 500	0.58041958	−0.022027972	0.000174825	1312.7
550	38 500	3 025 000	−0.022027972	0.00125641	−1.1655E−05	69 870
38 500	3 025 000	253 330 000	0.000174825	−1.1655E−05	1.1655E−07	5 017 446
Coefficients		Value	Uncertainty		Value	Uncertainty
	a0	99.99825175	1.88E−03	R0	99.99825175	1.88E−03
	a1	0.390874126	8.77E−05	A	3.908810E−03	8.77E−07
	a2	−5.87413E−05	8.44E−07	B	−5.874229E−07	−3.12E−04
Standard deviation in resistance (Ω)				0.0025		
Standard deviation in temperature (°C)				0.0064		

Figure 2.18 Example of a spreadsheet solution to a least-squares fit of DIN 43 760 platinum resistance data

problem. Note that the standard deviation of the resistance errors is very close to $0.0029\,\Omega$, which is the theoretical value for resistance measurements quantised to $0.01\,\Omega$ (Equation (2.10)).

Exercise 2.17

Apply the method of least squares to the equation $y = m$. That is, use least squares to fit a constant to a set of N data points, and hence show that

$$m = \frac{1}{N} \sum y_i,$$

$$s^2 = \frac{1}{N-1} \sum (y_i - m)^2,$$

$$s_m^2 = \frac{1}{N} s^2.$$

These are the standard equations for the mean, variance and variance in the mean (Equations (2.14), (2.15) and (2.18)).

Exercise 2.18

Apply the method of least squares to the equation of the straight line $y = ax + b$, and hence show that

$$b = \frac{\sum x_i^2 \sum y_i - \sum x_i \sum x_i y_i}{N \sum x_i^2 - \left(\sum x_i\right)^2}, \tag{2.80}$$

$$a = \frac{N \sum y_i x_i - \sum x_i \sum y_i}{N \sum x_i^2 - \left(\sum x_i\right)^2}, \tag{2.81}$$

$$s^2 = \frac{1}{N-2} \sum (y_i - ax_i - b)^2, \tag{2.82}$$

$$s_b^2 = \frac{s^2 \sum x_i^2}{N \sum x_i^2 - \left(\sum x_i\right)^2}, \tag{2.83}$$

$$s_a^2 = \frac{Ns^2}{N \sum x_i^2 - \left(\sum x_i\right)^2}. \tag{2.84}$$

These are the standard equations for a least-squares fit to a line.

2.13 The ISO Guide and its Application

Prior to the publication of the ISO Guide (ISO *Guide to the expression of uncertainty in measurement*) there was no consensus on methods for calculating uncertainty, nor a basis for comparing measurement results. For the 15 years between 1978 and 1993, a substantial effort on the part of several of the world's metrology organisations culminated in the ISO Guide, so far the only treatment of uncertainties recognised internationally.

Since 1993, the ISO Guide has revolutionised uncertainty analysis at the highest levels and its influence is gradually percolating through accredited laboratories into industrial practice. One of the most significant factors in the ISO Guide's utility is that it treats all uncertainties according to one set of principles based on the treatment of normal distributions. However, there are occasions when the application of the ISO Guide is not ideal or would give misleading results. Here we discuss some of the limitations.

2.13.1   Application to non-normal distributions

One of the most remarkable statistical facts is that many of the distributions that occur in statistical analysis and in measurement tend to the normal distribution when enough measurements are made. For most applications the assumption of a normal distribution is remarkably good. However, there are several areas where this assumption fails:

- All of the formulae involving the variance or standard deviation fail when the distribution does not have a variance. Such distributions occur in time and frequency analysis (how does one measure the stability of the best clock?), and alternative measures of uncertainty based on the Allan variance have been developed.

- All of the formulae involving high-order statistics of the normal distribution, for example the Student's t-distribution, the uncertainty in the variance (Equation (2.16)), and the Welch–Satterthwaite formula (Equation (2.32)), are strictly correct only for normal distributions. It is implicitly assumed by the ISO Guide that the formulae are a satisfactory approximation in most cases.

- The propagation of uncertainty formulae is an approximation that requires the function to be nearly linear. For grossly non-linear functions, such as $y = x^2$, it omits high-order terms that may be the most important. Full numerical models implemented in spreadsheets, for example, can be used to overcome some of these limitations.

There are several well-established techniques for handling each of these problems. We describe a solution for some of these problems in Section 2.13.4 below.

2.13.2 Application to distributed quantities

A key assumption in the ISO Guide is that 'the measurand can be characterised by an essentially unique value'. Unfortunately, in thermometry many Type A uncertainties tend to be significant, and are often due to quantities being distributed over temperature so that they are not unique or truly random. In Section 2.6.3, we provided formulae for evaluating the uncertainty of distributed quantities. In practice, uncertainties in measurements tend to be an amalgam of different effects, some of which are distributed and some single valued. The best estimate of the uncertainty lies somewhere between the two, and some judgement is required in the evaluation of the uncertainty. Again, a record of assumptions is important.

2.13.3 The nature of confidence intervals

The procedures described in the ISO Guide and in this text provide a means to represent uncertainties in terms of confidence intervals. The use of confidence intervals with distributed quantities and uncertain systematic errors means that confidence intervals do not have quite the same meaning as in normal statistics. For example, corrections with an expanded uncertainty at a 95% level of confidence applied to instrument readings could have several possible interpretations:

- The uncertainty, U, might characterise the dispersion of readings due to random noise. For example, when an instrument is used to measure a single temperature 95% of all readings will be within $\pm U$ of the true temperature.

- The uncertainty might characterise the dispersion of readings over the whole range of the instrument. There is a 5% chance that readings on some parts of the instrument's scale will always be more than $\pm U$ from the true temperature.

- The dispersion might characterise the dispersion of readings for all instruments subject to the same calibration process, and there is a 5% chance that any one instrument is always more than $\pm U$ from the true temperature for all parts of its measurement scale.

These three scenarios have quite different consequences for the user of the instrument, yet the uncertainty evaluation procedure given here and in the ISO Guide makes no distinction between the three. In practice a combination of all three effects will be present in any instrument, so the second and third scenarios are far less probable than 5%.

2.13.4   Alternative methods

With the availability of powerful computers, it is now practical to simulate the propagation of uncertainty. In particular, there are now several 'add-ins' for popular spreadsheet applications that carry out risk analysis. The procedures and terminology are, as should be expected, very similar to those for uncertainty analysis. The main advantage of these packages is that the level of mathematical skill required is less, the packages can manage a large variety of different distributions, including the troublesome ones with no variance, and they can manage all non-linearities and high-order effects. As with any uncertainty analysis a mathematical model relating all input quantities to the output is still required, and the resulting analysis is only as good as that model.

2.14   Reporting Uncertainties

2.14.1   How many decimal places?

The uncertainties in the estimates of the mean and variance (Equations (2.16) and (2.17)) have consequences on the reporting of measurements. The uncertainty in the variance means there is little point in reporting numbers with a huge number of decimal places because most of the trailing numbers will be random and contain no useful information. But how many decimal places should we use? Table 2.4 shows

Table 2.4   The uncertainty in the experimental standard deviation as a function of the number of degrees of freedom

Number of degrees of freedom, ν	Standard uncertainty in the standard deviation (%)
1	76
2	52
3	42
5	32
10	24
20	16
30	13
50	10

the standard uncertainty in the experimental standard deviation as a function of the number of degrees of freedom.

The values of the relative uncertainty can also be calculated from an approximation to Equation (2.17):

$$\frac{s_s}{s} = \frac{1}{\sqrt{2\nu}},$$ (2.85)

which works well for ν greater than three. Table 2.4 shows that the number of measurements required to obtain an accurate measure of the standard deviation is surprisingly high. For most measurements the uncertainty in the standard deviation is likely to be higher than 25%, and it requires at least 50 measurements to get the uncertainty below 10%.

For this reason, there is often little point in reporting the uncertainty to any more than one significant figure. Exceptions are when the most significant digit is a 1 or 2, in which case perhaps report to 5 or 2 in the next digit. Extra digits may also be warranted in very high-precision work where the number of degrees of freedom is large. The simplest rule is to report uncertainties to two significant figures.

The equation for the uncertainty in the mean has a form very similar to Equation (2.85):

$$\frac{s_m}{s} = \frac{1}{\sqrt{N}},$$ (2.86)

which is slightly higher than the uncertainty in the standard deviation. The rule for reporting the mean, or any result, is then very simple: report the result to the same decimal place as the standard uncertainty. This ensures that extra meaningless digits are not reported, while at the same time ensuring that rounding error is negligible.

Throughout the analysis of numerical data one or two extra *guard digits* should always be carried beyond the expected precision of the results. This is not because there is any meaningful information carried in the extra digits, but they are there to prevent cumulative rounding errors from contributing additional uncertainty. Once the final results and uncertainties have been calculated the best precision for reporting the numbers can be determined as above. This guide applies to all results, not just Type A uncertainties.

2.14.2   Presentation of uncertainty statements

The detail and amount of information presented with measurement results depends entirely on the client's needs. In order to reduce confusion a number of conventions have been promoted.

Algebraic conventions:

The symbol s is reserved for single Type A evaluations of the standard. uncertainty

The symbol u is reserved for Type B or combined (u_c) standard uncertainties.

The symbol U is reserved for expanded uncertainties.

Numerical conventions for standard uncertainties:

$M = 100.021\ 47\,\text{g}, u_\text{c} = 0.35\,\text{mg}$;

$M = 100.021\ 47(35)\,\text{g}$;

$M = 100.021\ 47(0.000\ 35)\,\text{g}$.

Numerical convention for expanded uncertainty:

$M = 100.02147 \pm 0.000\ 35\,\text{g}$.

Note that the $\pm$ symbol is usually reserved for use with expanded uncertainties.

When reporting measurements it may be useful to the reader to supply more information than just the bare numerical results. The information may include, depending on the purpose of the report and the needs of the client:

- The methods, or references to the methods, used to calculate the result and its uncertainty.

- All of the uncertainty components, how they were evaluated, the (effective) number of degrees of freedom for each and, if used, the covariances or correlation coefficients.

- All corrections, constants, models and assumptions employed in the calculation.

For calibration certificates the client needs the expanded uncertainty with the level of confidence and either the standard uncertainty or the coverage factor. It is helpful to include the effective number of degrees of freedom.

Example 2.24

Determine the appropriate rounding for the values of the mean and standard deviation calculated in Example 2.4.

Example 2.4 determined the mean and standard deviation of 20 measurements as

$$m = 6.485\,°\text{C} \quad \text{and} \quad s = 0.346\,°\text{C}.$$

Based on Equation (2.85) the uncertainty in s is known to about 16%. Therefore, the standard uncertainty should not be reported to any greater precision than about 0.05 °C. A reasonable approximation is:

$$s = 0.35\,°\text{C}.$$

The mean should be reported to the same precision:

$$m = 6.50\,°\text{C}.$$

The result may be presented as

$$temperature = 6.50(35) \, °C,$$

or if a 95% confidence interval is required, the same result could be presented as

$$temperature = 6.5 \pm 0.7 \, °C.$$

Note that $k = 2.09$ for $\nu = 19$ and $P = 95\%$ (see Table 2.2).

Further Reading

Basic texts and guides on uncertainty

C F Dietrich (1991) *Uncertainty, Calibration and Probability*, 2nd Edition, Adam Hilger, Bristol.
Guide to the Expression of Uncertainty in Measurement (1993) International Organisation for Standardisation, Geneva.
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P R Bevington (1969) *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York.
W R Press, B P Flannery, S A Teukolsky, and W T Vetterling (1986) *Numerical Recipes*, Cambridge University Press, Cambridge.

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D R White (2001) The propagation of uncertainty with non-Lagrangian interpolation, *Metrologia* **38**, 63–69.
D R White and P Saunders (2000) The propagation of uncertainty on interpolated scales, with examples from thermometry, *Metrologia* **33**, 285–293.

3

The ITS-90 Temperature Scale

3.1 Introduction

In principle, temperature is defined completely by thermodynamics, the science of heat. However, as we found in Chapter 1, thermometers based on thermodynamic laws are neither convenient nor sufficiently accurate for practical measurements. Instead, the international measurement community defines a practical temperature scale sufficiently reproducible to satisfy our needs in respect of science, trade and health. This scale is revised periodically to ensure that it covers a wide temperature range, is close to the thermodynamic scale, and is as available as practical to all users. The most recent revision was in 1990, so the current scale is known as the International Temperature Scale of 1990, or simply ITS-90.

ITS-90 has the same basic structure as the previous practical scales of 1968, 1948 and 1927. It approximates the thermodynamic scale using a number of defined temperatures (the fixed points) and highly reproducible thermometers to interpolate between the defined points. While in a few places the 1990 scale is a little more complex than the previous scales, the choice of temperature ranges is greater, and for most users it is more flexible and better suited to real thermometry needs.

The aims of this chapter are to provide procedures for the simplest and most useful parts of the scale, and to provide a background to enable the more general thermometer user to understand the temperature scale, the source of traceability for almost all temperature measurements.

We describe in detail the construction and use of the triple point of water and the ice point. The ice point, although not defined by ITS-90, is arguably the single most important tool in the thermometrist's kit. Because it is cheap, accurate and ready to use in 20 minutes, no self-respecting thermometrist should be without it. Those regularly involved in temperature measurement will find that the ice point is an essential tool for ensuring traceability.

An interesting feature of ITS-90 is that it enables users requiring high accuracy to establish the scale for themselves. This process is facilitated by the ready commercial availability of the components necessary to establish extensive parts of the scale, as well as the relative ease of use of these components. As we expect progressively more users to be interested in adopting this route, we introduce some of the procedures for realising ITS-90.

We focus particularly on the parts of the scale in the range from about $-200\,°C$ to $960\,°C$, which is based on platinum resistance thermometry, since it is by far the most commonly used part of the scale. The principles underlying the use of fixed

points and interpolation in the calibration of thermometers will also be of interest and directly applicable to more general thermometry. The chapter is, however, primarily an introduction to the scale. Readers requiring detailed information on the scale and its maintenance procedures should consult the official guidelines (see references at the end of the chapter).

3.2 The Triple Point of Water

3.2.1   The units of temperature

The fundamental physical quantity known as thermodynamic temperature is usually represented by the symbol T. The unit of thermodynamic temperature, the kelvin, symbol K, is defined as the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

A temperature is also commonly expressed in terms of its difference from 273.15 K, the ice point. To distinguish a thermodynamic temperature expressed this way, the temperature is known as a *Celsius temperature*, symbol t, defined by

$$t/^\circ\text{C} = T/\text{K} - 273.15. \tag{3.1}$$

The unit of Celsius temperature is the *degree Celsius*, symbol $^\circ$C. Thus the ice point is $0\,^\circ$C or 273.15 K, and the triple point of water is $0.01\,^\circ$C or 273.16 K. By definition the unit for the Celsius scale is the same size as the kelvin and differences of temperature may be expressed in kelvins or degrees Celsius. When reporting temperatures, kelvins are generally used for low temperatures, that is below $0\,^\circ$C, and degrees Celsius for higher temperatures, but there is no hard and fast rule. Small temperature differences are commonly expressed as millikelvin rather than millidegrees.

Because we have a thermodynamic temperature scale and a number of practical temperature scales that differ by small amounts, all with the same name for the units, it is occasionally necessary to distinguish between *scale temperature* and *thermodynamic temperature*. The symbols T_{90} and t_{90} are used for the current scale, ITS-90, and previous scales are denoted similarly, for example T_{68} and t_{68} for the International Practical Temperature Scale of 1968 (IPTS-68).

3.2.2   The triple point of water – defining the unit

The foundation of the temperature scale is the water triple point. It defines the unit of the thermodynamic temperature scale and is the most important defining point on ITS-90. Figure 3.1 shows the phase diagram for water. It plots three curves corresponding to the boiling, melting and sublimation points as a function of temperature and pressure. The water triple point occurs where all three curves meet at a single temperature and pressure. This is where all three phases of water, namely ice, liquid and vapour, are in thermal equilibrium with each other.

A practical realisation of a triple point is shown in Figure 3.2. The glass cell contains only water; the water and ice are visible in the figure and the space within the cell above the water contains only water vapour. The glass cell also has a thermometer well that allows the triple point to be used as a precision temperature reference.
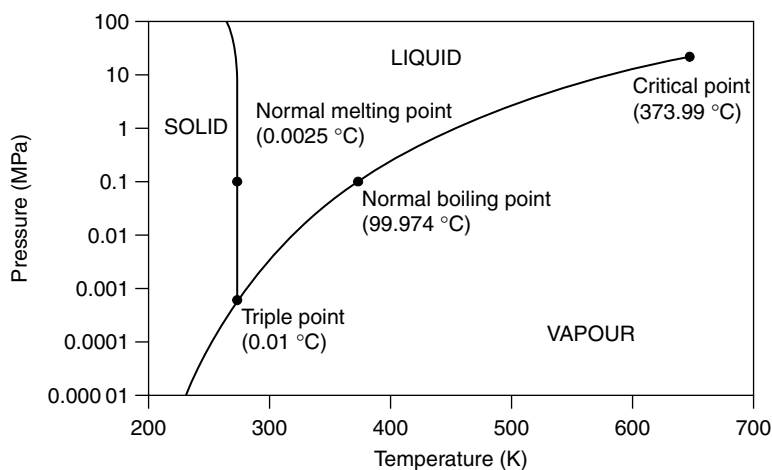
Figure 3.1   The phase diagram for pure water. Depending on the temperature and pressure, water may exist as ice, liquid or vapour. Under some conditions water may exist in two phases; these conditions are indicated by the melting, boiling and sublimation curves, each of which is sensitive to pressure. There is only one temperature and pressure where all three phases can coexist in thermal equilibrium: the triple point. At temperatures and pressures above the critical point, the vapour and liquid phases are indistinguishable

Triple-point cells are easily made by any competent glassblower, but particular attention must be given to cleanliness. Soluble impurities in the water of a triple-point cell depress the triple-point temperature by approximately 1.86 K per mole of impurity in 1 kg of water, and are a major factor in the performance of a cell. Many of the observed variable properties of the triple point of water appear to arise from the impurities, which are often added inadvertently during attempts to clean the glassware or purify the water. With care, the impurity level in a triple-point cell can be readily controlled to achieve an accuracy of better than 0.1 mK. Good procedures for freezing and using the cells help to reduce the effects of the impurities.

The main difference between the temperatures of the ice point, 0.0 °C, and water triple point, 0.01 °C, is due to pressure, which accounts for approximately 7.5 mK of the total 10 mK difference. The remaining 2.5 mK difference in the two temperatures is caused by dissolved air in the ice point. Therefore, the main impurity to be removed from the water during manufacture of a triple-point cell is air. A cell is easily tested for the presence of air as in Figure 3.3. The cell is tilted with the seal-off tube held downwards to trap a bubble of the gas. As the cell is tilted further, the pressure from the water increases causing the water vapour in the bubble to condense. The remaining bubble is almost entirely due to air contamination. If there is no significant air contamination, an audible click is heard as the cell is tilted, and the trapped bubble in the seal-off tube will diminish significantly. If the bubble volume is reduced by a factor of 3 when the bubble is trapped below a 50 mm head of water then the residual gas in the air makes an insignificant difference to the triple-point temperature, typically less than 50 μK. This test cannot reveal the presence of non-volatile impurities, however.

The isotopic composition of the water also alters the triple-point temperature. By definition, the water in the triple-point cell should have the isotopic composition of
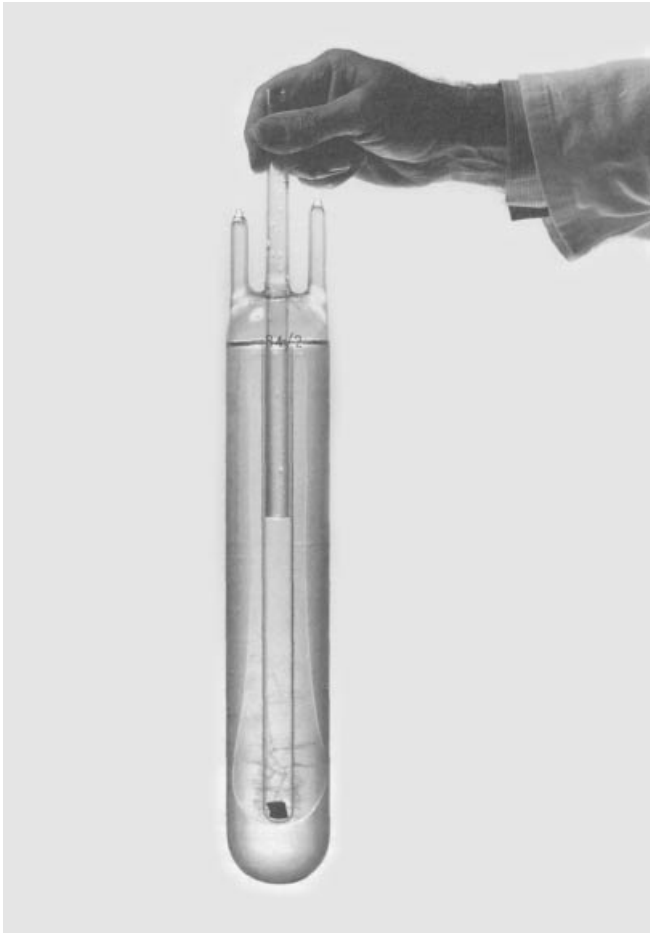
Figure 3.2   A water triple-point cell showing the frozen ice mantle and thermometer well containing some water and a small sponge. The space above the cell contains only water vapour at a pressure of about 600 Pa. The cell is stored in ice during use

seawater. Water consists of H_2O made from the light isotopes of hydrogen and oxygen, ^{1}H and [16]O. Seawater also contains about 158 µmol/mol of heavy water (deuterium oxide, ^2H_2O) and about 2000 µmol/mol of water with the heavy oxygen isotope ^{18}O, which contribute equally to a triple-point temperature about 1.3 mK above that for pure 'light water'. Most cells are made from fresh water, for which the isotopic composition varies approximately according to latitude. The variations cause a depression of about 10 µK for tropical fresh water and up to 200 µK for Antarctic snow water. Furthermore, each stage of distillation of the water may cause additional fractionation of the heavy isotopes leading to a further depression of up to 20 µK. The cumulative effect of these processes is that most triple-point cells have water with an isotopic composition that may be as much as 100 µK below the seawater definition.

A cell is best checked for accuracy by comparison with a second cell or bank of cells. Certification of a cell by a national standards laboratory is normally done this way.

(a)

(b)
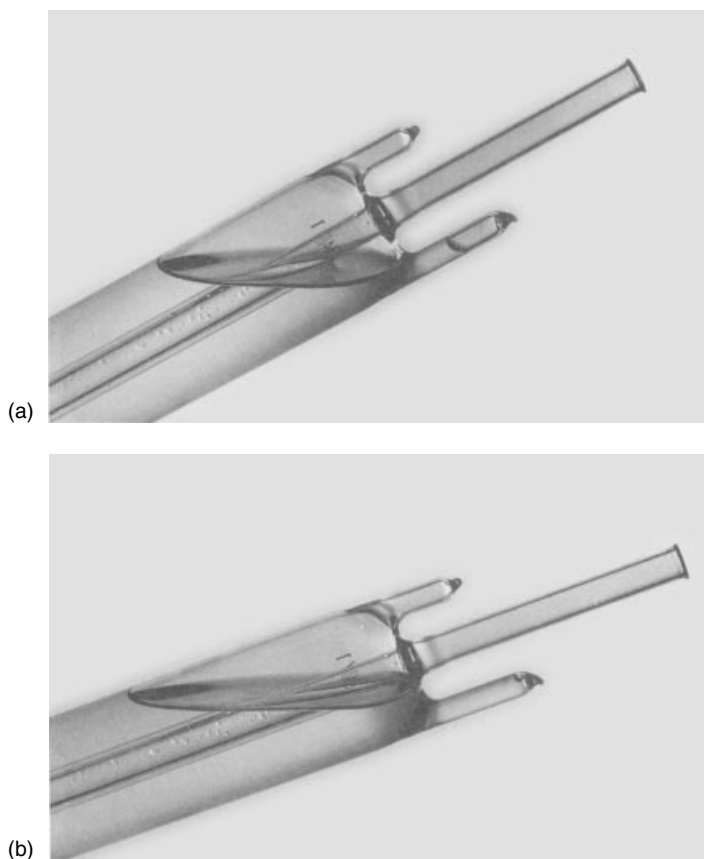
Figure 3.3   The air-bubble test for an air leak in a water triple-point cell; (a) Air and water vapour are trapped in the seal-off tube; (b) tilting the cell further compresses the trapped air bubble causing the water vapour to condense leaving only air in the bubble

Where the user has only one or two cells, certification is essential. Almost all of the effects that influence the triple point cause the temperature to be depressed. Therefore, if differences between cells are observed, the cell with the highest temperature is almost certainly the best.

In a sense, the temperature realised by a triple point of water cell is a matter of definition. However, there is some uncertainty associated with the degree to which the cell is manufactured and prepared according to the definition. It is relatively simple to make a cell with an uncertainty of 0.5 mK, and with good care cells can be manufactured to within 40 μK.

3.2.3   Using the triple-point cell

In principle, a water triple-point cell need only contain ice, water and water vapour in order to realise the triple point. In practice, we need to be able to immerse a

thermometer into a system where the temperature around the thermometer is entirely controlled by the phenomenon. Immersion is best achieved with an ice mantle surrounding the thermometer well, with a thin water interface between the ice and the well. The main benefit of this configuration is that it ensures that the water–ice interface is in close thermal contact with the thermometer. If one phase only, ice, water or water vapour, surrounded the well then the temperature in the well would be influenced by the temperature of the environment surrounding the cell. Having an ice mantle around the well also enables the reduction of impurity effects. As an ice crystal grows it tends to reject soluble impurities, so the growth of ice crystals is a purification process. When the ice mantle is frozen, the freeze process should start from the well and proceed slowly outwards. In this way, the ice near the well will be purer than the surrounding water. When the well is warmed to produce the water film between the well and the ice, the water will be purer than that in the rest of the cell, and the effects of any contamination originally present in the water or subsequently leached from the glass are minimised. The presence of the thin water film also eliminates the effect of mechanical pressure on the ice.

Procedure for preparing the triple point

- Pre-cool the cell by storing it near $0\,°C$ in crushed ice or a refrigerator (not a freezer) for a few hours.

- Hold the cell vertical. Once ice has formed any tilting or twisting of the cell should be done with care as the stress may cause the well to break.

- Fill the thermometer well uniformly with refrigerant. Crushed 'dry ice' (solid CO_2), cold nitrogen gas supplied through a tube from boiling liquid nitrogen, or metal rods cooled in liquid nitrogen all work well. There are also special heatpipe coolers available commercially for this purpose. It may help in obtaining a uniform mantle if the cell is gently rotated as the ice mantle freezes

- The outside of the cell, at the water–vapour interface, should be warmed to prevent ice from freezing completely across the surface of the water to the outer walls. Rapid ice expansion here may crack the cell.

- Once the ice mantle is large enough, stop the freezing by removing the refrigerant. The magnifying effect of the curved cell will make the ice mantle appear larger than it is, but the ice should fill three-quarters of the space if the triple point is to have a reasonable lifetime.

- Store the cell in an appropriate storage vessel and cover with crushed ice. Commercial storage units are available, but a tubular sleeve buried inside an insulating vessel packed with crushed or shaved ice works very well. Cells properly stored will stay frozen and ready to use for months.

- Immediately after freezing, the cell will realise the triple-point temperature with an uncertainty of about $1\,mK$. For improved accuracy the cell should be stored for 24 hours before it is used, to allow strain in the ice to relax; then the uncertainty will typically be less than $150\,\mu K$. For the highest accuracy, the cell should be stored for a further two weeks to allow the ice crystals to anneal fully. During the two weeks, the temperature will rise a further $50\,\mu K$ to $100\,\mu K$.

- Every day or so check the ice mantle and add ice to the storage vessel. When properly stored in ice the mantle will usually grow slowly. It may be necessary to warm the cell at the water–vapour interface if the ice grows across the surface.

- The cell's useful life depends on the storage method, and ends when the ice mantle no longer completely encloses the thermometer well. Usually the mantle thins slowly and fails at the bottom of the thermometer well owing to the pressure from the buoyancy of the ice. This effect is illustrated in Figure 3.2; the mantle in this cell is nearing the end of its useful life.

Procedure for using the triple point

- Half fill the thermometer well with cool water, if it is not already filled. This will ensure good thermal contact when a thermometer is inserted. There should be sufficient water so that the water rises to the height of the ice mantle when the thermometer is inserted. A small rubber sponge at the bottom of the well will help prevent breakage of the cell or the thermometer (see Figure 3.2).

- Free the ice mantle by inserting a metal rod into the well. A layer of ice will melt creating a thin water film around the well and holding the well temperature at a low-pressure melting point of the ice. The water film will allow the ice to float freely when the cell is (gently!) rotated.

- Once the mantle is free, replace the cell in its storage container and cover with ice. It is now ready for use. Storage in ice protects the measurement from heat influences, such as from leads, the body of the thermometer and radiant energy sources.

- Insert the thermometer. Thermometers can be pre-cooled in ice before insertion to save time.

- Once the thermometer is immersed, allow 15 to 20 minutes for thermal equilibrium to be reached. Triple-point measurements should be reproducible to better than $0.1\,\text{mK}$, and with care can be repeatable to $10\,\mu\text{K}$.

For the highest accuracy a temperature correction must be applied to triple-point measurements. Notice in Figure 3.2 that the only place where all three phases of water are actually present is at the surface of the water around the thermometer well. The water–ice interface around the well is at the melting point of water, which is pressure sensitive. Around the well, the temperature slowly decreases with depth as the pressure due to the head of water increases. The temperature measured in a triple-point cell is therefore given by

$$T = 273.16\,\text{K} - h \times 0.73\,\text{mK}\,\text{m}^{-1}, \tag{3.2}$$

where h is the height in metres from the centre of the temperature sensor to the surface of the water in the cell.

The triple point of water is the cheapest and most accurate of the ITS-90 fixed points, so it provides a very convenient check of the stability of thermometers used for the highest accuracy applications. The procedure is very quick, usually taking only a few minutes.

3.2.4 The ice point

Figure 3.1 shows that the melting point of water at atmospheric pressure is near 0.0025 °C. However, this is not the ice point as it is used as a temperature reference. The ice point is defined as the equilibrium temperature of ice and air-saturated water, which occurs at the lower temperature of 0.0 °C almost exactly. The 2.5 mK difference is caused by dissolved air in the water and ice.

Historically the ice point was the defining point for many temperature scales until the more precise triple-point cells were developed. It still has a major role in thermometry since it is a fixed point that can be readily achieved by almost any laboratory with a minimal outlay of resources. It is essential for people who take their temperature measurements at all seriously. Whether the accuracy required is ±100 °C or ±0.01 °C, the ice point is an invaluable aid for ensuring that a thermometer is functioning correctly.

One of the advantages of the ice point is that it can be made very simply and extremely cheaply and, so long as the basic principles are followed, it is relatively easy to realise an accuracy of ±0.01 °C. If the accuracy requirements are ±0.01 °C or better, then the water triple point should be used. The ice point can be used as a 'poor man's triple point' to achieve uncertainties of the order of ±2 mK but very close adherence to the procedure below is needed. The procedure is suitable for a reference standard and users should become sufficiently familiar with it to place a high level of confidence in it.

The equipment

To assemble an ice point you will need:

- An insulated container. A vacuum-insulated flask or expanded polystyrene flask approximately 300 mm to 400 mm deep and 80 mm to 100 mm in diameter is ideal. A vessel of this type retards the melting of the ice by its insulating properties. The flask should be deep enough to hold the full length of the thermometer below its ice point with 50 mm to 100 mm extra depth to accumulate meltwater. If a metal-sheathed thermometer is being checked it will need to be immersed to a minimum of about 300 mm.
- A siphon. A siphon is placed in the flask to enable the removal of excess water as the ice melts. Since the definition of the ice point is the equilibrium of melting ice with air-saturated water, air must be allowed to circulate through the meltwater on the surface of the ice. In addition, water has its maximum density at about 4 °C. If a large volume of water is allowed to gather at the bottom of the flask, it is possible for the water to become warm. Thus, the water level should never be allowed to rise to reach the bottom of the thermometer.
- Clean, shaved ice. The ice should be free of impurities so is ideally made from distilled or de-ionised water. Because freezing is also a purification process, food-grade ice made in freezers that employ a washing process is also satisfactory. Good, clean tap water is often satisfactory but should be avoided as it will occasionally be contaminated or have a high concentration of additives from the water treatment process. If tap water must be used check its electrical resistivity; at 10 °C its

resistivity should be higher than $0.5 \times 10^6 \, \Omega \, m$. Some tap water will be completely unsatisfactory in this respect and it pays to check. The ice must be shaved or crushed, ideally into small chips measuring less than 1 mm across. For liquid-in-glass thermometers, which have a poor thermal conductivity, larger chips up to 5 mm will be satisfactory. However, for steel-sheathed probes, such as platinum resistance thermometers, fine ice is essential if accuracies of $\pm 0.01\,^\circ$C are to be achieved. The ice may be shaved using commercial ice shavers ranging from cheap plastic bar accessories to professional ice shavers. A low-cost alternative, which is satisfactory for infrequent use, is a food processor with a grating disc. Note that discs with blades or knives are not suitable because they do not cut ice very effectively and the processor will be quickly damaged.

- A small quantity, approximately 300 ml, of clean water. Distilled or de-ionised water is ideal, as is the meltwater from the ice.
- A clean rod of a similar diameter to the thermometer.

The procedure

Assemble and use the ice point as follows:

- First, fill one-third of the flask with clean water. Freshly shaved ice is quite often colder than $0\,^\circ$C. By putting water into the flask first, we ensure that the ice is in fact melting. The difference in the condition of the ice is readily visible since cold ice freezes water vapour from the atmosphere giving it a white frosty appearance. By comparison the wet ice, at $0\,^\circ$C, is quite translucent (see Figure 3.4).
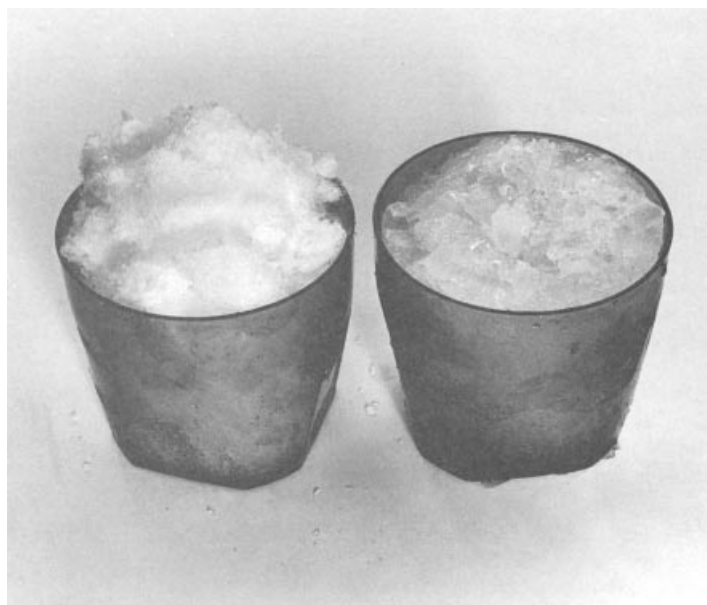
Figure 3.4   Shaved ice, with frosty ice on the left and ice after slushing on the right

- Add the shaved ice to a sufficient depth. For liquid-in-glass thermometers, the container should be filled to the top to allow the thermometer to be read without parallax errors. For other thermometers, there must be sufficient ice to ensure good immersion.

- Siphon off any excess water, and compress the remaining ice to form a tightly packed slush.

- Immerse the thermometer. For liquid-in-glass thermometers use the clean rod to make a hole beforehand to prevent breakage and undue stress on the bulb (see Figure 3.5).

- Wait approximately 15 to 20 minutes for thermal equilibrium to be reached before reading the thermometer. Read the thermometer several times at intervals of a few minutes to be sure that equilibrium has been reached. For steel-sheathed thermometers, it may be necessary to compress the ice quite firmly to achieve an accuracy of 0.01 °C.

- Periodically it will be necessary to add ice to the top of the container and siphon off the meltwater to prevent the level rising to the bottom of the thermometer.

This procedure may not be suitable for general thermocouple use (see Chapter 8). Although it is suitable for a single thermocouple reference junction, it will not cope with the large heat input from many thermocouples or a particularly heavy thermocouple. To ensure good thermal contact with the reference junction a well-stirred ice–water mixture or commercial ice-point apparatus may be more suitable. The ice–water mixture is, however, susceptible to temperature stratification, that is ice at 0 °C floating on top of the water and water at 4 °C (the temperature at which water is most dense)
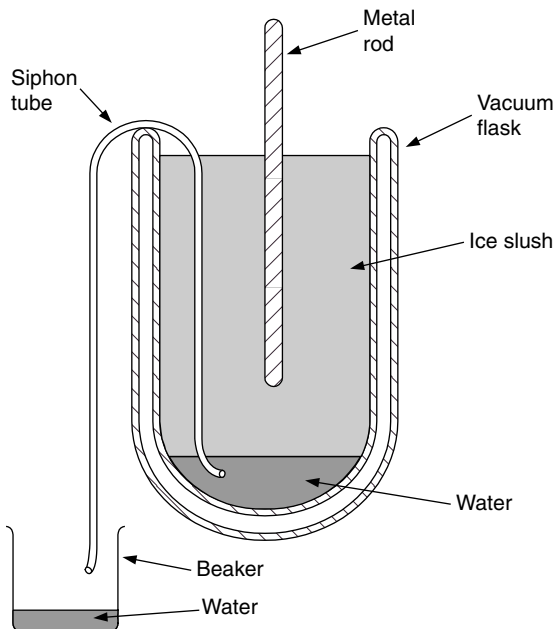
Figure 3.5   An ice-point apparatus for calibrating thermometers or for checking their stability

sinking to the bottom of the container. For this reason the ice–water mixture cannot be considered a temperature reference and its traceability must be demonstrated by an independent measurement of the ice–water temperature with a calibrated thermometer. This confirms that the water is well stirred and there is no excessive heat loading. If electrical insulation from the water is required, an oil-filled thermowell may be inserted into the ice.

The ice point can also be adapted to suit long-wavelength radiation thermometers. This is described in Section 9.6.2.

3.3 ITS-90

3.3.1 The principles of ITS-90

ITS-90 approximates the thermodynamic temperature scale over the range from 0.65 K up to the highest temperature practically measurable in terms of the Planck radiation law (see Section 3.3.6). ITS-90 is an example of the construction of an ordinal scale (Section 1.2.2) to approximate the metric scale for thermodynamic temperature. The approximation is based on three types of device, as summarised in Figure 3.6:

(1) Fixed points. These are the melting, boiling and triple points of pure substances. Each point is highly reproducible, and is assigned a temperature that is believed to be close to the thermodynamic temperature of the point.

(2) Interpolating thermometers. These are highly reproducible thermometers of four different types: helium vapour-pressure thermometer, helium- or hydrogen-gas thermometer, platinum resistance thermometer and radiation thermometer. Each is calibrated at one or more fixed points.

(3) Interpolating equations. The thermometer reading at each of the fixed points is used to construct an equation, of a specified form, that passes through each of the points. The interpolating equation is then used to provide readings for temperatures between the fixed points. About half of the ITS-90 interpolation equations are equivalent to Lagrange interpolation, as described in Section 2.11.

All of these instruments are tightly specified by ITS-90.

In the following sections, we describe the fixed points and the interpolating thermometers in more detail. We focus particularly on the platinum resistance thermometer sub-ranges of ITS-90 and the associated fixed points since they cover the most commonly used and easily realised parts of the scale.

3.3.2 The metal fixed points

Fixed points are systems whose temperatures are fixed by some physical process and hence are universal and reproducible. The most successful systems for temperature standards are phase transitions involving major changes of state. Figure 3.1, which shows the phase diagram for water, is characteristic of the phase diagrams for many simple substances, and provides some basic guidelines for the choice of fixed points. In the case of water, we have already exploited the triple point, which occurs at a
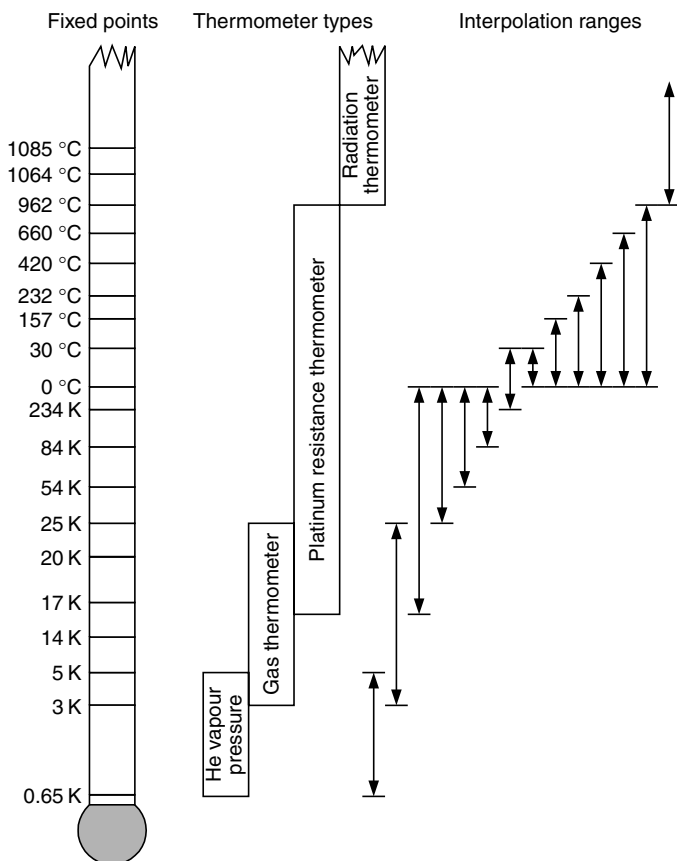
Figure 3.6 A simplified guide to the main features of ITS-90

single well-defined temperature and pressure. The second useful feature of Figure 3.1 is the almost vertical line representing the melting point. A vertical melting curve is characteristic of many substances and means that the melting point (or equivalently the freezing point) is relatively insensitive to pressure. The boiling-point curve by comparison has a very low slope indicating a very high pressure sensitivity. If, for example, we compare both the normal melting and boiling points of water with the triple point we see that the temperature change with 1 atmosphere change in pressure is about 13 000 times greater for the boiling point than for the melting point. Thus, melting points are preferred to boiling points for temperature references.

Phase changes involve *latent heat* or *heat of transition*. Latent heat is the heat required to break the binding forces that hold atoms or molecules in place. With melting, it is the heat required to change the state of the atoms or molecules from an ordered crystalline state to a disordered liquid state. The process is reversible so when the substance freezes the heat is released again. The latent heat allows us to exploit phase transitions as temperature references.

Figure 3.7 shows a melting and freezing curve for tin. As the sample of tin is heated, the temperature slowly rises until the melting point is reached. At the melting point,
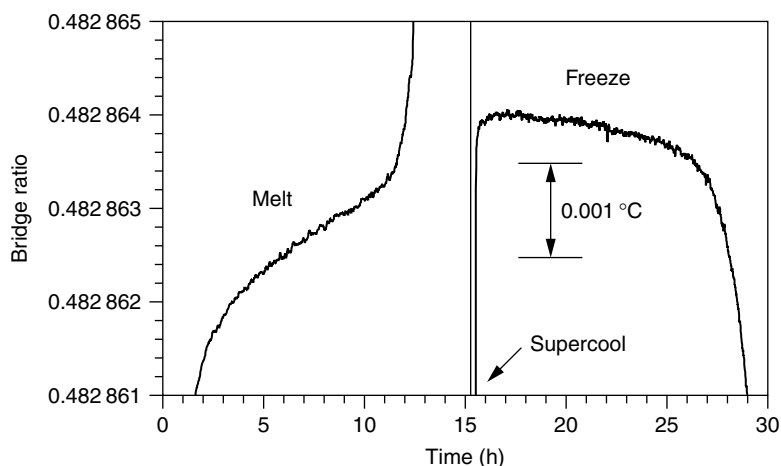
Figure 3.7 The melting and freezing curves obtained with a tin point

the heat applied to the sample is absorbed without any change in the temperature as the solid changes to liquid. For a typical metal fixed point, the total heat of transition is in the range 50 kJ to 500 kJ. With heating rates of a few watts, the sample can take several hours to melt. Once the sample has melted completely the temperature rises again. The reverse of the process occurs with freezing. As the sample is cooled slowly, the temperature becomes constant again once the freezing point is reached and the latent heat is being released.

The second feature of the freeze plateau is the supercool at the very beginning of the freeze. Extremely small crystals of any material are unstable and will contract rather than grow unless they are beyond a critical size. For materials that are close to the freezing point, the crystals are normally seeded on small foreign particles or the rough surface of the container. In very pure metals, there are few seeds for the crystals and it can take some time for the freezing to commence. In the meantime, the liquid continues to cool. Once the freeze has started, the latent heat released by the solidifying metal warms the sample and the temperature rises to the freezing point.

The factors affecting the performance of metal fixed points are very similar to those for the ice point. To provide a reproducibility of better than 1 mK the metals must be very pure, typically better than 99.9999% pure. Purity is a major factor contributing to the cost of these points. Purity concerns also have an influence on the construction of the fixed points. The high operating temperature of some of the points means that they are prone to oxidation and contamination from airborne impurities and atmospheric gases. For this reason most of the metal fixed points are operated under an inert gas environment, typically high-purity argon.

As expected of melting and freezing points, pressure has an influence on the fixed-point temperature. Since the fixed point is defined to be at standard atmospheric pressure, 101.325 kPa, corrections should be applied if the atmospheric conditions are extreme, the measurement is carried out at altitude, or the inert gas system is maintained at other than the standard pressure. Table 3.1 lists all of the fixed points employed in ITS-90, and the pressure coefficients for the points.

Table 3.1   Defining fixed points of the ITS-90 scale

Substance*†	Temperature		$dT/dP^{\ddagger}$	$dT/dl^{\S}$	$W_r(T_{90})^{\parallel}$
	T_{90}(K)	T_{90} (°C)			
^{3}He (V) or ^{4}He (V)	3 to 5	−270.15 to −268.15			
e-H$_2$ (T)	13.8033	−259.3467	34	0.25	0.001 190 07
e-H$_2$(V) or ^{3}He (G) or ^{4}He(G)	≈17	≈−256.15			
e-H$_2$(V) or ^{3}He (G) or ^{4}He(G)	≈20.3	≈−252.85			
Ne (T)	24.5561	−248.5939	16	1.9	0.008 449 74
O$_2$ (T)	54.3584	−218.7916	12	1.5	0.091 718 04
Ar (T)	83.8058	−189.3442	25	3.3	0.215 859 75
Hg (T)	234.3156	−38.8344	5.4	7.1	0.844 142 11
H$_2$O (T)	273.16	0.01	−7.5	−0.73	1.000 000 00
Ga (M)	302.9146	29.7646	−2.0	−1.2	1.118 138 89
In (F)	429.7485	156.5985	4.9	3.3	1.609 801 85
Sn (F)	505.078	231.928	3.3	2.2	1.892 797 68
Zn (F)	692.677	419.527	4.3	2.7	2.568 917 30
Al (F)	933.473	660.323	7.0	1.6	3.376 008 60
Ag (F)	1234.93	961.78	6.0	5.4	4.286 420 53
Au (F)	1337.33	1064.18	6.1	10	
Cu (F)	1357.77	1084.62	3.3	2.6	

*All substances except ^{3}He are of natural isotopic composition: e-H$_2$ is hydrogen at the equilibrium concentration of the ortho- and para-molecular forms.

†The symbols have the following meanings: V, vapour-pressure point; T, triple point; G, gas-thermometer point; M, F, melting point, freezing point (temperature, at a pressure of 101 325 Pa, at which the solid and liquid phases are in equilibrium).

‡dT/dP is the rate of change of the temperature with pressure. The units are 10^{-8} K Pa^{-1}, which is equivalent to millikelvin per atmosphere.

§dT/dl is the rate of change of the temperature with depth. The units are 10^{-3} K m^{-1}, which is equivalent to millikelvin per metre.

$\parallel$W$_r$ is the reference resistance ratio and is defined in Section 3.3.5.

Metal fixed-point cells are similar in construction to the water triple-point cell in that they have a cylindrical crucible containing the metal and a thermometer well immersed into the metal sample. They also exhibit a temperature dependence on the depth of the cell caused by the hydrostatic pressure of the metal, and corrections should be applied. Table 3.1 also lists pressure coefficients expressed as rate of change of temperature with the depth of the fixed point.

The detailed procedures for achieving a satisfactory freeze depend on the metals used. The following procedure outlines the realisation of the zinc point, which is typical of the procedures used for fixed points above 150 °C.

Equipment required

Figure 3.8 shows the main components for a metal fixed-point cell.

- The metal sample is contained within a high-purity graphite crucible. The thermometer well is also graphite. Graphite is not soluble in the particular metals used
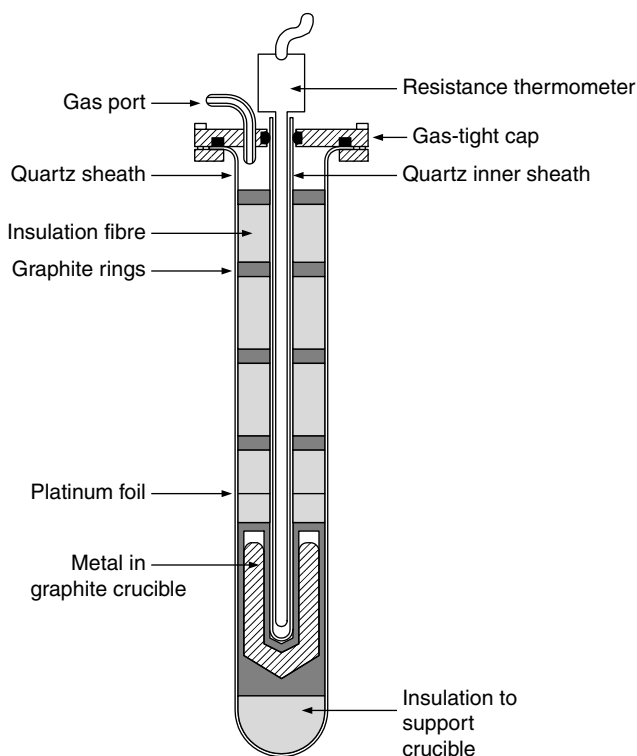
Figure 3.8 The basic construction for a metal freezing-point cell (not drawn to scale)

for ITS-90 and provides good thermal conduction with enough strength to withstand the freeze and any thermal stresses.

- A metal sample of about 100 ml to 250 ml is required. The ideal cell provides a thermometer with about 200 mm immersion within the molten metal.

- The fixed-point cell is assembled in a blind tube (glass or quartz depending on temperature). A second thermometer well of glass or quartz is inserted into the crucible. This thermometer well should be sand-blasted to prevent radiation from piping up the glass. The top of the assembly is made gas-tight with a port to supply the inert gas.

- Within the main glass tube are various layers of thermally insulating and thermally conducting material, as shown in Figure 3.8. The various layers are required to isolate the cell thermally from the outside of the furnace yet allow thermal contact with the furnace to keep the glass thermometer well warm and improve the thermometer immersion. Platinum foil may also be used in one or two of the layers of insulation to provide an infrared radiation barrier.

- The assembly is purged of air and filled with inert gas to prevent oxidation of the graphite and the metal. A dry gas is needed if the metal reacts with water, for example Al, Ag and Cu. The gas pressure should be kept at 1 standard atmosphere (see Table 3.1) because the freeze temperature is pressure sensitive.

- Once the cell is assembled, it can be inserted into a furnace. The typical furnace is a tube furnace able to accommodate the cell, which is 400 mm to 600 mm long, depending on the temperature of the fixed point. The temperature uniformity in the furnace should be within a few tenths of a degree over the length of the crucible. For the higher-temperature fixed points three-zone furnaces and heatpipe furnace liners are sometimes used to obtain the required uniformity.

From the above procedure, it can be seen that the fixed-point cell has to be carefully designed to ensure that the thermometer is in good thermal contact with the freezing-metal system. We now examine the main steps in obtaining a satisfactory freeze with such a cell.

The freezing procedure

- Place a known reference thermometer, ideally a standard platinum resistance thermometer (SPRT), in the thermometer well as a monitor. Any SPRT should be treated to reduce radiation effects as outlined in Section 6.5.3.
- Raise the temperature of the enclosure to about 5 K above the melting point to ensure a complete melt.
- From the graph of temperature versus time, a melt plateau is observed. Ideally, this should be flat, but in practice, there will be a small slope (as in Figure 3.7) due to the non-equilibrium distribution of the impurities from the previous freeze.
- Once the melt has been completed set the furnace to about 1 K below the freeze temperature. The exact set point varies considerably from system to system depending on the thermal properties of the furnace and the freeze duration required. The freeze duration should be a minimum of 3 hours, and preferably up to about 10 hours.
- Continue to monitor the temperature. With the exception of tin cells, the temperature will fall below the freezing point (the supercool in Figure 3.7) and then recover to the freezing point. With tin cells the supercool may be greater than 15 K so the cell must be removed (carefully) from the furnace for a minute or so to initiate the freeze.
- Once the thermometer indicates that a stable freeze plateau has been reached, remove the thermometer and insert a cold glass or quartz rod into the cell. In principle, a single continuous liquid–solid interface surrounding the thermometer well is satisfactory. In practice two interfaces are better. One interface starts on the inside surfaces of the outside walls of the crucible and encloses the remaining metal liquid. Inserting the cold rod induces a second solid–liquid interface surrounding the thermometer well. Because of the small temperature difference between the inner and outer interfaces the inner one grows very slowly allowing the freezing metal to reject any impurities.
- Reinsert the thermometer into the cell. The freeze plateau should last for a minimum of 3 hours, allowing several pre-heated thermometers to be calibrated. The uncertainty in the fixed point depends primarily on the purity of the metal and the quality of immersion of the thermometer. The low-temperature metal fixed points are typically repeatable to 0.1 mK or so. The higher-temperature points tend to be more

difficult and the repeatability is of the order of 2 mK to 5 mK. The quality of the immersion can be assessed by varying the immersion and tracking the hydrostatic correction with depth or by changing the furnace set point and confirming that there is no change in the measured temperature.

● Always check that the fixed point is still on the freeze plateau after each measurement by returning the monitoring thermometer to the well.

The procedure given here applies to so-called open cells. These cells have a gas port that allows the operator to control the gas pressure. Sealed cells, consisting of the crucible only within a sealed glass or quartz container, are also available. These are more convenient to operate and provide better protection against contamination of the cell. The disadvantage is that a leak may not be detected and, on heating, the pressure in the cell will alter the freeze temperature. Therefore, sealed cells should be treated as transfer standards requiring occasional certification rather than as primary standards.

All of the metal fixed points for ITS-90 are available commercially from several companies in convenient cells with furnaces and control equipment. Figure 3.9 shows a commercial gallium-point system. Unlike the other metal fixed points, gallium is
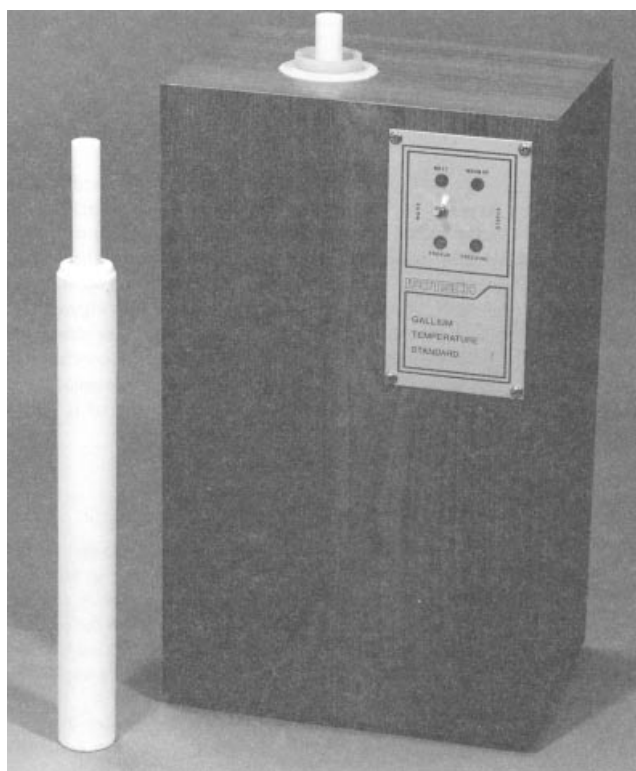
Figure 3.9   The gallium temperature standard, which includes the gallium cell and a fixed-point apparatus, is a convenient means for realising and maintaining the liquid–solid equilibrium (melting point) of gallium. This precision instrument provides laboratories and manufacturers with a standard for the calibration of laboratory transfer and industrial thermometers, at a temperature that is a constant of nature in the biological temperature range (29.7646 °C)

realised as a melting point. The melt plateau is used because, unlike the other metals, gallium expands on freezing making it difficult to prevent mechanical pressure from upsetting the fixed-point temperature. Fortunately, gallium is available in extremely high purity, better than 99.999 999%, so the fixed point is extremely good.

There is also a range of 'miniature' fixed-point cells available. These are intended for industrial usage, for calibrating rare-metal thermocouples (Chapter 8) and industrial resistance thermometers. The uncertainty of these systems is about ± 10 mK.

3.3.3   The cryogenic triple points

One of the big advances in reference standards for low-temperature thermometry is the increasing availability and use of sealed triple-point cells of gases, especially H_2, Ne, O_2 and Ar. The cells are available from some national standards laboratories, which also provide procedures for their use. In this section, we give a very brief outline of how they are used, mainly to illustrate how they differ from the other fixed points.

The most significant differences lie in the relatively small amount of gas used and the low latent heat of the gases. Whereas the metal fixed points have a total heat of transition in the range of 50 kJ to 500 kJ, the cryogenic triple-point systems have heats of transition more than a thousand times smaller, of the order of 5 J to 500 J. Therefore, unlike the metal fixed points we cannot rely on the latent heat alone to maintain the temperature of the system. A very well-controlled cryostat and delicate procedures are needed to realise the cryogenic triple points.

The cells must be filled with enough gas to ensure that there is sufficient material to have solid, liquid and vapour phases at the fixed-point temperature. If not then the pressure at the fixed-point temperature will be below the triple-point pressure, and only the sublimation point can be realised. This means that the room-temperature pressure of the cells can be quite high, in the range 0.5 MPa to 10 MPa. For this reason the cells should not be overheated. Gas cells are made in a very wide variety of shapes and profiles, and are usually made to hold several capsule-style SPRTs. An example is shown in Figure 3.10. Argon-point systems are also available for use with long-stem SPRTs.

Because of the low heats of transition, the cryogenic fixed points are operated in adiabatic conditions, that is zero heat flow. This is achieved by surrounding the cell with a radiation shield maintained at or very near the fixed-point temperature, with the whole system in vacuum. To prevent heat leaks via lead wires, thermometer leads have a small diameter (0.1 mm) and are thermally anchored to the radiation shield, with a minimum length of 300 mm to the cryostat to give sufficient thermal isolation.

The cell is cooled so that the gas condenses all around the thermometer block; this prevents drops of liquid or solid falling down during melting. The solidification should be slow to allow uniform crystallisation with little stress and to limit the temperature gradient in the solid. The shield is then adjusted to a few tenths of a kelvin below the triple-point temperature and held there while stresses in the solid anneal.

Because of the problems with the supercool and the thermal mass of the cell, the triple point is realised by controlled melting of the solid rather than freezing of the liquid. Once frozen, the cell is thermally isolated by evacuating the cryostat, and subjected to intermittent heating. Figure 3.11 shows the effect of the heating on the melt plateau. The
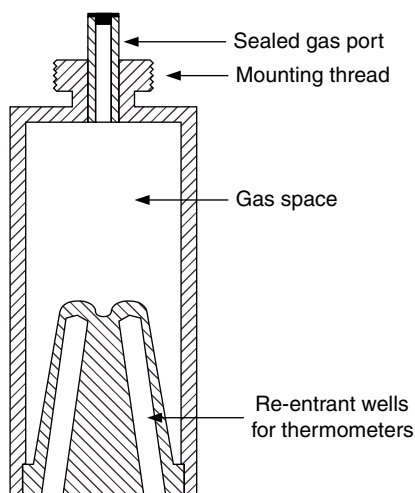
Figure 3.10   A sealed gas cell of a type suitable for establishing a gas triple point. The thermometer block can hold three capsule thermometers
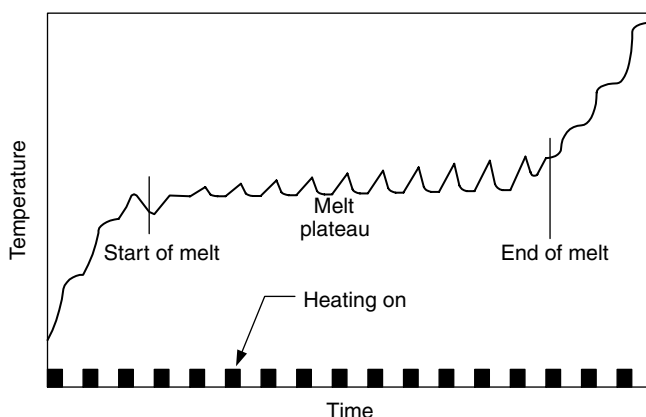
Figure 3.11   A schematic representation of a melt observed in a sealed gas triple-point cell

heating steps are chosen so that there are about 10 required to melt the sample. For each step an overheat is observed, initially around 0.1 mK and increasing to several millikelvin for the later steps. After each heating step, time is allowed for thermal equilibrium to be re-established. Once the cell is molten, the equilibrium temperatures measured following each pulse are analysed to determine the triple-point temperature. The uncertainty in the triple-point temperature is typically less than 0.2 mK.

3.3.4   The cryogenic vapour-pressure points

The cryogenic vapour-pressure points are very similar to the triple points, but are more difficult to realise because the pressure must be measured. This means that a capillary

must be connected to the cell and to pressure measurement equipment outside the cryostat. The capillary must always be warmer than the cell to prevent condensation yet not contribute a heat leak to the cell. This involves the use of large-diameter (2 mm) capillary with a vacuum jacket, thermal anchoring and radiation traps. Corrections must also be applied to account for the hydrostatic pressure of the gas in the capillary. Overall the uncertainties are not as good as the triple points but are usually better than 1 mK.

3.3.5   Platinum resistance thermometry

There are three different types of SPRT used for ITS-90:

(1)   Capsule SPRTs cover the temperature range from 13.8 K to 157 °C. These are small, typically 50 mm to 60 mm long by 5 mm diameter, with 30 mm to 50 mm platinum lead wires mounted in a glass seal at one end, as shown in Figure 3.12. The platinum sensor has minimal mechanical support, and has a resistance of 25.5 Ω at the triple point of water. Most capsule SPRTs are filled with helium gas at a pressure of 30 kPa (at room temperature) to improve the thermal contact and response time of the sensor.

(2)   Long-stem SPRTs cover the range 84 K to 660 °C. These are 450 mm long glass or quartz tubes of about 8 mm diameter, with the platinum sensing element mounted on a mica or quartz support, as shown in Figure 3.13. These too have a nominal resistance of 25.5 Ω. The connections to flexible lead wires are normally made in the handle mounted on the end of the tube. Chemical changes are an important
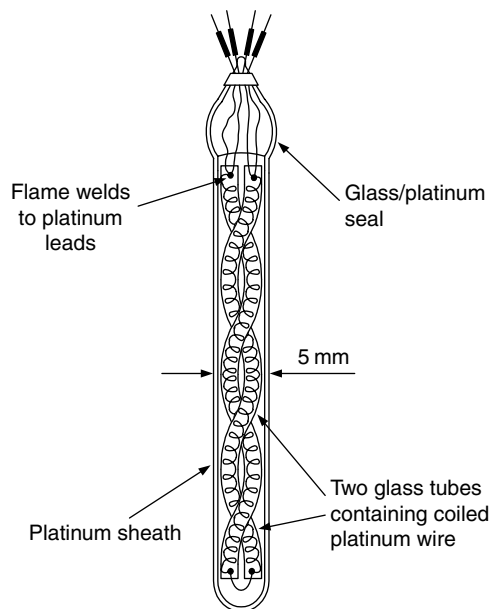
Figure 3.12   A typical 25 Ω capsule platinum resistance thermometer. The platinum sheath is 5 mm in diameter and 50 mm long

(a)

(b)

Figure 3.13 A long-stem SPRT made to ITS-90 requirements. The complete assembly in a carrying case is shown (top), with the tip showing details of construction of the resistance element (below)

consideration in the design of long-stem SPRTs. The sheath is normally filled with an inert gas plus oxygen at a partial pressure of 2 kPa. This concentration is chosen to control the oxidation state of the platinum wire and prevent impurity oxides from breaking down to metals, which can contaminate the platinum. Contamination from, and breakdown of, the supports or sheath also limit the acceptable upper temperature. For maximum stability the SPRTs with mica supports are best not taken over 450 °C.

(3) High-temperature SPRTs are long-stem SPRTs made for exposure to higher temperatures with a typical range of 0.01 °C to 962 °C. In these thermometers, all of the insulating components exposed to high temperatures are quartz. The nominal resistance is 0.25 Ω, much lower than the resistance of low-temperature long-stem thermometers, to reduce the influence of insulation leakage effects.

All three types of thermometer are readily available commercially in a form satisfying the ITS-90 requirements.

For platinum resistance thermometry the quantity of interest is not the absolute resistance of the thermometer, $R(T_{90})$, but $W(T_{90})$, the resistance ratio with respect to the resistance at the triple point of water:

$$W(T_{90}) = \frac{R(T_{90})}{R(273.16\,\text{K})}.$$ (3.3)

By using resistance ratio in the definition of the scale, we eliminate uncertainties associated with the measurement of the absolute resistance (see Example 2.19).

In order to ensure that the calibration equations for all SPRTs are very similar, and to reduce the uncertainty in the realisation of the temperature scale, ITS-90 requires the SPRT to be made out of platinum wire of sufficient purity such that

$$W(29.7646\,^\circ\text{C}) \geq 1.118\,07 \tag{3.4}$$

or

$$W(-38.8344\,^\circ\text{C}) \leq 0.844\,235. \tag{3.5}$$

In addition, if the SPRT is to be used up to the silver point then

$$W(961.78\,^\circ\text{C}) \geq 4.2844. \tag{3.6}$$

There are two problems to be solved in relating a resistance thermometer reading to temperature: one involves the relationship between resistance ratio and temperature while the other is the problem of calibrating individual thermometers. ITS-90 separates these two problems. Firstly, it specifies a reference function that characterises the relationship between resistance ratio and temperature, and secondly it employs relatively simple interpolation equations to provide for the calibration of individual SPRTs.

The reference function has two parts, one for the range 13.8033 K to 273.16 K and the other for 0.01 °C to 961.78 °C. In the range 13.8033 K to 273.16 K the reference function $W_\text{r}(T_{90})$ is defined by the equation

$$W_\text{r}(T_{90}) = \exp\left\{A_0 + \sum_{i=1}^{12} A_i \left[\frac{\ln[T_{90}/273.16\,\text{K}] + 1.5}{1.5}\right]^i\right\}. \tag{3.7}$$

An inverse function, equivalent to Equation (3.7) to within 0.1 mK, is

$$T_{90} = 273.16\,\text{K} \left\{B_0 + \sum_{i=1}^{15} B_i \left[\frac{W_\text{r}(T_{90})^{1/6} - 0.65}{0.35}\right]^i\right\}. \tag{3.8}$$

In the range from 0 °C to 961.78 °C the reference equation is

$$W_\text{r}(T_{90}) = C_0 + \sum_{i=1}^{9} C_i \left[\frac{T_{90}/\text{K} - 754.15}{481}\right]^i. \tag{3.9}$$

An inverse function, equivalent to Equation (3.9) to within 0.13 mK, is

$$T_{90}/\text{K} = 273.15 + D_0 + \sum_{i=1}^{9} D_i \left[\frac{W_\text{r}(T_{90}) - 2.64}{1.64}\right]^i, \tag{3.10}$$

where the coefficients A_i, B_i, C_i and D_i are set out in Table 3.2.

The two reference functions can be considered to represent idealised platinum thermometers; indeed, they were derived from the real data for two thermometers and they describe approximately the behaviour of all SPRTs. This approach is possible because

Table 3.2 The constants A_i, B_i, C_i and D_i in the reference functions of Equations (3.7), (3.8), (3.9) and (3.10) respectively

i	A_i	B_i	C_i	D_i
0	−2.135 347 29	0.183 324 722	2.781 572 54	439.932 854
1	3.183 247 20	0.240 975 303	1.646 509 16	472.418 020
2	−1.801 435 97	0.209 108 771	−0.137 143 90	37.684 494
3	0.717 272 04	0.190 439 972	−0.006 497 67	7.472 018
4	0.503 440 27	0.142 648 498	−0.002 344 44	2.920 828
5	−0.618 993 95	0.077 993 465	0.005 118 68	0.005 184
6	−0.053 323 22	0.012 475 611	0.001 879 82	−0.963 864
7	0.280 213 62	−0.032 267 127	−0.002 044 72	−0.188 732
8	0.107 152 24	−0.075 291 522	−0.000 461 22	0.191 203
9	−0.293 028 65	−0.056 470 670	0.000 457 24	0.049 025
10	0.044 598 72	0.076 201 285		
11	0.118 686 32	0.123 893 204		
12	−0.052 481 34	−0.029 201 193		
13		−0.091 173 542		
14		0.001 317 696		
15		0.026 025 526		

platinum has a very repeatable behaviour if sufficiently pure and free from undue mechanical stress. Two functions are used because no single platinum thermometer can cover the whole range from 13.8 K to 962 °C.

The calibration equations for individual thermometers are written as interpolations of the form

$$W_{\mathrm{r}}(T_{90}) = W(T_{90}) - \Delta W(T_{90}) \tag{3.11}$$

where the functions $\Delta W(T_{90})$ are called the deviation functions. There are 11 different sub-ranges using eight different deviation functions as shown in Table 3.3. Deviations from the reference values of resistance ratio (the last column in Table 3.1) are measured at the fixed points and used to calculate the coefficients of an approved deviation function.

While at first sight the many equations for the deviation functions may seem overly complex, the numerous sub-ranges make the scale more practical for a user wishing to implement the scale over a specific range of interest. For example, a user requiring temperature measurements from 0 °C to 100 °C would implement the 0 °C to 156 °C sub-range with only two fixed points. For measurements supporting biological and instrumentation measurements between 0 °C and 29 °C only two simple fixed points are required. The previous scale, IPTS-68, would have required four fixed points and exposure of the thermometer to temperatures around 420 °C for both of these cases.

The use of overlapping ranges does, however, lead to ambiguities in the temperature depending on the sub-range chosen. Non-uniqueness studies have shown that the ambiguity arising from different sub-ranges is no greater than that arising from different thermometers over the same range, and may lead to differences of 1 mK or so, but more typically 0.5 mK, which for many purposes is negligible.

SPRTs, although relatively fragile, are practical thermometers and should be used if uncertainties better than ±10 mK are sought. We outline here the practical concerns in the use of an SPRT; further details may be found in the manufacturer's instructions

Table 3.3 The sub-ranges, deviation functions and calibration points for platinum resistance thermometers used to define ITS-90

Temperature range	Deviation function	Fixed points
13.8033 K to 0.01 °C	$a(W - 1) + b(W - 1)^2 + \sum_{i=1}^{5} c_i \, [\ln(W)]^{2+i}$	e-H_2, Ne, O_2, Ar, Hg*
24.5561 K to 0.01 °C	$a(W - 1) + b(W - 1)^2 + \sum_{i=1}^{3} c_i \, [\ln(W)]^{i}$	e-H_2, Ne, O_2, Ar, Hg
54.3584 K to 0.01 °C	$a(W - 1) + b(W - 1)^2 + c \, [\ln(W)]^2$	O_2, Ar, Hg
83.8058 K to 0.01 °C	$a(W - 1) + b(W - 1) \ln(W)$	Ar, Hg
−38.8344 °C to 29.7646 °C	$a(W - 1) + b(W - 1)^2$	Hg, Ga
0.01 °C to 29.7646 °C	$a(W - 1)$	Ga
0.01 °C to 156.5985 °C	$a(W - 1)$	In
0.01 °C to 231.928 °C	$a(W - 1) + b(W - 1)^2$	In, Sn
0.01 °C to 419.527 °C	$a(W - 1) + b(W - 1)^2$	Sn, Zn
0.01 °C to 660.323 °C	$a(W - 1) + b(W - 1)^2 + c(W - 1)^3$	Sn, Zn, Al
0.01 °C to 961.78 °C	$a(W - 1) + b(W - 1)^2 + c(W - 1)^3 +$ $d \, [W - W(660.323 °C)]^2$	Sn, Zn, Al, Ag[†]

*For the sub-range 13.8033 K to 0.01 °C, two of the calibration points are points determined by gas thermometer or vapour-pressure thermometer (see Section 3.3.7 for details). [†]For the sub-range 0.01 °C to 961.78 °C the coefficients a, b, c are the same as used for the sub-range 0.01 °C to 660.323 °C, and the coefficient d is determined from the silver point.

and the BIPM guidelines. The minimum equipment requirement includes a calibrated SPRT, a triple point of water cell to enable you to measure $W(T_{90})$, and resistance bridge with a temperature-controlled reference resistor.

Accurate measurement of the temperature depends critically on accurate resistance measurement, which is covered more fully in Chapter 6. An a.c. or d.c. automatic resistance bridge using a four-lead definition of resistance is generally used. The bridge should display seven digits in resistance ratio and have a variable sensing current to enable corrections for self-heating (Section 6.5.4). While seven digit accuracy is preferred, adequate readings can be made with six digits if the reference resistor is specifically chosen to match the SPRT resistance over the range used. The bridge will probably be the most expensive component in your system.

Depending on the frequency and importance of the measurements the SPRT will need to be checked occasionally to verify that the calibration still applies. The check is best made with a water triple-point cell, although a very carefully prepared ice point may do (see Section 3.2.4). Equipment for the water triple point is relatively inexpensive and time saving in use. The ice point is even less expensive to establish but takes more care and is more time consuming if many accurate measurements are made.

When using capsule SPRTs, care must be taken to ensure good thermal contact, especially at lower temperatures. The capsule comprises the sensor only, unlike a long-stem SPRT, which also includes lead wires. The capsule should be totally immersed, using suitable grease to aid contact, in a well in the copper block whose temperature is being measured. The four, short, capsule lead wires are connected to longer leads of fine insulated copper wires that are thermally anchored to prevent heat transfer to the capsule.

With long-stem SPRTs radiation can be piped along the transparent sheath, upsetting the thermal balance. For example, incandescent room lighting can raise the apparent temperature of a water triple-point cell by 0.2 mK, and at higher temperatures radiation loss down the sheath can cool the thermometer causing errors of many millikelvin. To avoid radiation piping the sheath can be sand-blasted just above the sensor region or coated with graphite paint (see Section 6.5.3).

ITS-90 is the first scale to use SPRTs at high temperature. Of particular concern is the porosity of the quartz to some metal vapours, which can contaminate the platinum wire. A platinum-foil barrier over the quartz sheath is highly desirable if there is any risk of contamination. Electrical leakage also becomes a problem at very high temperatures. This is managed in part by using a low value of $0.25\,\Omega$ for the sensing resistance.

Mechanical vibration can cause strain and work hardening of the platinum wire and hence an increase in the resistance at the water triple point. Large knocks have been known to cause errors of the order of 10 mK. Annealing above 450 °C for several hours followed by gentle cooling to room temperature will usually restore the original resistance. For very severe knocks it may be necessary to anneal at 660 °C. The resistance should be repeatable to seven digits on a resistance bridge, that is to higher precision than the uncertainty in the value of the reference resistor. A capsule SPRT cannot be annealed and therefore should not be used for long periods where there is any vibration, for example in a stirred bath.

Strain due to thermal shock can also have a similar effect to mechanical shock. SPRTs should be inserted slowly into higher temperatures. A rate of 50 °C per minute is a good guide. The use of pre-heating furnaces may be useful if measurement time is an issue. The thermometer should also be removed with care. Table 3.4 gives recommended cooling rates for SPRTs.

The immersion depth for SPRTs is large, in part because of the high precision usually required and in part because of the length of the sensing element. SPRTs that have a high self-heating constant (see Section 6.5.4) require greater immersion. Adequate immersion depths are typically 150 mm to 200 mm at room temperature and up to 300 mm at 200 °C and above. If in doubt, perform a temperature profile versus immersion depth to give an indication of the required immersion depth.

Table 3.4 A typical cooling schedule for SPRTs. The SPRT may be cooled gradually or allowed to anneal at the lowest temperature of each of the three highest ranges

Range	Cooling rate	Period
From 960 °C down to 850 °C	25 °C per hour	4 hours
From 850 °C down to 630 °C	100 °C per hour	2 hours
From 630 °C down to 540 °C	400 °C per hour	30 minutes
From 450 °C to room temperature	50 °C per minute	10 minutes

3.3.6 Radiation thermometry

Above the freezing point of silver, 961.78 °C, ITS-90 uses the Planck blackbody radiation law (see Chapter 9) to define temperature in terms of the ratio of the spectral radiance at the temperature T_{90}, $L_\lambda(T_{90})$, to the spectral radiance at a fixed-point temperature, $L_\lambda(T_{90,X})$, where $T_{90,X}$ is the freezing point of silver, gold or copper. The ratio of the spectral radiances is

$$\frac{L_\lambda(T_{90})}{L_\lambda(T_{90,X})} = \frac{\exp(c_2/\lambda T_{90,X}) - 1}{\exp(c_2/\lambda T_{90}) - 1}, \tag{3.12}$$

where λ is the wavelength in vacuum, and $c_2 = 0.014\,388$ m K is the second radiation constant. Although the scale is defined in terms of a spectral radiance ratio at a single wavelength, practical radiometers must operate over a finite bandwidth. Typical bandwidths for primary radiometers are 10 nm to 100 nm. One of the more difficult tasks is to determine the mean effective wavelength to be used in Equation (3.12), which needs to be known to better than 0.1 nm for measurements made in the 600 nm to 900 nm range typical of modern radiometers. The mean effective wavelength depends on the radiometer's spectral responsivity, which must be measured to very high accuracy over a wide range of wavelengths, the spectral shape of the Planck radiation function, and the two temperatures in Equation (3.12). Several techniques have been developed for solving the resulting equations for temperature. More details on radiation thermometry are covered in Chapter 9.

The fixed points for radiation thermometry are similar to those for SPRTs but usually smaller. For radiation thermometry, the crucible is mounted horizontally in a furnace, and the graphite well is made into a blackbody cavity (see Figure 3.14). The cavity is typically 50 mm to 80 mm long with a 2 mm to 6 mm aperture.

Radiation thermometry has an accuracy of 0.1 K at the silver point where it meets the platinum resistance scale. If the scale is extrapolated to lower temperatures, it tends to have a similar accuracy so long as the radiometer is sufficiently sensitive. At higher temperatures, the uncertainty tends to increase in proportion to T^2. To measure to 0.1 K at the silver point the radiometer must measure radiance to an accuracy of better than 0.1%. The combination of the intensity ratios of the order of 1 in 10^4 that must be measured (Equation (3.12)) and the high accuracy means that corrections for the
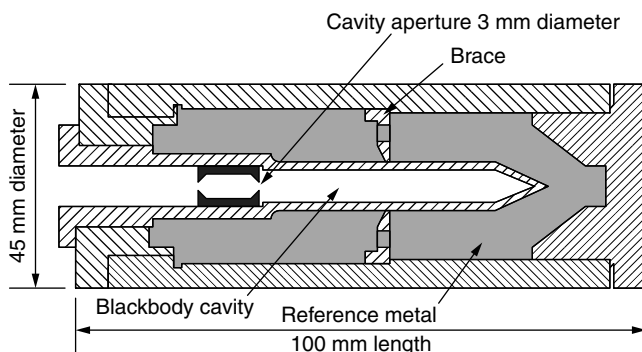
Figure 3.14 A metal fixed point with a blackbody cavity suitable for a radiation standard

non-linearity of the radiometer are essential. At this level of accuracy, the blackbody cavity must be characterised or be ideal to better than 1 part in 10^4. This in turn puts tight constraints on the design of the blackbody cavity (see Section 9.6).

Reference radiometers are used in two distinct ways. Conventionally they have been used as comparators to compare a blackbody directly with another radiant source, often a standard lamp, and hence only need a limited stability with time. As the optical detectors and filters improve in stability, the radiometers are beginning to be used as reference thermometers that need only occasional calibration. In both cases the radiometers are generally made by the national standards laboratory and are not readily available.

3.3.7 Cryogenic thermometry

Very low-temperature techniques are not considered in detail in this text. The unusual physical properties of materials at low temperatures, especially low heat capacity and high thermal conductivity, mean that both the materials used and the techniques involved are specialised. The interpolating thermometers defined by ITS-90, the helium vapour-pressure thermometer and the constant-volume gas thermometer, are also sufficiently complex and specialised that few national standards laboratories have implemented this part of the scale.

Vapour-pressure thermometers

If we refer to the water phase diagram in Figure 3.1, we can see that the temperature along the boiling-point curve depends only on pressure. What is more, the pressure changes rapidly for small changes in temperature. If we know the equation of the boiling-point curve, we need only measure pressure to a modest accuracy to make an accurate measure of the temperature. This is the principle underlying vapour-pressure thermometers.

Between 0.65 K and 5.0 K, ITS-90 is defined in terms of helium vapour-pressure thermometers. Two different thermometric liquids can be used:

(1)　^{4}He with equations for 1.25 K to 2.2 K and 2.2 K to 5 K;

(2)　^{3} He with an equation for 0.65 K to 3.2 K.

ITS-90 defines completely the numerical relationship between the temperature and the vapour pressure so no fixed points are required. While a thermodynamic equation can be given for the vapour pressure, it is approximate, so an empirical equation based on experimental data is used.

The vapour-pressure thermometer is designed to allow two phases of helium, the pure liquid and vapour phases, to come to thermal equilibrium in a similar manner to the cryogenic triple points. The absolute pressure at the interface between liquid and vapour is then measured, and the temperature is calculated. As with any cryogenic thermometry, heat losses and thermal gradients are a major concern. With care, an accuracy of around ± 0.5 mK is possible.

Gas thermometers

Constant-volume gas thermometers using helium, either ^{3}He or ^{4}He, cover the range 3 K to 24.6 K (the neon triple point), and require calibration at three temperatures. In principle, gas thermometers can be used to determine the thermodynamic temperature relative to a single fixed point (usually the neon triple point). However, they require considerable care if accurate results are to be achieved over a wide range of low temperatures. By using three well-placed fixed points according to ITS-90, the measurement difficulties are reduced, and the reproducibility of the scale is increased. Then accuracies of around ± 0.1 mK can be achieved. Over the range 4.2 K to 24.6 K for ^{4}He, a simple quadratic equation is used:

$$T_{90} = a + bp + cp^2, \qquad (3.13)$$

where p is the measured pressure. The coefficients a, b and c are determined at the triple point of neon, 24.5562 K, the triple point of equilibrium hydrogen, 13.8033 K, and at one further point between 4.2 K and 5 K as determined by the vapour-pressure thermometer.

With ^{3}He as the thermometer gas, or with ^{4}He below 4.2 K, Equation (3.13) must be modified to account for the non-idealities of the gas; specifically a term involving the second virial coefficient is added. The equations are firmly thermodynamically based with corrections to account for the known departures from ideal gas behaviour, for example finite atomic size and bonding.

Both the gas thermometer and the vapour-pressure thermometer are complex devices, further complicated by the fact that they have to be connected together to provide the third calibration point for the gas thermometer. Consequently, they are generally impractical for direct measurements so are used only to transfer the scale to more suitable temperature sensors.

3.4 The Propagation of Uncertainty on ITS-90

A full description of the uncertainties associated with the realisation of ITS-90 is beyond the scope of this text; indeed that is one of the purposes of the guidelines published periodically by the BIPM (see references at the end of the chapter). However, as users of SPRTs calibrated by another laboratory you will require an estimate of the uncertainty in the measured temperature. In this section, we provide an equation for the propagation of uncertainty on the SPRT sub-ranges of ITS-90 and explain the origin of the equation.

As a specific example of one of the SPRT interpolation equations, consider the water–tin–zinc sub-range (0.01 °C to 419.527 °C). The interpolation equation is

$$W_{\mathrm{r}} = W - a(W - 1) - b(W - 1)^2. \qquad (3.14)$$

The coefficients a and b are determined by requiring Equation (3.14) to be satisfied at the freezing points of tin and zinc. If the calculated values of a and b are substituted

back into the equation we find the interpolation can be rearranged into

$$W_r = L_{H_2O} + W_{r,Sn} L_{Sn} + W_{r,Zn} L_{Zn}, \tag{3.15}$$

where the L functions are Lagrange polynomials as a function of W (see Section 2.11). These are given by

$$L_{H_2O}(W) = \frac{(W - W_{Sn})(W - W_{Zn})}{(1 - W_{Sn})(1 - W_{Zn})},$$

$$L_{Sn}(W) = \frac{(W - 1)(W - W_{Zn})}{(W_{Sn} - 1)(W_{Sn} - W_{Zn})},$$

$$L_{Zn}(W) = \frac{(W - 1)(W - W_{Sn})}{(W_{Zn} - 1)(W_{Zn} - W_{Sn})}, \tag{3.16}$$

where W_{Sn} and W_{Zn} are the measured values of W at the tin and zinc points, and $W_{r,Sn}$ and $W_{r,Zn}$ are the reference resistance ratios at the tin and zinc points (see the last column of Table 3.1). We can now see that the ITS-90 interpolation equation is a Lagrange interpolation with the three defining points $(1, 1)$, $(W_{Sn}, W_{r,Sn})$, and $(W_{Zn}, W_{r,Zn})$.

All of the SPRT interpolation equations for the SPRT sub-ranges of ITS-90 are expressible in a form similar to Equation (3.15):

$$W_r = \sum W_{r,i} F_i(W), \tag{3.17}$$

which is of the same form as Equations (2.54) and (2.64). For the sub-ranges between the mercury point ($\sim -38\,°C$) and the aluminium point ($\sim 660\,°C$) the ITS-90 interpolation equations are equivalent to Lagrange interpolation, so the $F_i(W)$ functions are Lagrange polynomials and can be found easily. For the other sub-ranges, the functions are more complicated.

Calculation of the uncertainty from these equations is quite complicated but follows the procedures given in Section 2.11. Account must be taken of the correlation between uncertainties in the W values due to the use of the triple-point resistance in the calculation of each.

For the water–tin–zinc sub-range, when the same value of the triple-point resistance is used to calculate all W values, the uncertainty in the measured temperature is

$$U_T^2 = \left(\frac{dT_{90}}{dW_r}\right)^2 \left(\frac{1}{R_{H_2O}}\right)^2 \left(U_R^2 + L_{H_2O}^2 U_{R_{H_2O}}^2 + L_{Sn}^2 U_{R_{Sn}}^2 + L_{Zn}^2 U_{R_{Zn}}^2\right), \tag{3.18}$$

where R_{H_2O}, R_{Sn} and R_{Zn} are the measurements of the SPRT resistance at the fixed points, and R is the measurement of resistance at the unknown temperature. Because the terms due to the uncertainty in the triple point are quite small, this is a good approximation for the cases when different triple-point measurements are used to calculate the W values.

The pattern of Equation (3.18) is followed for all of the SPRT sub-ranges. For the sub-ranges between the mercury point ($\sim -38\,°C$) and the aluminium point ($\sim 660\,°C$)

all of the interpolation equations are equivalent to Lagrange interpolation, so the various sensitivity coefficients are Lagrange polynomials as shown here. For the other sub-ranges, the functions representing the sensitivity coefficients are no longer Lagrange polynomials but are quite well approximated by Lagrange polynomials.

Further Reading

ITS-90

Supplementary information for the international temperature scale of 1990 (1990) Working Group 1, BIPM, Sèvres, (includes the text of ITS-90).
Techniques for approximating the international temperature scale of 1990 (1990) Working Group 2, BIPM, Sèvres.

Propagation of uncertainty on ITS-90

D R White (2001) The propagation of uncertainty with non-Lagrangian interpolation, *Metrologia* **38**, 63–69.
D R White and P Saunders (2000) The propagation of uncertainty on interpolated scales, with examples from thermometry, *Metrologia* **37**, 285–293.

Precision thermometry and a description of the physics of temperature measurement

T J Quinn (1990) *Temperature*, 2nd Edition, Academic Press, London.
J F Schooley (1986) *Thermometry*, CRC Press, Boca Raton, FL.
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4

Use of Thermometers

4.1 Introduction

The concept of temperature is something of a paradox. On one hand temperature is fundamentally linked to heat transfer. Heat always moves from higher to lower temperatures, and often we measure temperature because we want to understand something about the movement of heat. On the other hand, temperature is strictly defined in conditions of thermal equilibrium, that is where there is no net transfer of heat in any direction. So, how do we make sense of the temperature measurement when we insert a thermometer into a system and cause heat to flow into and along a thermometer? In this chapter, we investigate a number of aspects of this contradiction: how thermometers affect systems in equilibrium, and how to make sense of measurements of temperature in systems that are not at equilibrium.

We begin by laying the foundations for the chapter with a description of the three main mechanisms of heat transfer: conduction, convection and radiation. Then, following a brief description of the thermal properties of materials, we investigate the effects that thermometers have on systems in thermal equilibrium or very near thermal equilibrium. This enables us to make simple models of the errors in temperature measurements arising from poor immersion and time constant effects. We also provide simple rules of thumb that enable the user to reduce any of the errors to a negligible level in all but the most difficult situations.

The final section extends the discussion on the thermal properties of materials and explains the use of electrical analogue models in the understanding of heat transfer. Electrical analogues are then used to explain the immersion and time constant effects in more detail and to develop a working definition of temperature that can be used in situations where there is no thermal equilibrium. Although this chapter should enable a very basic understanding of thermal design, its primary purpose is to provide guidelines for assessing and managing uncertainties in temperature measurement due to heat transfer effects.

Throughout the chapter, we emphasise the importance of simple experimental tests to expose and assess the magnitude of errors due to heat flow. In almost every situation, it is possible to change the ambient temperature, change the insulation, or change the immersion, and spend 20 minutes watching the effects of these changes.

4.2 Heat Transfer

4.2.1   Conduction

The flow of heat by conduction is familiar to all of us from everyday experience through the sensation of touch. When we place our hands around a hot cup of coffee, we feel our hands warm as the heat flows from the cup into our hands. The term 'heat' is synonymous with 'kinetic energy' (unit joules), and heat transfer can be thought of as energy on the move. The rate of heat flow is the amount of kinetic energy transferred per unit time (unit watts). Heat flow is always driven by a temperature difference.

As we discovered in Chapter 1, temperature is a measure of kinetic energy, the energy of movement. Thermal conduction occurs because of collisions resulting from that movement. Although the collision mechanisms vary between metals, non-metals, liquids and gases, conduction is the transfer of energy from more energetic atoms or molecules to less energetic ones. If there are no sources of heat within a system, then the kinetic energy is gradually redistributed until, on average, it is evenly distributed throughout all the atoms and molecules in the system. At this point thermal equilibrium is achieved; all parts of the system are at the same temperature and there is no net flow of heat in any direction.

If a temperature gradient is maintained across a region, then collisions between the atoms and molecules provide the mechanism for a continuous transfer of heat across the system from the higher-temperature region to the lower-temperature region. To maintain a temperature gradient an external source of heat is required at one end and a heat sink at the other.

In gases, collisions occur relatively infrequently because of the relatively large distances between molecules. Because there are so few atoms and so few collisions, gases are not good conductors of heat. Heat transfer in gases depends on the speed of the molecules or atoms. For a given kinetic energy (temperature), small atoms move most quickly, so the light gases, helium and hydrogen, are the best conductors.

In most solids, the atoms are constrained to fixed positions inside a crystal lattice, but are free to vibrate about these positions. Since temperature is a measure of kinetic energy, the strength and magnitude of the vibrations increases with temperature. Vibrations of neighbouring atoms affect one another through interatomic forces, and when there is a temperature gradient the net effect is a transfer of energy through the lattice in the form of lattice vibrations.

If the solid is an electrical conductor, such as a metal, then the electrons assist in the conduction. In a metal, many of the electrons are free to move about the lattice much like a gas, and constantly interact with each other and collide with the atomic lattice. Thus, in addition to heat flow by lattice vibrations, heat is transferred through electron collisions and diffusion as described above for gases. Because of the high density of free electrons, metals are very good thermal conductors. If the solid is not an electrical conductor, heat is transferred exclusively through lattice vibrations.

In both metals and non-metals, conduction of heat is impeded by impurities in the lattice. Impurities introduce local distortions in the lattice that scatter both lattice vibrations and electrons, causing the heat to diffuse more slowly. Because of the high levels of impurities and defects that cause scattering in metal alloys and non-crystalline solids, these materials tend to have a lower thermal conductivity than pure metals. An

interesting exception is diamond, which has a thermal conductivity of $2300\,\mathrm{W\,m^{-1}\,K^{-1}}$, about 10 times that of the best metals, due to its extremely regular and nearly defect-free crystalline structure.

Conduction in liquids is intermediate between that of gases and solids. The atoms and molecules are as closely spaced as in solids but the placement of the atoms is random. This means that the energy from collisions is scattered randomly, as it is in non-crystalline solids, so liquids have a thermal conductivity similar to the very poorest of solid conductors.

Regardless of the detailed mechanism, the rate of heat flow through an object by conduction is directly proportional to temperature difference, and is described by an equation known as *Fourier's law*:

$$\dot{q}_{\mathrm{cond}} = kA\frac{(T_1 - T_2)}{(X_1 - X_2)},\tag{4.1}$$

where $\dot{q}_{\mathrm{cond}}$ is the heat conducted per unit time (unit watts) (the dot above the q represents a change of heat with time), k is a quantity known as the *thermal conductivity* of the substance, A is the cross-sectional area perpendicular to the direction of heat flow, and T_1 and T_2 are the temperatures at the positions X_1 and X_2 respectively. Thus, we can see that increasing any of k, A or the temperature difference proportionally increases the rate of heat flow. In particular, the larger the difference in temperature between two points the faster the heat flows between these two points. Thus, for example, upon immersing a cold thermometer into a hot water bath, heat initially flows rapidly from the bath to the thermometer, but as the temperature of the thermometer increases, the flow of heat decreases and the temperature more slowly approaches that of the bath. The increase in heat flow with cross-sectional area is analogous to the flow of water through a hose: the larger the diameter of the hose, the larger the volume of water that can flow.

Figure 4.1 shows the typical range of thermal conductivities for various types of materials. As expected, the thermal conductivity of metals is generally significantly higher than that of non-metals owing to the additional transfer mechanism of the free electron cloud. The related property, thermal resistance, is discussed in more detail in Section 4.5.1.

4.2.2 Convection

The second mode of heat transfer is convection. Convection is an extension to heat flow by conduction with the added feature that energy is also transferred by bulk motion of a fluid. For example, the heat carried by the moving air from a hair dryer is carried by convection. We also experience convection when standing outside on a windy day and are exposed to wind-chill: that is, having heat removed from our bodies with the motion of the air. Heat flow by convection also occurs, for example, between a thermometer and a stirred liquid in a bath or between the non-immersed part of a thermometer and the air. These are examples of the two different types of convection that occur, namely forced convection and natural convection.

Our main interest in convection is in the understanding of heat transfer between a solid and a fluid. When a fluid moves over the surface of a solid, the fluid close to
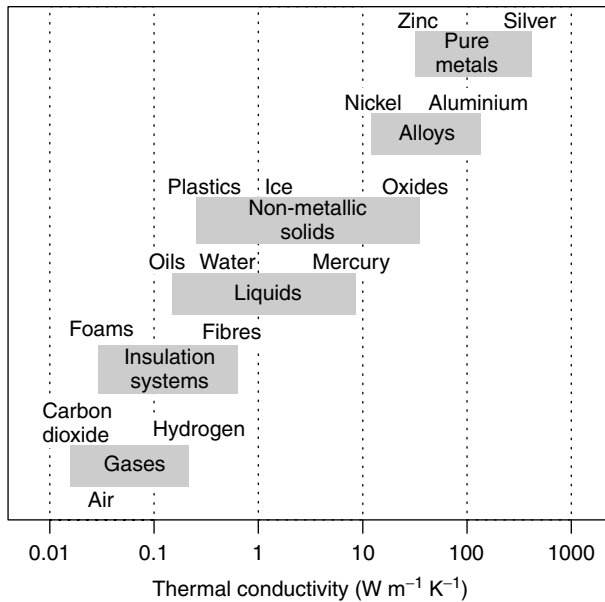
Figure 4.1   Range of thermal conductivities for various types of materials

the surface hardly moves at all. At some distance from the solid, the fluid motion is almost unaffected by the presence of the solid. The interaction between the solid and the fluid therefore creates a narrow region in the fluid in which the velocity of the moving fluid varies between zero and the natural velocity of the bulk of the fluid. This region is called the *boundary layer*. It is the properties of this layer that determine the rate of heat flow between the solid and the fluid. At the surface of the solid, where the velocity of the fluid is zero, heat flow occurs exclusively through conduction. With increasing distance from the surface, the velocity of the fluid increases as the viscous shearing forces in the fluid decrease. Heat is conducted through the fluid but is also progressively swept downstream.

Forced convection occurs when the fluid motion is a result of some external force, such as a fan, a pump, a bath stirrer, the wind, etc. Fans are commonly employed to provide convective cooling of hot electronic components. Pumping cold water through pipes is also an effective means of convective cooling.

Natural convection is the result of buoyancy effects in a fluid caused by density variations due to differences in temperature between different parts of the fluid. The air adjacent to a hot thermometer is heated by conduction, expands because of the increased movement of the molecules, and becomes less dense and therefore lighter than the surrounding air. The hot air rises, carrying the heat with it, and is replaced by an inflow of colder air from the surroundings.

As for conduction, the rate of convective heat transfer is proportional to temperature difference (in this case between the solid and the fluid outside the boundary layer) and to the cross-sectional area perpendicular to the direction of heat flow. It is also proportional to a quantity known as the *convection heat transfer coefficient*, h (analogous to the thermal conductivity). Thus the rate of heat flow by convection (unit watts)

Table 4.1   Indicative values of the convection heat transfer coefficient, h

Process	h (W m^{-2} K^{-1})
Free convection	
Gases	2–25
Liquids	50–1000
Forced convection	
Gases	25–250
Liquids	50–20 000
Convection with phase change	
Boiling or condensation	2500–100 000

is given by

$$\dot{q}_{\text{conv}} = h A \left(T_{\text{s}} - T_{\infty} \right), \tag{4.2}$$

where T_{s} is the temperature at the surface of the solid and T_{∞} is the temperature of the fluid beyond the boundary layer. When T_{∞} is higher than T_{s}, heat flows into the solid, and vice versa. Equation (4.2) is known as *Newton's law of cooling*.

The value of h is determined by many different factors including the conductivity and viscosity of the fluid, size, shape and texture of the surface of the solid, and the thickness of the boundary layer, which is reduced as the fluid velocity increases. Turbulence in the fluid also reduces the boundary layer thickness by mixing and transversely transferring heat across the boundary layer. Indicative values of h for liquids and gases are shown in Table 4.1.

In a stirred water bath, convection greatly increases the rate of heat transfer over that of pure conduction, leading to a more rapid attainment of thermal equilibrium within the bath. Convection also facilitates heat transfer between a thermometer and the bath and more rapidly removes any temperature gradients, which would persist in a non-stirred bath.

The convection heat transfer coefficient is significantly increased in cases involving latent heat exchange. This occurs when there is a phase change during the convective process. Two common examples of this are boiling and condensation. Imagine boiling a pot of water on a hotplate. Below the boiling point, heat is transferred through the water by the process of natural convection. However, as the water at the bottom of the pot reaches its boiling point it changes phase into steam (without changing temperature). This steam rises to the top of the water as a bubble carrying with it the latent heat of vaporisation. Condensation does the reverse: steam condenses into water droplets on a cold object releasing its latent heat. Devices designed to exploit this process are called *heat pipes*. Depending on the fluid employed, heat pipes can have effective thermal conductivities a million times that of copper. Latent heat is discussed in Section 4.3.3.

4.2.3   Radiation

Radiation is the third mode of heat transfer. Thermal radiation is energy in the form of electromagnetic waves, and covers the spectrum through radio waves, infrared, light, ultraviolet, and on through x-rays if the object is hot enough. We experience radiative

heat transfer when we warm our hands in front of a fire or an electric heater. Life as we know it owes its existence to radiative heating from the sun.

All matter with a temperature above absolute zero emits electromagnetic radiation, and generally in large quantities. This emission is due to spontaneous changes in the configuration of electrons in the constituent atoms and molecules of matter. Unlike conduction and convection, radiation does not require a physical medium for the transfer of heat and, in fact, is most efficient when taking place in a vacuum.

The rate that energy is radiated from an object per unit area, E (units $W\,m^{-2}$) is given by the Stefan–Boltzmann law:

$$E = \varepsilon \sigma T^4, \tag{4.3}$$

where σ is known as the Stefan–Boltzmann constant ($\sim 5.67 \times 10^{-8}\,W\,m^{-2}\,K^{-4}$), and ε is the total emissivity of the object's surface. The total emissivity is a quantity that characterises the ability of an object to emit radiation, and has a value between 0 and 1. When the emissivity is one the object is said to be a blackbody, and for a given temperature the amount of energy per unit area radiated from a blackbody represents an upper limit. A blackbody is an idealised concept, a perfect absorber and emitter of radiation, which can be approximated arbitrarily closely by creating an isothermal cavity containing a small aperture (see Section 9.6). Most ordinary objects have an emissivity somewhat less than one, with a value determined largely by the material properties of the object's surface. Objects with dark rough surfaces tend to have a higher emissivity than those with shiny smooth surfaces. Table 4.2 gives values of total emissivity for a range of materials.

The rate of emission predicted by Equation (4.3) is surprisingly large, and increases very rapidly with temperature. At room temperature ($\sim 300\,K$), all objects (including the human body) emit radiation at a rate of about $470\,W\,m^{-2}$. The reason we are not normally aware of this high rate of heat loss is that all of our surroundings are also emitting at approximately the same rate. So on balance, we absorb almost as much as we emit. However, if we go outside on a clear night, we cool down very quickly because of the radiation emitted into space. On a cloudy night, the radiation from the clouds replaces some of that heat.

Table 4.2   Total emissivity for a variety of materials at specified temperatures

Material	Temperature (K)	Total emissivity
Aluminium (highly polished)	300	0.04
Aluminium (anodised)	300	0.82
Stainless steel (polished)	300	0.17
Stainless steel (lightly oxidised)	800	0.33
Stainless steel (highly oxidised)	800	0.67
Glass	300	0.90–0.95
Ice	273	0.95–0.98
Paint	300	0.90–0.98
Wood	300	0.82–0.92
Alumina brick	800	0.40
Magnesia brick	800	0.45
Skin	300	0.95

The net heat transfer between an object and its surrounds is determined by the difference between the emitted radiation and the absorbed radiation. The net radiative heat flow (unit watts) is given by

$$\dot{q}_{\mathrm{rad}} = \varepsilon \sigma A \left(T_{\mathrm{s}}^4 - T_{\mathrm{sur}}^4 \right), \tag{4.4}$$

where T_{s} is the temperature of the object, T_{sur} is the temperature of the surroundings (the object is assumed to be completely surrounded by material at a constant temperature), and A is the area of the object's surface. Note that the term in T_{s} is the energy emitted by the object whereas the term in T_{sur} is the energy received by the object. For all objects the absorptivity is equal to the emissivity. This has to be, because when the two temperatures in Equation (4.4) are the same, there must be zero heat flow.

Because radiation propagates easily through a vacuum or through air, it is often difficult to identify objects in the surroundings that are in radiative contact with a thermometer. Heat flow between these objects and the thermometer can prevent thermal equilibrium from being reached, and introduce errors into the thermometer's reading. Typical radiant sources to be aware of include lamps, boilers, furnaces, flames, electric heaters and the sun. Cold objects too can be a problem because they do not return as much radiation as the thermometer emits, so allowing the thermometer to cool. Radiation errors are discussed in Section 4.4.5.

4.3 Thermal Properties of Materials

4.3.1   Thermal conductivity

We have already discussed heat transfer by conduction in Section 4.2.1. While most materials transfer heat by the conduction mechanism, there are many situations where two or perhaps all three mechanisms contribute to the heat transfer process.

Insulating materials are generally comprised of a solid of low thermal conductivity finely dispersed throughout an air space as fibres, powders or flakes. The resulting effective thermal conductivity of the insulating material is dependent on a combination of conduction in the solid, conduction and convection in the air spaces, and at high enough temperatures, radiation exchange between the solid surfaces. Because the conductivity of air is much less than that of solid materials, more effective insulation is achieved by decreasing the ratio of solid mass to total volume (this ratio is known as the bulk density). Very high-performance insulating materials are made using gases with a very heavy molecular weight to keep the molecular velocities low; for example, freons used in expanded foams yield a material with half the thermal conductivity of air-filled foams. Rigid insulation materials such as polystyrene are created by fusing or bonding parts of the solid, thus creating small pockets of gas.

Transparent materials also owe their conductivity to a combination of processes. Air is a good example since it allows heat transfer by conduction, convection and radiation. Because different mechanisms dominate at different temperatures and gases are opaque at some wavelengths, this can make for some unexpected behaviour. In high-temperature furnaces, the exhaust gases from invisible natural gas flames transfer most of their heat by radiation. Water vapour and carbon dioxide have broad absorption (and
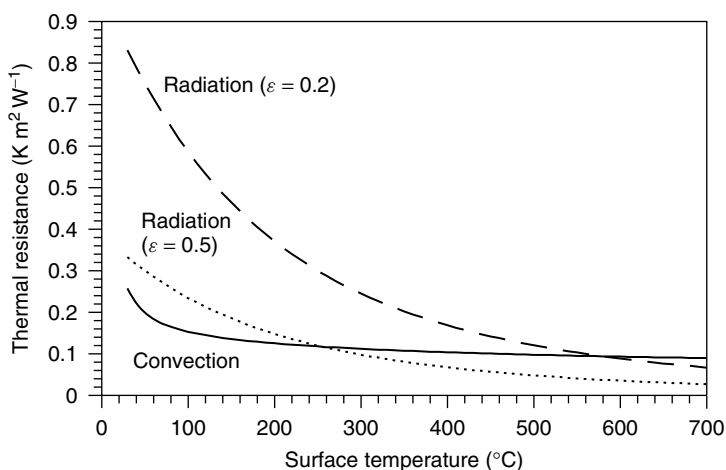
Figure 4.2   Comparison between the thermal resistances for convection and radiation for a $1\,m^2$ vertical plate in air

therefore also emission) lines in the near infrared, enabling the energy to be dumped quickly into the surfaces of objects some distance from the gas. Carbon dioxide is also one of the gases responsible for the greenhouse effect; it absorbs infrared radiation from the earth while transmitting the more energetic short-wavelength light from the sun. The effect is so named because the glass in a greenhouse is opaque in the infrared and has the same effect.

So far we have described the ability of a material to conduct heat in terms of conductance, which describes how much heat a material will conduct for a given temperature difference (unit $W\,°C^{-1}$). It also proves to be useful to discuss the same property in terms of thermal resistance (unit $°C\,W^{-1}$), which is the reciprocal of the conductance. Thermal resistance provides a measure of a material's ability to resist heat flow. Because of its analogy to electrical resistance (see Section 4.5), thermal resistance provides insight into many problems involving heat transfer.

Figure 4.2 gives a comparison between the thermal resistance for convection and radiation for a $1\,m^2$ vertical plate in air at an ambient temperature of $20\,°C$. This figure shows that when a surface with an emissivity of 0.5 is at about $250\,°C$ or higher, heat transfer by radiation dominates that by convection (i.e. the thermal resistance for radiation is lower than that for convection). For a surface with an emissivity of 0.2 (shiny metal), convection dominates up to about $600\,°C$.

As a general rule, for temperatures near $250\,°C$ heat transfer by radiation becomes significant in almost all situations, and by $400\,°C$ it usually dominates convection and conduction.

4.3.2   Heat capacity

Heat capacity is another thermal property that it is important to understand in order to reduce errors in thermometry. The heat capacity, C, of a substance is defined as the quantity of heat required to raise the temperature of that substance by $1\,K$. Thus, to

raise the temperature of a substance from T_1 to T_2 requires an amount of heat given by

$$q = C\,(T_2 - T_1) \tag{4.5}$$

to be absorbed by the substance.

The energy is stored in the material in essentially two different forms: as kinetic energy, through increased movement of all of the atoms and molecules in the material; and as potential energy, which is energy stored against interatomic forces in much the same way as rubber bands store energy. By definition, the kinetic energy is proportional to temperature, so for most solid and liquid materials the heat capacity is nearly constant. However, with the increased movement of the atoms, electrons and molecules in a material, the nature of the interatomic forces can change, so the potential energy can increase or decrease and cause variations from this rule. For isolated molecules, such as in gases, additional quantum mechanical effects cause the heat capacity to increase with temperature as internal vibrations become excited.

The heat capacity is also directly proportional to the mass of the substance, so an object twice as large as another, made from the same material, requires twice as much heat to raise its temperature by the same amount. Heat capacities for various materials are shown in Table 4.3, expressed both per kilogram and per cubic centimetre. An interesting feature of Table 4.3 is that although there is a large variation in heat capacity per unit mass, when

Table 4.3 Heat capacity per unit mass and per unit volume for various materials at $300\,\mathrm{K}$

Material	Heat capacity per unit mass $(\mathrm{J\,K^{-1}\,kg^{-1}})$	Heat capacity per unit volume $(\mathrm{J\,K^{-1}\,cm^{-3}})$
Copper	385	3.44
Gold	129	2.49
Silver	235	2.47
Aluminium	903	2.44
Zinc	389	2.78
Tin	227	1.66
Mercury	139.3	1.88
Stainless steel	480	3.83
Silicon	712	1.65
Water	4179	4.17
Ice*	2040	1.88
Methyl alcohol (CH_4O)	2500	1.98
Ethyl alcohol (C_2H_6O)	2500	1.98
Crown glass	670	1.74
Flint glass	500	2.10
Pyrex	835	1.85
Alumina	800	3.04
Magnesia	960	3.46
Polystyrene	1300	1.37
Silicone oil	1548	1.45
Engine oil	1909	1.69
Ethylene glycol [$C_2H_4(OH)_2$]	2415	2.69
Glycerin [$C_3H_5(OH)_3$]	2427	3.06

*At $273\,\mathrm{K}$.

expressed per unit volume most values for solids and liquids fall in the range $1\,\mathrm{J\,K^{-1}\,cm^{-3}}$ to $4\,\mathrm{J\,K^{-1}\,cm^{-3}}$. This allows us to make an adequate approximation of an unknown heat capacity when performing order-of-magnitude calculations or calculating uncertainties, simply by measuring volumes and assuming a heat capacity of $2\,\mathrm{J\,K^{-1}\,cm^{-3}}$.

4.3.3   Latent heat

Latent heat is the heat associated with the change of phase of a substance (i.e. from a solid to a liquid or from a liquid to a vapour, or vice versa). Each of the three phases of matter has a different atomic configuration with different associated energy states. Atoms in a solid are closely spaced and interact strongly; those in a liquid are less closely spaced and have a weaker interaction; atoms or molecules in a gas are widely separated with virtually no interaction.

When a solid is heated to its melting point and changes into a liquid, an extra quantity of heat is required for the atoms to break free of the forces holding them together. This extra heat is called the *latent heat of fusion*, L_f. A substance will not completely melt until this quantity of heat has been absorbed, during which time the temperature of the substance does not change. Similarly, if a liquid is cooled to its freezing point the heat released as the liquid freezes maintains the temperature at a constant value. Because materials in the process of changing phase absorb and release large quantities of heat without a change in temperature, they can be useful as temperature references, as described in Section 3.3.2.

When a liquid is heated to its boiling point, the energy required for the change of phase into a vapour is called the *latent heat of vaporisation*, L_v. In general, L_v is greater than L_f owing to the stronger interaction that must be overcome in changing a liquid into a vapour than in changing a solid into a liquid. When either phase change happens in reverse (i.e. freezing or condensation), the latent heat is released, again without a change of temperature.

4.4 Errors in the Use of Thermometers

A common fallacy held by many users of thermometers is that a thermometer will, when placed into a system, eventually indicate the temperature of that system. A number of errors occur in almost every measurement that make a perfect temperature measurement impossible. These errors are due to the fact that true thermal equilibrium between the thermometer and the system never exists or that the insertion of the thermometer disturbs the equilibrium. In this section we look at the errors in detail and give some simple rules that help us to assess the errors or make the errors negligible.

A common feature of all of these errors is that it is a simple matter to vary the measurement conditions to establish whether there is a significant problem, and if so to give an indication of the magnitude of the problem and enable an assessment of the uncertainty.

4.4.1   Immersion errors

Because thermometers are rarely totally immersed in the medium of interest, the immersion problem occurs in most temperature measurements. The thermometer stem, sheath
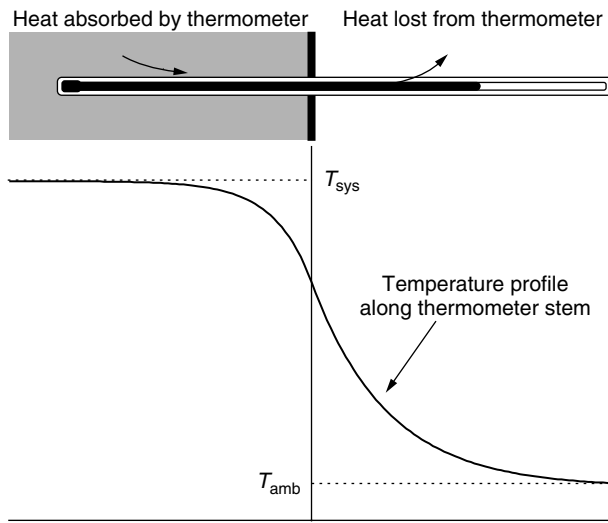
Figure 4.3   The flow of heat along the stem of a thermometer causes the thermometer to indicate temperatures slightly different to that of the medium of interest

and lead wires provide paths for a continuous flow of heat between the medium of interest and the outside world. Since heat can flow only where there is a temperature difference, the flow of heat is evidence that the tip of the thermometer is at a slightly different temperature from that of the medium of interest.

The heat flow along the stem of a thermometer is shown graphically in Figure 4.3. The temperature profile along the thermometer varies continuously. The hot end of the thermometer is close to the system temperature, while the cool end is near to the ambient temperature. The tip of the thermometer is surrounded in this case by a stirred fluid, which must transfer heat to the thermometer to replace that lost down the thermometer stem. The heat flow in the boundary layer around the thermometer and in the surface of the sensor means that the tip is not at the system temperature. Note too that the heat flow along the thermometer depends on the temperature gradient along the thermometer, and the further into the system the thermometer is, the less the heat flow.

A simple model of the heat flow in the thermometer near the tip relates the error in the thermometer reading to the length of immersion by

$$\Delta T_{\mathrm{m}} = \left(T_{\mathrm{amb}} - T_{\mathrm{sys}}\right) K \exp\left(\frac{-L}{D_{\mathrm{eff}}}\right), \tag{4.6}$$

where T_{sys} and T_{amb} are the system and ambient temperatures respectively, L is the depth of immersion of the sensor, D_{eff} is the effective diameter of the thermometer, and K is a constant approximately equal to, but always less than, one. Both K and D_{eff} depend on the thermal resistance between the thermometer and the system and on the heat capacities of the thermometer and system. This equation, which is plotted in Figure 4.4 for $K = 1$, is very useful for determining the minimum immersion that will ensure that the error is negligible.
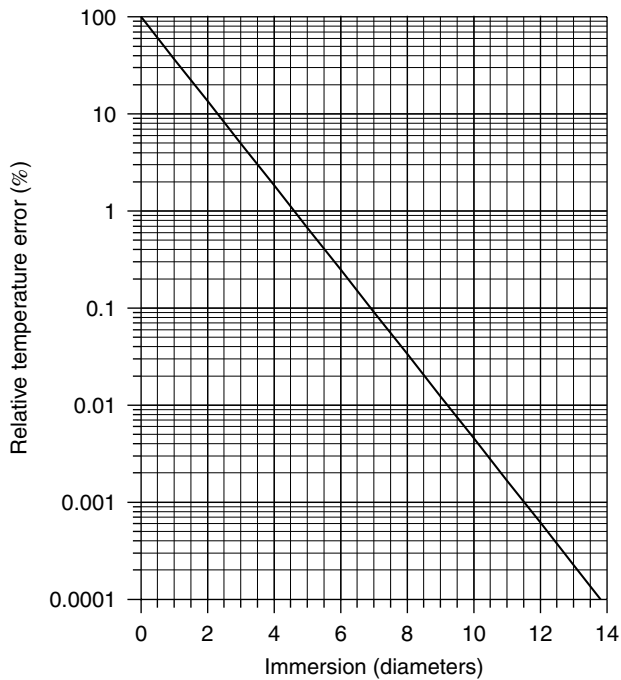
Figure 4.4 The relative temperature error $|\Delta T_m/(T_{sys} - T_{amb})|$ verus thermometer immersion length in diameters

Example 4.1

Determine the minimum immersion for a 4 mm diameter sheathed thermometer with the detecting element occupying the last 40 mm of the sheath. The measurement should have an immersion error of less than 0.01 °C for temperatures up to 100 °C.

Firstly, we determine the relative accuracy required in the measurement as

$$\left| \frac{\Delta T_m}{T_{sys} - T_{amb}} \right| = \frac{0.01}{100 - 20} \approx 0.01\%.$$

Then, referring to Figure 4.4, we find that the minimum immersion is a little more than nine diameters. To be conservative we will immerse the thermometer to 10 diameters beyond the sensing element, that is 80 mm total immersion.

Example 4.1 and Figure 4.4 provide some simple rules of thumb for determining thermometer immersion:

- For 1% accuracy, immerse to five diameters plus the length of the sensor. This level of immersion is typical of industrial measurements.

- For 0.01% accuracy, immerse to 10 diameters plus the length of the sensor. This level is typical of the immersion required for good laboratory measurements, as given in Example 4.1.

- For 0.0001% accuracy, immerse to 15 diameters plus the length of the sensor. This is typical of the accuracy required for the highest-accuracy laboratory measurements and for fixed-point measurements.

The main problem with Equation (4.6) for thermometer immersion is that the two constants, K and D_{eff}, are unknown and are dependent on the thermometer's surroundings as well as on the thermometer. This variable behaviour is due to the different thermal conductivities and heat capacities of different systems, and is demonstrated in Figure 4.5. In situations where the medium is well stirred, such as in an oil bath, the equation works well if the actual diameter of the probe is used for D_{eff}. However, in situations where the medium is not stirred, there is additional thermal resistance due to the boundary layer in the fluid. Then the effective diameter can be very much larger than the actual diameter of the probe. Other problems include uncertainty in the location of the sensing element, which is rarely the very tip of the thermometer, and difficulty in defining the diameter, for example with multiple sheaths or thermowells. In all cases, it pays to be pessimistic and add the detector length to the length determined from Figure 4.4, and use the outside diameter of any sheath or thermowell assembly.

The most difficult immersion problems occur when making measurements of air and surface temperatures. For air-temperature measurements, the effective diameters of
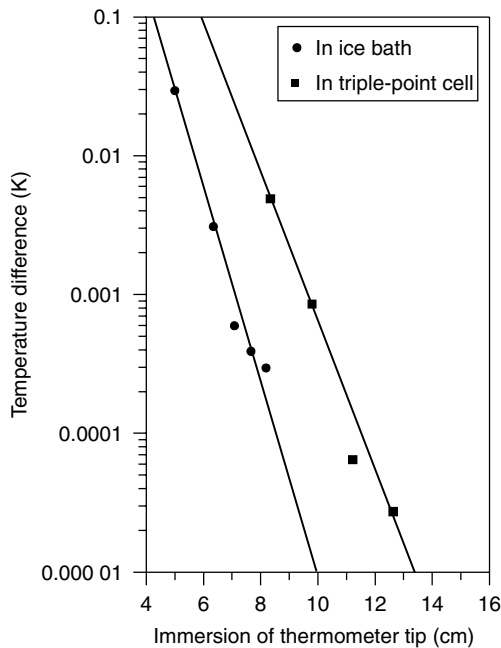
Figure 4.5 The immersion characteristics of an SPRT in an ice bath and triple point of water cell

probes may be more than 10 times the actual diameter; a probe requiring 10 diameters' immersion in the calibration bath may require more than 100 diameters' immersion in air. This is because the boundary layer effects, which increase the thermal resistance between the probe and air, are much higher in air (which has kinematic viscosity much like that of treacle) than in a stirred fluid.

In all cases where immersion errors are suspected it is a very simple matter to vary the immersion length by one or two diameters to see if the reading changes. As an approximation, about 60% of the total error is eliminated each time the immersion is increased by one effective diameter. In some cases, it may be practical to estimate the true temperature from a sequence of measurements at different immersions (see Exercise 4.2).

Example 4.2

Dry-block calibrators are small portable electric furnaces used to calibrate industrial temperature probes. Typically, the comparison medium is a cylindrical steel or aluminium block with two or more holes into which the thermometers are placed. The blocks are often removable, and fit into a small tube furnace of about 40 mm diameter and 150 mm length.

The immersion error in dry-block calibrators is usually large. The fundamental problem is that it is the immersion conditions of the block in the furnace (not the immersion of the thermometer in the block) that gives rise to the errors, and the length-to-diameter ratio of the block is about 5. Figure 4.4 suggests that this corresponds to a temperature measurement with an accuracy of only about 1%, and indeed this is the typical accuracy of most dry-block calibrators. They are intended only as portable calibrators for checking industrial control probes such as thermocouples and platinum resistance thermometers. They should not be used for comparisons requiring accuracies of better than about 1%. (See also Exercise 4.3.)

Exercise 4.1

Find the minimum immersion for a 6 mm diameter probe in a 10 mm diameter thermowell at 800 °C such that the immersion error is less than 1 °C.

Exercise 4.2

(a) Suppose that three measurements are made at immersion depths of L_1, L_2 and L_3, where $L_2 - L_1 = L_3 - L_2 = \Delta L$, and the resulting temperature readings are T_1, T_2 and T_3 respectively. By manipulating Equation (4.6) show that

$$T_{\text{sys}} = T_1 + \frac{(T_2 - T_1)^2}{2T_2 - T_1 - T_3}$$

and

$$D_{\text{eff}} = \frac{\Delta L}{\ln[(T_{\text{sys}} - T_1)/(T_{\text{sys}} - T_2)]}.$$

(b)   If three measurements are made at immersion depths of 3, 4 and 5 cm, giving temperatures of 115 °C, 119 °C and 121 °C, what is the system temperature and effective diameter of the thermometer?

(c)   The calculation of T_{sys} above is an extrapolation (see Section 2.11). What happens to T_{sys} and the uncertainty in T_{sys} if $T_2 - T_1 = T_3 - T_2$?

Exercise 4.3

If you have a dry-block calibrator, perform some simple experiments to expose the magnitude of the errors in these instruments. Try putting insulation, such as fibreglass wool, around the thermometer and over the top of the dry block. How much does the reading change? Also investigate the change in reading at different immersion depths, and see what effect a change in ambient temperature has.

   To make the best use of dry-block calibrators, exploit symmetry by using the same-size holes in the same radial position in the block and thermometers of the same diameter. Placing insulation material over the top of the block and using thermally conducting grease to improve the thermal contact between the thermometer and the block may help.

4.4.2   Heat capacity errors

When we immerse a cold thermometer into a hot system the thermometer must change temperature in order to read the temperature of the system. This requires the transfer of a quantity of heat to the thermometer. Clearly, the system must lose an equal amount of its own heat. If this heat is not replaced by some other source, such as from a heater driven by a temperature controller or latent heat from a fixed point, the temperature of the system will drop by an amount proportional to its own heat capacity. Provided there is no other heat flow, the thermometer and the system will eventually come to thermal equilibrium at a temperature somewhere between the initial temperature of the system and the initial temperature of the thermometer:

$$T_{\text{meas}} = T_{\text{s}} + \frac{C_{\text{t}}}{C_{\text{s}} + C_{\text{t}}} (T_{\text{init}} - T_{\text{s}}), \tag{4.7}$$

where C_{s} and C_{t} are the heat capacities of the system and thermometer respectively, and T_{s} and T_{init} are the initial temperatures of the system and thermometer respectively.

   There are several approaches to reducing or correcting for the heat capacity error. The most obvious is to use a thermometer with the smallest practical heat capacity. The second method, and often the most practical, is to pre-heat the thermometer to a temperature close to the system temperature. In some situations, it may be possible to measure

experimentally the drop in temperature with the immersion of a second thermometer, or to withdraw the thermometer, allow it to cool and then reimmerse it. An estimate of the size of a heat capacity error can also be based on estimates of the heat capacity of the thermometer and that of the system. The heat capacity of most solids and liquids varies between those of water, $4.2 \, \text{J K}^{-1} \, \text{cm}^{-3}$, and oil, $1.5 \, \text{J K}^{-1} \, \text{cm}^{-3}$ (see Table 4.3). A value of $2 \, \text{J K}^{-1} \, \text{cm}^{-3}$ is a reasonable estimate where no other data is available.

Example 4.3

A thermometer of unknown heat capacity is inserted into a large vacuum flask of hot fluid and indicates a temperature of $84.3 \, °\text{C}$. After withdrawing the thermometer, allowing it to cool to ambient temperature and reinserting it, the reading is $83.8 \, °\text{C}$. Estimate the initial temperature of the flask of fluid.

We assume that the change in temperature on the first immersion is the same as that on the second immersion, and that the temperature would otherwise be constant. The change on the second immersion was

$$\Delta T_\text{m} = 83.8 - 84.3 = -0.5 \, °\text{C}.$$

The initial fluid temperature is the first recorded temperature plus the correction for the error. Hence

$$T_\text{sys} = 84.3 + 0.5 = 84.8 \, °\text{C}.$$

Exercise 4.4

(a)   By summing the total heat of the thermometer plus the system before and after immersion of the thermometer derive Equation (4.7), and hence show that the heat capacity error in an uncontrolled system is

$$\Delta T_\text{meas} = \frac{C_\text{t}}{C_\text{t} + C_\text{sys}} (T_\text{init} - T_\text{sys}),$$

where C_t and C_sys are the heat capacities of the thermometer and system respectively, T_sys is the system temperature, and T_init is the initial thermometer temperature.

(b)   Find the heat capacity error that occurs when a large mercury-in-glass thermometer ($C_\text{t} \sim 20 \, \text{J K}^{-1}$) is used to measure the temperature of a hot cup of coffee. Assume one cup of coffee is equivalent to $250 \, \text{ml}$ of water, hence $C_\text{sys} = 1000 \, \text{J K}^{-1}$, and that $T_\text{sys} = 90 \, °\text{C}$.

4.4.3   Settling response errors

In systems where there is some temperature control mechanism or the system is very large, the heat capacity error is absent or negligible. However, it will take time for the

system to replace the heat lost in heating the thermometer, and for the thermometer to settle to the temperature of the system. If insufficient time is allowed for either process to occur, then there will be an error in the thermometer reading.

Equation (4.5) gives the amount of heat required to change the temperature of an object, while Equation (4.1) gives the rate that heat can be transferred from one object to another (or from location to location within an object). Thus, objects with larger heat capacities, as well as requiring more heat to change temperature, also take longer to do so than those with smaller heat capacities. In fact, it is the ratio of the heat capacity to thermal conductance that determines the heating or cooling rate. This ratio is called the time constant of the thermometer. It has the unit of time and characterises the time required for an object to respond to a temperature change. The typical response of a thermometer to a step change in temperature is shown graphically in Figure 4.6.

For thermometers of a given style of construction, the time constant increases with the diameter of the thermometer. For most probes and assemblies, the time constant increases as D^2. Exceptions include liquid-in-glass thermometers, for which the increase in time constant is in direct proportion to the diameter, and metal-sheathed probes with very small diameters (less than 1 mm), for which the time constant increases approximately as $D^{1.5}$.

A simple model estimates the error as

$$\Delta T_{\mathrm{m}} = \left(T_{\mathrm{init}} - T_{\mathrm{sys}}\right) \exp\left(\frac{-\tau}{\tau_0}\right), \tag{4.8}$$

where T_{init} and T_{sys} are the initial temperatures of the thermometer and the system respectively, τ is the time between immersion and reading, and τ_0 is the $1/e$ *time constant* of the thermometer. This equation allows us to estimate the minimum wait before we can read the thermometer with negligible error. To simplify calculations the equation is plotted in Figure 4.7.
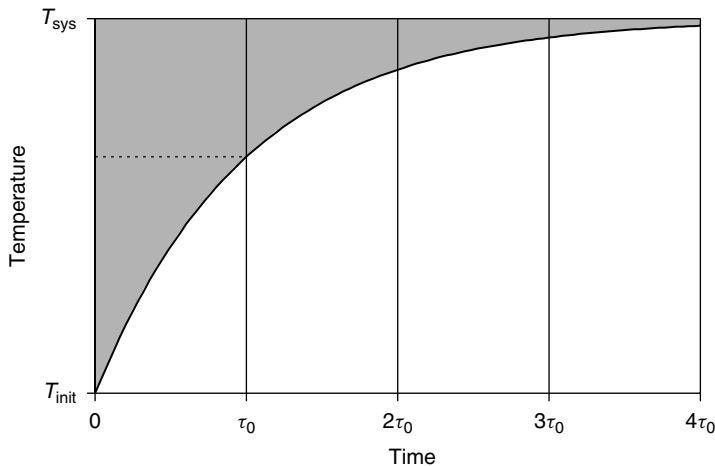
Figure 4.6   The settling response of a thermometer assuming that a single time constant, τ_0, is dominant. After each interval of τ_0 seconds the error is reduced by about 63%
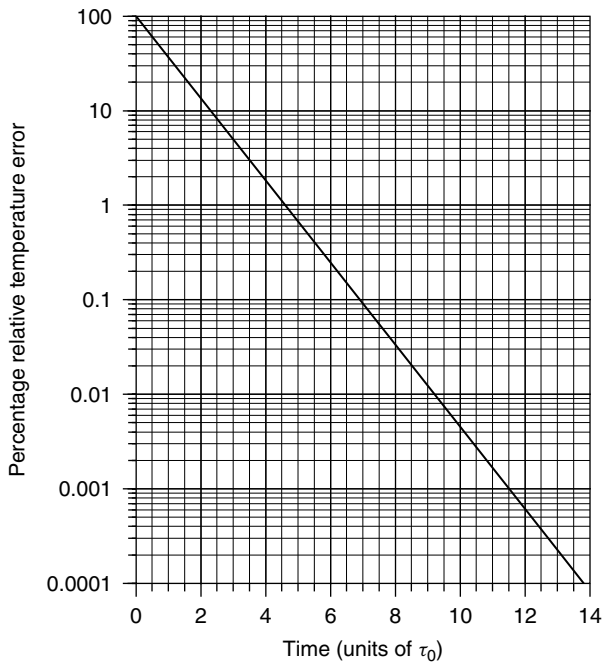
Figure 4.7 The relative temperature error $|\Delta T_m/(T_{\text{init}} - T_{\text{sys}})|$ verus measurement time in multiples of the time constant, τ_0

Example 4.4

Given a system with a response such as shown in Figure 4.6, estimate the minimum measurement time required to achieve an accuracy of 0.5 °C at temperatures near 150 °C. Assume that the initial temperature of the thermometer is 25 °C.

The relative error is required to be less than $0.5/(150 - 25) = 0.4\%$. Referring to Figure 4.7, it is found that at least $5.5\tau_0$ seconds must elapse before the error is less than 0.4%. The time constant of the thermometer is 20 s; hence the minimum measurement time is 110 s.

As with the immersion problems, the most difficult time constant problems occur in air-temperature measurements. Because of the extra thermal resistance of the boundary layer, the time constant of a thermometer in air may easily be 10 or 20 times that in a well-stirred calibration bath. Some particularly heavy thermometers may have time constants of 10 minutes or more, thus requiring an hour to settle for a single measurement.

One of the complicating factors with time constants is the limit of human patience. Once the measurement time gets beyond a minute or two it becomes very hard to bring oneself to wait long enough for the thermometer to settle. This is especially true when the last digit in the reading is changing very infrequently. In these situations it a matter

of discipline to record the reading after the required interval as measured by a clock. Only then can one be sure that the thermometer has settled properly.

An additional problem with time constants is that the assumptions leading to Equation (4.8) and Figure 4.7 are optimistic. There are some situations and probe designs where there is more than one time constant involved; a thermometer immersed in a thermowell measuring the temperature of a controlled process may have three time constants characterising the overall thermometer response. In these cases, there is simply no alternative to experimentation in order to expose potential errors in the indicated temperature.

Note too that Figure 4.7 is essentially the same graph as Figure 4.4. Therefore the rules of thumb that we developed for immersion have their counterparts for settling times:

- For 1% accuracy (industrial) wait at least five time constants.
- For 0.01% accuracy (laboratory) wait at least 10 time constants.
- For 0.0001% accuracy (best laboratory) wait at least 15 time constants.

Exercise 4.5

Compare the time constants of thermometers of different diameters by recording the settling response. Use an ice point or boiling water for a medium if you do not have a temperature-controlled bath. If you have only one thermometer try putting the thermometer in different-size tubes in order to change its heat capacity.

4.4.4   Lag errors with steadily changing temperatures

In systems where the temperature is changing at a constant rate the settling response of the thermometer causes a more serious error. The situation is shown graphically in Figure 4.8. There are two components to the error. The first component, the shaded portion of Figure 4.8, is the same as the time constant error discussed above and will gradually decrease to a negligible value. The main error is the *lag error*, which is proportional to the time constant and the rate of change of the bath temperature:

$$\text{lag error} \ = -\tau_0 \times \ \text{rate of change of temperature.} \tag{4.9}$$

The effect of the error is to cause the thermometer reading to lag τ_0 seconds behind the bath temperature.

Example 4.5

Calculate the lag error when a thermometer with a time constant of 20 seconds monitors a process temperature changing at $3\,^\circ$C per minute.

From Equation (4.9) the lag error is

$$\Delta T_m = \frac{-20 \times 3}{60} = -1\,^\circ\text{C}.$$
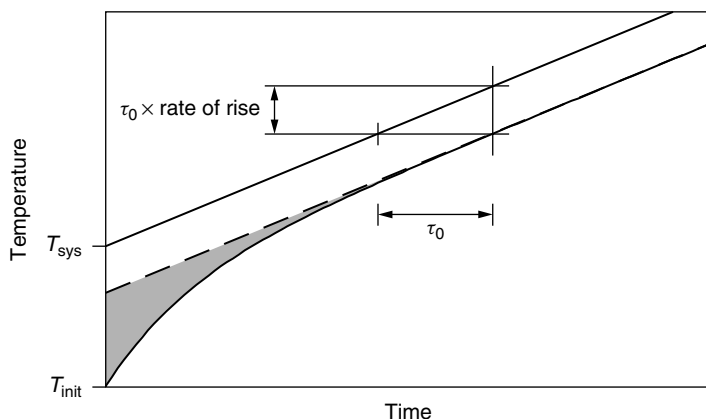
Figure 4.8 The temperature error due to the thermometer's time constant in a system with a steadily increasing temperature

Example 4.6

A very important example of lag error occurs in the rising-temperature method of calibration (see Section 5.5.3), in which measurements are compared while the bath temperature slowly and constantly increases. Consider, for example, the situation where we wish to calibrate a set of working thermometers with time constants of 5 s against reference thermometers that have time constants of 7 s. What is the maximum rate of rise in the calibration bath temperature if we require the lag errors to be less than 0.01 °C?

The lag error for the reference thermometers is

$$\Delta T_r = -7 \times \text{ rate of rise,}$$

and the error for the working thermometers is

$$\Delta T_w = -5 \times \text{ rate of rise.}$$

Hence the error in the comparison is

$$\Delta T_{cal} = (7 - 5) \times \text{ rate of rise.}$$

Since we require this error to be less than 0.01 °C, the maximum rate of temperature rise is

$$\text{maximum rate of rise} = 0.01/(7 - 5) = 0.005\,°C\,s^{-1} = 0.3\,°C\,min^{-1}.$$

It is instructive to investigate whether a limit on the lag error restricts the design and operation of a calibration bath. For a 25 l water bath heated by a 100 W heater, with

no heat losses, the rate of rise is approximately $1\,\text{mK}\,\text{s}^{-1}$. Thus controlling the heating rate to the nearest $100\,\text{W}$ is sufficient to allow quite high-accuracy calibrations to be feasible using the rising-temperature technique. In practice there are, however, additional complications in ensuring that the bath temperature is uniform. The maximum rate of rise of $5\,\text{mK}\,\text{s}^{-1}$ determined in the example above is very much a maximum. A more practical and conservative design figure would be a third or a fifth of that value.

4.4.5   Radiation errors and shielding

Radiation is one of the most insidious sources of error in thermometry. We often fail to recognise the physical connection between the radiant source and the thermometer, and overlook it as a source of error. Radiation errors are a particular problem in air and surface thermometry where there is nothing to obscure or shield the source, and where the thermal contact with the object of interest is already weak. Examples of troublesome radiant sources include lamps, boilers, furnaces, flames, electrical heaters and the sun. A particularly common problem to watch for is the use of incandescent lamps when reading thermometers. If you must use a lamp, then use a low-power fluorescent lamp, which will radiate very little in the infrared portion of the spectrum.

With more difficult measurements, such as air and surface temperatures, anything at a different temperature that has a line of sight to the thermometer is a source of error. This includes cold objects such as freezers, which act as radiation sinks and absorb radiation emitted by the thermometer. To put things in perspective, remember that at room temperature everything radiates (and absorbs from its neighbours) about 500 watts per square metre of surface area, so the radiative contact between objects is far greater than we would expect intuitively. In a room near a large boiler, a mercury-in-glass thermometer may exhibit an error of several degrees.

There are two basic strategies when you are faced with a measurement that may be affected by radiation. Firstly, remove the source; and secondly, shield the source. Removing the source is obviously the most effective strategy if this is possible. However, the thermometry is very often required in association with the source, particularly in temperature control applications. In these cases, it may be possible to change the shape or orientation of the source in a way that will give an indication of the magnitude of the error.

If you are unable to remove the radiation source then shielding is the only resort. A typical radiation shield is a highly reflective, usually polished, metal shield that is placed over the thermometer. The shield reflects most of the radiation away from the thermometer and itself. An example of a chrome-plated metal tube that can be used as a shield is shown in Figure 4.9. The shield will usually reduce the error by a factor of about 3 to 5. The change in the thermometer reading when the shield is deployed will give a good indication of the magnitude of the error and whether more effort is required. Successive shields will help but will not be as effective as the first. Suitable trial shields are clean, shiny metal cans and aluminium foil.

The disadvantage of using a radiation shield in air-temperature measurements is that the movement of air around the thermometer is greatly restricted, further weakening the thermal contact between the air and the thermometer. The problem is compounded
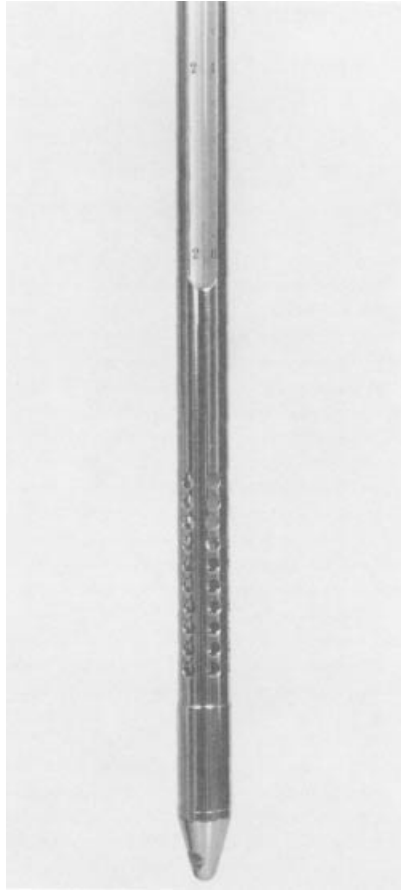
Figure 4.9   An example of a radiation shield for a mercury-in-glass thermometer

if the shield is warmed by the radiation and conducts the heat to the stagnant air inside the shield. Therefore, to be effective the shield must allow free movement of air as much as possible. In some cases a fan may be needed to improve thermal contact by drawing air over the sensor, and to keep the shield cool. Note that the fan should not be used to push the air over the thermometer as the air will be heated by the fan motor and friction from the blades.

4.5 Models and Methods

The previous sections of this chapter have provided a tutorial description of the errors and effects relating to heat transfer between the thermometer and the medium of interest. This section extends the description of the thermal properties of materials to enable more detailed modelling of the thermal properties of systems, including thermometers. This provides an extension to the discussion on immersion and time constant effects, explains how we can interpret temperature measurement in some

non-equilibrium situations, and provides an explanation of guarding techniques and temperature control.

4.5.1   Electrical analogue models

One of the difficulties of dealing with materials with mixed modes of heat transfer is in comparing materials or calculating the overall conductivity of combinations of materials. This can be overcome by exploiting the similarity of the heat transfer equations to those for electrical conduction. We do this by associating a thermal resistance with each mode of heat transfer.

Equation (4.1) gives the rate of heat flow by conduction between two points separated by a distance $\Delta x = X_1 - X_2$. If we denote the thermal resistance for conduction between these two points as R_{cond} then we can rewrite this equation as

$$R_{\text{cond}} = \frac{T_1 - T_2}{\dot{q}_{\text{cond}}} = \frac{\Delta x}{kA}. \tag{4.10}$$

Equation (4.10) is analogous to Ohm's law, which states that $R = V/I$. This suggests that heat flow through a set of thermal resistances can be modelled by an analogous electrical network of electrical resistances. Indeed this is the case. Additionally, heat capacity, fixed points and heaters all have electrical analogies. Table 4.4 lists the analogous quantities and relations that we will use here.

To exploit the analogies for thermal resistance we must first treat all of the different models of heat transfer in the same way. The *thermal resistance for convection*, R_{conv}, follows from Equation (4.2):

$$R_{\text{conv}} = \frac{T_s - T_\infty}{\dot{q}_{\text{conv}}} = \frac{1}{hA}. \tag{4.11}$$

The form for the *thermal resistance for radiation*, R_{rad}, is not immediately obvious from Equation (4.4). However, if we define a quantity called the *radiation heat transfer coefficient*, h_r, by

$$h_r = \varepsilon\sigma \left(T_s^3 + T_s^2 T_{\text{sur}} + T_s T_{\text{sur}}^2 + T_{\text{sur}}^3\right), \tag{4.12}$$

then Equation (4.4) can be written as

$$\dot{q}_{\text{rad}} = h_r A \left(T_s - T_{\text{sur}}\right). \tag{4.13}$$

Table 4.4   Analogous quantities and relations for electricity and heat transfer

Electrical quantity	Electrical symbol	Thermal quantity	Thermal symbol
Charge	Q	Heat	q
Current	$I = \dot{Q}$	Heat flow	$\dot{q}$
Voltage	V	Temperature	T
Electrical resistance	R	Thermal resistance	R
Electrical capacitance	C	Heat capacity	C

Electrical relation		Thermal relation	
Ohm's law	$V = IR$		$T = \dot{q}R$
Charge on capacitor	$Q = V/C$		$q = T/C$

This is now in the same form as Equations (4.1) and (4.2) and it follows that the thermal resistance for radiation is

$$R_{rad} = \frac{T_s - T_{sur}}{\dot{q}_{rad}} = \frac{1}{h_r A}. \tag{4.14}$$

Note that R_{rad} is highly temperature dependent (see Figure 4.2). Both R_{cond} and R_{conv} are also temperature dependent but to a much lesser extent.

4.5.2 Composite systems

Commonly we must calculate the thermal resistance of systems composed of more than one type of thermally conducting material, for example a kiln lined with a combination of fibrous ceramic insulation and brick. To determine the rate of heat transfer between any two points at temperatures T_1 and T_2, it is necessary to determine the total, or effective, thermal resistance, R_{total}, between these two points. The total thermal resistance may have contributions from all three modes of heat transfer. Firstly, we must learn how to calculate the total thermal resistance of several thermal resistances in combination.

Resistances in series

For heat flowing along a single path through various materials, the total thermal resistance is obtained by adding the various thermal resistances. The general formula is

$$R_{total} = R_1 + R_2 + R_3 + \dots. \tag{4.15}$$

Example 4.7   Heat flow through a composite material

Figure 4.10(a) shows a wall that is a composite of three different materials stacked together (this could be an insulating wall of a calibration bath, for example). The thermal resistances of the three layers are R_1, R_2 and R_3. The temperatures at the left and right faces are maintained at T_3 and T_0, respectively, where $T_3 > T_0$. Determine the rate of heat flow through the wall, and the temperature at each face of the insulating layers.

Because $T_3 > T_0$ the direction of heat flow is from left to right. This occurs in a series fashion (i.e. all the heat must flow through all three materials), so the total thermal resistance between the left and right sides of the wall is given directly by Equation (4.15):

$$R_{total} = R_1 + R_2 + R_3,$$

and the rate of heat flow is given by Equation (4.10):

$$\dot{q} = \frac{T_3 - T_0}{R_{total}}.$$
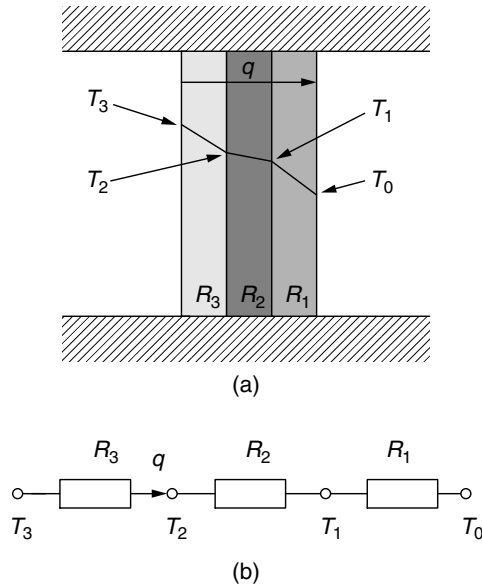
Figure 4.10 (a) Heat flow through a composite wall of three different materials; (b) the equivalent circuit representation

The electric circuit analogue is shown in Figure 4.10(b). The temperature at each of the internal faces is then found as

$$T_1 = T_0 + \dot{q} R_1,$$
$$T_2 = T_0 + \dot{q}(R_1 + R_2).$$

Note that the temperature varies through each layer according to

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \dot{q}\frac{R_i}{\Delta x} \tag{4.16}$$

where Δx is the thickness of each layer. The temperature profile through the three layers is also illustrated in Figure 4.10(a).

Resistances in parallel

When multiple paths or multiple modes of heat transfer exist between two points, the thermal resistances add in parallel. The general formula is

$$\frac{1}{R_{\text{total}}} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \dots \tag{4.17}$$

Example 4.8

Let us assume that the wall in Example 4.7 is indeed part of a calibration bath filled with water (see Figure 4.11(a)). A temperature controller is used to maintain the temperature of the water at T_w. The outside of the bath is exposed to air at ambient temperature T_a. Determine the rate of heat loss from the water to ambient through the wall.

Let us break this problem into two parts. Firstly, consider the heat transfer from the outside bath wall to the bath surroundings. The heat transfer takes place by convection because of the air movement, and by radiation. These two paths occur in parallel. If the parallel combination of the thermal resistances for convection and radiation from the outside wall to ambient is denoted R_a then, according to Equation (4.17),

$$\frac{1}{R_a} = \frac{1}{R_{a,conv}} + \frac{1}{R_{a,rad}}.$$

Equivalently, this can be written

$$R_a = \frac{R_{a,conv} R_{a,rad}}{R_{a,conv} + R_{a,rad}}.$$

This thermal resistance between the wall and the surroundings is in series with the thermal resistance through the wall. We calculated the thermal resistance

(a)

(b)
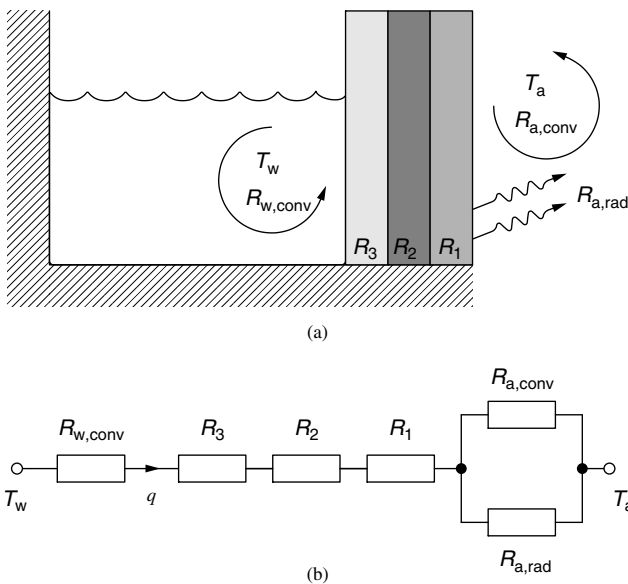
Figure 4.11 (a) Heat flow through the wall of a calibration bath, including convection within the bath liquid, convection in the air on the outside of the bath, and radiation from the outside of the bath to the surroundings; (b) the equivalent circuit representation

of the bath wall in Example 4.7. There is also a thermal resistance $R_{\text{w,conv}}$ due to the convection of the water in the bath. Thus, the total thermal resistance between the water and ambient is given by

$$R_{\text{total}} = R_{\text{w,conv}} + R_1 + R_2 + R_3 + R_\text{a},$$

where R_1, R_2 and R_3 are the thermal resistances of the wall components as given in Example 4.7. The rate of heat flow is given by

$$\dot{q} = \frac{T_\text{w} - T_\text{a}}{R_{\text{total}}}.$$

The electrical analogue is given in Figure 4.11(b). Note that in practice, for a water bath, the radiation loss will be negligible compared with the convection loss to ambient. So in this case the parallel combination of $R_{\text{a,rad}}$ and $R_{\text{a,conv}}$, denoted R_a, will be almost identical to $R_{\text{a,conv}}$.

4.5.3 Temperature in non-equilibrium situations

The formal definition of temperature (Section 1.3.2) relates to the mean translational kinetic energy of the particles in a system at thermal equilibrium. Throughout the discussion in this chapter we have been using temperature to characterise the behaviour of systems with heat flowing through them, that is systems demonstrably not in thermal equilibrium. In these cases, what does temperature mean?

The essence of the formal definition is that temperature is a single-valued statistical quantity, an average over a long period of time, over many atoms or molecules, each with nominally the same average kinetic energy. Because of the huge number of atoms in a small quantity of material ($\sim 10^{22}$ per gram), and the tremendous speed at which things happen at the atomic level ($\sim 10^{-12}$ s), we can argue that the concept of thermal equilibrium can apply to very small volumes of matter, and over very short periods of time. This stretching of the concept of thermal equilibrium then allows us to make sense of concepts such as temperature gradients, as shown in Figure 4.10.

When we measure temperatures in the presence of rapidly changing heat flows, extra uncertainties in the measurement must be considered. The principal differences are that temperature is no longer single valued. Consider, for example, a thermometer of 10 mm diameter immersed in a system with a temperature gradient of $1\,^\circ\text{C}\,\text{mm}^{-1}$. Then by measuring a temperature with the thermometer we attribute a single value to a system with a temperature range of $10\,^\circ\text{C}$. Thus, there is an additional uncertainty due to the range of temperature. A similar effect occurs when temperatures are changing quickly and a thermometer has a finite response time.

As we highlighted in the meteorological temperature example of Section 1.3.3, having alternative forms of heat transfer taking place in the same material can also lead to ambiguities in the measurement. This is especially a problem for radiative contact. It is possible, for example, to take a volume of air that is both isothermal and stable with time, insert a thermometer and completely change the temperature profile in the
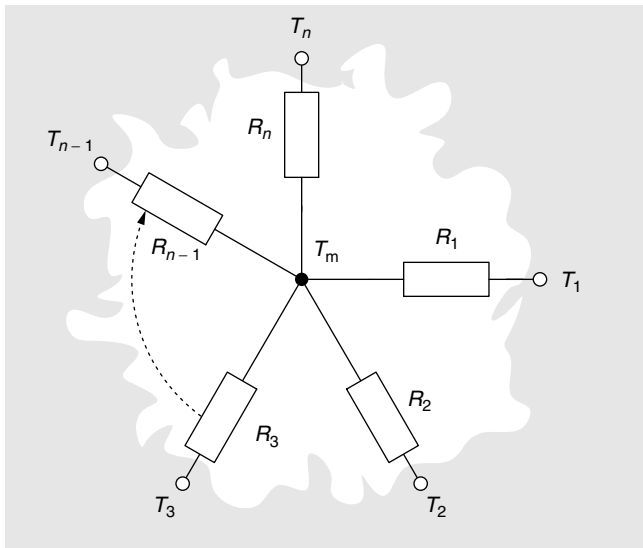
Figure 4.12   A representation of the general temperature measurement, showing the thermal connections between the thermometer and all of the other objects in thermal contact, including the object of interest at temperature T_1

air because the thermometer absorbs radiation that previously passed through the air with no effect.

Figure 4.12 illustrates the general problem. A thermometer inserted into a medium may be in thermal contact with many different objects in the surroundings, each with a different temperature. The thermometer indicates a temperature that is a weighted average of all of the temperatures of the objects it is in thermal contact with:

$$T_{\mathrm{m}} = \left[\sum \frac{T_i}{R_i}\right]\left[\sum \frac{1}{R_i}\right]^{-1}. \tag{4.18}$$

The thermometrist, who may wish to measure T_1 say, must ensure through various means that $T_{\mathrm{m}} = T_1$. The three distinct options include:

(1)   making R_1 small by improving the thermal contact with the object of interest by increasing the immersion, or by using heat-sink grease, or stirring the medium, for example;

(2)   making the other R_i large by weakening the thermal contact with other objects by using insulation or radiation shields, for example;

(3)   making the other $T_i = T_1$ by heating or cooling the other objects until they have the same temperature as the indicated temperature.

The last strategy may seem a little strange; it seems unlikely that we could have the freedom to change the temperature of the surrounding objects. However, there are guarding techniques that exploit this principle (see Section 4.5.6). In addition, one can often change the orientation or position of the thermometer so that the thermal contact

with objects at a similar temperature is improved, while the contact with those at different temperatures is weakened. The simplest practical cases are where thermometers are immersed into strong temperature gradients. The thermometer should always be immersed along an isotherm.

In many situations (the meteorological temperature measurement is a good example) all of these strategies can be applied to some degree, but it is usually not possible to eliminate all of the influences from the other objects. In that case, it may be easier to define a measurement protocol that controls the magnitude of the various influences, so that measurements are repeatable and comparable.

4.5.4 Immersion revisited

A complete evaluation of all the various conduction, convection and radiation paths for a thermometer in use is reasonably complicated, comprising a large number of series and parallel combinations of thermal resistances. Identifying and then evaluating the influence of each object can be a long process. Consider the case of the simplest immersion problem. The corresponding thermal resistance network is shown in Figure 4.13. There are three nodes of interest: the object of interest with a temperature T_s, the sensor of the thermometer indicating a measured temperature T_m, and the surroundings at ambient temperature T_a. These points are connected through two thermal resistances: R_b, between the object of interest and the sensor, and R_a, between the sensor and ambient.

Equating the heat flows through the two thermal resistances (i.e. applying Equation (4.10) to each), we arrive at an equation relating the measurement error, ΔT_m, to the true temperature:

$$T_m = \frac{R_a}{R_a + R_b}T_s + \frac{R_b}{R_a + R_b}T_a = T_s + \frac{R_b}{R_a + R_b}(T_a - T_s). \qquad (4.19)$$

Now we can see how the ambient temperature influences the measured temperature. Note that the larger the value of R_a and the smaller the value of R_b, the closer T_m will be to T_s. This is simply telling us that good thermal contact between the thermometer and the object of interest reduces the error, as this reduces R_b. In a stirred bath, for example, increasing the velocity of the liquid increases the value of the convection heat transfer coefficient, h, thereby decreasing the thermal resistance for convection (see Equation (4.11)).

To estimate the magnitude of the temperature error we can change one of the quantities in Equation (4.19) and determine its effect on the measured temperature,
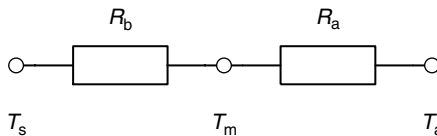
Figure 4.13 Equivalent circuit for the multiple heat transfer paths between the object of interest at temperature T_s and the sensor of the thermometer indicating a temperature T_m, and between the sensor and ambient at temperature T_a

T_m. For example, it may be possible to vary the ambient temperature by turning up the air-conditioning. The expected sensitivity to ambient temperature is determined by differentiation of Equation (4.19) with respect to T_a. The result is

$$\frac{\Delta T_m}{\Delta T_a} = \frac{R_b}{R_a + R_b}. \tag{4.20}$$

$\Delta T_m/\Delta T_a$ is the sensitivity coefficient of the measured temperature to ambient temperature. This is the factor in front of the error term of Equation (4.19), and it enables us to make corrections or calculate the uncertainty for poor immersion.

> **Example 4.9   Determining the thermometer error due to heat flow to ambient**
>
> A thermometer is immersed into a water bath and indicates a temperature reading of 80.50 °C when the ambient temperature is 20 °C. After raising the ambient temperature to 25 °C the thermometer reads 80.55 °C. What is the true temperature of the water?
>
> Since the increase in thermometer reading was 0.05 °C for an increase of 5 °C in ambient temperature, we have $\Delta T_m/\Delta T_a = 0.05\,°C/5\,°C = 0.01$. From Equation (4.19) we can estimate the true temperature as
>
> $$T_s \approx T_m - \frac{\Delta T_m}{\Delta T_a}(T_a - T_m) = 80.50 - 0.01 \times (20 - 80.50) = 81.1\,°C.$$
>
> That is, the correction is about 0.6 °C. Note that we only know the sensitivity coefficient with a relative uncertainty of 20% (0.01 °C in 0.05 °C) so the uncertainty in the correction is about 0.13 °C.

Surface temperatures

Surface-temperature measurements are fundamentally difficult. The problem is that a surface is an infinitely thin boundary between two objects, and therefore there is no 'system' into which to immerse a thermometer. 'What is the surface temperature?' is therefore a silly question. With surface-temperature measurements, the answer to the measurement problem often lies in analysing the purpose for making the temperature measurement (see Section 1.2.3). For example, if we need to know how much energy the surface radiates, we should use a radiation thermometer (see Chapter 9); if we want to know the likelihood of the surface posing a human burn risk then we should use a standard finger as specified by a safety standard; and if we require a non-intrusive measurement of the temperature of the object behind the surface, then a measurement using one of the techniques in Figure 4.14 may be the answer. Note that, as with any situation where there is a large heat flow, one should always immerse the thermometer along an isotherm.

In recent years, there has been a huge increase in the number of commercially available surface probes, which are often thermocouple based. Unfortunately, the inherent design of most of them is seriously flawed. They often use quite heavy thermocouple
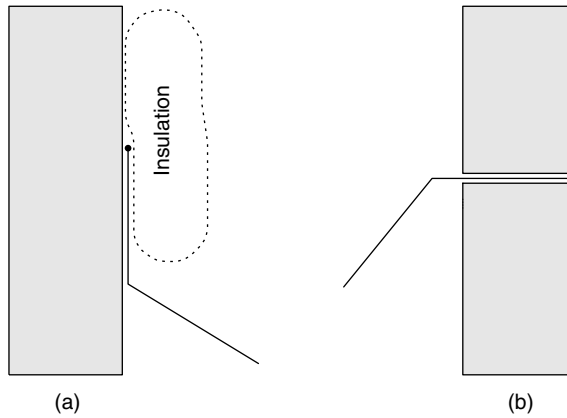
Figure 4.14 Two solutions to the problem of surface-temperature measurement: (a) attaching a length of the probe to the surface so the probe is immersed along an isotherm improves immersion — in some cases, insulation may be helpful in reducing heat losses by radiation or convection, although it can cause the surface to become hotter; (b) approaching the surface from the side that has the least temperature gradient will give the least error

wire, the measurement junction is not isothermal in use, and they approach the surface at right angles where the greatest temperature gradients occur. As a result, most commercial surface probes are in error by about 5% to 10%. With careful design, fine wire placed along the surface, and insulation behind the wire, accuracies of about 1% are readily achievable.

Surface-temperature measurements are also subject to errors caused by the probe inhibiting the emission of radiation from the surface. At high temperatures ($1000\,°C$) especially, where the emission rates are in excess of $100\,kW\,m^{-2}$, the surface will warm very quickly. In these situations, the probe must be very fast so the measurement can be made before significant heating has occurred.

4.5.5   Time constants revisited

Electrical analogues are also useful for analysing the thermal response of thermometers to temperature changes. Figure 4.15 shows the simplest electrical analogue that yields a response time. In this figure, R represents the thermal resistance to the object of interest and C the heat capacity of the thermometer. This same model yields Equations (4.8) and (4.9) for the time response error and the lag error, which apply when the temperature of interest is constant or changing uniformly.

In more difficult cases, where the temperature is changing in a more complicated fashion, it becomes far more difficult to estimate the errors. However, it is possible to gain a qualitative picture of the thermometer's behaviour under these circumstances. By considering the effect of the time constant on a periodic temperature variation it can be shown that the thermometer's response is less than the actual variation by the factor

$$G(f) = \frac{1}{\left(1 + 4\pi^2\tau_0^2 f^2\right)^{1/2}}, \tag{4.21}$$
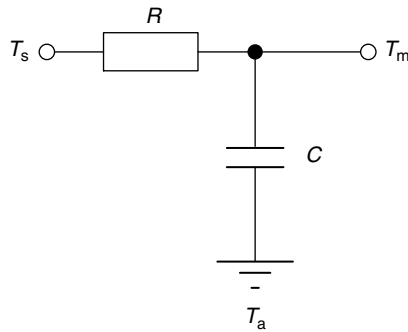
Figure 4.15 Electric circuit analogue for the heat flow into an object with a heat capacity C

where f is the frequency of the periodic variation, and $\tau_0 = RC$ is the time constant of the thermometer. Those familiar with electronics will recognise Equation (4.21) as the response of a first-order filter. At frequencies less than about $1/(2\pi\tau_0)$, the thermometer will follow the changes in temperature well. Variations at frequencies higher than $1/(2\pi\tau_0)$ are effectively filtered out by the thermometer's response.

Equation (4.21) has practical consequences when choosing thermometers for applications where a fast response or detection of short-term events is required. A simple rule of thumb is to choose thermometers with time constants six times faster than the event to be measured.

One of the advantages of thermometers with long time constants is that they can be used to measure average temperatures. The meteorological air-temperature measurement described in Chapter 1 is an example.

4.5.6 Guarding

In Section 4.5.3 we indicated that one of the ways of improving immersion is to adjust the temperature of the surrounding objects to be the same as the temperature of interest. Consider the simplest case with the two thermal resistances (Figure 4.13 and Equation (4.19)). The measured temperature is given by

$$T_m = T_s + \frac{R_b}{R_a + R_b}(T_a - T_s).$$

By making $T_a = T_s$, the error can be reduced to zero. This is occasionally a useful method for improving immersion, for example by heating the stem of the thermometer. Figure 4.16 shows a surface thermometer based on this principle.

The thermocouple mounted on the surface measures the surface temperature. Normally, this measurement would have substantial errors due to the poor thermal contact between the thermocouple and the surface, and because of the temperature gradient over the thermocouple junction. However, by heating the end of the thermocouple wire so that the second measuring junction is at the same temperature as the first, we ensure that both junctions are enclosed in a volume that is isothermal, overcoming both of the errors.
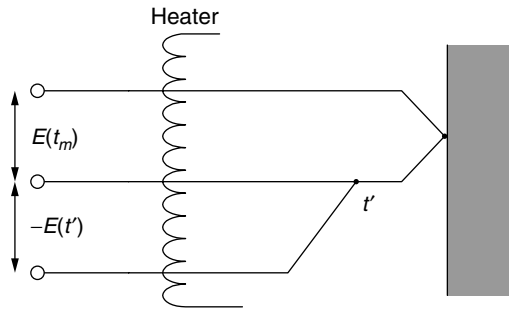
Figure 4.16 A guarded thermocouple for measuring surface temperatures

The underlying principle of guarding is that no heat will flow between two objects if they are at the same temperature. The same principle is exploited in multi-zone furnaces and cryostats (Section 3.3.7).

4.5.7 Temperature control

An electrical analogue model also explains the benefits and limitations of temperature control loops. Consider the model in Figure 4.17. In the figure, R represents the thermal resistance between the calibration bath and ambient, C the heat capacity of the bath, K the gain of the controller (unit $W\,°C^{-1}$), and T_0 the set point of the controller. When the bath is stable, the heat lost to the surroundings is equal to the heat supplied by the controller:

$$\frac{T_{\text{bath}} - T_{\text{a}}}{R} = K(T_0 - T_{\text{bath}}), \tag{4.22}$$

from which it follows that

$$T_{\text{bath}} = T_0 + \frac{(T_{\text{a}} - T_0)}{1 + RK}. \tag{4.23}$$
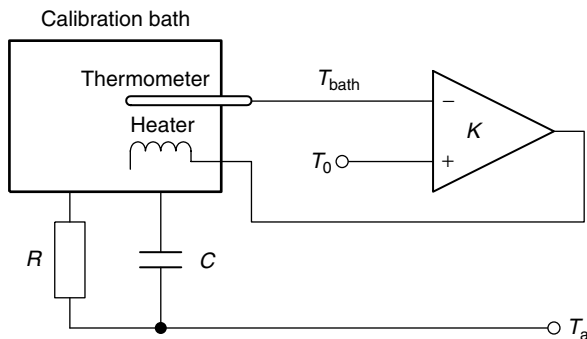
Figure 4.17 Electrical analogue of a proportional temperature controller

This equation tells us that the controller reduces the influence of the ambient temperature by the factor $1 + RK$, known as the *loop gain*. In good-quality calibration baths the loop gain is about 1000, while for industrial furnaces, ovens, etc., the loop gain can be lower than 5.

The time constant of a controlled system is also improved. For the calibration bath the time constant RC may be as high as one day. With the controller operating, the $1/e$ time constant is also reduced by the factor $1 + RK$, so the calibration bath will settle within a few minutes following small set-point changes. Note that the sensitivity to ambient temperature indicated by Equation (4.22) can be reduced by using PID (proportional, integral, differential) controllers. The integral term eliminates the sensitivity to ambient temperatures, while the differential term enables the use of a higher loop gain before the control system becomes unstable. However, PID controllers are generally not so useful for calibration baths because they take about four times longer to settle.

Further Reading

Heat transfer and thermal models

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H S Carslaw and J C Jaeger (1973) *Conduction of Heat in Solids*, 2nd Edition, Oxford University Press, London.
F P Incropera and D P DeWitt (1996) *Fundamentals of Heat and Mass Transfer*, 4th Edition, John Wiley, New York.
M Kutz (1968) *Temperature Control*, John Wiley, New York.

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T W Kerlin and R L Shepard (1982) *Industrial Temperature Measurement*, Instrument Society of America, Research Triangle, NC.
J F Schooley (1986) *Thermometry*, CRC Press, Boca Raton, FL.

5

Calibration

5.1 Introduction

Most of us have had the experience of making measurements using different methods, getting different answers, and then being left to wonder which is correct. The experience is common because very few instruments are as accurate as they appear to be. The experience of most calibration laboratories is that as many as one in five of all instruments are faulty or outside the manufacturer's specifications. This failure rate is almost independent of the instrument type or manufacturer, and tends to increase with the increasing cost and capability of instruments.

There is something about measurement scales, especially those marked to high precision or indicating many digits, that lead us to trust them. For thermometers at least, this is hopelessly optimistic. Liquid-in-glass thermometers with errors of two to five scale divisions are usually within the manufacturer's specifications; platinum resistance thermometers capable of accuracies of a few millikelvin are only accurate to about 0.3 °C when uncalibrated; and some thermocouples having been used once are forever outside their specifications. Even when we are aware of the possibility of error we tend to take it on faith that the probability of error is sufficiently low that we can ignore the consequences. It is only when we compare measurements from different instruments that our faith is shaken.

The only way of ensuring that an instrument's readings are accurate and trustworthy is by regular calibration. In this chapter, we consider calibration in detail beginning with a discussion on the meaning of calibration. We then progress through the principles underlying the design and development of calibration procedures to equipment requirements, reporting and recording of calibration results, and finally to descriptions of the two calibration techniques employed in thermometry. Examples of calibration procedures are given for the single-point calibration of a liquid-in-glass thermometer used as a working instrument, and of a direct-reading electronic reference thermometer. We will provide thorough examples for other types of thermometer in later chapters.

While this chapter is designed primarily as guidance for those laboratories establishing calibration systems and possibly seeking accreditation under ISO 17025 *General requirements for the competence of testing and calibration laboratories*, the chapter should also help users of calibrations interpret their certificates and improve the reliability of their measurements.

5.2 The Meaning of Calibration

5.2.1   What is a calibration?

In Chapter 1 we established a definition of traceability: 'the property of a result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons, each with a stated uncertainty'. Calibrations are the comparisons that establish the links in the traceability chain.

> **Calibration:**
> The set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards.
>
> Notes
>
> (1)   The result of a calibration permits the assignment of values of measurands to the indications or the determination of corrections with respect to the indications.
> (2)   A calibration may also determine other metrological properties such as the effect of influence quantities.
> (3)   The result of a calibration may be recorded in a document, sometimes called a calibration certificate or a calibration report.

This definition clearly establishes the main purpose of a calibration, namely to supply the link between a measurement scale on an instrument and the SI definition of the scale. As with many technical definitions the meaning of some of the clauses and notes is only apparent once one considers how calibrations are used.

By itself, a table of corrections or an equation that relates the readings of an instrument to the SI is insufficient. To compare results meaningfully, optimise production and meet tolerances in specifications and documentary standards, it is necessary to know the uncertainty in the corrected readings of the instruments. Unlike many experimental uncertainties, the uncertainty in the readings of an instrument can only be determined by comparison with a more accurate instrument, that is by calibration. If the uncertainty is not provided at any point in the traceability chain, then all downstream users are deprived of information that is essential for the evaluations of the uncertainty in their measurements.

For many users of calibrations a calibration certificate is almost irrelevant. Often it is simply filed in a cabinet in an office somewhere rarely to be retrieved. Why then do these users bother getting the instrument calibrated? As we indicated in the introduction, the authors' experience with liquid-in-glass thermometers is that one in five of new thermometers fail to meet the manufacturer's specifications or the appropriate documentary standard. Of those thermometers that do meet the specifications, about 50% are more than one scale division in error at some point on their scale. For other types of thermometers, the failure rate is not quite so high, perhaps about one in eight. These failure rates are by no means unique; similar rates are found in most calibration

laboratories and are typical for other instruments besides thermometers. The only factor that has a significant effect on this failure rate is whether the owner operates a QA system requiring regular calibration and checking of instruments, in which case the failure rate can drop to 1 in 30. Since measurements are used to make decisions, what is the cost of the resulting poor decisions made using uncalibrated instruments? How many products have to be recalled? How many manufacturing hours are lost? How many lives are lost? Thus the most common use for calibration is to identify instruments that are untrustworthy or do not meet some minimum level of performance. This is the rationale for QA systems' insistence on the calibration of all instruments used to make measurements that may affect the quality of a product.

We have now identified the three main factors that must be assessed in a calibration:

(1)   the link to the SI; for thermometers the link to the ITS-90 temperature scale;

(2)   the uncertainty in the readings of the instrument;

(3)   the reliability of the instrument.

Before we investigate these three factors and the process for assessing them, let us investigate the meaning of calibration in more detail.

5.2.2   What is not a calibration?

The word 'calibration' has developed several meanings over the last couple of hundred years, and depending on context, now has three distinct meanings. The root for the word 'calibration' is an Arabic word for a mould for casting metal. This is probably the origin of the oldest meaning for calibration, which is associated with the casting of metal for cannon and guns. Specifically, calibration may refer to the determination or adjustment of the calibre (or bore) of a gun, or the adjustment or determination of the range of a gun.

The second and most common meaning of the word 'calibration' is the marking or adjustment of an instrument's scale, often by the manufacturer. That is, a calibration refers to the set of operations carried out by an instrument manufacturer in order to ensure that the equipment has a useful measurement scale. This second meaning will be referred to in this text as *adjusting* the instrument. Adjustment is also something performed by instrument servicers to instruments that have drifted with time or have needed repair. The more modern meaning of calibration, which we use in the context of traceable measurement and which we described in the previous section, does not appear in dictionaries before 1940 and indeed not all modern dictionaries give it. Dictionaries, of course, follow the general use of a term and not necessarily the technical usage.

The colloquial definition of calibration as an adjustment is the one given by most dictionaries and is most easily confused with the metrologist's definition. Manufacturers particularly confuse the two meanings because the purpose of adjustment and checking of an instrument on an assembly line is to ensure that the instrument is reading correctly and within specifications, the same reason most users seek calibration. However, the adjustment and checks are not always independent, and are rarely certified. Indeed some manufacturers now supply calibrations with new instruments, but usually only as an optional extra and at additional cost.

So-called 'self-calibration' further highlights the distinction between the two common meanings for calibration. Many modern instruments implement complex signal processing algorithms in the process of converting a signal to a digital reading. A degree of artificial intelligence is often added to enable the instrument to check itself against an internal reference and adjust its scale. This is a self-calibration in terms of the second meaning (adjustment) but not in terms of the third meaning (establishing traceability). Calibration in the metrological sense has three distinguishing features:

(1) Independence. Any comparison or measurement of the instrument's performance must be carried out against a calibrated independent reference standard.

(2) Permanent record. The calibration should produce a record of the results used in the evaluation of the instrument's performance and, ideally, a calibration certificate.

(3) User control. The user should always have control over the time and place of the calibration.

Quite a number of 'self-calibrating' instruments implement two of the three features (not always the same two) and in doing so greatly enhance the reliability and accuracy of the instrument. However, there are also examples of 'self-calibrating' instruments where none of these features are implemented, and while they may well be more accurate and reliable, the seemingly random and uncontrolled adjustments make them indistinguishable from an instrument with an intermittent fault. Most measurement and calibration procedures try to minimise human interference because it is unpredictable. Yet many of these intelligent instruments do the opposite; improperly implemented artificial intelligence and multiple menu trees make operator error and erratic behaviour a design feature. In general, self-adjustment does not do away with the need for calibration, but properly implemented improves accuracy and reliability and extends the time between calibrations.

Figure 5.1 When is a calibration certificate not a calibration certificate? The type of document shown here provides no measure of the instrument's relationship to ITS-90, or uncertainty in readings; indeed it does not mention temperature at all. It is a manufacturer's warranty indicating that the manufacturer has made the appropriate adjustments, and not a calibration certificate

Many manufacturers of measuring instruments offer calibration services for their instruments. Ideally, this serves the best interests of both the client and the manufacturer. The manufacturer knows more about the instrument than anybody else and therefore is more able to recognise faults and ensure reliability. The manufacturer gains by finding out how instruments perform in the long term and is able to identify successful features that can be included in later models. Unfortunately, some manufacturers refuse to provide the full complement of calibration information to their clients (see Figure 5.1). It is common, for example, for manufacturers to adjust all instruments returned for calibration but not advise the client that they have done so. This means that the client builds up an entirely false picture of the stability of the instrument. The authors are also aware of manufacturers who have implemented software upgrades to fix bugs and denied the changes. It is notable that one of the new requirements of ISO 17025 for reference instruments is for calibration laboratories to provide a record of performance both before and after adjustment, if adjustments are made.

5.3 Calibration Design

The initial phases of calibration design are primarily information-collecting exercises. In the first part of this section, we describe how and where to gather the information. We then consider how this information is used to design a calibration that will establish the reliability of an instrument and traceability of its measurements.

5.3.1   The thermometer under test

The first information to gather is that relating to the thermometer under test. This covers a huge range including:

- operating principles;
- typical construction of the probe;
- the type of temperature indicator (direct reading or not);
- typical temperature ranges;
- typical accuracies;
- suitable and unsuitable applications;
- sensitivities to environmental factors;
- common manufacturing defects;
- common faults arising in use.

Information on the thermometer can be found from:

- manufacturers' specifications (check more than one manufacturer);
- operators' manuals;
- application notes published by manufacturers;
- textbooks (like this one and those given in the references at the end of each chapter);

- guidelines and technical notes published by national measurement institutes and accrediting organisations;
- documentary standards for the same or similar thermometers;
- other people working in the same area;
- scientific papers and conference proceedings.

In some cases the information may require interpretation. A manufacturer's specification for input impedance on an electronic thermometer is a clue to sensitivity to sensor impedance or long lead wires. Tests in documentary standards for the change in ice-point reading following exposure to high temperatures is a clue to problems with hysteresis.

The biggest influence on calibration design is the type of the thermometer. The following chapters in this book provide sufficient information for the design of calibrations for the most common temperature sensors. If you are working to very high accuracy or have an unusual application, you will need to add to the information we provide.

In addition to the type of sensor, the presence or absence of an indicator also influences calibration design. This applies to some degree to all types of sensors. There are very broadly three main categories, as follows.

Sensor only

Commonly when calibrating platinum resistance thermometers, thermocouples, thermistors and occasionally radiation thermometers, we are required to calibrate the sensor only. Because we must measure resistance, voltage, or current, against temperature, we require traceability to the SI standard for the corresponding electrical quantity as well as for temperature. In these cases, the staff involved in the calibration must also have the appropriate expertise in the measurement of electrical quantities.

Almost all temperature sensors are non-linear; that is, their response cannot be represented by a straight line on a graph. Therefore, a non-linear (in temperature) equation must be found to represent the response of the sensor. In general the most acceptable form of calibration is by least squares as described in Section 2.12. For platinum resistance thermometers, thermistors and radiation thermometers the equation usually relates the sensor response directly to temperature (see Sections 6.7.1, 6.8.1 and 9.7.2 respectively). For thermocouples the sensor response is sufficiently complex that calibration equations of this form are not especially useful. More often the calibration equation is a correction equation in voltage:

$$\Delta V = a + bV + cV^2 + dV^3, \tag{5.1}$$

which describes the departure of the thermocouple response from the response defined in the appropriate documentary standard. Where the sensor is manufactured and used in accordance with a documentary standard the calibration equation can also be expressed as a temperature correction:

$$\Delta t = a + bt + ct^2 + dt^3, \tag{5.2}$$

where t is the temperature inferred from the definition of the sensor response given in the documentary standard.

Sensor plus indicator (not direct reading)

Commonly with platinum resistance thermometers and thermocouples, the resistance meter or voltmeter is submitted with the sensor for calibration. The resistance meter or voltmeter is usually calibrated separately in terms of the appropriate electrical quantity. This ensures that the meter is subjected to a complete complement of tests and analysis to ensure its reliability and accuracy with respect to the SI. Separate calibrations on the probe and indicator also allow multiple sensors to be used with the indicator.

Sensor plus indicator (direct reading in temperature)

Direct-reading thermometers have features in common since they must all linearise the response of the sensor. Usually each indicator is adjusted to suit one sensor only; thus the sensor and indicator combined are the thermometer, and the two are usually calibrated together. These considerations are additional to those for the sensor itself. There are three basic categories of linearisation.

Segmented linearisation   Low-cost instruments often approximate the response of the sensor by a few (typically one to four) straight lines. This was one of the earliest techniques and is no longer common in electronic instruments. The only common cases now occur in wide-range precision liquid-in-glass thermometers. The residual error from this technique has a rather jagged shape that does not lend itself to accurate interpolation between calibration points (see Figure 5.2).
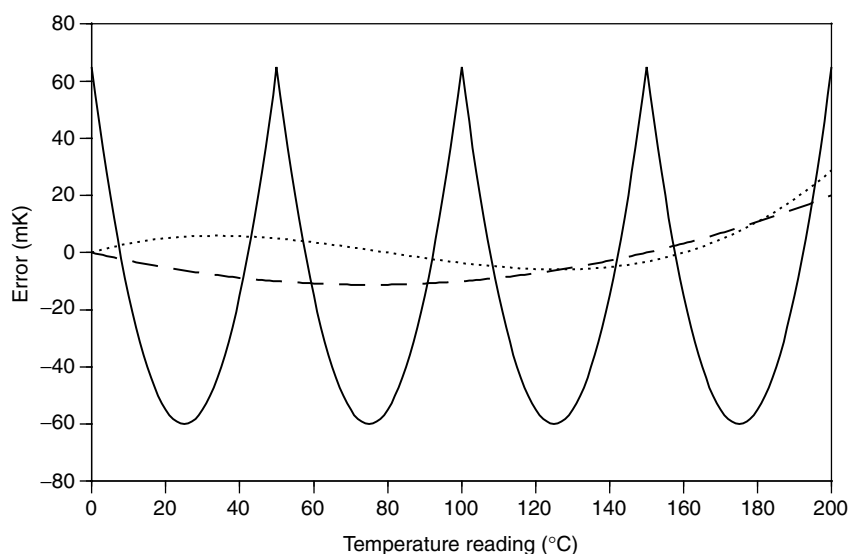
Figure 5.2   Linearisation strategies for a platinum resistance thermometer. Solid curve: segmented linearisation leaves a non-smooth error curve so that interpolation between calibration points may not be valid; dashed curve: analogue linearisation matches the general shape of the curve at the expense of a complex but smooth error curve; dotted curve: the residual errors from microprocessor linearisation change very slowly with the reading

Analogue linearisation   Linearisation can be accomplished using a variety of non-linear electronic circuits such as function generators, negative resistance circuits, analogue multipliers and logarithmic amplifiers to make smooth approximations to the sensor response. For example, a common approximation is based on the equation

$$L(T) = k\frac{R(T) - a}{R(T) - b},\tag{5.3}$$

where $R(T)$ is the sensor response to temperature, $L(T)$ is the linearised response, and a, b and k are constants corresponding to offset, linearity and range adjustments. This equation is easily implemented using analogue-to-digital converters, which are used in every digital indicator. This is a low-cost option, moderately accurate, and well suited for temperature ranges of $100\,°C$ to $200\,°C$. The most important feature from the calibration point of view is that, although the linearisation is not perfect, the residual error curve is smooth. This ensures that accurate interpolation between calibration points is practical.

Microprocessor linearisation   Microprocessor linearisation is common amongst the better-quality electronic thermometers. Three approaches are used: a look-up table plus linear interpolation, which is essentially the segmented approach but with very many segments; interpolation through measured points, which is often Lagrange interpolation (Section 2.11); and direct implementation of the non-linear calibration equation. Generally, the residual non-linearities are negligible. The largest errors tend to be due to small departures (i.e. within tolerance) of the sensors from the sensor definition in the corresponding documentary standard.

For thermometers with a smooth error characteristic there are four basic forms of error in the readings. The first, the offset error, is constant for all temperatures, and is similar to the ice-point shift in mercury-in-glass thermometers. The second error is proportional to the temperature and is essentially a range or scale error. For these two effects, we expect the error to take the form

$$\text{linear error} = -A - B \times \text{reading},\tag{5.4}$$

where A and B are constants.

Non-linear errors also occur in two forms. Even-order non-linearity causes a U-shape in the thermometer's error curve. Odd-order error introduces an S-shape in the error curve. So long as the non-linearities are not severe, they are well approximated by

$$\text{non-linear error} = -C \times (\text{reading})^2 - D \times (\text{reading})^3,\tag{5.5}$$

where C and D are coefficients for the even-order and odd-order errors respectively. This equation is particularly appropriate for instruments using analogue linearisation techniques, which are designed to remove the second-order (terms in t^2) behaviour at the expense of a smaller third-order (term in t^3) non-linearity. Equation (5.5) would describe the residual t^2 errors and the additional t^3 errors.

When the instrument is calibrated, we expect the correction, which is added to the reading to compensate for an assumed error, to have the form

$$\Delta t = A + B \times \text{reading} + C \times (\text{reading})^2 + D \times (\text{reading})^3,\tag{5.6}$$

where Δt is the correction to the reading. The four constants are best determined by a least-squares fit to the comparison data. An equation of this form, with the same quantity on both sides of the equation (temperature in this case), is called a *deviation function* for the thermometer. The deviation function style of calibration may also be used to determine the departure of thermocouples and resistance thermometers from standard tables of voltage or resistance versus temperature, as with Equations (5.1) and (5.2) above.

5.3.2   The client's needs

When we commence each new calibration, we should establish the needs of our client, the owner or user of the thermometer. There are two factors to consider to ensure that measurements made by the user are traceable. Firstly, because thermometers are often sensitive to factors other than temperature, the relationship must be established under well-defined conditions that are readily accessible to the user. This ensures that the user can establish the same conditions as employed during calibration, and therefore be confident that the relationship to the ITS-90 temperature scale is unchanged. Secondly, there are often occasions when the thermometer is in good condition, yet inappropriate for the application envisaged by the user. Examples include bare thermocouples in some chemically aggressive environments, platinum resistance thermometers in high-vibration environments, and mercury-in-glass thermometers in food applications. While we cannot always gather the required information from the client or prevent the user from using the thermometer in adverse or inappropriate situations, there is a duty of care on the part of the calibration laboratory to seek the information and advise the client.

Topics that should be addressed in the discussion with the client include:

- temperature range;
- required uncertainty (as opposed to the expected uncertainty);
- conditions of use, especially unusual ambient or operating conditions, and associated instrumentation;
- type of use, especially whether the thermometer is a reference or working thermometer.

Temperature range

Users are often tempted to calibrate thermometers over the full specified range of an instrument. However, the performance of most thermometers deteriorates as the range is extended. In addition, most manufacturers' specifications cover the extreme range of applicability of the instrument, including temperatures where it may be suited for intermittent use only. It pays to limit the calibration range to that which satisfies the client's needs, and no more. This yields a thermometer less likely to have been damaged from the extreme exposure and with a lower calibration uncertainty.

Accuracy

It is often necessary for the calibration laboratory to advise a client that the uncertainty required is unrealistic; either the need is overstated or the thermometer is not good

enough. While the laboratory may well lose a calibration fee, clients appreciate the early advice rather than being told after an expensive calibration that the instrument is not suitable.

Users are often tempted to overspecify the accuracy they require for their measurements. This has the effect of unnecessarily increasing the cost of the equipment and procedures associated with their measurements. A very approximate rule of thumb for the cost of thermometers used near room temperature is US$100 divided by the required accuracy in degrees Celsius. A thermometer with an accuracy of 1 °C costs about US$100, a thermometer system with an accuracy of 0.001 °C costs about US$100 000. The cost of overspecifying needs can be very high.

Conditions of use

For the calibration to satisfy its prime purpose of relating measurements to ITS-90, the client must be able to reproduce the calibration conditions. If the conditions are not accessible to the client then an additional, usually unquantifiable, error occurs, and measurements are no longer traceable. There are several common examples where this is a consideration, including the immersion conditions of liquid-in-glass thermometers and thermocouples, the sensing current of platinum resistance thermometers, and the instrumental emissivity setting of radiation thermometers.

It is important that the client's needs in respect of operating conditions are recognised before comparison measurements are carried out. Usually there is an expectation that the calibration laboratory will adapt its measurements to suit the client, but this is not always practical. Base-metal thermocouples should be calibrated *in situ*, and deep-sea thermometers cannot always be calibrated at the appropriate operating pressures without specialised equipment. In these cases, the calibration laboratory should ensure that the client is aware of the different conditions, and in some cases measure sensitivity coefficients that will allow the user to make corrections or estimates of uncertainty.

Reference and working thermometers

When designing calibrations it is useful to distinguish reference thermometers from working thermometers. Put simply, *reference thermometers* are used to calibrate other thermometers while *working thermometers* measure temperatures for any other purpose. Working thermometers are at the end of the traceability chain, while reference thermometers are links in the chain. The distinction has an impact on both the choice of calibration method and the treatment of uncertainties.

Working thermometers are usually used at a few well-determined temperatures, often only one temperature. Calibrations for working thermometers should therefore be designed to assess the performance over a narrow range near each of the specified temperatures.

Because working thermometers are used to make single temperature measurements that are not subject to averaging or other statistical processing, the uncertainty reported on the calibration certificate should measure the uncertainty in a single corrected reading. Following the discussion in Section 2.6.3, this leads us to the conclusion

that the component of the uncertainty derived from the analysis of the comparison measurements has the form

$$U_{\text{fit}} = k(1 + \rho/N)^{1/2}s, \tag{5.7}$$

where s is the standard deviation of the measured errors in the thermometer readings, k is the required coverage factor, ρ is the number of variables determined in the calibration ($\rho = 1$ for a correction), and N is the number of comparison measurements used to determine the correction or calibration equation. The uncertainty tends to ks when N is large.

Reference thermometers are used to calibrate other thermometers often at temperatures that are not known in advance. Calibrations for reference thermometers must therefore cover a range of temperatures. Since the thermometer cannot practically be compared at every possible reading, the corrections applied to the reference thermometer readings must be interpolated. The calibration procedure should therefore demonstrate that there are no erratic jumps in the thermometer characteristic and that corrections can be interpolated. There should also be a sufficient number of points measured to allow interpolation either linearly or according to an equation determined by least squares.

When reference thermometers are used, typically several readings are taken and averaged. Because the readings for the reference thermometer are averaged in the process the uncertainty reported on the certificates for reference thermometers should correspond to the uncertainty in the correction rather than the uncertainty in a corrected reading. The discussion in Section 2.6.3 (and Section 2.12.1 for an interpolation equation determined by least squares) leads us to the conclusion that the component of the uncertainty derived from the analysis of the comparison measurements has the form

$$U_{\text{fit}} = \left(\frac{\rho}{N}\right)^{1/2} ks, \tag{5.8}$$

where ρ is the number of parameters fitted in the analysis, and N is the number of measurements.

There is, however, one important caveat to the use of Equation (5.8). When in use, the reference thermometer measurements should completely sample the same distribution as during calibration. If, for example, the reference thermometer is used to carry out short-range calibrations of working thermometers and the corrections for the reference thermometer are distributed (discussed in Section 2.6.3) the errors in the reference thermometer readings will be highly correlated and there will be little benefit from averaging. Then the uncertainty in the correction is best characterised by $U_{\text{fit}} = ks$. Thus in cases where the thermometer is used for short-range calibrations use $U_{\text{fit}} = ks$.

5.3.3 Establishing the link to the SI

The prime purpose of calibration is to determine the relationship between the thermometer readings and the ITS-90 temperature scale. For direct-reading thermometers the relationship is usually a table of corrections. For temperature sensors, such as resistance thermometers, it is an equation relating resistance or voltage to temperature.

Figure 5.3 shows a graphical representation of the relationship between the readings of an uncalibrated thermometer and those of a reference thermometer. In simplest terms,
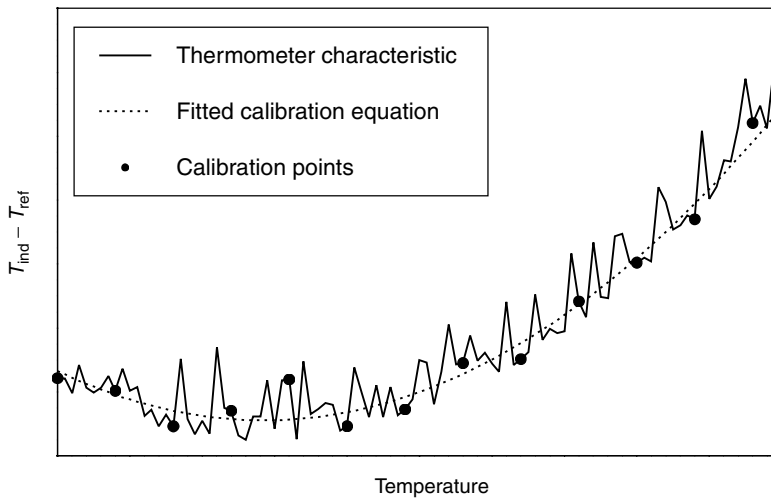
Figure 5.3   The basic problem of thermometer calibration is to sample enough of the thermometer characteristic to be able to find a correction equation and a measure of the accuracy of the equation

the problem is to sample this relationship and find an equation that passes through or near the set of sample points. Mathematically, establishing the link to the SI is the process of determining an interpolation equation (Section 2.11). There are several approaches providing different compromises between simplicity and the completeness of the information conveyed in the calibration certificate.

Single-point comparisons

The simplest comparisons involve a single measurement of the difference between the thermometer reading and a reference temperature. These are commonly carried out at experimentally important temperatures such as 37 °C for medical work, 44.5 °C for water quality work and 121 °C for sterilisation work. The result of the comparison is a single measure of the correction to the reading of the thermometer. However, to be classified as a calibration this approach requires an estimate of the uncertainty in the value of the correction. Since a single measurement is made, this must be a Type B assessment because it cannot be made based on sample statistics (a Type A assessment).

Where estimates of the uncertainties are not available, measurements of this type are strictly verifications, not calibrations. They are a confidence-building activity, which may postpone calibration by demonstrating the continued good behaviour of an instrument, but cannot replace calibration.

Short-range comparisons

Making multiple comparisons at one temperature immediately provides information on the dispersion of the readings of the thermometer under calibration, and enables a

calculation of uncertainty. To be a useful assessment of the uncertainty, the measurements must sample the range of errors likely to occur in use. Thus the measurements should not all be made at exactly the same temperature but should vary over a narrow range of temperatures around the temperature of interest, with the range determined by the likely use of the thermometer. With a liquid-in-glass thermometer, for example, an assessment over the range covering a few scale divisions either side of the nominal calibration point will assess the dispersion of readings caused by variations in the bore diameter and quality of the scale markings. The procedure is repeated for each calibration point and is the simplest approach for working thermometers used at a few specific temperatures. The results are most simply presented as a correction and uncertainty for each calibration point.

This procedure is also useful for calibrating reference thermometers. In this case, enough points must be taken to characterise accurately the behaviour of the thermometer over the entire range of interest. Corrections for temperature readings in between the calibrated points can then be determined by interpolation. Since it is common practice to use linear interpolation, the points should be close together. This approach has the advantage of mathematical simplicity but requires a large number of comparisons to be carried out. For example, we recommend one calibration point for every 50 to 100 scale divisions on liquid-in-glass thermometers. A good reference thermometer requires 10 to 12 calibration points, each based on perhaps six measurements. That is, 60 to 70 separate measurements may be necessary to calibrate a reference thermometer.

Wide-range comparisons

In Chapter 2 we introduced the method of least-squares fitting for determining the best values for the constants in a calibration equation. It is a technique well suited for the calibration of reference thermometers, though it may also be used with working thermometers.

Least-squares interpolation trades mathematical complexity for a reduced number of calibration points. Since we recommended three or four calibration points per unknown constant in the least-squares fit, only 12 to 16 measured points are required for a typical cubic calibration equation. This represents a reduction in the number of measurements of about five times over a multi-point calibration based purely on linear interpolation. On the complexity side, we have traded a table of corrections and uncertainties, which can be calculated simply from means and standard deviations, for a cubic equation and more complicated mathematics.

Least-squares interpolation also has other advantages: it demonstrates the suitability of the calibration equation by highlighting any interpolation error, and provides a measure of the uncertainty that is appropriate for all temperature readings within the calibration range. The measurements should be equally spaced over the temperature range of interest. The results are typically expressed as a correction equation and a single uncertainty. A least-squares fit to a recognised calibration equation is the most appropriate calibration method for non-linear sensors, such as resistance thermometers and thermocouples.

5.3.4 Assessing the uncertainty

In most calibrations, there are several sources of uncertainty not assessable by the user of the calibrated thermometer. These include the effects of the reference thermometer, transfer medium (e.g. a calibration bath), and effects originating within the thermometer itself. Because they affect every measurement made with the thermometer, it is the calibration laboratory's responsibility to assess them.

Occasionally calibration certificates report uncertainties that are of no practical use to the client. The most common examples are certificates reporting the uncertainty in the reference thermometer used in the calibration or the best measurement capability according to the laboratory's accreditation. Neither provides the user with any information about the dispersion of error in the readings of the calibrated thermometer.

With most thermometers the accuracy is dependent on use, maintenance and how the readings are interpreted. For the uncertainty to be of most use to the client the calibration laboratory must assume the best conditions accessible to the user. That is, the laboratory must eliminate all errors that the user can readily eliminate or assess, and must include in the estimate of the total uncertainty, the uncertainty caused by all the errors that the user will be unable to assess.

In thermometry there are generally at least four factors that contribute to the calibration uncertainty, including:

(1) uncertainty in the reference thermometer readings;

(2) variations in the stability and uniformity of the calibration medium;

(3) 'random' departures from the determined ITS-90 relationship; and

(4) uncertainty due to hysteresis.

We now discuss each of these contributions in more detail.

Uncertainty in the reference thermometer readings

The reference thermometer is the link between the thermometer under calibration and ITS-90; any errors in the scale of the reference thermometer will be transferred to the newly calibrated thermometer. The uncertainty in the reference thermometer readings, which is reported on the certificate for the reference thermometer, must therefore be included in the total uncertainty of the calibrated thermometer. If the reference thermometer certificate does not report the correct uncertainty, or reports it for an inappropriate level of confidence, then additional work may be required to determine the uncertainty or to scale it to the correct level of confidence (see Example 2.12).

Variations in the stability and uniformity of the calibration medium

Throughout the calibration we assume that the reference thermometer and the thermometer under test are at the same temperature. However, no matter how well controlled the calibration medium (bath, furnace, cavity or cryostat) there will always be residual spatial and temporal fluctuations in the temperature, which lead to differences

in the temperatures of the two thermometers. The distribution of these differences has two components: a fluctuating component and a steady component.

Random fluctuations in bath temperature cause random differences in the two thermometers' readings and already contribute to the uncertainty through the dispersion of the readings; they will thus contribute to the standard deviation in the corrections or least-squares fit. Therefore it is unnecessary to add to the total uncertainty a term for the uncertainty due to the fluctuations. Although we do not need to include the uncertainty for the random error caused by the fluctuations, it must still be measured to ensure that it is not a major contributor to the total uncertainty.

The systematic part of the error, due to temperature gradients within the bath, is not directly apparent in the calibration results and some prior assessment must be made of the contribution to the total uncertainty. The stability and uniformity tend to deteriorate as the temperature difference with respect to ambient increases, so we recommend surveys at three temperatures, at least, over the operating range: the lowest operating temperature, the highest operating temperature, and a middle temperature or near room temperature. A regular assessment every year or two will monitor the quality of the medium in case of deterioration in the performance, caused by thickening of the oil, for example, or failure of the stirring mechanism.

Departures from the determined ITS-90 relationship

All thermometers have at least one accepted calibration equation. These equations are good descriptions of the thermometer's response and are well established in respect of the mathematical form and typical values for the constants in the equations. For example, platinum resistance thermometers above $0\,°C$ have a quadratic relationship between resistance and temperature, and the parameter values are usually close to those for the appropriate documentary standard. However, all such relationships are idealised and small departures from the accepted relationship occur for many reasons. In most cases, the equation approximates very complex real behaviour. These non-idealities in the thermometer's behaviour lead to small and generally unpredictable departures from the simple calibration equation reported on the calibration certificate. In the following sections and chapters we will use the uncertainty symbol U_{fit} to characterise the uncertainty due to these effects. It is usually a Type A estimate based on the standard deviation of results used to calculate a single correction or calibration equation. Note that the experimental determination of U_{fit} usually includes the effects of fluctuations in temperature of the calibration medium as described above.

Uncertainty due to hysteresis

Hysteresis is a property of a thermometer whereby the readings depend on previous exposure to different temperatures (Example 2.10). Unfortunately, it is a property of most thermometers, and it is usually impractical to eliminate the effects of hysteresis from measurements. Not only would the calibration time become excessive because of the long preconditioning required for each measurement, but also the procedures for the usage of the thermometer would become so restrictive as to make the thermometer useless. However, some simple procedures can yield useful reductions in the effects.

To minimise the effects of hysteresis, reference thermometers are often used such that the measured temperature is approached from room temperature. This effectively halves the contributing uncertainty. However, in adopting this procedure the hysteresis effects are still present but hidden within the measurements. In order to assess the resulting uncertainty at least one measurement must be made that assesses the width of the hysteresis loop. In some cases the difference between two ice-point measurements, made before and immediately after the comparison, may provide sufficient information to allow an assessment.

The total uncertainty

Once all of the uncertainties have been considered, including those terms specific to the particular type of thermometer, the total uncertainty can be determined according to Section 2.8. The simplest approach is to adopt Equation (2.30):

$$U_{\text{cal}}^2 = U_{\text{ref}}^2 + U_{\text{bath}}^2 + U_{\text{fit}}^2 + U_{\text{hys}}^2 + \cdots, \tag{5.9}$$

where each of the uncertainties is determined and reported at the same level of confidence. If the client has not requested any particular level of confidence then they may be reported at any appropriate level, with 95% being preferred. The certificate must state the uncertainty and level of confidence, and should state either the coverage factor or the standard deviation to allow the client to change the level of confidence if required.

5.3.5   Reliability and generic history

Most clients buy a calibration for the assurance of reliability; few buy the calibration for the improvements in accuracy alone. With this in mind it is somewhat surprising that some calibration certificates have statements like 'These results are valid only at the time of test'. Clearly, such a certificate is of no use to anyone who wishes to interpret the readings of the thermometer for a period up to five years beyond the date of calibration. However, this is precisely what we want of calibrations, and this should be recognised at the outset. By issuing a calibration certificate, a calibration laboratory is supplying assurance that both the ITS-90 relationship and the uncertainty will be valid for a reasonable period.

An assurance of reliability begs the obvious question: how, on the basis of a calibration performed over a period of a few days, can we assess the likely stability of the instrument over the next month, year, or even five years? The answer is a two-stage process that places considerable demands on both the calibration laboratory and the user of the thermometer.

The calibration laboratory must:

- Have experience and/or knowledge of similar thermometers that have proved to be stable over long periods when subject to normal usage and reasonable care.
- Show that the thermometer under calibration is no different from those with the established history.

- Assert that the thermometer under calibration will have a similar stability to those with the established history, so long as it is subjected to the same usage and care.

The user of the thermometer (who may also be the supplier for in-house calibrations) must:

- Demonstrate, through regular ice-point checks, or other simple verification checks, that the instrument continues to behave as it did at the time of calibration.
- Demonstrate that the thermometer has not been exposed, during use or storage, to conditions that may adversely affect its performance.
- Evaluate the additional uncertainty due to drift in the thermometer behaviour with time.

The two components of this process are essentially histories: firstly, the collected knowledge on the typical behaviour of similar thermometers, which we call the *generic history* of the thermometer; and secondly, technical procedures, the calibrations and service records relating to an individual thermometer, which we call the *specific history*.

The most general aspects of generic history include:

- the typical relationship between the response of the sensor and temperature;
- the typical accuracy of the thermometer;
- the typical stability of the thermometer;
- the typical construction of the thermometer;
- the typical errors and faults in the thermometer;
- the typical usage and non-usage of the thermometer.

The presence of the positive factors and absence of the negative factors is a signature of reliability of a thermometer. Departure from this signature is deviant behaviour and therefore an important indicator of potential errors or faults. Calibrations are designed to verify the positive generic signature for each thermometer and detect the presence of any of the negative factors. Let us consider some examples.

Typical relationship

All thermometers are based on sensors, that is devices with a physical property that changes with temperature. For example, the volume of mercury changes with temperature, as does the resistance of platinum wire. For any type of thermometer to be a suitable candidate for maintaining the temperature scale, the relationship between the physical property and the temperature must be well established. Any individual thermometer that departs from this norm should be considered unreliable. For example, platinum thermometers with excessive departures from the expected relationship are often contaminated or have been subjected to excessive stress.

Typical uncertainty

The total calibration uncertainty of a thermometer normally depends on a large number of factors: the method of construction, the temperature range, the environment it is

exposed to, and how it is used. A part of the generic history of a reliable thermometer is that its accuracy will fall within a well-known range provided that it is constructed along certain well-known guidelines and its exposure is restricted to a certain range and environment. A calibration uncertainty that falls outside this range is usually an indicator of a damaged or faulty thermometer. For example, most calibrated mercury-in-glass thermometers have a total calibration uncertainty between one-fifth and one-half of a scale division. Thermometers with larger uncertainties may have non-uniform bores, poor scale markings, or may be made from poorly annealed glass.

Typical stability

Stability is the most important part of the generic history. It is impractical to hold a thermometer for years just to prove that it has certain stability over this period. Instead, we must rely on records of similar thermometers that have been proved to be stable over periods of years. The evidence and criteria relating to stability of thermometers are well documented in the measurement literature. For example, over the last two decades or so there have been significant advances in the manufacturing techniques for thermistors. Their generic history now includes records of glass-encapsulated thermistors that are stable to fractions of a millikelvin over periods in excess of a year.

Typical construction

One of the key factors in the development of thermometers is the means of constructing them so that they are least affected by environmental conditions, especially the aggressive environments associated with high operating temperatures. Eliminating the air-pressure effect in early gas thermometers and radiation errors in air-temperature measurements are two other examples. Thermometers that do not adhere to proven design and construction practices almost certainly compromise their short-term and long-term accuracy, and their reliability.

Typical errors and faults

Each type of thermometer, because of its construction and materials, is prone to particular manufacturing defects or physical damage. Thermometers with evidence of these defects are likely to exhibit high uncertainty and long-term instability. For example, a low insulation resistance between the detector element and the sheath of a resistance thermometer indicates that it has excess moisture in the probe assembly and will give unreliable temperature measurements Figure 5.4 shows two extreme examples of thermometers exhibiting physical damage.

Typical usage

More than most instruments, thermometers suffer simply because they are used. In order to withstand very high- or very low-temperature exposure, compromises must be made in their construction. Again, the generic history of thermometers includes the various constructions and purposes for which they are intended. Thermometers manufactured for one purpose may be quite unsuitable for another. The need to match
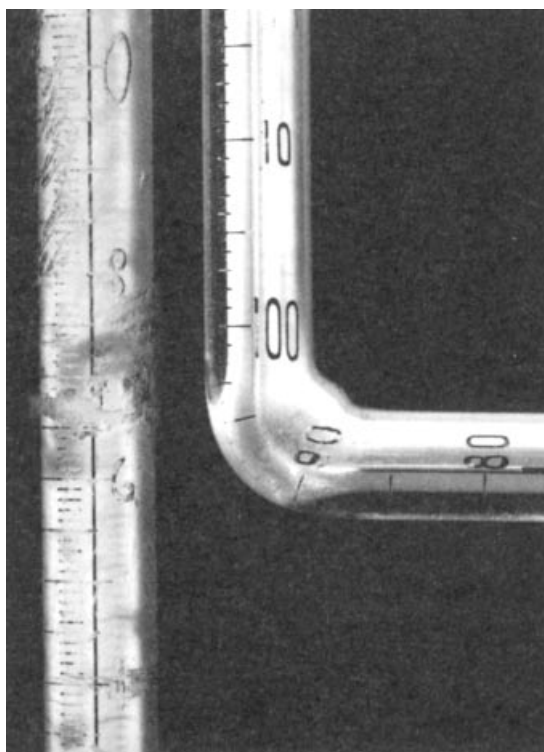
Figure 5.4 Two thermometers that have clearly been exposed to conditions that might adversely affect their reliability. One has a waist ground into the stem; the other has been bent to allow horizontal reading of the scale. Neither should be certified

construction and calibration with use arises often with thermocouples, which will maintain calibration only under very specific conditions.

One thing that is sure to make a calibration laboratory uneasy is a homemade instrument. Homemade instruments are often assembled using inappropriate materials and techniques, or used in environments where they have a high likelihood of being damaged. They are often not suitable for calibration. Fortunately, many of these cases sort themselves out; instruments that are poorly made usually fail the short-term tests, and instruments that pass the short-term tests are usually manufactured according to accepted design principles. The problem of determining reliability is not unique to homemade instruments. Every time a new model of instrument is released on the market, calibration laboratories must carry out extra tests to prove the reliability of the new model. Likewise, as with any new instrument, the owner must treat the instrument with a little more scepticism until a reasonable history of good behaviour is established.

5.3.6 Recalibration and specific history

By issuing a certificate the calibration laboratory is providing a conditional assurance of reliability, and asserting that the thermometer is capable of long-term stability.

However, the calibration laboratory cannot control the way in which the thermometer is used. Proof of the long-term validity of the certificate rests almost entirely with the user, who must demonstrate that the thermometer is continuing to behave the same way as it did on the day of calibration. As we noted in the previous section, to prove the validity of the certificate the user must:

- Demonstrate through regular ice-point checks, or other simple verification checks, that the instrument continues to behave as it did at the time of calibration.
- Demonstrate that the thermometer has not been exposed to use or conditions that may adversely affect its performance.
- Apply corrections and include a component of uncertainty to account for any drift uncovered in the instrument's readings.

The first requirement is the single most important factor in the proof of validity of a certificate. With liquid-in-glass and platinum resistance thermometers, about 95% of all possible faults appear as a change in the ice-point reading. For thermometers that cannot read an ice point (as with some radiation thermometers) or the ice point provides little information about the integrity of the thermometer (as with thermocouples), regular verification checks against other thermometers or fixed points are required.

To meet the second requirement the user of the thermometer must be able to demonstrate that the thermometer has always been used with due care. Here the ISO 17025 standard has recommendations based on an equipment log, which includes:

- a full description (identification) of the instrument;
- procedures for use, including a copy of the manufacturer's instructions;
- the complete calibration and verification history of the instrument;
- dates when the instrument is due for recalibration and service;
- a complete service and repair history; and
- restrictions on the use of the equipment to approved sites and approved personnel.

This information constitutes the specific history of the thermometer.

Drift in thermometers usually arises because of gradual dimensional or compositional changes. The changes may occur predominantly with time, as with bulb contraction in liquid-in-glass thermometers, or may depend on use, as with platinum resistance thermometers. Drift assessments are usually based on changes in the ice-point reading with time or from the historical record of calibrations. Example 2.13 illustrates an assessment based on a calibration record.

Because the stability of instruments depends strongly on use, most laboratory accreditation organisations discourage the inclusion of a time component in the calibration uncertainty. Instead, it is the owner's responsibility to make that assessment. For the same reason ISO 17025 also forbids, except if regulations require it, the inclusion of a recalibration interval on calibration certificates.

The question of when to recalibrate is one of the more confused areas of calibration. The answer is very simple: the calibration certificate is valid so long as the user is able to demonstrate its validity. If the ice-point record suggests that the thermometer has drifted too far for comfort then it is time for the thermometer to be recalibrated. Thermometers should be calibrated as new, after one year of use, to measure the drift

rate and identify premature failures, and then as necessary up to a maximum period of five years. If at any time the accumulated uncertainty due to drift in the thermometer becomes excessive (i.e. it no longer satisfies the user's needs) then the thermometer is due for recalibration. If the rate of drift is excessive compared with the manufacturer's specification then the thermometer may need adjustment or service. Thermocouples and radiation thermometers that do not have the ice point or triple point within their range may need to be recalibrated more frequently.

Ice-point checks should always be made immediately before and after calibration, to check that the thermometer has survived shipment, and to ensure that the ice-point record is continuous in the event that adjustments are required.

5.4 Documentary Requirements

One perspective that helps to draw attention to the practical meaning of traceability is to replace the term traceable by auditable. For a measurement to be traceable there must be a chain of measurement records that relate the measurement to the appropriate measurement standard. ISO 17025 requires five technical aspects of calibrations to be documented.

5.4.1   Staff training

The staff in a calibration laboratory must be well informed if a laboratory is to perform high-quality calibrations (satisfying the clients' needs). Staff should have:

- relevant knowledge of the way clients' and the laboratory's instruments are to be used and tested;
- knowledge of the typical defects or degradations that may occur during use of a particular instrument;
- knowledge of the general requirements expressed in relevant legislation and documentary standards; and
- understanding of the significance of deviations found with regard to the normal use of instruments.

The laboratory must therefore record staff training and experience to support their claims of competence, including qualifications, training, experience and demonstrated skills. Staff should be supervised when undergoing training.

5.4.2   Calibration procedures

With each calibration, information and expertise are acquired that make the next calibration easier and better. Fully documented technical procedures provide a means for ensuring that this information is not lost or forgotten. In particular, written procedures provide a means for retaining information in the event of key staff leaving, and so simplify the training of new staff.

The most time-consuming calibrations are those for instruments that fail to meet the client's requirements. When faults are uncovered there is often double-checking and repetition of measurements. The better specified the calibration procedure, the less the results will be questioned. One particularly useful time-saving device is a list comprising the criteria for failure. For liquid-in-glass thermometers, the list may include quality of marking and uniformity of bore, as well as performance-related criteria such as maximum error and maximum rate of change of error.

Procedures should be developed before being performed and should contain at least the following information:

- appropriate identification, for example a procedure number and/or a title;
- statement of the scope of the procedure;
- description of the types of instruments covered by the procedure;
- a statement of the quantities, ranges and uncertainties covered by the procedure;
- a description of the equipment required and the performance of that equipment;
- any documentary standards or reference materials required;
- environmental conditions required;
- a detailed description of the actions taken in the procedure including:
  - affixing of identification marks, and handling, storage and shipment of items;
  - checks to be made before the calibration work is started;
  - checks that the equipment is working properly;
  - the method of obtaining and recording results;
  - any safety measures to be observed;
- criteria for approval and rejection;
- data to be recorded and the method of analysis;
- the uncertainty or a procedure for calculating the uncertainty.

Note that a procedure that is excessively complicated or detailed can be very expensive to maintain. There should be no more detail than necessary to provide reminders to trained staff. Flow charts can be very useful.

5.4.3   Uncertainty analysis and best measurement capability

The ISO 17025 standard also requires evidence validating the technical procedures. For calibration procedures, this must include a full uncertainty analysis of the method, supported by comparisons with other laboratories or comparisons of results based on alternative methods. As we discussed in Chapter 2, emphasis is placed on the uncertainty analysis because it is a very convenient way of assessing the competence of a laboratory.

The uncertainty analysis should summarise all the physical effects known to the staff that are within, say, a factor of 10 of their best measurement capability. This can take any form that the staff find convenient. The combination of a cause and effect

diagram, with a short statement or paragraph on each influence variable, and a table summarising the numerical contribution of the most significant effects, works very well. Note that the statement on each influence effect or source of uncertainty need not be complicated. For example, the statement

> Self-heating: according to Nicholas and White [ref], the variations in the self-heating effect, caused by the current passing through the sensing resistance, are less than 2 mK for measurements in stirred baths, and therefore negligible for our purpose.

is perfectly satisfactory. The main point is that the laboratory should be aware of the effect, its cause and its magnitude. While some of the effects may well have negligible influence on most calibrations, there will be occasions when some of the effects are significant, and staff should be able to recognise and manage these effects.

More detailed descriptions of uncertainties are required where the effect or influence is significant; say, within a factor of 3 of the best measurement capability. The description should then include a detailed derivation of the numerical value for the uncertainty supporting its inclusion in the total uncertainty. Detailed explanations and supporting evidence should be provided for all uncertainties relating to the laboratory's equipment.

Two important sources of uncertainty in thermometer calibrations are the reference thermometer and the calibration medium (bath, furnace, cavity, cryostat), collectively the calibration system. In an ideal situation, the uncertainties arising from the calibration system should have a negligible influence on the thermometer being calibrated. The client can then expect the same calibration from every calibration laboratory. Let us investigate the conditions for this to be so.

The total calibration uncertainty typically has the form

$$U_{cal}^2 = U_{ref}^2 + U_{bath}^2 + U_{fit}^2 + U_{hys}^2 + \cdots, \qquad (5.10)$$

where the contributing terms in sequence are: the uncertainty in the readings of the reference thermometer; the uncertainty due to non-uniformity of the calibration medium; the uncertainty calculated from the statistical analysis of comparisons; then one or more terms based on Type B assessments of various effects associated with the thermometer under test. The first two terms relate purely to the calibration system, and the remaining terms to the thermometer under test. If we can make the uncertainties due to the reference thermometer and the bath so small that they are negligible, then the calibration uncertainty is a property of the thermometer only and is independent of the calibration laboratory.

Let us say, for argument's sake, that the contribution of the reference and bath uncertainties should be less than 10% of the total calibration uncertainty. It follows that

$$U_{ref}, U_{bath} < \tfrac{1}{3} \left(U_{fit}^2 + U_{hys}^2 + \cdots \right)^{1/2}. \qquad (5.11)$$

That is, the uncertainties due to the reference thermometer and the bath must be at least a factor of 3 less than the expected uncertainty of the thermometer. The factor of 3 is a useful rule of thumb for determining the quality of the equipment required to carry out a calibration, or alternatively the best uncertainty in a calibration. It is sometimes called the $3 \times$ *rule*, and corresponds to a *test-uncertainty ratio* of 3.

It should be recognised that the $3\times$ rule arises from a 'fair-trading' argument based on the client's reasonable expectations that the calibration of a thermometer does not depend on how it was calibrated. It is not a definition of what is technically feasible. A test-uncertainty ratio smaller than 3 is acceptable for in-house calibrations or where a very high level of transfer is required and there is no alternative supplier.

The total uncertainty due to all of the terms associated with the calibration system, comprising terms due to the reference thermometer, non-uniformity of the medium, and short-term temperature fluctuations in the medium, is called the *best measurement capability*, or *bmc*. It is the lowest possible uncertainty that the calibration laboratory can achieve when calibrating an ideal thermometer. More typically, following the fair-trading argument given above, routine calibrations should not normally achieve uncertainties much better than $3 \times bmc$. One of the most important tasks required of the calibration laboratory is regular assessment of its *bmc*. This involves regular uniformity and stability surveys of all calibration media.

5.4.4   Calibration records

Detailed records for each calibration job should also be kept. These records may be required in the event of customer complaints, reviews of procedures, or reissue of certificates. Because the records contain information not contained on the calibration certificate, they constitute part of the traceability chain for the thermometer. The records should include:

- any notes listing the client's requirements and operating conditions (if available);
- a detailed description of the item under test including, if necessary, any software identification and menu options;
- a detailed description of the reference instruments used including, if necessary, any software identification and menu options;
- the results of all of the checks carried out on the instrument;
- notes on any adjustments made, for example photocopies of key parts of the operator's manual;
- a complete record of comparison measurements including identification of the calibration procedure;
- relevant notes on the analysis;
- a copy of the calibration certificate and/or covering letters to the client;
- copies of paperwork relating to financial matters such as work orders and invoices.

All of this should be auditable and traceable from the number reported on the calibration certificate.

5.4.5   Calibration certificates

As with any formal report of a measurement, the calibration certificate must include sufficient information to identify uniquely the equipment tested, the nature of the tests, and present an unambiguous statement of the results. The certificate must have:

- the title 'calibration certificate';
- a means to identify the certificate uniquely, usually a unique number that is traceable to the calibration records;
- the page number and total number of pages on each page;
- the name, address and location of the calibrating laboratory;
- the name and address of the client;
- a means to identify uniquely the equipment tested, for example the manufacturer, model and serial numbers of all items submitted for test;
- the date when the calibration was carried out;
- a brief description of the calibration method, for example comparison with reference thermometer or fixed points;
- where relevant the conditions under which the measurements were carried out;
- the results, observations and conclusions derived from the results;
- a statement of the quantity measured, for example temperature according to ITS-90;
- a statement of the uncertainties in the results;
- the names, functions and signatures of personnel responsible for the tests and the certificate;
- the conditions under which the report may be reproduced; and
- an endorsement by an independent accrediting body.

The certificate should not normally contain recommendations on the recalibration interval, unless it is requested by the client or required by regulations. Also certificates do not normally contain statements of professional opinion, with the exception of statements of compliance with a documentary standard. Note, too, that it is not necessary for the certificate to identify the reference thermometer used for the calibration. This information is not of any use to the client. For a calibration to be traceable, it is sufficient that the test equipment be identified in the test record held at the calibration laboratory. If necessary, the information can be traced through the report number.

The statement of traceability is implied through the endorsement by an independent accrediting body. The certificate is itself a statement that all measurements reported on the certificate are traceable to the appropriate national or international standards; the endorsement is an assurance that all measurements are indeed traceable and that all of the appropriate records have been kept. In this respect, ISO 17025 provides a practical working definition of traceability.

This may look like an excessive amount of information. However, all of it is necessary to ensure traceability, and to avoid possible confusion. In many cases, it will all fit on a single A4 page. Examples of completed certificates are given in Section 5.5.

5.5 Calibration Methods

5.5.1   Collating the information

Once all of the information on the thermometer, the client's needs and the calibration system has been gathered it is time to decide what tests and measurements must be
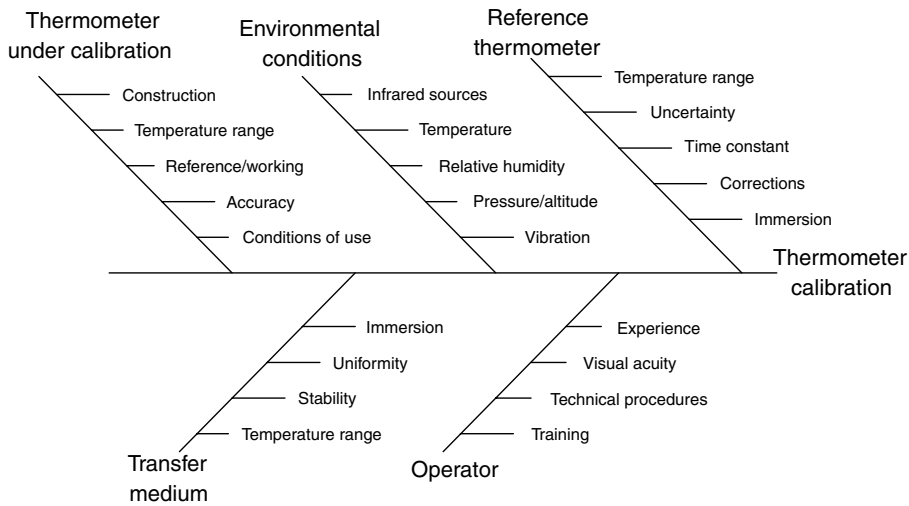
Figure 5.5 A cause and effect diagram for a thermometer calibration. The branch labelled 'Thermometer under calibration' should be expanded to include the influences specific to each type of thermometer

carried out. A lot of the information can be classified as influence variables of various sorts, which can be summarised in a cause and effect diagram such as Figure 5.5. Once the influences and effects have been recorded, we suggest that they be classified into three main groups, as follows.

Influences or effects that are indicative of faults or unreliable behaviour

These influences tend to be manufacturing defects or damage acquired through use. Since they result in an unreliable measuring instrument, each effect identified translates into a criterion for failure or rejection. The calibration procedure should include a test to check for the presence or absence of these effects.

An example of an effect of this type is the presence of moisture in the sheath of a platinum resistance thermometer. A simple test is to measure the insulation resistance between any of the lead wires and the steel sheath. If moisture is found the probe should be dried or discarded (see Section 6.5.10).

Effects easily eliminated by good practice

Quite a number of the effects identified will be easily eliminated by good practice. Examples include immersion effects and operator effects. In any good measurement, the user should always be striving to ensure there is sufficient immersion, and the operator is trained to avoid effects such as parallax and stiction. Some of these effects may translate into calibration conditions to be reported on the calibration certificate; for example, 'the minimum immersion of the platinum resistance thermometer was 160 mm'.

Influences or effects that are unavoidable

The remaining effects that have been identified are those that cannot be eliminated by good practice. They include the uncertainty in the reference thermometer readings, the non-uniformity and instability of the calibration medium, and any instrumental effects associated with the thermometer under test. The calibration procedure should therefore include methods (Type A or Type B) for assessing the respective contributions to the total uncertainty in the calibration.

5.5.2   A calibration procedure

In this section, we outline a calibration method built on the recommendations given in the preceding sections. The eight steps given below are intended to be an outline of a suitable method for inclusion in a calibration procedure. Before using it, we suggest you adapt it to suit your own needs or incorporate any additional requirements specified by your organisation.

Step 1: Start record keeping

The calibration begins formally with the order for the work to commence and receipt of the instrument. Record the client's name, address, order number and a complete description of the thermometer submitted for testing, including the make, model and serial numbers. Any specific requirements of the client should also be noted, such as the range and accuracy required, particular temperatures of importance, relevant documentary standards, the intended use of the thermometer and any potential influence variables in the working environment. Questions to ask the client include:

- What are the temperature range and accuracy required?
- How is the thermometer to be used, for example as a reference or a working thermometer?
- Must it conform to any documentary standards?
- Will it be exposed to any difficult environments, for example corrosive chemicals, vibration, pressure, moisture, rapid cycling, or electromagnetic or ionising radiation?
- Are there any departures from normal usage, for example in respect of immersion, response times, and other sources of error normally excluded from measurements?
- Is it likely to need adjustment?
- Can we please have a copy of the operator's manual and manufacturer's specifications?

Step 2: General visual inspection

Immediately after receipt of the thermometer, make a simple visual check and record the state of the instrument. Note the packaging used for shipment and examine the thermometer for any damage that may have occurred during shipping. Quickly check that it works, and that all of the required leads, software and manuals are present.

Step 3: Conditioning and adjustment (if required)

For many thermometers, some form of conditioning or pre-calibration adjustment may be required. For example, rare-metal thermocouples and SPRTs require annealing. Similarly, many electronic thermometers benefit from adjustments for offset, range and linearity.

Instruments that have user-serviceable adjustments (ice points, range and linearity) should *not* be adjusted except in consultation with the client. Adjustments will prevent the client from being able to use the calibration retrospectively and will interrupt the ice-point record that is the client's proof of stability. If adjustments are made to a reference instrument, measurements of the performance (Step 5 below) must be made both before and after adjustment.

A calibration does not normally cover the servicing or repair of the thermometer. If the client expects this, then it should be sought from the manufacturer of the thermometer. It would be unusual for the calibration supplier to have the expertise and equipment required, and servicing by a person not approved by the manufacturer may invalidate any warranty.

Step 4: Generic checks

Carry out all of the pass/fail checks required to establish consistency of the thermometer with the positive aspects of generic history. Many of these measurements may be carried out at any time, but some, such as maximum rate of change of error for liquid-in-glass thermometers, require the comparison data and are best carried out at the end of a calibration. Others, such as checks of the insulation resistance of resistance thermometers, are more efficiently carried out before the comparison. Where possible, ice points should be determined before and after all comparisons; in the absence of previous calibration data this may be the only specific information available on the stability of a thermometer.

Step 5: Comparison

The thermometer is compared either with a reference thermometer or with fixed points using one of the three comparison methods outlined in Section 5.3.3. Enough measurements should be taken to ensure confidence in the determined relationship and uncertainty. The comparison should also be carried out in such a way as to avoid as many influence effects as is practical, while ensuring that the conditions are still readily accessible to the user.

Step 6: Analysis

Once all the data has been gathered, the results are processed to determine the best ITS-90 relationship for the thermometer.

Step 7: Uncertainties

The uncertainty for the calibration is established by considering the four general sources of uncertainty described in Section 5.3.4, as well as uncertainties specific to the thermometer being calibrated.

Step 8: Complete records

It is first necessary to decide if the thermometer should be certified. If at any of the Steps 2 to 7 there is evidence that the thermometer deviates strongly from expected behaviour, then a certificate should not be issued. In cases where a certificate is not issued, a covering letter should be supplied to the client explaining why. This information may be invaluable in uncovering poor handling or for making warranty claims. All information relating to a thermometer, whether or not a certificate is issued, should be kept for a reasonable period. A copy of the letter or certificate is placed in the file, the client invoiced and the file closed.

5.5.3   Rising-temperature comparisons

Ideally, mercury-in-glass thermometers should be calibrated in baths that enable the temperature to be set and changed by a fraction of a scale division. This allows an accurate assessment of the quality of the thermometer bore and markings near the calibration point. The method described here achieves the same end without the use of a sophisticated controller. The method uses a well-stirred bath with a simple heater powered from a variable power supply such as a variable a.c. transformer.

The power provided for the heater is a few watts more than required to keep the bath stable, so the bath temperature rises very slowly and steadily. By placing the thermometers in the bath and reading them in a timed sequence it is possible to ensure that the average reading for all the thermometers is the same. Figure 5.6 shows a graphical representation of the technique, and Figure 5.7 shows a suitable placement of the thermometers in the bath.

The process shown in Figure 5.6 is repeated several times (three or more) for each calibration point in order to build up statistical information about the distribution of the errors near the calibration point.

The technique has a number of advantages over fixed-temperature calibrations:

- By design, the readings are taken at temperatures distributed randomly over several scale divisions, ensuring that the bore and scale markings are well sampled.

- The mercury column rises steadily as the temperature is increased, ensuring that the mercury meniscus is properly shaped.

- The technique has a relatively low cost and is quicker than the fixed-temperature technique described in Section 5.5.5 below.

- By using stirred-alcohol baths, cooled initially with dry ice or liquid nitrogen, the technique gives access to temperatures down to $-80\,^\circ$C without the need for refrigerators.
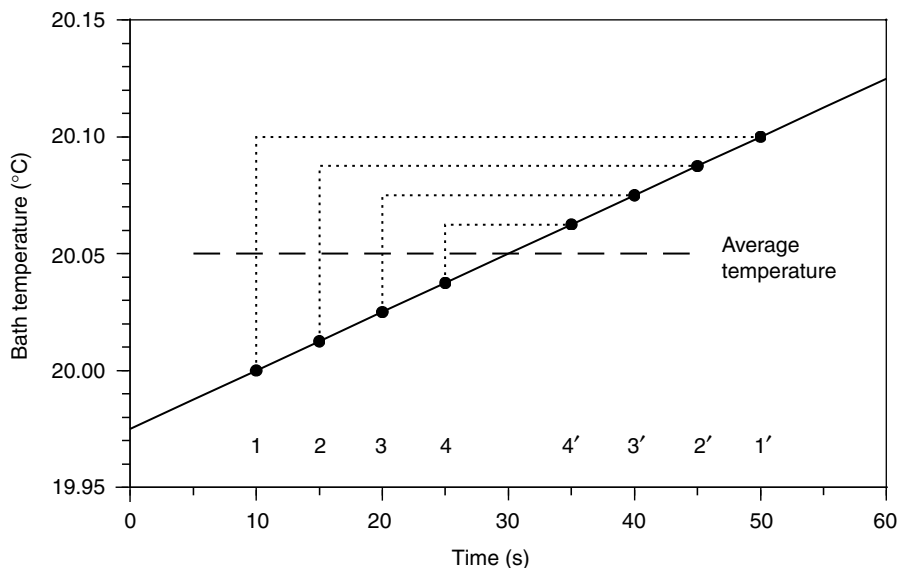
Figure 5.6   The rising-temperature calibration method. In this comparison the four thermome-ters are read at 5 second intervals with a slightly longer delay before they are read at 5 second intervals in the opposite sequence. The average bath temperature is the same for all the ther-mometers
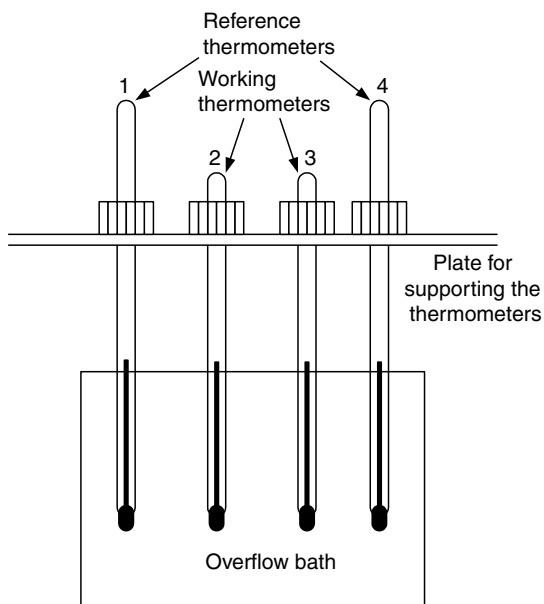
Figure 5.7   The thermometers are placed in the calibration bath in the sequence in which they will be read to prevent recording errors

The technique has a number of small disadvantages:

- A variable rate of rise of the bath temperature will lead to the average temperatures not being the same for all sets of readings. The problem is not serious so long as the variations do not correlate with the movement of the operator reading the thermometers.

- When thermometers with different time constants are used, they will lag behind the bath temperature by different amounts (see Section 4.4.4), leading to a systematic error in the calibration. Example 4.6 considers this problem and yields a useful rule of thumb: the rate of rise should be less than $1\,\mathrm{mK\,s^{-1}}$.

- The strict timing requirements are quite demanding for the operator who must read the thermometer, record the results, and move the viewing telescope to the next thermometer in time to take the next reading. Careful planning is required to avoid reading and transcription errors, particularly if the reference thermometers and thermometers under test have different scale markings.

- The steadily rising mercury column will almost certainly suffer from stiction: the mercury moving up in fits and starts. It is important that the thermometer is tapped lightly immediately before the reading to encourage the mercury to move to its equilibrium level and so minimise the stiction error.

- It is likely that the uniformity and stability of the calibration medium are not as good as for a fixed-temperature system.

- The method does not provide as much information about the distribution of the errors as does the fixed-temperature calibration (see following example).

5.5.4   Example: Calibration of a short-range working thermometer

In this section, we provide a summary of an actual calibration of a mercury-in-glass thermometer using the rising-temperature method.

Let us assume that an order is received from ACME Thermometer Co. for the calibration of two ASTM 121C kinematic viscosity mercury-in-glass thermometers. The procedure given in Section 5.5.2 is followed, using the rising-temperature method described above.

Step 1: Start record keeping

A file is opened with an order number for the job. This file contains the client's address, the contact person, the contact telephone and/or fax number, a copy of the order, a complete description of the thermometers including the manufacturer, type number and serial numbers, and the calibration points required. The file will be continually updated to include summaries of the test records, calibration results and a copy of the certificate if one is issued. The thermometers are short-range thermometers with an auxiliary ice-point scale and a main scale covering the range 98.5 °C to 101.5 °C, marked to 0.05 °C. Calibration is required at 0 °C, 100 °C and 101 °C.

Step 2: General visual inspection

The thermometers are unpacked and inspected immediately on receipt. They are found to be in good condition. The packaging is satisfactory.

Step 3: Conditioning and adjustment

The thermometers are subjected to a three-day wait at room temperature to allow the bulb to relax following possible previous use. They are stored horizontally in a secure cabinet to protect them from risk of mechanical and thermal shock that might accompany the other activities in the laboratory.

Step 4: Generic checks

Detailed inspection shows that the markings on both thermometers are clear, well formed and unambiguous. There are no visible constrictions or obstructions in the bore. The mercury column is intact and there are no signs of mercury in any of the chambers above the meniscus.

An ice-point measurement is made so that it can later be compared with a post-calibration ice point to check on the thermometer's stability. The ice-point reading is found, as required by the ASTM standard, to be within two scale divisions of $0\,°C$. The ice points on the two reference thermometers that will be used in the comparison are also checked now.

Step 5: Comparison

The comparison follows the guide in Section 5.3.3 for the short-range calibration of liquid-in-glass thermometers. The ASTM standard requires comparisons at $100\,°C$ and $101\,°C$. The rising-temperature technique is used at both points.

The calibration bath is first warmed to a couple of degrees below $100\,°C$ and the thermometers are then located in the bath as indicated in Figure 5.7, with the mercury column just visible above the surface of the oil. Once the telescope has been positioned and the operator is ready to record the results, the bath heater is adjusted to bring the bath slowly through the $100\,°C$ mark. The heat capacity of oil is about one-quarter that of water so the bath requires about 1 watt per litre of oil in excess of the bath losses to rise at $1\,mK\,s^{-1}$ (see Section 4.3.2).

Readings commence once the reference thermometers indicate that the temperature is within about three scale divisions of $100\,°C$. A wristwatch with an alarm indicating 10 second intervals is used to alert the operator to take a reading. The record of the comparison at $100\,°C$ is shown below, where the values of the reference thermometer and the thermometers being calibrated are tabulated in the columns marked as 'Ref' and 'Working' respectively. The record is arranged in the same sequence as the sequence of thermometers in the calibration bath to help prevent transcription errors, and the

readings are taken in the order indicated by the arrows.

Reading	Ref 1	Working 1	Working 2	Ref 2
Set 1 →	99.740	99.740	99.720	99.770
←	99.750	99.750	99.720	99.780
Set 2 →	100.040	100.050	100.030	100.078
←	100.042	100.045	100.030	100.078
Set 3 →	100.180	100.190	100.175	100.220
←	100.182	100.190	100.180	100.224

Once the comparisons at $100\,°C$ and $101\,°C$ are complete, the thermometers are removed from the bath, cleaned to remove the oil, and returned to the cabinet to allow recovery from the high-temperature exposure. An ice-point measurement is carried out then to help assess the recovery of the thermometer.

Step 6: Analysis

The first step in the analysis is to calculate the average reading for each set of results. Guard figures are retained to avoid round-off errors during the calculation.

Reading	Ref 1	Working 1	Working 2	Ref 2
Set 1	99.745	99.745	99.720	99.775
Set 2	100.041	100.0475	100.030	100.078
Set 3	100.181	100.190	100.1775	100.222

The reference thermometer readings are now corrected using the corrections given on their calibration certificates and averaged to determine the calibration temperatures. The corrections given at $100\,°C$ are:

$$\text{correction for Ref 1 at } 100\,°C = +0.045,$$

$$\text{correction for Ref 2 at } 100\,°C = +0.010.$$

Hence the statistics for the reference thermometers are as shown below.

Corrected readings	Ref 1	Ref 2	Mean	Difference
Set 1	99.790	99.785	99.7875	+0.005
Set 2	100.086	100.088	100.087	−0.002
Set 3	100.226	100.232	100.229	−0.006

The reference thermometers disagree by at most $+0.005\,°C$ and $-0.006\,°C$, which is consistent with the reference thermometers each having reported uncertainties of $0.008\,°C$. The corrections for the two working thermometers are now determined along with the means and standard deviations.

These corrections to the working thermometers (correction = true temperature − mean reading) are given below.

	Temperature	Working 1	Working 2
Set 1	99.7875	0.0425	0.0675
Set 2	100.087	0.0395	0.0570
Set 3	100.229	0.0390	0.0515
Mean	100.0345	0.0403	0.0587
Standard deviation		0.0019	0.0081

These tables are calculated for each calibration point and a summary prepared for each thermometer. The summary for Working Thermometer 2 is as follows.

Temperature	Reading	Correction	Standard deviation
0 (ice point)	−0.020	+0.02	
100.03	—	+0.059	0.0081
101.02	—	+0.047	0.0071
	Cumulative standard deviation		0.0076

The cumulative standard deviation is calculated from the variance of the residual errors of both of the calibration points (100 °C and 101 °C). The total number of degrees of freedom used to calculate the variance is equal to four, calculated as the number of measurements of error (six, three per point) minus the number of corrections calculated (two, one per point).

Step 7: Uncertainties

In order to determine the total uncertainty the various contributing factors identified in Section 5.3.4 are evaluated.

Uncertainty in the reference thermometer readings   This is read directly off the calibration certificates for the two reference thermometers,

$$U_{\text{ref}} = 0.008\,°\text{C},$$

and is already reported at the 95% level of confidence.

Variations in the uniformity of the calibration medium   It is known from commissioning tests that the bath non-uniformity is no greater than 0.005 °C per 200 mm, with most of the gradient in the vertical direction. Since the thermometers have been placed in the bath within 100 mm of each other, the non-uniformity is treated as the

semi-range on a rectangular distribution and the uncertainty is estimated as

$$U_{\text{bath}} = 0.0025\,°\text{C},$$

which closely approximates a confidence interval of 95%.

Departures from the determined ITS-90 relationship: The uncertainty associated with the calculation of corrections from the experimental data is 0.0076 °C. This is a Type A uncertainty with four degrees of freedom. The 95% confidence interval is found using Equation (5.7) where the k value from the Student's t-distribution (Table 2.2) corresponding to $P = 95\%$ and $\nu = 4$ is found to be 2.78. The value of N used is the number of measurements contributing to the calculation of each correction ($N = 3$). Hence

$$U_{\text{fit}} = k(1 + 1/N)^{1/2}s = 0.024\,°\text{C}.$$

Uncertainty due to hysteresis   The likely uncertainty due to hysteresis is indicated by the difference between the precalibration and postcalibration ice points, in this case 0.005 °C. Treating this as a rectangular distribution, the 95% confidence interval is estimated as the semi-range:

$$U_{\text{hys}} = 0.0025\,°\text{C}.$$

Total uncertainty   The total uncertainty is the quadrature sum of the individual uncertainties:

$$U_{\text{total}} = \left(0.008^2 + 0.0025^2 + 0.024^2 + 0.0025^2\right)^{1/2} = 0.026\,°\text{C}.$$

As is typical, the total uncertainty is very nearly equal to that for the greatest contributor. On the certificate, the uncertainty will be quoted as 0.026 °C, which is equivalent to about half a scale division, and is typical for a high-resolution mercury-in-glass thermometer.

Step 8: Complete records

After comparison of the results with ASTM specifications the decision is made that the thermometer is within the specifications so a certificate is prepared with the results rounded to the appropriate decimal place. The completed certificate for Working Thermometer 2 is shown in Figure 5.8.

5.5.5 Fixed-temperature comparisons

For calibrations to have the highest accuracy, all settling and response errors must be eliminated. This is achieved only with the fixed-temperature calibration method. The equipment required is a bath (furnace, cryostat, cavity) with a high uniformity. A

CALVIN, DEGRIES AND CO

1 TRACEABILITY PLACE, PO BOX 31-310, LOWER HUTT, NEW ZEALAND
TELEPHONE (64) 4 569 0000   FAX (64) 4 569 0003

CALIBRATION CERTIFICATE

Report No: T92-2001.

Client: ACME Thermometer Co, 100 Celsius Avenue, P O Box 27-315, Wellington, New Zealand.

Description of Thermometer: ASTM 121C kinematic viscosity thermometer divided to 0.05 °C, serial number 2925, manufactured by Zeal.

Date of Calibration: 22 to 23 January 2000.

Method: The thermometer was compared with standard thermometers held by this laboratory. All measurements are traceable to the New Zealand National Standards. The temperature scale used is ITS-90.

Conditions: The thermometer was calibrated in total immersion.

Results:

Thermometer Reading (°C)	Correction (°C)
0 (ice point)	+0.02
100.04	+0.06
101.02	+0.05

Note: Corrections are added to the reading to obtain the true temperature.

Accuracy: The uncertainty in the corrected thermometer readings is ±0.026°C at the 95% confidence level.

Checked:_____   Signed:_____

W Thomson   R Hooke

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page 1 of 1

Figure 5.8   A typical calibration certificate for a working thermometer

controller should control the temperature of the bath with a high short-term stability so that the uncertainty due to bath-temperature fluctuations is negligible. For liquid-in-glass thermometer calibrations, the controller should also have a sufficiently fine set-point adjustment to enable the small increments in temperature, which are required to assess the bore and scale markings.

In a fixed-temperature calibration, all calibration temperatures are determined and the controller set point is set to each of the nominal calibration temperatures in turn. The bath and thermometers are allowed to settle for several minutes (or longer as required) once the bath has reached the set point. The calibration readings are then taken and the bath moved to the next temperature.

The advantages of the fixed-temperature method are:

- settling and response errors are eliminated;
- the bath has higher uniformity than with a rising-temperature calibration enabling a better best measurement capability;
- there is more accurate control over the calibration temperatures;
- the operator has greater flexibility over when the readings are taken, and this results in fewer recording and transcription errors;
- the method provides more information (larger number of degrees of freedom) than the rising-temperature method for the same number of measurements.

Disadvantages of the method include:

- the cost of the bath and controller is higher;
- for a given number of calibration points the calibration time is longer because of the additional settling time.

5.5.6 Example: Calibration of a reference thermometer

In this section, we summarise an actual calibration of an electronic reference thermometer using the fixed-temperature calibration method.

A platinum resistance thermometer, with a resolution of $0.01\,°C$, is received from ACME Thermometer Co. and requires calibration between $-20\,°C$ and $180\,°C$. The thermometer is used to calibrate mercury-in-glass thermometers, often over short ranges (i.e. working thermometers). The thermometer is calibrated against an SPRT.

Step 1: Start record keeping

A file is opened with an order number for the job. This file contains the client's address, the contact person and contact details, a copy of the order, a complete description of the thermometer including the manufacturer, type number and serial number, and the temperature range required. The file is continually updated to include summaries of the test records, calibration results and a copy of the certificate if one is issued. In this case, the thermometer is a platinum resistance thermometer with a direct-reading electronic indicator, with a total range specified by the manufacturer of $-50\,°C$ to $200\,°C$.

Step 2: General visual inspection

The thermometer is unpacked and inspected immediately on receipt. The packaging is satisfactory. The probe, indicator, power cord and operator's manual are all found

to be present and appear to be in good condition. The thermometer is plugged in and turned on to check that it is in working order.

Step 3: Conditioning and adjustment

Although the operator's manuals for such thermometers include instructions for resetting the ice point, range and linearity immediately prior to calibration, this is not carried out since the client has asked that the instrument not be adjusted unless the ice point is in error by more than $0.05\,°C$.

Step 4: Generic checks

Four checks are carried out on the thermometer.

Detailed visual inspection   The instrument is inspected for bends and dents in the probe, damage to the leads, plugs, sockets, cable strain relief, etc. The electronic unit appears to be well maintained and nothing is loose or broken. The general condition of the instrument is consistent with its age and usage and indicates that the instrument is well maintained.

Insulation check   The probe assembly is first disconnected from the instrument. The insulation resistance between the steel sheath and one of the four lead wires is measured using a low-voltage insulation tester. The resistance is found to be in excess of $1\,G\Omega$, which is typical of probes assembled using alumina insulation and which are free of moisture.

Ice-point check   Carrying out ice-point checks on stainless steel sheathed probes can be quite difficult and errors of several hundredths of a degree are possible. The high thermal conductivity and thermal mass of the stainless steel probe make it difficult to keep the ice well packed and in good contact with the sheath. This is aggravated by heat being dissipated in the sensing element. With instruments that read to $0.01\,°C$ or better, it is extremely important to use very finely shaved ice. The probe is allowed to settle for at least 10 minutes, and the ice is pushed firmly down around the probe immediately before reading.

Hysteresis check   The hysteresis is assessed by comparing readings before and after exposure to high temperatures. In this case the range extends below $0\,°C$ so that the change in ice point before and after the comparison is indicative of the width of the hysteresis loop.

Step 5: Comparison

Since the comparison is to provide the data for a least-squares fit to a calibration equation (Equation (5.2)) with four unknown constants, a total of 19 points (17 comparison points plus two ice points), are measured giving more than four data points per constant. These points are distributed over the calibration range $-20\,°C$ to $180\,°C$, as requested by the client.

Table 5.1 Comparison results for a platinum resistance thermometer

Reading no.	Temperature (°C)	Reading (°C)	Correction (°C)	Residual errors (°C)
1	−19.9504	−19.96	0.00	+0.0096
2	−7.4467	−7.46	+0.01	+0.0033
3	5.0430	5.045	0.00	−0.0020
4	17.5320	17.535	0.00	−0.0030
5	30.0153	30.015	0.00	+0.0003
6	42.4994	42.50	0.00	−0.0006
7	54.9758	54.975	−0.01	+0.0108
8	67.5422	67.55	−0.01	+0.0022
9	80.0084	80.005	−0.01	+0.0034
10	92.4734	92.49	−0.01	−0.0066
11	104.9527	104.97	−0.02	+0.0027
12	117.4225	117.44	−0.02	+0.0025
13	129.8958	129.915	−0.02	+0.0008
14	142.3688	142.39	−0.01	−0.0062
15	154.8518	154.86	−0.01	+0.0018
16	167.3067	167.305	0.00	+0.0017
17	179.7642	179.755	+0.01	−0.0008
18	0.0000	0.00	0.00	0.0000
19	0.0000	0.005	0.00	−0.0050

Ice-point shift $= 0.0050\,°C$
Standard deviation of residuals $= 0.0048\,°C$

The first three columns in Table 5.1 summarise the comparison. The reference SPRT is interfaced to a computer through a high-accuracy a.c. resistance bridge. The computer calculates the temperature according to ITS-90. At each calibration point, the thermometer under test is read by the operator and the result entered into the computer. A reading is reported to 0.005 °C when the display flickers between two adjacent numbers. The computer then interrogates the bridge and calculates the temperature. The two ice-point readings are added to the table after the comparison is completed.

Step 6: Analysis

The readings and temperatures recorded in the first three columns of Table 5.1 are now analysed. The computer carries out a least-squares fit on all of the results including the two ice points. As described in Section 5.3.3, the fit determines the values of the constants in the cubic correction equation (Equation (5.2)) that best describes the measured data. The correction calculated for each calibration point is rounded to the nearest 0.01 °C, the resolution of the thermometer, and recorded in the fourth column of Table 5.1. The residual errors in the corrected readings (reading + correction) are listed in the fifth column.

Figure 5.9 graphs the results of the comparison and gives a visual summary of the performance of the thermometer. There are two notable features of the calibration curve. Firstly, the non-linearity is quite evident, with some even (U-shaped) and some
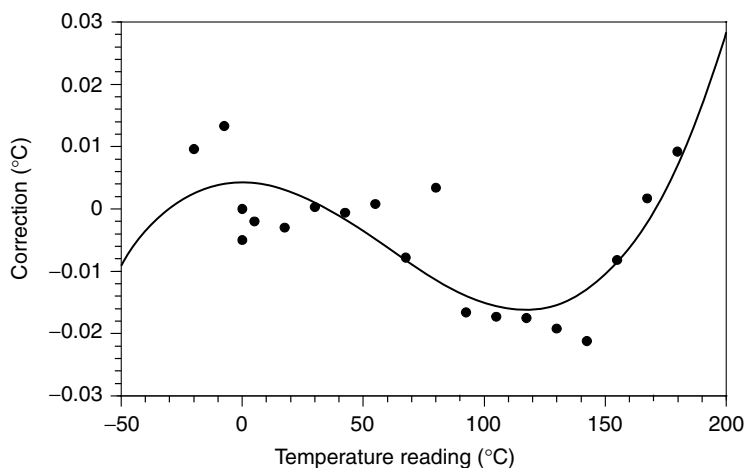
Figure 5.9   The calibration data and fitted deviation function for an electronic reference ther-
mometer, as determined from Table 5.1

odd (S-shaped) non-linearity. Secondly, there is a 0.01 °C step in the data at 0 °C.
This step feature is quite common in electronic thermometers that display both +0.00
and −0.00; internal switches change the mode of operation for positive and negative
signals.

   The table and graph are also examined in order to answer the following questions:

- Are there any large residual errors in the residual column that would indicate an
  incorrect reading or gross misbehaviour of the sensor?

- Are the residual errors of random sign? Randomness is a good indicator that the
  thermometer behaves as expected. A regular pattern of + and − signs is indica-
  tive of a gross departure from the expected curve, perhaps because the resistance
  thermometer has been damaged through poisoning or excessive moisture.

- What is the overall shape of the error curve? If the error is too great the thermometer
  may need adjustment. This is also often evident from a large ice-point correction.

- How large is the standard deviation of the residual errors? The value should be
  typically between 0.3 digits and 2 or 3 digits. At 0.3 digits the residual errors
  are entirely due to quantisation (Section 2.3.2). At 3 digits the errors are getting
  suspiciously large. Large and random residuals may be indicative of a poorly stirred
  bath or a faulty thermometer. With some high-resolution thermometers, high levels
  of noise in the last digit may be typical behaviour.

   The thermometer appears to be quite satisfactory in all respects.

Step 7: Uncertainties

The uncertainties are now analysed as discussed in Section 5.3.4.
Uncertainty in the reference thermometer reading   The uncertainty of the reference
SPRT is found from the calibration certificate to be 2 mK, and reported as a 95%

confidence interval:

$$U_{\text{ref}} = 0.002\,{}^\circ\text{C}.$$

Variations in the uniformity of the calibration bath   From commissioning tests for the bath it is known that the gradients are less than 2 mK over the 300 mm wide controlled volume. Since the reference thermometer and the thermometer under test were within 100 mm, the maximum error is 0.6 mK, and the 95% confidence interval is approximated by the semi-range of a rectangular distribution:

$$U_{\text{bath}} = 0.0003\,{}^\circ\text{C}.$$

Departures from the determined ITS-90 relationship   Since the thermometer is used to calibrate short-range working thermometers the uncertainty in the corrections is estimated as the coverage factor times the standard deviation of the fit (see Equation (5.8) and accompanying discussion). There were a total of 19 data points and four unknown parameters; thus the number of degrees of freedom is $\nu = 15$, and the appropriate k value from the Student's t-distribution corresponding to a 95% level of confidence is $k = 2.13$. Hence

$$U_{\text{fit}} = ks = 2.13 \times 0.0048 = 0.010\,{}^\circ\text{C}.$$

Hysteresis   The change in ice-point reading before and after the comparison was 0.005 °C. This value is used to approximate the semi-range of a rectangular distribution characterising the hysteresis errors:

$$U_{\text{hys}} = 0.005\,{}^\circ\text{C}.$$

Self-heating   For platinum resistance thermometers that are not calibrated at zero current there is an additional uncertainty due to the likely variation in the self-heating between the calibration bath and the media in which the thermometer may be used (Section 6.5.4). For 100 Ω sheathed elements operated at 1 mA sensing current the variations are usually less than 2 mK. The 95% confidence interval for the uncertainty is approximated by this figure. Hence

$$U_{\text{self-heating}} = 0.002\,{}^\circ\text{C}.$$

Total uncertainty   Summing all of these terms in quadrature, the total uncertainty is found to be

$$U_{\text{total}} = \left(2^2 + 0.3^2 + 10^2 + 5^2 + 2^2\right)^{1/2} = 11.6\,\text{mK}.$$

For the presentation in the certificate, this is rounded to 0.012 °C.

Step 8: Complete records

The entire performance of the thermometer is reviewed before the decision is made to issue a certificate. The thermometer is found to be satisfactory and a certificate prepared, as shown in Figure 5.10.

CALVIN, DEGRIES AND CO

1 TRACEABILITY PLACE, PO BOX 31-310, LOWER HUTT, NEW ZEALAND
TELEPHONE (64) 4 569 0000 *FAX (64) 4 569 0003*

CALIBRATION CERTIFICATE

Report No:	T92-2002.
Client:	ACME Thermometer Co, 100 Celsius Avenue, P O Box 27-315, Wellington, New Zealand.
Description of Thermometer:	An electronic platinum resistance thermometer, model RT200, manufactured by PEL, serial number 001, probe serial number SDL11.
Date of Calibration:	13 to 16 July 2000.
Method:	The thermometer was compared with standard thermometers held by this laboratory. All measurements are traceable to the New Zealand National Standards. The temperature scale used is ITS-90.
Conditions:	The probe was immersed to a minimum depth of 200 mm.

Results:

Thermometer Reading (°C)	Correction (°C)
−19.60	0.00
−7.46	+0.01
5.05	0.00
17.54	0.00
30.02	0.00
42.50	0.00
54.98	−0.01
67.55	−0.01
80.01	−0.01
92.49	−0.01
104.97	−0.02
117.44	−0.02
129.92	−0.02
142.39	−0.01
154.86	−0.01
167.31	0.00
179.76	+0.01
0 (ice point)	0.00

Note: Corrections are added to the reading to obtain the true temperature.

Accuracy: The uncertainty in the corrected thermometer readings is ±0.013°C at the 95% confidence level.

Checked:_____   Signed:_____
W Thomson   R Hooke

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Figure 5.10 Example of a calibration certificate for an electronic reference thermometer

Further Reading

ISO 10012-1:1992 *Quality Assurance Requirements for Measuring Equipment, Part 1: Metrological Confirmation System for Measuring Equipment*, International Organisation for Standardisation, Geneva.

ISO 10012-2:1997 *Quality Assurance Requirements for Measuring Equipment, Part 2: Guidelines for Control of Measurement Processes*, International Organisation for Standardisation, Geneva.

ISO 17025:1999 *Requirements for Technical Competence of Calibration and Testing Laboratories*, International Organisation for Standardisation, Geneva.

J A Wise and R J Soulen (1986) Thermometer Calibration: *A Model for State Calibration Laboratories*, NBS Monograph 174, US Department of Commerce.

6

Platinum Resistance Thermometry

6.1 Introduction

Platinum resistance thermometers are remarkable instruments. In various forms they operate over the range $-260\,°C$ to $960\,°C$, with accuracies approaching $1\,mK$. They can be cycled repeatedly over hundreds of degrees Celsius and still provide a very severe test of the best resistance bridges. Few material artefacts can be treated in this manner and remain as stable.

A wide range of platinum thermometers is available, from the very accurate standard thermometers defined by ITS-90 to robust industrial thermometers, which may be accurate to several tenths of a degree. The lower overall cost and higher accuracy of platinum thermometers compared with other thermometers make them the thermometer of choice for many applications. In precision applications, their accuracy is second to none.

Resistance thermometers are unlike other temperature sensors in that they require external stimulation in the form of a measuring current or voltage. This gives rise to errors associated with resistance-measuring instruments that must be considered in addition to those due to the sensor itself. Therefore, this chapter covers resistance measurement as well as the construction, use and calibration of resistance thermometers.

The chapter begins with a discussion of the nature of electrical resistance in metals, as an aid to understanding the properties and limitations of resistance thermometers. We then investigate the various forms of construction of platinum resistance thermometers, resistance measurement, sources of error in platinum thermometry, leading to the choice, use and calibration of platinum thermometers. This chapter is primarily about industrial and laboratory thermometers, but we include advice on the use and calibration of standard platinum resistance thermometers (SPRTs) as well. Those readers establishing or maintaining the ITS-90 scale should refer to Chapter 3, and particularly the two BIPM publications (see references at the end of this chapter), which contain more detailed advice on scale maintenance and excellent bibliographies.

The chapter concludes with a brief discussion of other types of resistance thermometer, namely other metal resistance thermometers, thermistors and germanium resistance thermometers.

6.2 Resistance in Metals

6.2.1 Introduction

All metals are good electrical conductors. This is because the electrons in metals are not bound to atoms but are free to move randomly throughout the metal. In other materials such as insulators, electrons are unable to move so freely, if at all. Let us consider a simple model that will help explain the electrical properties of metals.

Imagine the inside of a section of platinum wire: a huge lattice of platinum atoms (actually positively charged ions) all in neat rows, in three dimensions. Amongst the atoms are electrons moving about at random. When a voltage is applied, the electrons accelerate and move towards the positive terminal of the voltage source. The moving electrons constitute an electric current.

In a perfect metal lattice, the free electrons are completely unimpeded in their movement, so that a perfect metal crystal has zero electrical resistance. This is never observed in practice because there are two basic mechanisms that scatter the electrons and restrict their movement. One mechanism is due to temperature; the other is due to impurities and lattice defects.

6.2.2 The effects of temperature on resistance

The temperature of any material is a measure of the energy of motion of the atoms and electrons. In a crystal lattice, the movement of atoms is very restricted and they cannot easily change their position within the lattice. However, they can vibrate about their positions. This temperature-related vibration is the major cause of electron scattering. As the temperature of the lattice increases, the vibrations increase and the scattering of the electrons increases.

When a voltage is applied to the ends of metal wire, the electrons move towards the positive terminal, all the time accelerating then colliding with the vibrating atoms. The kinetic energy given to the lattice by the electrons is what we observe as electrical heating. The greater the voltage across the wire, the faster the electrons move towards the terminal, and the greater the current. For metals the current, I, is proportional to the voltage, V:

$$I = V/R, \tag{6.1}$$

where R is a constant called the electrical resistance, which depends on the amount of electron scattering. This relationship, known as *Ohm's law*, is followed so accurately by metals that it is possible to define and measure resistances to a few parts per billion (a few parts in 10^9).

As the temperature of the lattice increases, the vibrations and the resistance to the flow of electrons increase in proportion to the absolute temperature. The resistance–temperature relationship is usually written in terms of the Celsius temperature, t:

$$R(t) = R(0\,^{\circ}\text{C})(1 + \alpha t), \tag{6.2}$$

where α is the temperature coefficient of resistance, approximately equal to $1/273.15\,\text{K} = 3.66 \times 10^{-3}\,\text{K}^{-1}$. Figure 6.1 shows that this simple model is very good.
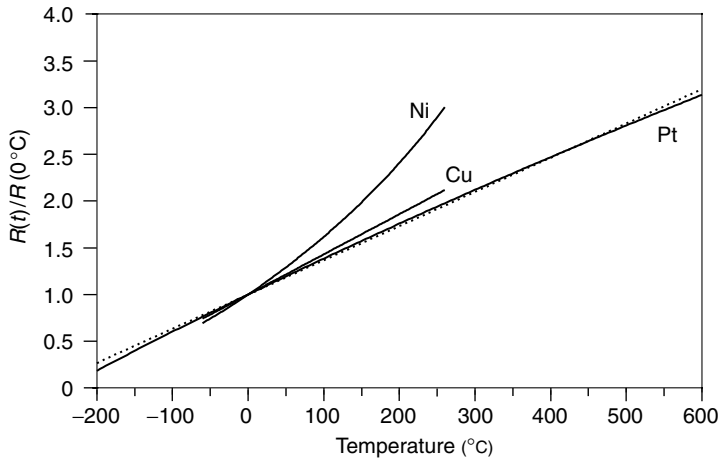
Figure 6.1   The resistance of nickel, copper and platinum as a function of temperature. The dotted line is the resistance according to simple theory, Equation (6.2)

6.2.3   The effects of impurities on resistance

Detailed understanding of resistance beyond the simple model presented here is extremely complicated. It is, for example, very difficult to predict the curvature in the resistance–temperature curves of Figure 6.1. One of the few simple improvements we can make to the model is to include the effects of impurities. If a different-sized atom is placed in the lattice, it causes additional scattering of the electrons, in a manner that is almost independent of temperature. That is, impurities in the lattice tend to increase the resistance by a constant amount:

$$\hat{R}(t) = R(t) + \Delta R, \tag{6.3}$$

where ΔR is the resistance due to the impurities. This equation, known as *Mathiessen's rule*, can be rewritten as

$$\hat{R}(t) = \hat{R}(0\,^{\circ}\mathrm{C})(1 + \hat{\alpha}t), \tag{6.4}$$

where

$$\hat{\alpha} = \alpha \frac{R(0\,^{\circ}\mathrm{C})}{R(0\,^{\circ}\mathrm{C}) + \Delta R}. \tag{6.5}$$

That is, impurities increase the ice-point resistance and decrease the temperature coefficient of resistance. In turn this means that the higher the temperature coefficient of a metal wire, the purer it is.

The most important impurities are defects, that is points or planes in the lattice where atoms are missing or doubled up. These are always present even in the purest of metals. Working the metal by bending, drawing or hammering can also create defects very easily, by breaking and distorting the lattice, forcing atoms to become misplaced. This process, which causes the metal to become harder and resist further deformation, is known as work hardening.

A large proportion of defects can be removed by annealing. This is accomplished by heating the metal and causing the atoms to vibrate sufficiently that they can fall back into place. However, heating also causes defects. At temperatures above about 450 °C in platinum, the concentration of defects quickly reaches a state of equilibrium where the rate of creation is equal to the rate of removal by annealing. Because the equilibrium concentration of defects increases with temperature, thermometers used at high temperatures must be cooled slowly to ensure that these thermal defects are not quenched into the lattice and allowed to affect the resistance at lower temperatures.

6.3 Platinum Resistance Thermometers

6.3.1   Electrical properties of platinum thermometers

All metals behave very much as the simple model suggests, but few metals are suitable as resistance thermometers. A good thermometer must be able to withstand high temperatures, be chemically inert, and be relatively easy to obtain in a pure form. Platinum is one of the few suitable metals.

In the early days of platinum thermometry, Callendar found that the resistance of platinum was well described by a simple quadratic equation with constants A and B:

$$R(t) = R(0\,°C)\left(1 + At + Bt^2\right). \tag{6.6}$$

Historically this was rewritten in an alternative form:

$$R(t) = R(0\,°C)\left[1 + \alpha t + \alpha\delta\left(\frac{t}{100}\right)\left(1 - \frac{t}{100}\right)\right], \tag{6.7}$$

which simplified the calculations required to determine the calibration constants α and δ from fixed-point measurements at the boiling point of water (100 °C) and the sulphur point (~440 °C). This form also explicitly defined the *alpha value* of the thermometer:

$$\alpha = \frac{R(100\,°C) - R(0\,°C)}{100R(0\,°C)}, \tag{6.8}$$

which was readily determined from measurements at the ice point (0 °C) and the water boiling point. This measure of the α value is still used today as a measure of the purity of platinum and to define the various grades of platinum thermometer. Because the boiling point is no longer defined by ITS-90, the α value is likely to be replaced by an alternative measure of purity. One candidate is the resistance ratio at the gallium point, namely ρ (Greek symbol rho):

$$\rho = \frac{R(29.7646\,°C)}{R(0\,°C)}, \tag{6.9}$$

where 29.7646 °C is the melting point of gallium (see Chapter 3, Figure 3.9).

Van Dusen later found that an additional term is required to describe the resistance–temperature relationship below 0 °C:

$$R(t) = R(0\,°C)\left[1 + At + Bt^2 + C\left(t - 100\right)t^3\right], \tag{6.10}$$

where C is zero above $0\,°C$. This equation, known as the *Callendar–van Dusen equation*, was the basis for the temperature scales of 1927, 1948 and 1968, and continues to be used to define the resistance–temperature relationship for industrial resistance thermometers. Typical values for the coefficients for an SPRT are

$$A = 3.985 \times 10^{-3}\,°C^{-1},$$
$$B = -5.85 \times 10^{-7}\,°C^{-2},$$
$$C = 4.27 \times 10^{-12}\,°C^{-4},$$
$$\alpha = 3.927 \times 10^{-3}\,°C^{-1},$$
$$\rho = 1.118\,14.$$

For an industrial platinum resistance thermometer (PRT) more typical values are

$$A = 3.908 \times 10^{-3}\,°C^{-1},$$
$$B = -5.80 \times 10^{-7}\,°C^{-2},$$
$$C = 4.27 \times 10^{-12}\,°C^{-4},$$
$$\alpha = 3.85 \times 10^{-3}\,°C^{-1},$$
$$\rho = 1.115\,817.$$

The constants are similar for different grades of platinum, with the α value varying between the two values shown above. The α value may also be expressed in several different ways; for example:

$$0.385\,\Omega\,°C^{-1} \text{ for a } 100\,\Omega \text{ PRT},$$
$$3.85 \times 10^{-3}\,°C^{-1},$$
$$0.385\%\,°C^{-1},$$
$$3850 \text{ ppm}\,°C^{-1},$$

all of which are equivalent. We later use an approximation $\alpha = 4 \times 10^{-3}\,°C^{-1} = 1/250\,°C$ to estimate the magnitude of some of the errors in resistance thermometry.

A short summary of the resistance–temperature relationship for industrial PRTs is incorporated as Appendix C.

6.3.2   Construction of platinum thermometers

The main aim when assembling a resistance thermometer is to ensure that the metal is allowed to respond to temperature, while being unaffected by all other environmental factors, including corrosive chemicals, vibration, strain, pressure and humidity. For platinum thermometry, the most serious concern is instability caused by mechanical shock and strain due to thermal expansion.

In its simplest form, a resistance thermometer is a coil of wire loosely mounted on an insulating support. However, the thermometer is susceptible to mechanical shock

when mounted in this way. Small knocks and vibration cause the unsupported parts of the wire to flex. This works the wire, introducing defects and increasing the resistance.

The logical solution to this flexing problem is to support the wire fully by mounting it on a solid bobbin so that it is unable to flex. Now we have a different problem. When the thermometer is heated, the wire and the bobbin expand at different rates, causing the wire to be stretched or compressed. If the strain is small, the resulting deformation of the wire will be elastic and temporary, as with a rubber band. If the strain is too large then the deformation will be plastic, as with putty, and any dimensional changes will be permanent. This process also work-hardens the wire and further increases the resistance.

PRTs therefore have several different forms that make a compromise between mechanical robustness and precision. In the following sections, we describe these in more detail so users can make an informed choice for their application. The information is not intended as a guideline for construction. At higher temperatures especially, there is considerable art and proprietary knowledge involved in the manufacture of PRT assemblies, and users are well advised to buy assembled probes rather than build their own.

6.3.3   Standard platinum resistance thermometers

The construction and basic limitations of the three forms of SPRT are described in detail in Section 3.3.5. The long-stem SPRT, which is the most common, is a coil of very pure platinum wire loosely supported on a mica or quartz cross, and sheathed in a glass or quartz tube. Cleanliness of the various components is critical for these thermometers, especially at high temperatures where contaminants migrate very quickly.

Standard thermometers are extremely delicate instruments; shock, vibration or any acceleration that causes the wire to flex will strain the wire and change its resistance. Large knocks have been known to cause errors of the order of 10 mK, while long exposure to vibration may cause errors as large as 100 mK. However, with care an SPRT can be used regularly for periods well in excess of a year with cumulative drifts of less than 1 mK.

6.3.4   Partially supported platinum thermometers

The extreme fragility of SPRTs generally limits their use to maintenance of the ITS-90 scale, calibration and the very highest-accuracy applications. The first step in making a more robust PRT is to support the wire as much as practical while still allowing it to expand and contract with temperature. Two successful industrial resistance-element designs are shown in Figure 6.2. The first uses a bobbin formed from high-purity alumina to support a tightly wound helix of the platinum wire. The second supports the tightly wound helix inside the bore of a high-purity alumina insulator. The wire may be restrained further with alumina powder, which fills the spaces in the bores. In some designs ceramic cement fills about one-third of the insulator bores further to restrain the wire movement. In elements designed for aerospace applications, the case or sheath may be oil filled to dampen vibrations.

Depending on the intended application and accuracy, there are three basic grades of wire used in partially supported PRTs. Note that the different grades specified
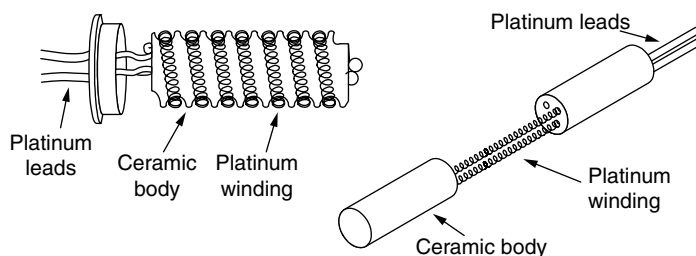
Figure 6.2 Two practical designs for partially supported PRTs

in different documentary standards may differ slightly. As the standards are reissued to conform to ITS-90 following the change of temperature scale in 1990, some of these standards are becoming harmonised. The wire is usually manufactured as a highest-purity grade then doped with the required concentration of impurities to bring the α value down to conform with the standard. The three basic grades of wire are:

(1) $\alpha = 3.926 \times 10^{-3}\,°\text{C}^{-1}$ This is the same grade of wire as required by ITS-90 for SPRTs. However, the additional support of the wire degrades the performance of the thermometers to about $\pm 5\,\text{mK}$ and reduces the maximum continuous upper temperature exposure to about $500\,°\text{C}$, depending on the sheath material.

(2) $\alpha = 3.916 \times 10^{-3}\,°\text{C}^{-1}$ This grade is a compromise between the SPRT grade and the more common industrial grade. It is primarily a standard for laboratory instruments. The main advantage over lower-grade industrial thermometers is the higher reproducibility between thermometers.

(3) $\alpha = 3.85 \times 10^{-3}\,°\text{C}^{-1}$ This is the grade of wire used most commonly for industrial PRTs. The exact temperature dependence of the wire depends on which metals are used to dope the wire. In most cases a rare metal from the same chemical family as platinum is used, so that the shape of the resistance–temperature curve and other physical properties are similar to those for pure platinum. The temperature dependence is sufficiently different from the ITS-90 reference function to limit the fitting of the ITS-90 calibration equations to about $\pm 10\,\text{mK}$. Usually the Callendar–van Dusen equation (Equation (6.10)) is almost as good a fit as the ITS-90 functions.

Overall, the partially supported PRTs used in a laboratory situation achieve typical accuracies between $2\,\text{mK}$ and $20\,\text{mK}$, with a variable sensitivity to vibration and shock depending on the degree to which the wire is supported. Some of the best of these elements will withstand intermittent use to $850\,°\text{C}$ with accuracies of a few tenths of a degree. The performance is limited by hysteresis and drift caused by the different thermal expansions of the wire and ceramic substrate. The ice-point resistance values for partially supported thermometers are normally in the range $10\,\Omega$ to $500\,\Omega$, with the $100\,\Omega$ units being the most common. The dimensions of the elements are also varied with diameters between $0.9\,\text{mm}$ and $4\,\text{mm}$ and lengths from $6\,\text{mm}$ to $50\,\text{mm}$.

6.3.5   Fully supported platinum thermometers

The most robust of the PRTs are fully supported elements mounted either in glass or in alumina ceramic (Figure 6.3). By encapsulating the wire completely the susceptibility to mechanical vibration and mechanical shock is made minimal. The penalty for increased robustness is a much poorer long-term stability and large hysteresis due to differential thermal expansion and contraction of the substrate and the wire.

Almost all fully supported PRTs are manufactured with the $\alpha = 3.85 \times 10^{-3}\,°C^{-1}$ grade wire. As with the partially supported PRTs, the temperature range depends very strongly on the sheath material, which is a major source of contaminants. Ceramic substrates have a temperature coefficient of expansion that is closer to that of platinum than glass, so ceramic-based PRTs exhibit less hysteresis than glass elements. However, the cement used to bond the wire in ceramic elements is often porous, as is the ceramic itself, so ceramic elements can be more susceptible to contamination. Ceramic elements are sometimes encapsulated in glass to overcome the porosity, and to protect against contamination.

Glass elements, although of low cost and impervious to fluids, have a number of serious drawbacks. At high temperatures, glasses undergo a rapid change in their coefficient of expansion associated with the softening of the glass. This causes hysteresis and work hardening due to the greatly increased strain on the platinum. An increase in the mobility of the metal components in the glass (sodium, lead, boron, etc.) also causes the glass to become electrically conductive, especially to a.c. current (see Section 6.5.11), and allows the metal atoms to contaminate the platinum.
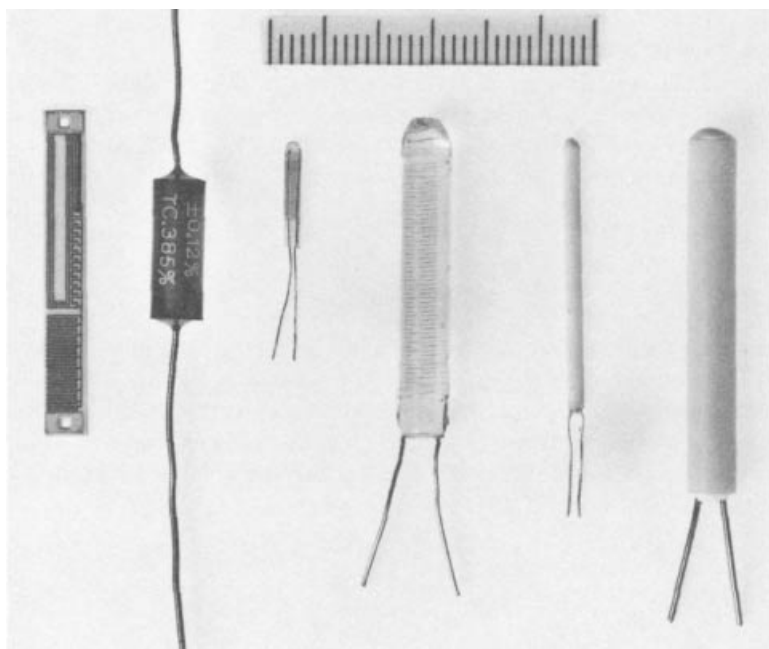
Figure 6.3   Examples of industrial PRT elements. From the left: a thick film element, a PRT designed for printed circuit mounting, two glass PRTs and two ceramic PRTs

Overall, the fully supported PRTs achieve typical accuracies of 20 mK to 200 mK with minimal sensitivity to mechanical shock and vibration. The range of fully supported elements available is very similar to that for partially supported elements with ice-point resistances in the range 10 Ω to 1000 Ω, with the 100 Ω units again being the most common.

6.3.6   Platinum film thermometers

One of the disadvantages of PRT elements manufactured from wire is that the construction does not lend itself to automation. Another disadvantage in some applications is the moderately long time constant of 2 to 6 seconds. For some applications such as the control elements in household irons, where speed and low cost are important, the thick film element is an attractive alternative. Film elements are made by sputtering platinum onto an alumina substrate in a meandering pattern. The resistance is then trimmed to the nominal value, and the element coated with a glaze, which provides protection. Film elements are about one-third of the cost of other elements and have time constants as low as 0.2 s.

Flexible platinum film elements are also available and are very useful for applications requiring a fast response and for surface-temperature measurements. In these elements, platinum foil is adhered to a high-temperature plastic substrate, which allows the entire element to flex. Usually they are available with an adhesive back so that they can be attached to a surface. The temperature range is limited by the highest temperature the plastic will withstand, typically 150 °C to 200 °C. With all film PRTs the lead wires have a tendency to break free, and must be restrained when the element is installed.

Overall, the accuracy is similar to that of the fully supported elements but over a slightly reduced temperature range. Because the wire is bonded to the substrate, the film elements are more susceptible to thermal expansion effects. The increased strain in film elements may also cause large departures from the resistance–temperature tables at high temperatures. Film thermometers usually have higher resistances than other types, ranging from 100 Ω to 2000 Ω. The dimensions are highly variable, from 2 mm square to some in excess of 100 mm long, with a large number of dimensions similar to fully supported and partially supported elements.

6.3.7   Sheathing

The choice of sheath for platinum resistance elements is a key factor in determining the temperature range of the thermometer. There are two classes of sheathing materials: metallic, such as stainless steel or inconel; and non-metallic, including glass, alumina and quartz.

Metallic sheaths are the least fragile and easiest to manufacture, but most likely to cause contamination. For continuous use, they are limited to temperatures below 450 °C and preferably below 250 °C. At higher temperatures, the metal atoms in the sheath become mobile and can contaminate the platinum wire. For use at temperatures above 250 °C, stainless steel and inconel sheaths should be heat treated in air or oxygen before assembly to build an impervious layer of oxide on the inside of the sheath and

drive off lubricants used in the drawing process for the tubes. Glass elements and glass-encapsulated ceramic elements, which are less susceptible to contamination by the sheath, may be more suited to operation above 250 °C.

At temperatures above 450 °C all platinum elements become increasingly susceptible to contamination and any metallic component of an assembly should be viewed as a source of impurities, and the sheath material must be correspondingly cleaner. At the highest temperatures only quartz and high-purity alumina are suitable sheaths. Both are normally baked at 1100 °C to drive off impurities before the thermometer is assembled. Above 600 °C some metals, especially copper and silver, will migrate through quartz, so a sacrificial sheath of platinum foil should be used for extra protection. Quartz sheaths also have problems with devitrification: impurities causing the quartz to change from a glassy form to a crystalline form. The crystalline form is more porous and very brittle.

6.3.8   Lead wires

The lead wires, which conduct the current to and from the thermometer, should also be seen as a potential source of impurities. For the highest temperature applications platinum is the only suitable lead wire, but for most applications the cost is not warranted. At low temperatures (up to 250 °C) glass-insulated copper or silver wire is used. The glass prevents oxidation of the wire and migration of the metals. For high-temperature assemblies, nickel alloy or platinum-coated nickel wires are often used.

6.3.9   Electrical insulation

The electrical insulation for the lead wires is also a crucial component in the thermometer assembly. For the highest accuracy and stability, quartz spacers and supports, as used in high-temperature long-stem SPRTs, are best. Partially supported PRTs are often assembled using four-bore alumina insulators, sometimes with alumina powder to restrict their movement in the sheath. The lowest-grade ceramic insulation material is magnesia. This is usually found in sheaths assembled from mineral-insulated metal cable. Magnesia has the unfortunate property of absorbing moisture, which can lead to low values of insulation resistance and problems with moisture-induced hysteresis.

6.4 Resistance Measurement

In order to realise the full potential of resistance thermometers we must know how to measure resistance. To achieve an accuracy in temperature measurement of ± 1 °C, the resistance must be measured to better than $0.4\,\Omega$. Even an apparently ordinary temperature measurement requires a non-trivial resistance measurement. Fortunately, resistance measurement is a well-developed science and for most thermometry measurements the errors are not only well known but also simple to model.

In this section, we give an overview of resistance measurement as it relates to platinum thermometry. It will provide the basis for understanding some of the sources of error and for a critical assessment of the suitability of instruments for temperature measurement.

6.4.1   General principles

Ohm's law (Equation (6.1)) suggests that resistance can be measured very simply by measuring the voltage across a resistor and the current through it, and then calculating the ratio

$$R = V/I. \tag{6.11}$$

However, electrical current is not easily measured or defined except in terms of a voltage and a second, known, resistance. In practice, resistances are measured by comparison with other resistances to eliminate the need to know or measure the current directly. There are two basic methods, as follows.

Potentiometric methods

Figure 6.4 shows a simplified circuit diagram for a *potentiometric* resistance measurement. The term potentiometric is derived from the historical use of potentiometers to measure resistance before the invention of digital voltmeters. To measure a resistance in this way, a standard resistor and two good voltage measurements are required. A current is passed through both the standard resistor, R_S, and the unknown resistor, $R(t)$ (i.e. the PRT). Since the current through the resistors is the same, the two measured voltages are in the ratio of the resistances:

$$R(t) = \frac{V_t}{V_S} R_S. \tag{6.12}$$

The essential features of the circuit are that we must know the value of one resistor and measure accurately one voltage ratio. This technique is particularly suited to measurements based on integrated circuit analogue-to-digital converters so it is used in almost all digital multimeters, hand-held and bench thermometers.
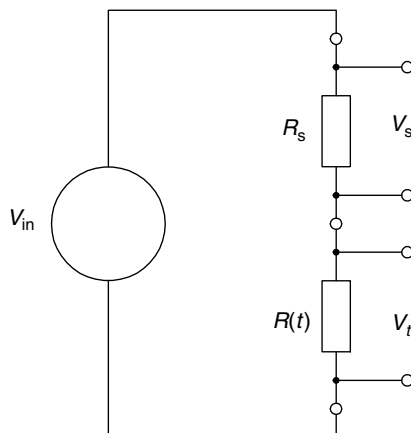
Figure 6.4   A potentiometric resistance measurement

Bridge methods

The second group of resistance measurements is based on the Wheatstone bridge, as shown in Figure 6.5. A null detector compares the output voltage from two voltage dividers, one of which includes the resistance thermometer. The output voltage of the bridge is

$$V_{out} = V_1 - V_2 = \frac{R_2 R(t) - R_3 R_1}{(R_2 + R_3)(R_1 + R(t))} V_{in}. \tag{6.13}$$

There are two modes of operation. In the balanced mode one of the bridge resistors is adjusted until the output voltage is zero, and then the unknown resistance is determined as

$$R(t) = \frac{R_3}{R_2} R_1. \tag{6.14}$$

The thermometer resistance can then be determined in terms of three well-defined resistances. When Equation (6.14) is satisfied, the voltages from the two arms of the bridge are equal, and the bridge is said to be balanced. The advantage of this technique is that the voltmeter only has to detect a null, greatly easing its accuracy requirements. The accuracy demands on the variable resistors, however, are high, generally making this option expensive. With the advent of modern electronic components, bridge methods have been largely superseded, except for the very highest-accuracy instruments. Indeed, the highest-accuracy instruments tend to be called bridges, even when they employ the potentiometric method.

In the second mode of operation of the Wheatstone bridge, the variable resistors are adjusted so that the bridge is balanced at one temperature, say t_0; that is, from Equation (6.14), $R(t_0) = R_3 R_1 / R_2$. Then the output voltage becomes the measure of temperature:

$$V_{out} = \frac{R(t) - R(t_0)}{(R_1 + R(t))(R_1 + R(t_0))} R_1 V_{in}. \tag{6.15}$$

Now if R_1 is also large relative to $R(t)$ the output voltage is approximately

$$V_{out} = \frac{V_{in}}{R_1} R(t_0)\alpha t. \tag{6.16}$$
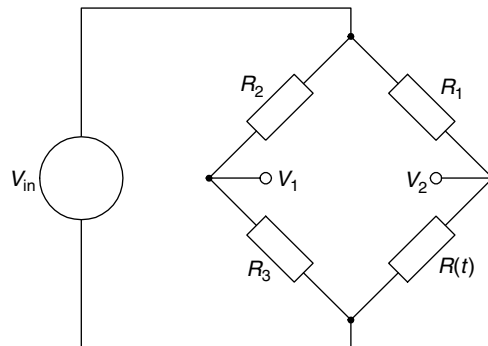
Figure 6.5   The Wheatstone bridge eliminates the need to measure voltages accurately

That is, the output voltage is approximately proportional to temperature. The output signal is slightly non-linear with temperature but sufficient for temperature control systems, which attempt to restore the bridge back to the balanced condition where $R(t) = R(t_0)$, that is $t = t_0$. Most high-precision temperature controllers operate on this principle.

6.4.2   Two-, three- and four-lead measurements

The most significant error in resistance thermometry is caused by the resistance of the lead wires that connect the sensing element to the resistance-measuring instrument. Figure 6.6 illustrates the problem. Because the lead resistances are indistinguishable from the resistance of the PRT, the resistance meter infers a value of $R(t) + R_{L1} + R_{L2}$ for the resistance of the thermometer. The error in the temperature measurement is approximately

$$\Delta T = \frac{2R_L}{\alpha R(0\,°C)} \approx \frac{500R_L}{R(0\,°C)} \, °C. \tag{6.17}$$

In a typical hand-held thermometer with leads 1 or 2 metres in length, the total lead resistance is of the order of $1\,\Omega$, giving rise to an error of $2.5\,°C$. While the error can be compensated by adjusting the zero and range of the indicator, the meter has no immunity to changes in the lead resistance. Such changes may be due to the temperature dependence of the leads, deterioration of plug and socket contacts, or deterioration of the cable as strands of wire break. Most two-lead measurements are limited to accuracies of about $\pm0.3\,°C$.

The ideal solution to the lead-resistance problem is to measure resistance by a four-lead method as illustrated in Figure 6.7. The sensing current is passed through one pair of leads and the voltage measured across the other pair. Because there is no current flowing in the leads to the (ideal) voltmeter, there is no voltage drop due to the resistances in those leads, and therefore no error. Note that the resistance of a four-lead resistor is well defined, being the resistance between the points where the two pairs of leads meet. In a good four-lead measurement, the errors due to the lead resistances can be reduced to negligible levels, and most instruments will accommodate several metres of leads with no measurable error.

One of the advantages of the potentiometric method is that it is very easy to make a four-lead resistance measurement. A close look at Figure 6.4 shows that both the resistors already have four leads, and the voltage across each resistor is measured according
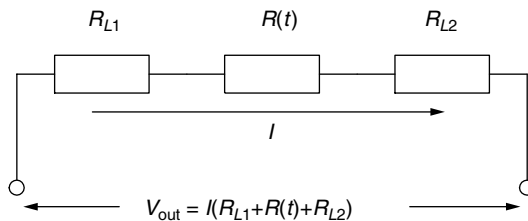
Figure 6.6   In a two-lead resistance measurement the resistance of the leads is indistinguishable from the resistance of the sensing element
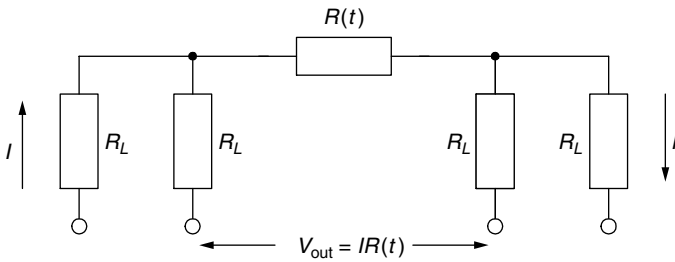
Figure 6.7 In a four-lead resistance measurement the measured resistance is independent of the lead resistances

to Figure 6.7. Because most hand-held and bench instruments use the potentiometric method, the inclusion of a four-lead measurement of resistance ought to be trivial, yet few manufacturers do so.

Historically, bridge instruments were common in industrial applications. Unfortunately, the four-lead measurement principle is not so easily incorporated into resistance bridges. Instead a three-lead technique was developed, which makes a first-order correction for the lead resistances. Nowadays bridge methods are no longer used, but three-lead thermometers are still very common. Figure 6.8 shows how the correction works in a modern three-lead instrument. Two voltages are measured, one across the sensing resistance plus one lead resistance, the other across a lead resistance only. The difference between the two voltages yields a measure of the resistance, given by

$$R_{\text{meas}} = R(t) + R_{L1} - R_{L2}. \tag{6.18}$$

Thus, if the two lead resistances are equal there is no error in the measurement. The three-lead method is common in industrial applications, especially when the lead wires must be very long, and in some laboratory bench meters. As with the two-lead method, the three-lead method is sensitive to changes in either of the leads. Such damage tends to occur with use as leads, plugs and sockets wear. The accuracy is limited to a few tenths of a degree depending on the length of the leads.

A fourth technique is the pseudo four-lead method (Figure 6.9). In this case, the sensor has only two leads, but the probe assembly has a second set of leads without
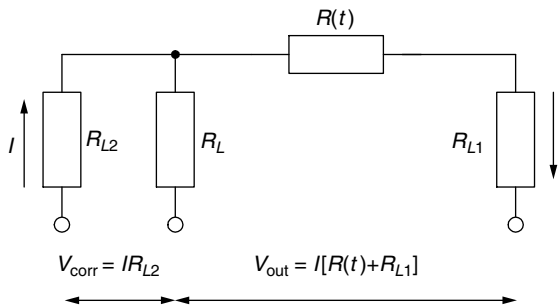
Figure 6.8 In a three-lead measurement, two voltage measurements are made. The voltage measured across the spare lead is used to correct the main measurement

a sensing element. As with the three-lead method, this method makes a correction for the lead resistances:

$$R_{\text{meas}} = R(t) + 2R_{L1} - 2R_{L2}. \tag{6.19}$$

As with the three-lead design, it requires the two sets of resistances to be equal and provides no immunity to deterioration in the cables or plugs and sockets.

6.4.3   D.C. resistance measurement

Potentiometric and bridge methods both rely on voltage measurements to establish either voltage ratios or the equality of voltages. Any extraneous voltages in these measurements therefore cause errors. In d.c. systems there are three main sources of these extraneous voltages: thermoelectric effects, as with thermocouples; amplifier offset voltages and currents; and electrolytic effects, as exploited in batteries.

Thermoelectric voltages are generated in conductors by temperature gradients. The voltage generated is the product of the temperature gradient and the thermoelectric constant of the wire (the Seebeck coefficient), which is different for different materials. In an ideal resistance measurement all the lead wires have the same temperature profile so the voltage generated in one lead will be equal to the voltage generated in all other leads. The meter will then measure the correct voltage difference across the PRT. However, if the materials differ, for example the lead wire changes from platinum to copper, and the temperature profile across the leads is different, then the thermoelectric voltages will not balance. This leads to an error that depends on the relative temperatures of the platinum–copper junctions (see Section 8.2). Since the difference in the Seebeck coefficients for platinum and copper is about $7\,\mu\text{V}\,^{\circ}\text{C}^{-1}$, the error in a typical measurement of a resistance with a $1\,\text{mA}$ measuring current corresponds to about $0.02\,^{\circ}\text{C}$ error per degree Celsius difference in the junction temperatures. Thermoelectric effects are particularly troublesome at exposed instrument terminals subject to heating by convection or radiation.

In an ideal voltmeter, the reading is zero when both of the input connections are held at zero potential. Any non-zero reading that occurs under this condition measures the input offset voltage of the meter. The offset voltage is additive for all voltage measurements so it will affect both the voltage ratio in potentiometric systems and the null measurement in bridge systems. For most modern electronic meters the offset
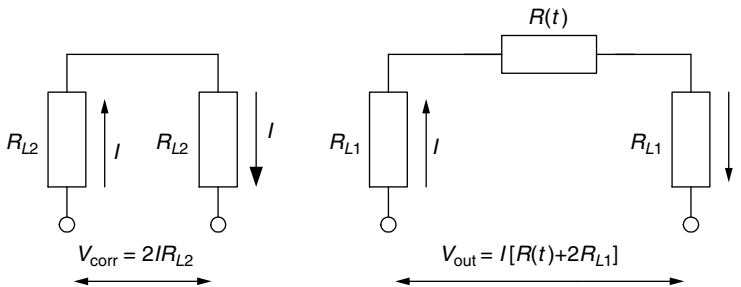
Figure 6.9   In the pseudo four-lead measurement a set of dummy leads is used to provide the lead correction

voltage may be between $0.1\,\mu\text{V}$ and $40\,\mu\text{V}$, causing errors of up to $0.1\,°\text{C}$. In practice, it is the temperature dependence of offset voltages that limits the performance of d.c. instruments. Accurate d.c. instruments are usually restricted to temperature-controlled laboratories.

When thermometers are operated in wet environments, there is the possibility of electrolytic activity. This occurs if there is any moisture connecting the lead wires to any earthed metal in the vicinity. The metal and the lead wires will behave as a small electrolytic cell and cause currents to flow along the lead wires to the meter or through the PRT resistance, in either case causing a significant and generally unpredictable error. In a wet environment, all effort must be made to ensure that there is no electrical connection between the leads and the outside world other than through the measuring instrument itself. Errors due to electrolytic effects are normally seen as very noisy and erratic readings.

Overall, the combination of thermoelectric effects and offset voltages limits simple d.c. measurements to accuracies of about $\pm0.02\,°\text{C}$.

6.4.4   A.C. resistance measurement

All of the d.c. voltages giving rise to the errors described above are constant, whereas the voltage across the resistor changes with the sensing current. By reversing the current systematically and averaging pairs of readings, all of the d.c. voltage errors are eliminated from the measurement of resistance. This is the principle behind a.c. resistance measurement. In practice, the measuring current or voltage may be either switched d.c. ('chopped'), or true sinusoidal a.c. All of the highest-accuracy d.c. systems are in fact a.c. systems since they all employ alternating sensing currents. The only fundamental distinction between these so-called d.c. instruments and a.c. instruments is the operating frequency.

The use of a.c. techniques has additional benefits. Firstly, the offset voltage of the detectors and amplifiers varies erratically owing to electronic noise, including *1/f noise*, so called because of its spectral distribution. The noise is overcome by averaging signals for long periods. By operating at frequencies above a few hertz the $1/f$ noise is all but eliminated, and measurement times are substantially reduced. In addition, at frequencies above a few tens of hertz, transformers can be used to establish extremely accurate ratios of a.c. voltage.

Figure 6.10 shows a simplified diagram of one type of a.c. resistance bridge. The circuit is a rearrangement of the potentiometric measurement given in Figure 6.4. The voltages across the two resistors are compared using a ratio transformer and balance detector so that the bridge reading is in resistance ratio and the value of the unknown resistance is inferred as

$$R(t) = \frac{n}{N} R_\text{S}. \tag{6.20}$$

Because the bridge employs the potentiometric principle lead resistances in the four leads to each resistor are eliminated. With the best a.c. bridges, multi-stage transformers are used to obtain an effective number of turns exceeding $1\,000\,000\,000$, so that resistance ratios can be measured with a precision corresponding to a few microkelvin, far in excess of the practical needs of resistance thermometry.
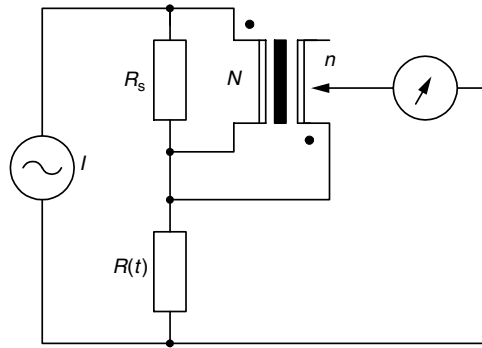
Figure 6.10   A simple schematic diagram of a potentiometric a.c. resistance bridge. The bridge uses a ratio transformer to measure resistance ratio by comparing the voltages across the two resistors. When the detector indicates that the bridge is balanced the ratio of the resistances is equal to n/N

With a.c. systems, part of the electrical energy conducted by electrical components is carried by the electric and magnetic fields around the components. If an external object alters those fields then the impedance of the component (resistance, inductance or capacitance) will change. Thus for the highest-accuracy a.c. measurements it is necessary to confine the fields so they are immune to external influence. This is achieved by using coaxial connections to the components. There are a variety of coaxial connections possible. Figure 6.11 shows the one most commonly employed in resistance bridges used for thermometry. Note that equal currents flow on the inner and outer conductors of the current leads so that there is no magnetic field outside the cable. Similarly, the electric field is contained entirely within the outer conductor of the two cables.

Some manufacturers of d.c. bridges argue that a.c. bridges are less accurate because of sensitivity to stray capacitance, but in practice this is not a problem so long as lead lengths are kept reasonably short. The coaxial connection of Figure 6.11 shows that the capacitance of the coaxial cables short-circuits the sensing resistance and reduces the measured resistance to

$$R_{\text{meas}} = \frac{R(t)}{1 + \left[2\pi f C R(t)\right]^2}, \tag{6.21}$$

where C is the capacitance of the cables, and f is the frequency of the sensing current. For a worst case of, say, $R(t) = 200\,\Omega$, $f = 100\,\text{Hz}$, $C = 1000\,\text{pF}$ (corresponding to about $10\,\text{m}$ of coaxial cable), the error is only a few parts in 10^9, so is negligible.
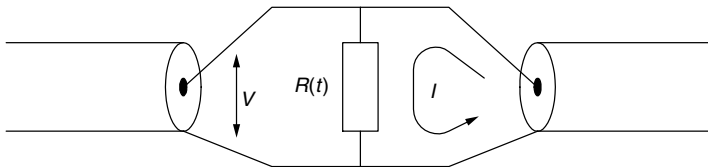
Figure 6.11   The four-terminal coaxial resistance definition used for a.c. measurements of resistance

6.4.5   Verification and calibration of resistance bridges

Regular ice-point or triple-point measurements of PRTs confirm not only the stability of the PRT but also that of the resistance bridge. Because it is possible that the PRT and bridge are both in error, it helps to check more than one PRT, or to check the bridge against a stable reference resistor. Some resistance bridge manufacturers sell suitable resistors.

There are also two simple techniques for checking bridges, which do not require calibrated resistors.

Example 6.1   The complement check

A seven-digit a.c. bridge that measures resistance ratio is used to measure the ratio of two nominally equal $100\,\Omega$ resistors. Two measurements are made. One of the ratio R_1/R_2, then the resistors are swapped and a measurement of R_2/R_1 is made. Ideally, the product of the two measurements is equal to 1.0.

Measurement of R_1/R_2	0.999 987
Measurement of R_2/R_1	1.000 015
Product	1.000 002

The error in the product of the two readings is two counts in the last digit, indicating that the error in each of the individual readings is probably one count in the last digit. Note that it is possible that the ratio readings have large errors that almost cancel. Thus the check builds confidence in the bridge accuracy but cannot prove that it is accurate.

Example 6.2   The linearity check

Figure 6.12 shows the circuit diagram for a set of four resistors connected together so that they can be measured both individually and in series while retaining their four-lead electrical definition. Similar networks, which are available commercially, are called Hamon resistors. The network makes it possible to measure the linearity of a resistance bridge, as summarised in the table below.

Resistor	Measurements of individual resistors	Accumulated sum of individual measurements	Measurements of resistors connected together	Differences between measured and calculated sums
1	0.250 007	0.250 007	0.250 007	0 (by definition)
2	0.250 015	0.500 022	0.500 020	0.000 002
3	0.250 002	0.750 024	0.750 026	−0.000 002
4	0.249 994	1.000 018	1.000 019	−0.000 001
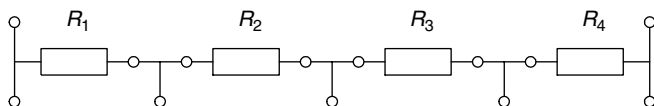
Figure 6.12   A simple resistance network that can be used to check the linearity of a resistance bridge. Note that each resistor can be measured as a four-lead resistor

The results show that the bridge non-linearity is probably less than one or two counts in the last digit of the bridge reading. Note that the linearity check is insensitive to errors proportional to readings, so as with the complement check, the linearity check is not a proof of absolute accuracy.

The availability of calibrations for resistance meters and bridges depends on the type and accuracy. Calibrations for d.c. and low-frequency ($<$0.1 Hz) switched d.c. resistance meters are readily available from many national measurement institutes and the larger accredited electrical calibration laboratories.

Reference systems have been built for some types of a.c. bridge. Unfortunately, the systems tend to be fussy about operating frequency and connections to the bridges. Consequently, suitable a.c. reference systems are not common and are still not suitable for the highest-accuracy a.c. bridges.

A recently developed solution to the calibration problem is based on the observation that the combination of the complement check and the linearity check will detect all types of errors that occur in resistance ratio bridges. By measuring the resistance of a small number of resistors, connected in series and parallel, in a large number of different combinations, we are sampling the distribution of the bridge errors. A least-squares fit then allows the determination of a calibration equation and the uncertainty in the bridge readings. In effect, the technique exploits the additive and ratio properties of a metric scale (see Section 1.2.2). The method requires a resistance network similar to the Hamon resistor used in the linearity check, and which is available commercially. The method is applicable to all types of resistance measurement: a.c., d.c. and switched d.c. It can also be done in-house making it unnecessary to ship an expensive and fragile bridge.

6.5 Errors in Resistance Thermometry

The errors in resistance thermometry fall naturally into four main groups, as summarised in Figure 6.13. Most of the errors are easily recognised from simple tests and comply with the general measurement model given in Figure 2.10. With all of the errors it is relatively easy to identify the causes and to separate the various functional elements in the PRT's construction. It is this clarity of operation that has allowed the PRT to develop into such a reliable and accurate thermometer.

6.5.1   Immersion errors

The immersion considerations for PRTs are relatively straightforward and follow the general guide given in Section 4.4.1. The main concern with PRTs is that the sensing
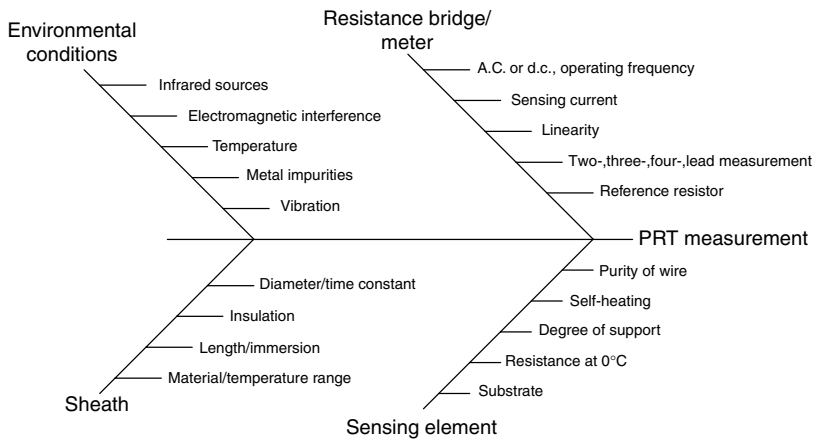
Figure 6.13 A summary of the errors arising in platinum resistance thermometry

element is relatively large, so that extra immersion is required beyond that implied by Figure 4.4. Also, except for flexible-film types, PRTs are generally too bulky for surface-temperature measurement.

Ice points can be difficult, particularly with stainless steel sheathed PRTs; the combination of the thermally conductive sheath and the self-heating can make it difficult to realise the ice point to better than $\pm 0.01\,°C$. It is important that the ice is very fine and well packed. For measurements requiring accuracies better than $\pm 0.01\,°C$ a water triple point should be used in preference.

SPRTs have quite demanding immersion requirements simply because of the high precision required. At the zinc point, for example, the SPRT is required to measure the temperature to about 0.0001% ($\pm 0.5\,mK$ at $400\,°C$), which requires a minimum immersion of about 14 diameters. Additionally the open structure of the assembly and transparent sheath make the effective length of the sensing element longer than just the length of the coil of wire (see Section 6.5.3 on radiation errors).

6.5.2 Lag and settling errors

The errors due to the response time of PRTs follow the general guide given in Sections 4.4.3 and 4.4.4. Time constants for PRTs vary considerably: 0.2 seconds for film types; 2 to 6 seconds for larger fully and partially supported types; 5 seconds for SPRTs; and 5 to 20 seconds for stainless steel sheathed assemblies. Additionally many of the larger sheathed assemblies exhibit a second and longer time constant. While 95% of the settling may occur very quickly, in 20 seconds or so, the remaining 5% of the error takes minutes to die away. A simple experiment, such as withdrawing and reinserting the thermometer, will normally reveal any problems.

6.5.3 Radiation errors

The most common situations in which radiation errors affect measurements made with PRTs are covered in Section 4.4.5. For glass or quartz sheathed SPRTs, however, the considerations go beyond those for other thermometers.

The sheath of the long-stem SPRTs provides a transparent 'light pipe' along which radiation can carry heat to and from the sensing element. Because of the radiation the PRT is not only in thermal contact with the medium immediately surrounding the platinum element but is also in radiative contact with whatever it 'sees' down the sheath. At low temperatures this error will cause temperature readings to be high. Poorly placed incandescent room lights, for example, can heat an SPRT in a water triple point by a few tenths of a millikelvin. At high temperatures the error will cause readings to be low, by an amount in excess of 30 mK at the aluminium point ($\sim$660 °C) and 5 mK at the zinc point ($\sim$420 °C).

The error can be substantially reduced by roughening the lower part of the thermometer sheath from just above the sensor for about 20 cm. This can be done either by sand-blasting or by coating the sheath with graphite paint. Note that the thermometer still 'sees' the lower portion of the sheath, so long-stem SPRTs have more demanding immersion characteristics than other thermometers.

6.5.4 Self-heating

Because a current is passed through the sensing element to measure its resistance, the element dissipates heat, which in turn causes the temperature of the element to increase. This self-heating error is very simply modelled as the power dissipated divided by the dissipation constant, h. The error in the temperature measurement is

$$\Delta T = R(t)I^2/h, \tag{6.22}$$

where $R(t)$ is the resistance of the sensing element and I is the sensing current. The dissipation constant h is normally expressed in milliwatts per degree Celsius. The dissipation constant may also be expressed in terms of the self-heating coefficient, $s = 1/h$. Hence

$$\Delta T = sR(t)I^2. \tag{6.23}$$

The self-heating coefficient is normally given in kelvins per milliwatt. The range of typical values for h is wide, varying from 1 mW °C^{-1} for very small film elements in still air to 1000 mW °C^{-1} for large wire-wound elements in moving water. Table 6.1 gives typical values for the dissipation constant, self-heating coefficient and the self-heating error for different sensing elements in air and water.

Table 6.1 The typical range of dissipation constants for unsheathed platinum resistance elements. The error is calculated for 100 Ω elements and 1 mA sensing current

Condition	Dissipation constant (mW K^{-1})	Self-heating coefficient (K mW^{-1})	Error (mK)
Still air	1 to 10	0.1 to 1	10 to 100
Still water	2 to 400	0.0025 to 0.5	0.25 to 50
Moving water	10 to 1000	0.001 to 0.1	0.1 to 10

Example 6.3   Self-heating of a sheathed PRT

Estimate the self-heating of a $100\,\Omega$ stainless steel sheathed PRT at $80\,°C$ in a water bath, operated at a sensing current of $1\,mA$. The manufacturer's specification for the dissipation constant is $30\,mW\,°C^{-1}$ in water moving at $1\,ms^{-1}$.

From Equation (6.2), the resistance of the element at $80\,°C$ is about $130\,\Omega$. Hence by applying Equation (6.22) we obtain

$$\Delta T = \frac{130 \times (0.001)^2 \times 1000}{30} \, K = 4.3\,mK.$$

The factor of 1000 in the numerator converts the power unit from milliwatts to watts.

Because the self-heating error increases as the square of the current, the current is probably the most significant factor in self-heating. For example, the errors in Table 6.1 are given for a $1\,mA$ sensing current, and for typical applications the error is quite tolerable. However, for most PRT elements the sensing current may be as large as $10\,mA$, for which the errors would be 100 times greater, and the error then becomes a problem in almost every situation. As a rule most PRTs are operated at power dissipations of less than $1\,mW$; for a $100\,\Omega$ sensor typical sensing currents are in the range $0.1\,mA$ to $2.5\,mA$.

One of the problems with the self-heating error is that it is highly dependent on the immediate environment of the thermometer. The sheathing of elements may increase the error by as much as a factor of 5, and use in air by as much as 100. Clearly, it is not possible to improve the accuracy of a measurement significantly by applying a correction based on the manufacturer's estimate of the dissipation constant. The specification is indicative only.

Corrections for self-heating can be made by altering the sensing current and making a second measurement. The pair of results can then be used with Equation (6.22) to calculate the zero-current reading (Exercise 6.2). For a pair of readings T_1 and T_2, made with currents I_1 and I_2, the zero-current reading is

$$T_0 = T_1 - \frac{I_1^2}{I_1^2 - I_2^2} (T_1 - T_2). \tag{6.24}$$

The correction formulae for common ratios of I_1 and I_2 are given in Table 6.2.

Table 6.2   Self-heating correction formulae for common ratios of sensing currents

I_2	T_0
$\sqrt{2}I_1$	$2T_1 - T_2$
$I_1/\sqrt{2}$	$2T_2 - T_1$
$2I_1$	$T_1 - (T_2 - T_1)/3$
$I_1/2$	$T_2 - (T_1 - T_2)/3$

In making the correction it is assumed that the temperature T_0 does not change. This is the case when PRTs are used in fixed points; indeed the ITS-90 scale is defined entirely in terms of the zero-current resistance of SPRTs. For most SPRTs the self-heating effect for a 1 mA sensing current is between 0.3 mK and 3 mK, depending in part on the fixed point. Unfortunately, in practice there are few other situations where the temperature is sufficiently stable to allow accurate corrections to be applied.

Exercise 6.1

A bare 100 Ω detector element is used to measure air temperature near 40 °C. The manufacturer's specification for the dissipation constant in still air is 1.3 mW °C^{-1}. Estimate the self-heating when the sensing current is (a) 1 mA, (b) 2.5 mA.

Exercise 6.2

(a)   Use Equation (6.22) to derive Equation (6.24).

(b)   Assuming the uncertainties in T_1 and T_2 are the same and equal to σ_T, show that the uncertainty in the corrected temperature T_0 is

$$\sigma_{T_0} = \frac{\left(I_1^4 + I_2^4\right)^{1/2}}{|I_1^2 - I_2^2|}\sigma_T.$$

(c)   A self-heating assessment employs two sensing currents related according to $I_2 = \sqrt{2}I_1$ (the first entry of Table 6.2). Show that an estimate of the zero-current temperature, $T_0 = 2T_1 - T_2$, has a higher uncertainty than an estimate based on two separate measurements of T_1 and correction equation $T_0 = T_1 - T_2 + T_1'$.

6.5.5   Mechanical shock and vibration

Vibration and mechanical shock are the main contributors to long-term drift in PRTs. Rapid acceleration of the thermometer will cause unsupported wire to flex against the supports or substrate. The flexing in turn causes work hardening and an increase in the resistance of the thermometer. Stainless steel sheathed partially supported PRTs used in laboratory applications should be treated as fragile instruments despite their robust appearance. In high-vibration industrial applications, fully supported PRTs should be used, and, if possible, the source of vibration should be damped or isolated. In extreme cases, prolonged exposure can cause the element to fail, often by causing the connection between the lead wires and the element to break. While most manufacturers specify the shock and vibration that the PRTs will withstand, the specifications are usually for a once-only event.

6.5.6 Thermal expansion effects

In industrial PRTs deformation of the wire due to various thermally driven mechanical effects is the single greatest source of uncertainty. There are two main effects, both caused by the differential expansion of the platinum wire and the substrate: firstly, elastic deformation, which gives rise to hysteresis; and secondly, plastic deformation and work hardening which give rise to drift.

All materials change their dimensions with temperature. For platinum wire, this change is about 9 ppm (parts per million) for every degree Celsius change in temperature. Similarly, all the materials used as substrates for PRTs expand or contract with temperature. Ideally, the substrate should expand and contract at exactly the same rate as the platinum. This would ensure that there would be no strain on the wire. The two most common substrates, glass and alumina ceramic, very nearly satisfy this requirement.

Glasses designed to support platinum thermometers usually have a coefficient of expansion within 1 ppm $°C^{-1}$ or so of that of the platinum, which for most purposes is a good match. One of the problems with glass is that the coefficient of expansion increases by a factor of 3 or more above the softening temperature of the glass. The softening temperature is typically 400 °C to 500 °C, but for some glasses it is as low as 250 °C.

Ceramic alumina substrates also have expansion coefficients of about 8 ppm $°C^{-1}$ to 10 ppm $°C^{-1}$. The structure of ceramics is quite different from that of glass. They are not a uniform solid but a mass of very small crystals bonded together. Alumina crystals have several forms, each of which has a different coefficient of expansion. Furthermore, the crystals have different coefficients of expansion depending on alignment. For individual alumina crystals, the coefficient varies between about $+13$ ppm $°C^{-1}$ and -5 ppm $°C^{-1}$, both extremes being very different from that of platinum. In general, the finer the raw alumina used to make the ceramic, the more uniform the coefficient of expansion and the lower the porosity of the ceramic. The net coefficient of expansion is also process dependent. Thus, although alumina is better than glass in respect of electrical resistivity and purity, it is porous and may have a non-uniform and slightly unpredictable coefficient of expansion.

Elastic deformation and hysteresis

For both types of substrate there will be some *differential thermal expansion*, typically 1 ppm $°C^{-1}$, or less for the better substrates. As the wire is stretched the length of the wire increases. The dimensional changes are not permanent deformations since the wire is elastic for small strains, and as soon as the strain is released the wire returns to its original shape. Because the lattice is distorted as the wire is stretched, a differential expansion coefficient of 1 ppm $°C^{-1}$ results in increases or decreases of about 5 ppm $°C^{-1}$ in the temperature coefficient of platinum. Since the temperature coefficient is about 4000 ppm $°C^{-1}$, the error introduced is usually within $\pm0.1\%$ of the temperature change.

In most elements, the substrate will be unable to maintain the strain on the wire. This allows the wire to relax and slip against the substrate. A thermometer undergoing
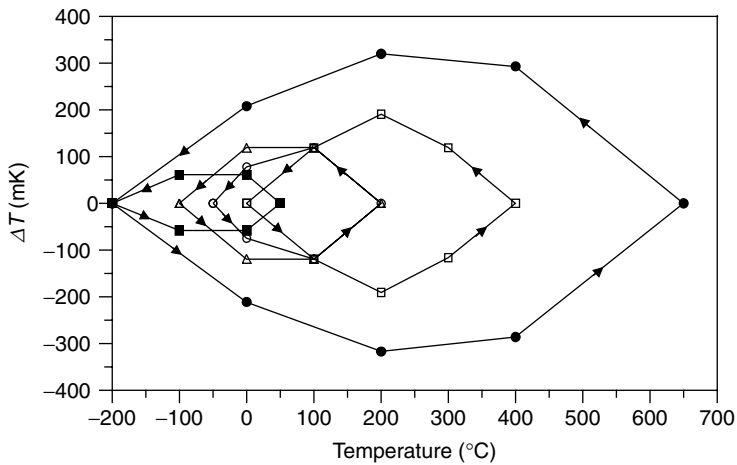
Figure 6.14 Hysteresis in a fully supported industrial PRT. The hysteresis error is proportional to the temperature range covered

stretching on the way to high temperatures will first relax and undergo compression as it returns to low temperatures. This gives rise to hysteresis as shown in Figure 6.14. Some PRTs also exhibit relaxation with time, with a relaxation period as long as several hours. The relaxation can also give rise to erratic behaviour if it occurs in fits and starts. Above 250 °C most PRTs exhibit relaxation as the strain is removed by annealing.

The typical hysteresis in the fully supported PRT of Figure 6.14 ranges between ±0.02% and ±0.05% and is very dependent on the range. For the best partially supported PRTs the maximum strain that the substrate (alumina powder) will support is low, so the hysteresis may be as low as 0.0002%, almost as good as SPRTs. Curiously, hysteresis is also quite low (0.01%) in some thick-film elements because the platinum is bonded to the substrate and is not as free to relax.

Plastic deformation and drift

Metals including platinum cannot be stretched indefinitely. Once the strain exceeds about 0.1% the metal yields, and the deformation is said to be plastic. Superficially, this would not seem to be a problem; resistance elements with a differential thermal expansion of about 1 ppm °C^{-1} would have to be cycled about 1000 °C to reach the required strain levels. However, the platinum wire is not supported uniformly along its length. For example, platinum wire supported on an alumina insulator, which is microscopically rough, may be supported by only a few per cent of its surface area. Thus very small localised areas of the platinum wire are subject to high strain and undergo plastic deformation on every cycle.

Plastic deformation has two detrimental effects. Firstly, it permanently changes the dimensions of the wire. Secondly, the deformation introduces defects into the wire as the crystal structure is deformed and fractured. Both of the effects increase the ice-point resistance of the wire and can be distinguished by determining the temperature coefficient. If the ice-point resistance increase is associated with a decrease in temperature

coefficient then by Mathiessen's rule (Section 6.2.3) the increase in resistance is probably due to defects. In this case, the increase in ice-point resistance can be removed by annealing. Usually both effects are present so that annealing will not completely restore the thermometer to its original condition.

6.5.7   Other thermal effects

Thermal expansion of the lead wires in PRTs is one of the main causes of failure at high temperatures. For both stainless steel and quartz sheathed PRTs, differential thermal expansion can easily cause the lead wires to be strained beyond the yield point. High-temperature SPRTs are probably the extreme example. The thermal expansion of quartz is close to zero so the differential expansion is about $10 \, \text{ppm} \, ^{\circ}\text{C}^{-1}$. Over $800 \, \text{mm}$ of sheath and a $960 \, ^{\circ}\text{C}$ cycle to the silver point, the leads expand nearly $8 \, \text{mm}$! It is essential that the leads be allowed to move freely to prevent tangles and breaks.

Stainless steel sheaths are also a problem since the coefficient of expansion of steel is about $16 \, \text{ppm} \, ^{\circ}\text{C}^{-1}$. Consequently PRTs manufactured for use above a few hundred degrees use alloy lead wires with a coefficient of expansion close to that of steel. Nevertheless, PRTs used above $400 \, ^{\circ}\text{C}$ and exposed to rapid thermal cycling are prone to breaking leads.

At high temperatures, the thermal energy (lattice vibrations) is sufficient to cause atoms to form dislocations and other defects. The equilibrium concentration of defects, η, usually grows exponentially with increasing temperature according to

$$\eta = \eta_0 \exp\left(-E_{\text{d}}/kT\right) \tag{6.25}$$

where η_0 is a constant, E_{d} is the energy required to create the defect and k is Boltzmann's constant. For SPRTs at temperatures above $600 \, ^{\circ}\text{C}$, the defect concentration is sufficient to upset the resistance at lower temperatures, if the defects are allowed to remain. Therefore, standard thermometers used at high temperatures must be cooled slowly to allow the defects to anneal out of the metal. To cool a thermometer from $960 \, ^{\circ}\text{C}$ to $450 \, ^{\circ}\text{C}$, for example, requires in excess of 6 hours. The sheaths of high-temperature SPRTs also become very fragile with exposure to temperatures above $600 \, ^{\circ}\text{C}$.

6.5.8   Contamination

At temperatures above $250 \, ^{\circ}\text{C}$ platinum thermometers become progressively more susceptible to contamination. The effect of the contaminants is to increase the impurities in the metal and hence increase the resistance. If the level of impurities is high, the resulting departures from the resistance tables can be in excess of several degrees, effectively destroying the thermometer. The damage is irreparable since, unlike crystal defects, the impurities cannot be removed by annealing.

Probably the most common cause of contamination is the migration of iron, manganese and chromium from stainless steel and inconel sheaths. An overnight exposure of an unprotected ceramic element at $500 \, ^{\circ}\text{C}$ can easily cause several degrees' error. The migration of contaminants can be reduced by heat treating the sheaths in

air or oxygen before the thermometer is assembled. This builds a layer of metal oxide, which is relatively impervious to metal atoms. The heat treatment can also drive off the lubricant used to draw the tube, another source of contamination.

Above 450 °C ceramic elements require additional protection. The main drawback of ceramic elements is that the ceramic is porous, particularly where the lead wires are cemented onto the substrate. Glass substrates on the other hand are very effective at blocking the migration of impurities from sheaths. Some manufacturers supply glass-encapsulated partially supported elements, which have the advantages of both ceramic and glass types. In some cases, secondary glass sheaths are used inside stainless steel sheaths to protect ceramic elements.

Glass and glass-encapsulated elements are prone to contamination from within the element itself. Above the softening point of the glass, typically 400 °C to 500 °C, the metallic constituents of the glass are able to move readily. Therefore glass elements should never be used above the softening point. Unfortunately, few manufacturers supply information on the softening points of their glasses, some of which are usable up to 600 °C. In principle, the onset of the softening point can be detected by comparing a.c. and d.c. resistance measurements of the elements, but this is rarely practical.

Above 500 °C, the only robust strategy for preventing contamination is to use quartz (fused silica) sheaths. Very high-purity alumina may also be used if there are no other metallic contaminants in the environment. For high-temperature SPRTs even a quartz sheath may be insufficient. Above 800 °C, the only reliable protection for SPRTs is a secondary platinum sheath. When used in the silver point, the platinum sheath (0.2 mm thick) is mounted in the graphite well of the fixed point and protected from mechanical damage by a second quartz well.

All contamination causes an increase in the ice-point resistance of the PRTs. When significant, it also causes changes in the curvature of the resistance–temperature curve. Any probe exhibiting a large ice-point change that cannot be removed by annealing has usually been contaminated and should be discarded as unreliable.

6.5.9 Compensation and assessment of drift

The cumulative effect of work hardening, contamination and plastic deformation is to increase the resistance of the PRT element. By following Mathiessen's rule (Equation (6.3)) and assuming only a linear dependence of resistance with temperature, we can use the change in ice-point resistance to assess the likely temperature errors. The drift-affected resistance is

$$\hat{R}(t) = [R(0\,°\text{C}) + \Delta R_\text{d}]\,(1 + \alpha t) + \Delta R_\text{i}, \tag{6.26}$$

where ΔR_d is the change in resistance due to dimensional changes and ΔR_i is the change induced by impurities and defects. We can estimate the magnitude of the error caused by the increase in resistance by assuming the original value for the ice-point resistance, and that the PRT has a linear resistance–temperature relationship. The error-affected temperature is calculated as

$$\hat{t} = \frac{1}{\alpha}\left[\hat{W}(t) - 1\right], \tag{6.27}$$

where

$$\hat{W}(t) = \hat{R}(t)/R(0\,°\text{C}), \tag{6.28}$$

for which the temperature error is

$$\Delta t = \hat{t} - t = \frac{\Delta R_\text{d} + \Delta R_\text{i}}{\alpha R(0\,°\text{C})} + \frac{\Delta R_\text{d}}{R(0\,°\text{C})}t. \tag{6.29}$$

The first term of Equation (6.29) is a constant temperature error due to the ice-point shift, while the second describes the effect on the temperature coefficient. There are two alternative methods of calculating the temperature that reduce the error.

Method 1: Use the most recent value of the ice-point resistance

The error indicated by Equation (6.29) can be reduced considerably by using the most recent value of the ice-point resistance to calculate the temperature. That is, instead of Equation (6.28) we calculate

$$\hat{W}(t) = \hat{R}(t)/\hat{R}(0\,°\text{C}). \tag{6.30}$$

Then the error is

$$\Delta t = -\frac{\Delta R_\text{i}}{\hat{R}(0\,°\text{C})}t \tag{6.31}$$

and depends purely on impurity- and defect-induced resistance effects.

Method 2: Subtract the ice-point shift from the reading

This time we calculate the resistance ratio according to

$$\hat{W}(t) = \frac{\hat{R}(t) - \Delta R}{R(0\,°\text{C})}, \tag{6.32}$$

where $\Delta R = \Delta R_\text{i} + \Delta R_\text{d}$ is the total ice-point shift. The temperature error in this case is

$$\Delta t = +\frac{\Delta R_\text{d}}{R(0\,°\text{C})}t, \tag{6.33}$$

which depends only on dimensional changes induced by plastic deformation.

Both of the compensation methods substantially reduce the effects of the increase in resistance, especially at temperatures near $t = 0\,°\text{C}$. By substituting the measured ice-point shift ΔR into Equations (6.31) and (6.33) we obtain estimates of the range of possible values of the error, namely the uncertainty. If the likely value of the error is characterised by a rectangular distribution, the uncertainty is

$$U_{\Delta R} = \pm\frac{\Delta R}{R(0\,°\text{C})}t. \tag{6.34}$$

Example 6.4 demonstrates an uncertainty assessment based on these equations.

Example 6.4 ***The assessment of uncertainty due to ice-point shifts in PRTs***
A $0.1\,\Omega$ shift has occurred in the ice-point resistance of a $100\,\Omega$ PRT. Evaluate the two extremes of the likely error at $100\,°C$ and $500\,°C$ by substituting $0.1\,\Omega$ for ΔR_d and ΔR_i in the above equations. Use $\alpha R(0\,°C) = 0.4\,\Omega\,°C^{-1}$. The results are summarised in Table 6.3.

Table 6.3 The temperature error due to a 0.1% change in ice-point resistance versus the three methods of calculating $W(t)$

Method	$t = 100\,°C$		$t = 500\,°C$	
	$\min(\Delta R_\mathrm{d} = 0)$	$\max(\Delta R_\mathrm{i} = 0)$	$\min(\Delta R_\mathrm{d} = 0)$	$\max(\Delta R_\mathrm{i} = 0)$
No compensation Equation (6.29)	+0.25	+0.35	+0.25	+0.75
Method 1 Equation (6.31)	−0.1	0.0	−0.5	0.0
Method 2 Equation (6.33)	0.0	+0.1	0.0	+0.5

Table 6.3 shows that either of the two compensation methods provides a significant reduction in the temperature error. A combination of the two correction methods would yield a method with equal maximum and minimum error. However, the increase in resistance is most commonly due to impurity and defect effects, so Method 2 is generally best.

6.5.10 Leakage effects

Accurate resistance measurements require all of the measuring current to pass through the PRT element. This is relatively easy at low temperatures where insulators have a very high resistance. However, at high temperatures even the very best insulators break down and form a short circuit around the sensing element. Moisture is the other main cause of leakage effects, particularly at lower temperatures where there is insufficient heat to drive the water out of the assembly.

The effect of any leakage resistance on the measurement is well modelled by a leakage resistance in parallel with the sensing resistance. The total resistance of the assembly, $\hat{R}(t)$, is

$$\hat{R}(t) = \frac{R(t)R_\mathrm{ins}}{R(t) + R_\mathrm{ins}}, \tag{6.35}$$

where $R(t)$ is the resistance of the PRT alone and R_ins is the resistance of the insulation; ideally R_ins is infinite. For large values of the insulation resistance, Equation (6.35) is

well approximated by

$$\hat{R}(t) = R(t)\left(1 - \frac{R(t)}{R_{\text{ins}}}\right). \tag{6.36}$$

By substituting $R(t) = R(0\,^{\circ}\text{C})(1 + \alpha t)$ we can obtain an expression for the temperature error caused by the poor insulation resistance:

$$\Delta t \approx -\frac{(1 + \alpha t)^2}{\alpha}\frac{R(0\,^{\circ}\text{C})}{R_{\text{ins}}} \approx -\frac{(250 + t)^2}{250}\frac{R(0\,^{\circ}\text{C})}{R_{\text{ins}}}. \tag{6.37}$$

This equation assumes that no correction for the change in ice-point resistance has been made. Equation (6.37) shows that the error increases very rapidly at temperatures above $250\,^{\circ}\text{C}$. In fact, the problem increases more quickly than this because the insulation resistance normally falls with increasing temperature. The equation also shows that the problem is much worse for PRTs with a high ice-point (or triple-point) resistance. This is the reason that high-temperature SPRTs have a nominal triple-point resistance of about $0.25\,\Omega$. A rearrangement of Equation (6.37) allows us to calculate the minimum insulation resistance for a given maximum temperature error:

$$R_{\text{ins,min}} = \frac{(250 + t)^2}{250\Delta t_{\text{max}}}R(0\,^{\circ}\text{C}). \tag{6.38}$$

Example 6.5   Calculation of errors due to insulation resistance

Calculate the error due to a leakage resistance of $10\,\text{M}\Omega$ on a $100\,\Omega$ sensor at $0\,^{\circ}\text{C}$.

Substitution into Equation (6.37) yields

$$\Delta t = \frac{250 \times 100}{10\,000\,000} = 2.5\,\text{mK}.$$

Specifications vary but most documentary standards for PRTs require an insulation resistance at $0\,^{\circ}\text{C}$ that exceeds $100\,\text{M}\Omega$ or $1000\,\text{M}\Omega$; this is usually measured at $100\,\text{V}$ d.c. The reason why the resistance of the insulator has to be so high at $0\,^{\circ}\text{C}$ is that it does not remain high as the temperature increases. In fact, insulators behave very differently from metals and their resistance decreases rapidly with increasing temperature according to the exponential relationship

$$R_{\text{ins}} = R_0 \exp\left(\Delta E / kT\right). \tag{6.39}$$

The similarity of this equation to Equation (6.25) for the defect concentration in metals is no coincidence; it is the thermally excited electrons in insulators that aid electrical conduction. As the temperature rating of the thermometer increases, the purity requirements on the insulation also increase.

The main cause of leakage errors at low temperatures is moisture. The combination of soluble impurities and moisture in a thermometer assembly can cause errors of

several degrees. Moisture is also a major cause of hysteresis in thermometer assemblies. The hysteresis effects depend on how the thermometer is constructed. The parts of the assembly that are particularly prone to leakage resistances are the connections between the element and the lead wires, the connections between the lead wires and the flexible cable, and if a ceramic element is used, the element itself. When a thermometer is left unused for a period of time the water diffuses evenly throughout the assembly. This even distribution will correspond to a particular value for the leakage error. When the thermometer is used, the distribution of the moisture changes as it diffuses to the cooler parts of the thermometer, changing the error.

Moisture is a problem for most industrial assemblies because it is almost impossible to make a reliable, low-cost and airtight seal on steel sheathed thermometers. As the temperature of the thermometer is cycled, the air within the assembly expands and contracts and, with time, moisture is drawn into the assembly. This is a serious problem for thermometers with magnesia insulation, which has a strong affinity for water.

Some thermometer manufacturers pack the sensing element in thermally conducting grease to prevent the ingress of moisture into the ceramic elements and to improve the thermal response times of the thermometers. The elements using these constructions should be selected carefully as the grease can seriously damage some ceramic elements. Because ceramic is porous the grease will gradually invade the pores and cause the wire to be stressed as the ceramic swells. With thick-film elements, the grease will strip the thin outer layer of ceramic. Thermometers using glass elements are better suited to these applications.

Exercise 6.3

Calculate the minimum insulation resistance that ensures that the leakage error is less than 0.01 °C at 400 °C. The sensor is a 100 Ω PRT.

6.5.11   A.C. leakage effects

A.C. measurements are different from d.c. measurements because energy may be dissipated by the alternating electromagnetic fields around the conductors (resistors, lead wires, etc.). To make a high-quality a.c. measurement we must consider not only the conductors in a circuit, but also their placement and the materials between them. The main concern is with the substrate materials and insulators.

Glass elements exhibit the largest a.c. leakage effects in thermometry. These effects also occur in many other substrates including quartz and alumina. With glasses, however, the effects are more pronounced because they occur at low temperatures within the operating range of industrial PRTs (250 °C upward). Generally, glass elements should not be used on a.c. systems unless it can be proven that a.c. leakage is absent.

Glass elements used at temperatures near the softening point, typically 400 °C to 500 °C, become highly conductive to a.c. as the metallic ions become mobile and the glass behaves as a lossy capacitor. The d.c. conductivity also rises, although usually well past the softening point and beyond temperatures where the element would normally be used. The problem with a.c. leakage is that it may begin 100 °C or more

below the glass softening point, and has been observed at temperatures as low as 100 °C with a resulting error of about 10 °C.

Other situations where a.c. leakage effects are important are generally restricted to high-accuracy applications. For example, PTFE-insulated leads and cables should always be used in preference to PVC to prevent errors of a few millikelvin. The effect is also known to afflict high-temperature SPRTs used near the silver point. The silver point is sufficiently close to the softening point of quartz for errors of several millikelvin to be apparent if too high a frequency is used.

Tests to expose a.c. leakage errors exploit their frequency dependence. The effect is absent at d.c. (zero frequency) and gets progressively worse as the frequency increases. It is for this reason that resistance thermometry bridges operate at very low frequencies, typically in the range 10 Hz to 100 Hz. The simplest test that exposes a.c. leakage is to change the carrier frequency of the bridge, and some thermometry bridges have this facility.

6.5.12   Electromagnetic interference

Electromagnetic interference (EMI) is any unwanted voltage or current that originates outside the measurement circuit. Sources of EMI include electric motors, transformers, power cables, radio and TV transmissions, leakage currents from electric heaters, and ground loops.

It is commonly believed that EMI due to magnetic fields can be reduced by metal screens. However, a screen must be several metres thick to have a significant effect on the field at d.c. and the low frequencies used in resistance thermometry. There are two basic techniques for reducing magnetic EMI. Firstly, separate the EMI source and the thermometer as much as possible. This exploits the fact that the coupling between the source and the thermometer falls off as the distance cubed. Secondly, ensure that all lead wires are kept close together. Twisted-pair and coaxial cables are very effective in reducing the loop area exposed to magnetic fields. Some examples are shown in Figure 6.15.
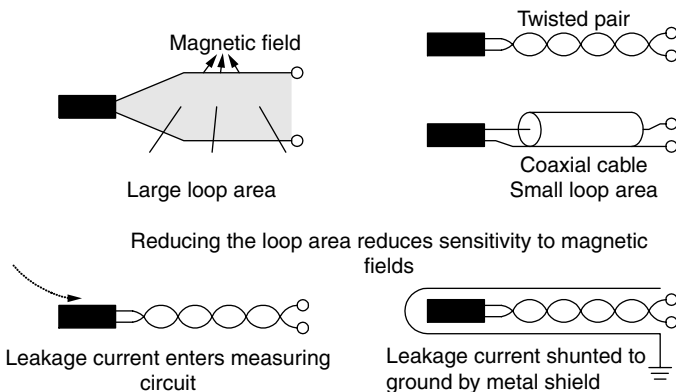
Figure 6.15   Examples of measurement practices which are susceptible to EMI (left), and relatively immune to EMI (right)

The main benefit of screens in low-frequency instruments is that they can be used to eliminate the effects of leakage currents and ground loops. A common example of leakage currents affecting resistance thermometry occurs in electric furnaces, where the heaters are wound on ceramic. At high temperatures, the ceramic will conduct very slightly, allowing small currents to flow into an unscreened thermometer assembly. An earthed metal screen surrounding the thermometer will intercept the leakage current and shunt it harmlessly to ground. Earthed screens are also effective in intercepting capacitively coupled EMI.

Ground-loop effects are very similar to the leakage current problem except that differing ground voltages or magnetic fields induce the currents. The solution is also the same: surround the thermometer by an earthed screen that intercepts the current. For screens to be effective there must be high insulation resistance between the screen and the thermometer and between the screen and the lead wires.

6.5.13 Lead-resistance errors

The errors due to lead resistances were discussed in Section 6.4.2. In most measurements, the errors can be estimated based on the measurement technique, estimates of the lead resistance, and knowledge of the thermometer resistance.

For a two-lead measurement the temperature error is

$$\Delta t \approx 250 R_L / R(0\,^{\circ}\text{C}), \tag{6.40}$$

where R_L is the combined resistance of the two leads. The error can be large. For example, a $0.5\,\Omega$ lead resistance in each lead of a $100\,\Omega$ thermometer gives rise to an error of approximately $2.5\,^{\circ}\text{C}$.

For ideal three-lead and pseudo four-lead measurements the errors are less and depend on the difference in lead resistances, which are characterised by the uncertainty in the match of the leads:

$$U_t = 250 U_{R_L} / R(0\,^{\circ}\text{C}). \tag{6.41}$$

In true four-lead resistance measurements the errors should be negligible.

For all measurement techniques, a simple check will expose any susceptibility to lead-resistance errors. Simply insert a small resistance successively into each of the leads and measure the change in reading. Then with estimates of the lead resistances it is relatively easy to estimate the error and uncertainty. This check is necessary where an instrument is used with excessively long lead wires or there are doubts about the instrument's sensitivity to lead resistances.

Example 6.6 Assessing errors due to lead resistances

A three-lead resistance thermometer indicator is to be connected to a remote $100\,\Omega$ thermometer probe. The lead resistances are all measured and found to be within $7\pm1\,\Omega$. Estimate the expected error and uncertainty due to the lead resistances.

The error   A $1\,\Omega$ resistor is successively inserted into each of the three leads to the thermometer and the changes in reading are

$$\text{lead 1:} \quad \Delta T = 2.6\,°\text{C}\,\Omega^{-1},$$
$$\text{lead 2:} \quad \Delta T = -4.1\,°\text{C}\,\Omega^{-1},$$
$$\text{lead 3:} \quad \Delta T = 0.1\,°\text{C}\,\Omega^{-1},$$

where ΔT is the change in reading with the $1\,\Omega$ resistor inserted into the respective lead. The changes in temperature reading suggest that the instrument does not compensate correctly for lead resistance. In a good three-lead or pseudo four-lead resistance measurement the sum of the changes should be zero. In a true four-lead measurement each of the changes should be zero. For this example, there would be an expected error of

$$\Delta t = (2.6 - 4.1 + 0.1) \times 7 = -9.8\,°\text{C}.$$

Equivalently, the correction for lead resistance error is $+9.8\,°\text{C}$. For this case, the fact that the sum of the errors is not close to zero suggests that a lead correction circuit in the thermometer is faulty and that the instrument should be serviced rather than any readings corrected.

The uncertainty   The measurements tabulated above are the sensitivity coefficients for the lead-resistance errors. If it is assumed that the uncertainties in the resistance of the three leads are uncorrelated then the total uncertainty is

$$U_{R_L} = \left(2.6^2 + 4.1^2 + 0.1^2\right)^{1/2} \times 1 = 4.9\,°\text{C}.$$

This is the uncertainty in the lead-resistance correction.

6.5.14   Thermoelectric effects

Thermoelectric effects, as discussed in Section 6.4.3, potentially affect only high-accuracy measurements not employing switched d.c. or a.c. sensing currents. The few microvolts generated by thermoelectric effects are not significant compared with the $0.4\,\text{mV}\,°\text{C}^{-1}$ output voltage of most resistance thermometers. The problem is serious only in extreme cases where, for example, a lead wire has been replaced by a dissimilar metal, or connection terminals are exposed to high temperature gradients.

When voltage errors are expected or known to exist, their influence on the measurement can be assessed as

$$\Delta t = 250 \frac{V_{\text{TE}}}{I\,R(0\,°\text{C})}, \tag{6.42}$$

where I is the sensing current through the PRT, V_{TE} is the error voltage, and $R(0\,°\text{C})$ is the ice-point resistance of the PRT. The typical error for a $1\,\text{mA}$ sensing current and a $100\,\Omega$ PRT is about $2.5\,\text{mK}\,\mu\text{V}^{-1}$.

6.5.15   Reference resistor stability and accuracy

Ultimately the accuracy of a resistance thermometer depends on the accuracy of one or more reference resistances. For example, for the balance equation for the Wheatstone bridge (Equation (6.14)) any changes in the values of R_1, R_2 and R_3 will be interpreted incorrectly as changes in the value of $R(t)$. For small changes, the perceived change in $R(t)$, namely $\Delta R(t)$, is given by

$$\frac{\Delta R(t)}{R(t)} = \frac{\Delta R_1}{R_1} - \frac{\Delta R_2}{R_2} + \frac{\Delta R_3}{R_3}, \tag{6.43}$$

where ΔR_1, ΔR_2 and ΔR_3 are the changes in each of the reference resistors. This equation provides us with the information to assess the stability and accuracy of the bridge. By expressing the percentage changes in resistance in terms of the temperature coefficients of the resistors, β_i, we obtain

$$\Delta t = \frac{(\beta_1 - \beta_2 + \beta_3)}{\alpha} \Delta t_a, \tag{6.44}$$

where α is the temperature coefficient of the PRT and Δt_a is the change in the temperature of the reference resistors.

Example 6.7   *Temperature stability of a resistance bridge*

A platinum thermometer bridge is required to indicate temperature to an accuracy of $\pm 0.1\,°C$. The bridge will be exposed to ambient temperatures between $10\,°C$ and $40\,°C$. Estimate the maximum temperature coefficients required of the reference resistors.

By matching the temperature coefficients of R_1 and R_2 we need consider only the temperature coefficient of R_3. Then, by rearranging Equation (6.44) we obtain the maximum acceptable value for β_3:

$$\beta_3 < \alpha \frac{\Delta t}{\Delta t_a}.$$

Now, by substituting $\Delta t = 0.1\,°C$ and $\Delta t_a = 30\,°C$, and using $\alpha = 4000\,ppm\,°C^{-1}$, we find that the temperature coefficient for R_3 must be less than $13\,ppm\,°C^{-1}$. Since we must also accommodate some mismatch between R_1 and R_2, resistors with temperature coefficients of less than $10\,ppm\,°C^{-1}$ would be appropriate.

Typical temperature coefficients for ordinary resistors used in electronic assembly are $50\,ppm\,°C^{-1}$ to $200\,ppm\,°C^{-1}$, and $0.2\,ppm\,°C^{-1}$ to $15\,ppm\,°C^{-1}$ for precision resistors. For accuracies of $0.01\,°C$ or better, it is usually necessary to restrict the ambient temperature range, or to control the precision resistors with a thermostat.

Equation (6.43) can also be modified (see Example 2.17) to estimate the uncertainty in temperature caused by uncertainties in the reference resistors:

$$U_T = \frac{1}{\alpha} \left[\left(\frac{U_{R_1}}{R_1} \right)^2 + \left(\frac{U_{R_2}}{R_2} \right)^2 + \left(\frac{U_{R_3}}{R_3} \right)^2 \right]^{1/2}. \qquad (6.45)$$

Example 6.8   *Estimating the accuracy of a resistance bridge*

A simple Wheatstone bridge is assembled using resistors with a 0.01% tolerance. Estimate the accuracy of the bridge.

Substituting the values directly into Equation (6.45) and using $\alpha = 0.4\% \, ^{\circ}\mathrm{C}^{-1}$ we obtain

$$U_T = \frac{\left(0.01^2 + 0.01^2 + 0.01^2 \right)^{1/2}}{0.4} = 0.043 \, ^{\circ}\mathrm{C}.$$

All direct-reading platinum thermometers include some form of linearisation in their electronic systems. As discussed in Section 5.3.1, linearisation is required to convert the non-linear response of the platinum thermometer into a signal that is directly proportional to temperature. Because the resistance–temperature characteristic for platinum is nearly linear, the linearisation is relatively simple to achieve in comparison with other temperature sensors. Indeed most of the residual error after linearisation is due to small departures of the sensing element from the standard tables, and would typically be less than $0.1 \, ^{\circ}\mathrm{C}$ over a $200 \, ^{\circ}\mathrm{C}$ range.

6.6 Choice and Use of Resistance Thermometers

6.6.1   Choosing and using a thermometer

If a reference thermometer is required for any temperature below $200 \, ^{\circ}\mathrm{C}$, then a PRT should be the first choice. Although the initial cost of a PRT may be higher than that of a liquid-in-glass thermometer, the maintenance and recalibration costs of PRTs are much less, and PRTs are less fragile. If accuracies of $0.1 \, ^{\circ}\mathrm{C}$ or better are required then PRTs should be the only choice.

At temperatures above $200 \, ^{\circ}\mathrm{C}$ the limitations of PRTs begin to affect their suitability, especially if the PRT is subject to regular cycling. Figure 6.16 summarises the best temperature range and accuracy that can be expected from the three main types of PRT.

There are four main factors to consider in the choice of industrial platinum thermometers, as follows.

Accuracy

The accuracy of a calibrated PRT is between $\pm 1 \, \mathrm{K}$ and $\pm 1 \, \mathrm{mK}$, depending on the construction and the required temperature range. A good rule of thumb is that the cost
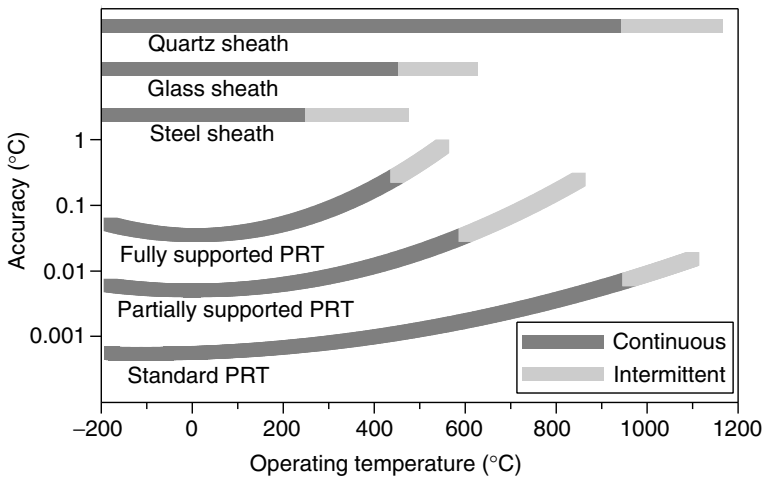
Figure 6.16 Approximate accuracy and range that can be achieved with fully supported, partially supported and standard PRTs

of the thermometer is inversely proportional to the required accuracy. A $\pm 1\,\mathrm{mK}$ system will cost about 1000 times more than a $\pm 1\,^\circ\mathrm{C}$ system, with most of the cost in the bridge.

The accuracy of industrial PRTs is also strongly dependent on the temperature range. It is typically below 0.1% of the range for fully supported PRTs and below 0.005% for partially supported PRTs. For the highest-accuracy applications, PRTs can be selected for low hysteresis by cycling them, for example between $100\,^\circ\mathrm{C}$ and $-196\,^\circ\mathrm{C}$ (liquid nitrogen). Measuring the change in triple-point or ice-point resistance between exposures to the high and low temperatures will reveal the amount of hysteresis. The best partially supported PRTs have less than 0.0002% hysteresis.

D.C. instruments are suitable for accuracies between $\pm 0.02\,^\circ\mathrm{C}$ and $\pm 1\,^\circ\mathrm{C}$. A.C. bridges or switched d.c. systems are necessary for accuracies better than $\pm 0.02\,^\circ\mathrm{C}$, with the a.c. systems having the faster measurement time.

Temperature range

As the temperature range increases, the lower-grade PRTs are excluded, and demands on the quality of the environment and sheath increase.

Above 250 °C   The environment should be free of contaminants. Ceramic elements in stainless steel sheaths are suitable only for intermittent use unless they are specially constructed for this range. Fully supported elements should not be exposed to regular (e.g. daily) cycling.

Above 450 °C   Silica or quartz sheaths only should be used. Fully supported and some partially supported assemblies have a limited life at these temperatures due to the eventual fatigue and failure of lead wires.

Above 650 °C   Only high-temperature SPRTs survive readily, although some of the best of the partially supported PRTs will survive intermittent use to $850\,^\circ\mathrm{C}$.

To obtain the best accuracy from reference PRTs (other than SPRTs) it is worth restricting their use to narrow ranges in order to limit the hysteresis and drift. Depending on the accuracy required, one PRT per 200 °C range is a reasonable guide.

Environment

The major environmental considerations are vibration and mechanical shock. If either of these is present, fully supported elements should be used. Partially supported elements may be suitable if the vibration is small or if the assembly can be mechanically decoupled from the source of the vibration. In a very wet or humid environment, glass elements should be used to prevent excessive leakage current and moisture-induced hysteresis.

Construction

Most manufacturers of PRT elements also assemble and sell sheathed PRTs. Since sheathing is required for most applications, elements should be purchased sheathed. The differential expansion of the sheath and lead wires makes construction of a reliable sheathed PRT something of an art, especially at high temperatures, and is best left to the experts. In addition, the best techniques often involve proprietary information. Remember that a calibration laboratory may be unwilling to certify a thermometer that has obviously not been manufactured using well-established techniques.

For laboratory applications, for example as a reference thermometer, the main cost of a platinum thermometer is the electronic display unit or bridge so there is little point penny-pinching on the PRT. A good-quality PRT is partially supported, has four leads and a good seal where the cable joins the sheath. The connecting cable should have a braided screen that is connected to the sheath if it is metal, and use PTFE insulation. PTFE exhibits less a.c. loss and withstands temperatures of up to 200 °C. The length of the sheath should be chosen according to the application and temperature range. As a guide, the minimum sheath length should be about 200 mm plus 100 mm per hundred degrees of duty above 200 °C. For example, a minimum length for duty at 400 °C is 400 mm.

6.6.2   Care and maintenance

PRTs are relatively easy to care for. They have a long life so long as they are not exposed to vibration, temperature cycling and potentially contaminating environments.

All PRTs should be checked regularly at the ice point or triple point, since a change in the ice-point resistance will expose almost all signs of faulty behaviour or misuse. A decrease in ice-point resistance is normally an indicator of excessive leakage due to moisture. With steel sheathed PRTs this can be checked very easily by measuring the insulation resistance between the sheath and element. The moisture can be removed by drying the thermometer in a drying oven for a day or so. The assembly should not be heated above the maximum specified temperature of the head and leads, typically 65 °C for PVC cable. PTFE-insulated assemblies may be dried at 100 °C.

An increase in ice-point resistance caused by work hardening can be removed by annealing. This is accomplished by heating the thermometer to 400 °C to 450 °C for several hours. This should be repeated until the ice-point resistance of the PRT stabilises at a single value. Only appropriately constructed metal sheathed partially supported PRTs and SPRTs should be annealed. Other constructions will be damaged by the exposure to 450 °C.

All SPRTs should be annealed regularly (e.g. at least annually). This should be repeated until the triple point resistance of the PRT has stabilised. For SPRTs not used above 700 °C, this value should be stable to the equivalent of better than 1 mK for periods of years. In some cases, where very severe mechanical shock is known to have caused a large resistance shift, the annealing temperature may need to be increased to 660 °C or up to the working temperature limit, whichever is lower. If the triple-point resistance increases on annealing at 450 °C, the thermometer may be suffering from an auto-catalytic oxidation that can occur on occasions. Annealing at 600 °C also suppresses this process.

PRTs that exhibit large, permanent ice-point resistance shifts should be treated with suspicion. If the permanent shift exceeds 0.1% the PRT should be discarded as unreliable.

6.7 Calibration of Resistance Thermometers

PRTs have been a part of all of the temperature scales since 1927. Consequently, there has been a great deal of research on calibration and interpolation equations, with over a dozen equations recommended at various times for various applications. The ITS-90 formulation, which is suited to SPRTs and the best of the partially supported PRTs, is discussed in Chapter 3. In this section, we recommend two formulations based on the Callendar–van Dusen (CVD) equation, which are simpler and better suited to second-tier and laboratory applications. Both recommendations apply to reference thermometers that are calibrated in terms of resistance. Direct-reading thermometers should be calibrated according to the procedure outlined in Chapter 5 (Section 5.5.6).

As with all high-accuracy calibrations, a high level of expertise is required of personnel involved in the calibration of PRTs. In particular, good algebraic and computing skills are required to handle both the ITS-90 formulation and the simpler CVD equation. Additionally, for the CVD equation an understanding of least-squares fitting is essential.

6.7.1   Calibration equations

For all of the earlier temperature scales the CVD equation was the accepted interpolation equation for PRTs. It is also the defining function for all the industrial PRTs. The general form of the equation is

$$W(t) = 1 + At + Bt^2 + Ct^3(t - 100), \tag{6.46}$$

where C is zero above 0 °C, and $W(t) = R(t)/R(0\,°C)$. Note that ITS-90 uses the triple-point ratio rather than the ice-point ratio. The CVD equation is very much simpler than the ITS-90 formulation and is well suited to least-squares fitting.

For thermometers used below $-40\,°C$ and above $150\,°C$ to $200\,°C$ the simple quadratic equation given as Equation (6.46) with $C = 0$ may prove to be inadequate. Most PRTs do not conform exactly to the documentary standards, which use the CVD equation and exhibit a t^3 dependence that begins to dominate the residual errors when the temperature range gets large. For large ranges above $0\,°C$ the equation may be extended to

$$W(t) = 1 + At + Bt^2 + Dt^3. \tag{6.47}$$

Use of this equation is equivalent to the deviation function approach described in Section 5.3.1.

After the thermometer has been calibrated using Equation (6.47), the temperature can be calculated from the measured resistance and the calibration constants by successive approximation. For the cubic equation the temperature is calculated by repeated application of

$$t_n = \frac{W(t) - 1}{A + Bt_{n-1} + Dt_{n-1}^2}. \tag{6.48}$$

This gives an improved estimate of the measured temperature t_n, based on the previous estimate t_{n-1}. With repeated application of Equation (6.48), the estimate of the temperature improves steadily, and after a few iterations, the accuracy of the result will be close to the full computer accuracy. Alternative algorithms that solve the equation directly can be susceptible to round-off errors on some computers. The iterative technique can be implemented in spreadsheet applications by enabling the iteration or recursion features, and on some pocket calculators.

The recursion relation for the CVD equation is

$$t_n = \frac{W(t) - 1}{A + Bt_{n-1} + Ct_{n-1}^2(t_{n-1} - 100)}. \tag{6.49}$$

When $W(t)$ is very different from one, five or six iterations of Equations (6.48) or (6.49) may be necessary before t_n converges to the correct value.

Exercise 6.4

Apply the recursion equation, Equation (6.48), to find the temperature reading of a PRT with $W(t) = 2.6$. The calibration constants for the PRT are $A = 4 \times 10^{-3}\,°C^{-1}$, $B = -6 \times 10^{-7}\,°C^{-2}$, $D = 0$.

6.7.2   Calibration at fixed points

There are two basic methods for calibrating PRTs, namely calibration at fixed points, as described in this section, and calibration by least squares, as described in the next section.

Calibration by direct comparison with fixed points has been described in Chapter 3. This technique is the more accurate but is subject to some serious restrictions when applied to industrial PRTs. The advantages include the following:

- It provides an accurate determination of the calibration constants.
- Since all measurements are normally corrected for self-heating errors (Section 6.5.4), the effects of self-heating are eliminated from the calibration.
- Relatively few points are required: typically two or three, depending on which ITS-90 interpolation equation is used.
- ITS-90 provides five convenient fixed points at approximately $-38\,°C$, $30\,°C$, $157\,°C$, $232\,°C$ and $420\,°C$. This is sufficient choice for most calibration ranges.

  Disadvantages include the following:

- By using the same number of fixed points as unknown constants, no additional information is made available on the likely uncertainty in the calibration. For SPRTs, which are always calibrated at the fixed points, there is enough generic knowledge available to make a good Type B assessment. This is not true for industrial PRTs, which differ considerably between grades and manufacturers, and exhibit significant levels of interpolation error.
- In many cases, the user of calibrated industrial or laboratory PRTs does not have access to bridges with the facility to change the measuring current. All measurements made with the thermometer will therefore be subject to self-heating errors of between 5 mK and 30 mK which the user is unable to assess. This will make the full accuracy of the thermometer unrealisable and introduce a serious systematic error. Again, this is not a serious problem for SPRTs because the self-heating error is usually less than 2 mK and users of SPRTs use bridges that allow the current to be changed.
- An assessment of the uncertainty in a thermometer's readings is essential for a calibration to satisfy the requirements described in Chapter 5. For industrial PRTs it is necessary to make more measurements than is required simply for determination of the calibration constants. Least squares provide the best means for analysing the results.

6.7.3   Calibration by least squares

In a least-squares calibration, the data is typically acquired by comparison with an SPRT. There are several choices of calibration equation but for most applications Equation (6.46) or (6.47) is more than adequate. The measurements required are one measurement of the triple-point or ice-point resistance, and a number of measurements of $W(t)$ distributed evenly over the calibration range. The exact number of points required depends on the number of parameters to be fitted; about four points per unknown parameter are sufficient.

Once all the measurements have been made, the values of A and B are determined by the method of least squares described in Section 2.12. For the quadratic equation version of the CVD equation (Equation (6.46) with $C = 0$) the best values of A and B are

$$
\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} \sum t_i^2 & \sum t_i^3 \\ \sum t_i^3 & \sum t_i^4 \end{bmatrix}^{-1} \begin{bmatrix} \sum t_i \left(W(t_i) - 1 \right) \\ \sum t_i^2 \left(W(t_i) - 1 \right) \end{bmatrix}, \tag{6.50}
$$

where $W(t) = R(t)/R(0\,°C)$ or $R(t)/R(0.01\,°C)$ as appropriate.

The standard deviation of the fit (Equation (2.73)), which describes how well the equation fits the measurements, and the uncertainties in the values of A and B (Equation (2.74)) can then be computed.

The advantages of this method include the following:

- It provides an assessment of the uncertainty in temperatures measured by the PRT, the standard deviation of the fit. Just as a low value for the standard deviation shows the thermometer has the expected resistance–temperature relationship, so a very high value for the standard deviation is indicative of a faulty thermometer. The fault may be excessive hysteresis and relaxation, contamination, or an excess of moisture.
- The calibration is carried out under the same conditions as those in which the thermometer will be used. This ensures that the relationship determined is realisable by the user of the thermometer. Such conditions might be a 1 mA sensing current and 200 mm immersion in a stirred fluid bath. The effects of self-heating will then be the same (or very similar) in use as in calibration.
- It can be applied to any calibration range. For most calibrations, only the quadratic form of the CVD equation is required. For very wide-range calibrations, a cubic term (and even a quartic term) may need to be added.
- It provides an assessment of the uncertainties in the fitted values, A and B. This is also useful in determining the precision for reporting the values.

Disadvantages include the following:

- It requires more calibration points. However, unlike measurements at fixed points, the measurements are more amenable to automation and the sensing current is constant.
- The conditions under which the thermometer may be used with full accuracy are restrictive, although they are probably less restrictive than for a fixed-point calibration.

Both methods described above (here and in Section 6.7.2) are quite complicated. While this would traditionally have been considered an impracticality, this is no longer the case. The availability and power of even the lowest-cost computers now mean that algebraic complexity is no longer an issue, at least for laboratory applications.

6.7.4   A calibration procedure

The calibration procedure for a PRT follows closely the outline given in Section 5.5.2. In this section, we highlight additional features relevant to PRTs.

Step 1: Initiate record keeping

Resistance bridges are normally calibrated independently of the thermometer. Direct-reading thermometers follow the example in Section 5.5.6. Otherwise, proceed as for Section 5.5.2.

Step 2: General visual inspection

As for Section 5.5.2.

Step 3: Conditioning and adjustment

SPRTs and partially supported PRTs in silica sheaths are appropriately constructed to withstand duty at 450 °C and may therefore benefit from periodic annealing to relieve accumulated strain in the wire. The annealing procedure should be repeated until the triple-point (or ice-point) resistance becomes stable. If the ice point increases steadily on annealing then the PRT may have been contaminated.

Step 4: Generic checks

Detailed inspection   As for the example in Section 5.5.2.

Insulation resistance   The insulation resistance of metal sheathed resistance thermometers should be checked to confirm that there is no build-up of moisture in the insulation.

Ice-point or triple-point resistance   Measurement of one of these will confirm that the lead wires are intact, and indicate whether the thermometer has been exposed to damaging environments. For industrial PRTs the resistance should be within 0.2% of the nominal resistance. This allows for 0.1% on initial tolerance plus a further 0.1% shift due to drift. Brand-new thermometers should be within 0.1%. Resistance values that are high are indicative of contamination or exposure to vibration and shock. Low resistance values are indicative of moisture build-up in the insulation, and occasionally short-circuited lead wires. The resistance should be measured before and after the calibration to enable assessment of the stability of the thermometer:

Hysteresis assessment: There are two situations depending on the expected usage of the thermometer:

(1)   The measured temperature will always be approached from room temperature. This follows the rationale of Example 2.10 for reducing the uncertainty due to hysteresis. To assess the likely uncertainty due to hysteresis a number of additional points must be included in the comparison on return from the highest (or lowest) temperatures. Once the width of the hysteresis loop has been determined, the uncertainty is estimated as half of the loop width.

(2)   The measured temperature may be approached from either direction. In this case the comparison must cover the required calibration range in both directions to avoid biasing the measurements. If the data for both directions is included in the least-squares fit then the uncertainty due to hysteresis will be included in the error of fit and no additional uncertainty need be included in the total.

Self-heating assessment   This applies only to thermometers that are calibrated at non-zero current. The self-heating effect in resistance thermometers can depend on the environment in which they are used. Because the self-heating error in use will be different from the self-heating in calibration, the additional uncertainty must be included in the assessment of total uncertainty. For all 100 Ω sheathed PRTs operated at 1 mA the variation in self-heating when used in oil baths, water baths, ice points and triple points is

usually less than ± 2 mK. If the thermometer is unsheathed or is to be exposed to an environment very different from the calibration environment then a subsidiary experiment must be designed to enable estimation of the likely change in self-heating.

Step 5: The comparison

For SPRTs and the very best of the partially supported PRTs a fixed-point comparison (Section 6.7.2) is appropriate. Otherwise, the least-squares fit approach (Section 6.7.3) should be adopted. For most PRTs the simple quadratic version of the CVD equation is adequate so that a minimum of eight comparison points is required. These should be distributed evenly over the calibration range. The comparison must also duplicate the expected usage in respect of hysteresis as described above. If the thermometer is expected to be used so that the measured temperature is always approached from room temperature (to reduce the hysteresis) then the comparison should be carried out in the same way. If the thermometer usage is not expected to be controlled and significant hysteresis is expected, the comparison should cover the expected temperature range in both directions. This doubles the number of calibration points in the comparison.

Step 6: Analysis

The analysis comprises the determination of the constants in the calibration equations. We demonstrate the analysis for an industrial PRT in Example 6.9 below.

Step 7: Uncertainties

As for Section 5.5.2, and Example 6.9 below.

For SPRTs the assessment of uncertainty is based entirely on assessments of the uncertainty at each fixed point propagated according to the uncertainty in interpolations as described in Sections 2.11.2 and 3.4.

Step 8: Complete records

As for Section 5.5.2.

> ### Example 6.9   Calibration analysis for a PRT
>
> A fully supported steel sheathed PRT is calibrated over the range $-10\,°C$ to $180\,°C$. The calibration data and the results of a least-squares analysis are summarised in Table 6.4 below. Figure 6.17 is a graphical summary of the results and includes the results of the hysteresis measurements.
>
> The precalibration triple-point resistance has been used to determine the resistance ratio and the data has been fitted to the simple quadratic version of the CVD equation (Equation (6.46)) to determine the values for A and B. A check of the residual errors in the fit shows that there is a slight pattern in the signs of the errors which suggests a small cubic or S-shaped non-linearity (Section 5.3.1).

Table 6.4   Summary of initial readings and comparison

Insulation resistance: greater than $1000\,\text{M}\Omega$
Precalibration triple-point resistance $= 100.0384\,\Omega$

Reading number	Measured resistance	Measured temperature	Fitted temperature	Residual error
1	96.1462	−9.9482	−9.9443	−0.0039
2	100.7751	1.9065	1.8858	0.0207
3	105.4064	13.7761	13.7633	0.0128
4	110.0186	25.6411	25.6332	0.0079
5	114.6116	37.5020	37.4952	0.0068
6	119.1831	49.3438	49.3433	0.0005
7	123.7829	61.3051	61.3070	−0.0019
8	128.3179	73.1410	73.1442	−0.0032
9	132.8424	84.9942	84.9960	−0.0018
10	137.3440	96.8296	96.8298	−0.0002
11	141.8415	108.6959	108.6953	0.0006
12	146.3178	120.5399	120.5473	−0.0074
13	150.7780	132.3917	132.3993	−0.0076
14	155.2155	144.2333	144.2337	−0.0004
15	159.6404	156.0842	156.0773	0.0069
16	164.0506	167.9291	167.9246	0.0045
17	168.4467	179.7764	179.7773	−0.0009

Standard deviation of fit (Ω)	$= 0.0030\,\Omega$
Standard deviation of residual temperature errors (°C)	$= 0.0078\,°\text{C}$
$R(0.01\,°\text{C})$	$= 100.0384\,\Omega$
Fitted parameters:	$A = 3.906\,703 \times 10^{-3} \pm 2.8 \times 10^{-5}\,°\text{C}^{-1}$
	$B = -5.728 \times 10^{-7} \pm 2.0 \times 10^{-7}\,°\text{C}^{-2}$
Mean hysteresis error	$= -0.0150\,°\text{C}$
Post calibration triple-point resistance	$= 100.0438\,\Omega$

Determining the total uncertainty

The contributing factors are as follows.

Reference thermometer   The uncertainty in the reading of the reference thermometer is determined from its certificate and already given for a 95% level of confidence:

$$U_{\text{ref}} = 2.0\,\text{mK}.$$

Calibration medium   The expanded uncertainty due to non-uniformity of the calibration bath has been previously determined from commissioning tests to be

$$U_{\text{bath}} = 1.0\,\text{mK}.$$

Uncertainty in the fit   The standard deviation of the residual errors in the least-squares fit is 7.8 mK. The number of degrees of freedom in the fit is 15, and

the coverage factor for an expanded uncertainty with a 95% level of confidence is 2.13. Since the thermometer will be used as a reference thermometer to calibrate working thermometers the expanded uncertainty is (see Equation (5.8) and accompanying discussion)

$$U_{\text{fit}} = 16.6\,\text{mK}.$$

Hysteresis   In this example the average hysteresis error is $-15\,\text{mK}$. The halfwidth of the loop is used as an estimator of the uncertainty; hence

$$U_{\text{hys}} = 7.5\,\text{mK}.$$

The change in triple point resistance of $-5.4\,\text{m}\Omega\,(-14\,\text{mK})$ also shows the effect of hysteresis. The jagged appearance of the hysteresis loop (Figure 6.17) is due to relaxation.

Self-heating   The PRT is steel sheathed, nominally $100\,\Omega$, and is operated at a measuring current of $1\,\text{mA}$. Therefore the Type B assessment recommended in the procedure gives an estimate of the uncertainty as

$$U_{\text{sh}} = 2\,\text{mK}.$$

The *total uncertainty* is the quadrature sum of these terms:

$$U_{\text{total}} = 18.5\,\text{mK}.$$

This is rounded up to $20\,\text{mK}$ for the certificate.
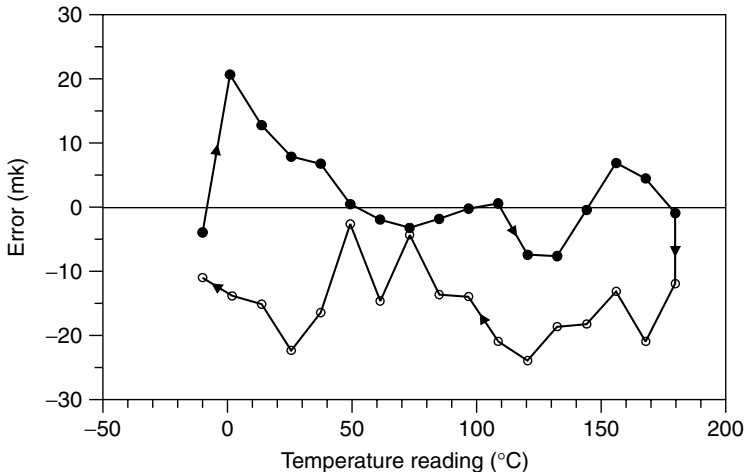
Figure 6.17   A graphical summary of the PRT calibration data for Example 6.9. The ascending sequence of measurements (filled circles) is used to determine the coefficients in the CVD equation, while the descending sequence of measurements (open circles) is used to determine the amount of hysteresis. The jagged appearance of the curves is due to relaxation associated with the hysteresis

Continued from page 248

Figure 6.18 shows a completed certificate for the thermometer.

CALVIN, DEGRIES AND CO

1 TRACEABILITY PLACE, PO BOX 31-310, LOWER HUTT, NEW ZEALAND
TELEPHONE (64) 4 569 0000   FAX (64) 4 569 0003

CALIBRATION CERTIFICATE

Report No: T92-2003.

Client: ACME Thermometer Co, 100 Celsius Avenue, P O Box 27-315, Wellington, New Zealand.

Description of Thermometer: A stainless steel sheathed platinum resistance thermometer manufactured by ACME, serial number GRT10.

Date of Calibration: 13 to 16 August 2000.

Method: The thermometer was compared with standard thermometers held by this laboratory. All measurements are traceable to the New Zealand National Standards. The temperature scale used is ITS-90.

Conditions: The thermometer was immersed in a stirred bath to a minimum depth of 200 mm. The sensing current for all resistance measurements was 1 mA.

Results: The temperature, $t \, °C$, was related to the thermometer resistance, $R(t \, °C)$, and the resistance at the triple point of water by the equation

$$\frac{R(t \, °C)}{R(0.01 \, °C)} = 1 + At + Bt^2$$

The constants $R(0.01 \, °C)$, A and B were found to be

$R(0.01 \, °C) = 100.0384$ ohm
$A = 3.9067 \times 10^{-3} \, (°C)^{-1}$
$B = -5.728 \times 10^{-7} \, (°C)^{-2}$

Note: $R(0.01 \, °C)$ should be measured with the user's instrument and the value obtained used in the equation.

Accuracy: The uncertainty in temperatures measured with the thermometer over the range $-10 \, °C$ to $180 \, °C$ and determined using the above constants is estimated to be $\pm 0.02 \, °C$ at the 95% confidence level.

Checked:_____   Signed:_____
W Thomson   R Hooke

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Figure 6.18 A completed certificate for an industrial PRT, based on the information given in Example 6.9

6.8 Other Resistance Thermometers

6.8.1 Thermistors

Thermistors are semiconducting ceramic resistors made from various metal oxides. They have one outstanding advantage over all other resistance thermometers, namely very high sensitivity. It is not difficult to build thermistor thermometers with sensitivities of $50 \, \text{mV} \, °\text{C}^{-1}$ or more, more than 100 times that of most platinum thermometers

and more than 1000 times that of most thermocouples. They are also very small and fast.

There are two main classes of thermistor, namely PTC or positive temperature coefficient thermistors, and NTC or negative temperature coefficient thermistors, the latter being the most suitable for thermometry. An approximate equation relating the resistance of the NTC thermistor to temperature is

$$R(T) = A \exp(B/T), \tag{6.51}$$

which is of the same form as that for the leakage resistance of insulators (Equation (6.39)). Values of $R(T)$ range from less than $100\,\Omega$ to more than $100\,M\Omega$, depending on the temperature and the values of A and B. For convenience Equation (6.51) is usually written

$$R(T) = R(T_0) \exp\left(\frac{B}{T} - \frac{B}{T_0}\right), \tag{6.52}$$

where T_0 is 298.15 K (25.0 °C) or 273.15 K (0 °C). The resistance typically varies by a factor of 100 000 or more over the $-100\,°C$ to 150 °C operating range. Some thermistors are available for temperatures outside this range but the performance deteriorates quite quickly with extremes of temperature. The temperature coefficient of thermistors is approximately

$$\alpha = \frac{-B}{T^2}, \tag{6.53}$$

with typical values between $-3\%\,°C^{-1}$ and $-6\%\,°C^{-1}$.

The main disadvantages of thermistors include the extreme non-linearity of the resistance with temperature, and instability with time and cycling. The best thermistors are glass-encapsulated or epoxy-encapsulated beads, which are available with an interchangeability of 0.1 °C. The long-term stability of the best thermistors approaches a few tenths of a millikelvin per year.

Equation (6.52) is a satisfactory calibration equation for only very narrow ranges (10 °C) or for low-accuracy applications. A better equation is

$$\frac{1}{T} = a_0 + a_1 \log\left(R/R_0\right) + a_2 \log^2\left(R/R_0\right) + a_3 \log^3\left(R/R_0\right), \tag{6.54}$$

where R is the measured resistance and R_0 is a convenient normalising constant (e.g. $1\,\Omega$ or $1\,k\Omega$). This equation fits most thermistor responses over ranges of 100 °C or more to within a few millikelvin.

The high sensitivity and fast response of thermistors make them ideally suited to precision temperature control and differential temperature measurement where resolutions better than $5\,\mu K$ can be obtained. They are also attractive for simple hand-held thermometers because the sensitivity and high resistance make them relatively immune to lead-resistance errors. Thermistors are available in a wide variety of sheathed assemblies including air-temperature, surface-temperature, veterinary and hypodermic probes.

6.8.2 Copper and nickel resistance thermometers

Platinum is not the only metal used for resistance thermometry, although it is the most widely used. Other metals include copper, nickel and nickel–iron, as well as the rhodium–iron thermometer.

The main attraction of copper resistance thermometers is their very high linearity, within $0.1\,°C$ over ranges less than $200\,°C$. The disadvantages are their low resistance, typically $10\,\Omega$ at $25\,°C$, and their susceptibility to corrosion. Typical operating ranges are from $-80\,°C$ to $260\,°C$. The temperature coefficient, $\alpha = 4.27 \times 10^{-3}\,°C^{-1}$, is marginally higher than that for platinum.

Nickel resistance thermometers are chosen principally for their low cost and high sensitivity. They are also subject to greater standardisation than copper thermometers. The DIN 43 760 standard defines a nickel thermometer for the range $-60\,°C$ to $180\,°C$ with a resistance–temperature relationship similar to the CVD equation (Equation (6.46)), although C is differently defined:

$$R(t) = R_0 \left(1 + At + Bt^2 + Ct^4\right), \tag{6.55}$$

where $R_0 = 100\,\Omega$, $A = 5.450 \times 10^{-3}\,°C^{-1}$, $B = 6.65 \times 10^{-6}\,°C^{-2}$, $C = 2.605 \times 10^{-11}\,°C^{-4}$.

The α value for nickel is $6.18 \times 10^{-3}\,°C^{-1}$, nearly twice that of platinum. The non-linearity of nickel thermometers is about three times that of platinum.

Nickel–iron resistance thermometers are used for their high sensitivity and resistance, in air-conditioning systems, for example. A typical nickel–iron thermometer has a resistance of $100\,\Omega$ at $21.1\,°C(70\,°F)$, and an α value marginally less than that of nickel. They have a useful temperature range of $-20\,°C$ to $150\,°C$.

6.8.3 Rhodium–iron thermometer

The rhodium–iron resistance thermometer is the most stable and reliable cryogenic thermometer. It is constructed, similarly to the platinum capsule thermometer (Figure 3.12), from rhodium wire doped with 0.5% of iron to give a resistance between $20\,\Omega$ and $50\,\Omega$ at $0\,°C$. The rhodium–iron thermometer is preferred over the range $0.5\,K$ to $30\,K$ where it has a greater sensitivity than PRTs. While it is still useful up to room temperature, the platinum thermometer gives superior performance. A suitable calibration equation is of the form

$$R(T) = \sum_{i=0}^{n} b_i \left[\ln(T + g)\right]^i, \tag{6.56}$$

where the b_i are to be determined and g is a constant between $0\,K$ and $10\,K$. With $n = 6$ the equation fits to within about $0.3\,mK$. Thin-film versions of these thermometers are now available.
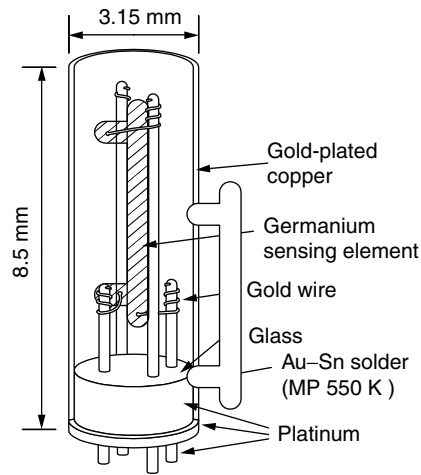
Figure 6.19 Example of one type of construction for a germanium thermometer. The germanium is in the form of a bridge, with current contacts on the ends and potential contacts on side arms

6.8.4 Germanium resistance thermometer

Germanium thermometers are semiconductor thermometers that may be used at cryogenic temperatures where very high sensitivity is required. The thermometer is generally constructed as a single crystal of germanium with 'n' or 'p' doping, and four leads are attached in a can filled with ^{4}He or ^{3}He gas (see Figure 6.19). Individual germanium thermometers can exhibit good stability but should be selected as some instabilities arise from thermal cycling or from sources that are unknown. A variety of types are available and are best used for narrow temperature ranges below 30 K. They are very non-linear and a suitable calibration equation is of the form

$$\ln(T) = \sum_{i=0}^{n} A_i \left\{ [\ln(R) - M] / N \right\}^i \, , \tag{6.57}$$

where N and M are suitable constants and the A_i are to be determined by least-squares fitting, thus requiring $3n$ calibration points; n is about 12 for a wide temperature range and 5 for a narrow range. As with all resistance thermometers, self-heating errors occur. Because the resistance can be very high there are also leakage resistance problems, and the a.c. and d.c. resistances are different.

Further Reading

Standard platinum resistance thermometry

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Resistance measurement

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Low Level Measurements Handbook, Keithley Instruments, Inc. cleveland,O H.

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7

Liquid-in-glass Thermometry

7.1 Introduction

Liquid-in-glass thermometers were one of the earliest types of thermometer developed. Because their use has dominated thermometry for at least 200 years, they have had a profound effect on the development of thermometry practice and philosophy, and in popular opinion they are the only 'real' thermometers. Liquid-in-glass thermometers have been developed to fill nearly every niche in temperature measurement from $-190\,°C$ to $600\,°C$, including the measurement of temperature differences to a millikelvin. In spite of the fragile nature of glass and the toxicity of mercury, the popularity of the thermometers continues, largely because of the chemical stability of glass, the apparent ease of use, and the self-contained nature of the thermometer.

The trend is, however, to move away from liquid-in-glass thermometers. Platinum resistance thermometry gives superior performance at lower overall cost, and is readily accessible with easy-to-use electronic resistance bridges and high-quality probes available commercially. Even at the low end of the market, simple battery-operated thermometers now replace many liquid-in-glass thermometers; they have a similar convenience in use, without the disadvantages of glass or mercury. However, liquid-in-glass thermometers are still specified in many documentary standards for test procedures, and they still represent a cost-effective solution in a few situations where measurements are made over a narrow temperature range.

In this chapter we first examine the construction of liquid-in-glass thermometers and show they are not as simple as they first appear. The multi-purpose nature of the glass as container and sensor, the liquid as sensor and indicator, and the scale as lineariser and indicator, means several aspects of the performance of the thermometers are compromised. Quite a number of sources of error need to be taken into account in order to achieve high accuracies, and this is reflected in the more complex procedures for both the use and calibration of liquid-in-glass thermometers.

We focus our attention on solid-stem mercury-in-glass thermometers, since they are the most common and amongst the most reliable. Additional advice is given on enclosed-scale thermometers, since they are more common in some parts of the world, and on thermometers employing organic liquids, which may be required for some low-temperature applications.

7.2 Construction of Liquid-in-glass Thermometers

7.2.1   Solid-stem thermometers

Figure 7.1 illustrates the various parts of a solid-stem liquid-in-glass thermometer. Four of the parts are common to every thermometer: the bulb, the capillary, the thermometric liquid and the scale. Very simply, the operation of liquid-in-glass thermometers is based on the expansion of the liquid with temperature. As the temperature of the liquid in the bulb increases, the liquid expands and is forced up the capillary. The temperature is indicated by the position of the top of the liquid column against the marked scale. Figure 7.1 identifies the various parts of solid-stem thermometers while typical examples of solid-stem thermometers are illustrated in Figure 7.2.

The various thermometric fluids commonly used in liquid-in-glass thermometers are listed in Table 7.1. Mercury is the least sensitive of the liquids but the most linear. Unlike other thermometers, which have a separate sensor and indicator, liquid-in-glass thermometers use the temperature sensor as the indicator. This feature compromises the immersion conditions of the sensor, and in some situations necessitates 'stem corrections' to account for the poor immersion.

Most of the organic fluids used for liquid-in-glass thermometers are transparent, so they make the thermometer difficult to read. Often a coloured dye is used to make the liquid column more visible. One fluid not shown explicitly in Table 7.1 is mercury–thallium alloy. Mercury freezes at about $-38\,°C$, limiting the utility of mercury-filled thermometers at low-temperatures. However, the alloy of mercury with 8.6% thallium has a freezing point at about $-60\,°C$, so it is occasionally used in low-temperature thermometers. They are more accurate and easier to use than those with
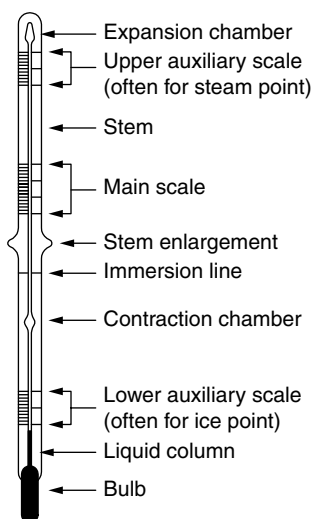
Figure 7.1   The main features of a solid-stem liquid-in-glass thermometer. The thermometer may have an enlargement in the stem or an attachment at the end of the stem to assist in the positioning of the thermometer
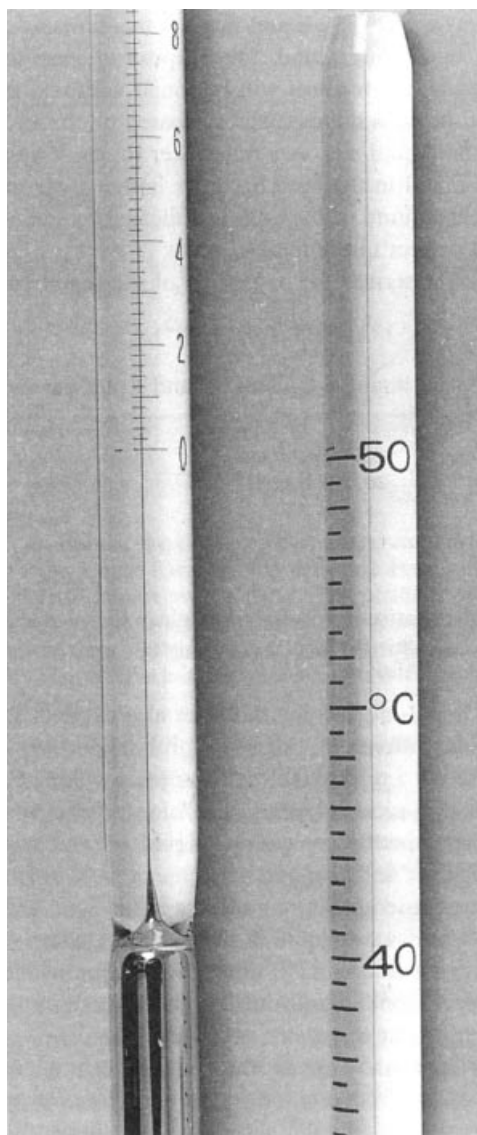
Figure 7.2 Pointing marks are usually scratched at both ends of a thermometer's stem to locate the scale. The proximity of the scale to the pointing marks is a good indicator of the quality of a thermometer. In a good-quality thermometer (left), the 0 °C pointing mark is immediately alongside the corresponding scale mark. In a general-purpose thermometer (right), the 50 °C pointing mark is about one-quarter of a scale division above the scale mark

organic fluids, but thallium is highly toxic, far more so than mercury, and appropriate safety precautions should be taken when these thermometers are used.

The volumetric thermal expansion of the mercury is well known since it is used as a density standard:

$$V = V_0 \left(1 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4\right), \qquad (7.1)$$

Table 7.1 Working range of some thermometric liquids and their apparent thermal expansion coefficient in thermometer glasses around room temperature

Liquid	Typical apparent expansion coefficient $(°C)^{-1}$	Possible temperature range
Mercury	0.000 16	−35 °C to 510 °C
Ethanol	0.001 04	−80 °C to 60 °C
Pentane	0.001 45	−200 °C to 30 °C
Toluene	0.001 03	−80 °C to 100 °C

where V_0 is the volume of the liquid at $0\,°C$ and the a_i are the coefficients of thermal expansion, with values

$$a_1 = 1.815\,868 \times 10^{-4}\,°C^{-1},$$
$$a_2 = 5.458\,43 \times 10^{-9}\,°C^{-2},$$
$$a_3 = 3.498 \times 10^{-11}\,°C^{-3},$$
$$a_4 = 1.5558 \times 10^{-14}\,°C^{-4}.$$

The expansion is such that there is about 6250 times more fluid in the bulb than each $1\,°C$ interval in the capillary. The high-order terms of Equation (7.1) show that the expansion is also slightly non-linear with temperature.

The bulb is the thin glass envelope containing most of the fluid. Because the indication of the thermometer changes if the volume of the bulb changes the stability of the bulb is paramount. For this reason the glasses used for bulbs are carefully designed and selected, often being different to that used in the stem. Thermometers are always well annealed after manufacture to remove any residual strain in the glass. The volume of the bulb is, however, temperature sensitive having an expansion coefficient about 10% of that of mercury, and unfortunately contributes about 90% of the non-linearity in mercury thermometers.

The capillary transforms the volumetric change of the liquid into a linear change that is interpreted in terms of temperature. It is important that the bore of the capillary has a uniform diameter, and is clean and smooth. In good-quality reference thermometers, the uniformity of the capillary used to make the thermometer is checked beforehand by measuring the length of a small drop of mercury as it is moved up the capillary. Any impediments or dirt within the bore will also cause a discontinuity in the thermometer reading and may cause the mercury column to stick as the temperature changes.

Not all glasses are suitable for thermometric use. Table 7.2 lists some of the glasses approved by the British Standards Institution. Note that several types have colour stripes in the stem to identify them. Most thermometers made in accordance with a documentary standard indicate the make of glass. The bulb glass is not necessarily the same as the stem glass. All glass changes with time and temperature, so glass composition is a major factor in the long-term drift of liquid-in-glass thermometers.

In order to mark the scale on the thermometer the manufacturer first 'points' the thermometer. This involves placing scratch marks on the outside of the capillary tube (see Figure 7.2) at points on the scale corresponding to a number of different temperatures within the thermometer's range. A ruling machine is then used to engrave, etch

Table 7.2 Thermometer glasses

Glass	Identification stripe(s) or approved abbreviation	Normal maximum working temperature (°C)
Normal glass, made by Whitefriars Glass Ltd	Single blue stripe	350
Normal glass, Dial, made by Plowden and Thompson Ltd	Double blue stripe	350
Normal glass, Schott-N16, made by Jenaer Glaswerk Schott and Genossen, Mainz	Single red stripe	350
Normal glass, 7560, made by Corning Glass Co.	CN	350
Corning borosilicate glass, made by Corning Glass Co.	CB	450
Thermometric glass, Schott 2954, made by Jenaer Glaswerk Schott and Genossen, Mainz	Single black stripe	460
Borosilicate glass, made by Whitefriars Glass Ltd	Single white stripe	460
Corning glass, 1720, made by Corning Glass Co.	C1720	600
Schott-Supremax R8409, made by Jenaer Glaswerk Schott and Genossen, Mainz	SPX8409	600

Note: The maximum temperatures given in the last column of the table are a guide to normal practice. The performance of a thermometer depends greatly on the stabilising heat treatment that it has been given during manufacture, and a well-made thermometer of 'normal glass' may be satisfactory for many purposes at temperatures as high as 400 °C. On the other hand, for the best accuracy it may be preferred to use one of the borosilicate glasses for temperatures lower than 350 °C. In general the lower the maximum temperature of use in relation to the approved temperature of the glass the better will be the 'stability of zero' of the thermometer.

or print a scale onto the stem by linearly interpolating (i.e. marking equal subdivisions) between the pointing marks. To overcome the effects of the non-linear expansion of the mercury and glass with wide-range or high-precision thermometers, the scale is often ruled in several segments, with each scale segment in a precision thermometer typically no more than 100 scale divisions long. Figure 7.3 shows an example of a thermometer scale ruled in five segments. This is an example of segmented linearisation as described in Section 5.3.1.

Liquid-in-glass thermometers may also have additional features or parts depending on the purpose for which they are designed. Some have auxiliary scales, commonly at 0 °C and 100 °C, so they can be checked at the ice point and the water boiling point. To accommodate the scales at disparate temperatures while still achieving high resolution without having thermometers metres in length, it is necessary for the thermometers to have contraction chambers between the different scales. The chambers must be smooth to ensure that bubbles are not trapped as the mercury rises.

The main purpose of the expansion chamber at the top of the thermometer is not to allow the mercury to expand, but to prevent the build-up of pressure in those thermometers that are gas filled. A visual inspection of the back of the thermometer will show whether the thermometer is gas filled or vacuous (sometimes referred to as 'vacuum filled'). Especially in high-temperature thermometers, the gas is a short-term
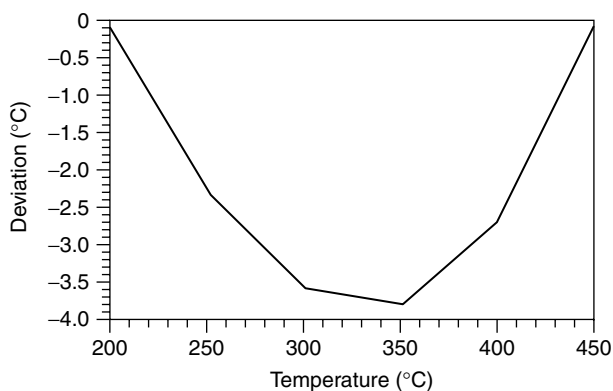
Figure 7.3   The deviations of markings on a high-temperature thermometer scale from length linearity. The scale has been ruled in five segments to approximate a curve. The positions of the scale markings were measured with an automatic laser length-bench as if the thermometer was a ruler. The length of the scale and deviations from linearity have been expressed in equivalent temperatures

measure (i.e. only effective for minutes) to stop the mercury from evaporating from the column, diffusing to the top of the thermometer, and condensing. The pressure of the gas must be greater than the vapour pressure of the mercury at the highest temperature to prevent the mercury from boiling, so very high-temperature thermometers must withstand internal pressures as high as several atmospheres.

Also visible on the thermometer is an indication of the immersion condition. This may be written as total immersion, partial immersion (often 75 mm, 100 mm or 175 mm) or there may simply be a ring around the stem at the appropriate immersion depth. We discuss immersion conditions in detail in Section 7.3.9.

The construction of most liquid-in-glass thermometers is covered by documentary standards published by several organisations. The ISO standards do not appear to be greatly followed, but many thermometers are manufactured and used according to the specifications of the British Standards Institution (BSI), the American Society for Testing and Materials (ASTM), or the Institute of Petroleum (IP). Some of the documentary standards are given in the references at the end of the chapter.

7.2.2   Enclosed-scale thermometers

In a solid-stem thermometer, the capillary is very thick, and serves the additional purposes of supporting the scale and being the main structural member of the thermometer. In an enclosed-scale thermometer (see Figure 7.4) the capillary serves no other purpose than to indicate the change in volume of the liquid. The other purposes are satisfied by two separate structures. The scale is marked on a flat strip of opaque glass that lies behind the capillary, and the whole assembly is contained within a larger glass tube.

The separation of the scale from the capillary in enclosed-scale thermometers makes slightly different compromises in performance from solid-stem thermometers. The main advantage of enclosed-scale thermometers is that the parallax errors can be, depending

Figure 7.4   The top of an enclosed-scale thermometer showing the capillary, scale with pointing marks, and the end stop for the scale

on the design, much reduced. On the negative side, they are slightly more fragile, there is the possibility that the scale separates from the capillary, and the time constant to warm the mercury in the enclosed part of the column is longer. The mounting of the capillary against the scale is usually the biggest problem with quite a number of different devices used including wire ties, glue, and glass end stops fixed to the capillary, with the last being the most satisfactory. Overall, there seems to be very little difference in performance between the enclosed-scale and solid-stem thermometers.

7.3 Errors in Liquid-in-glass Thermometry

The apparent simplicity and ease of use of liquid-in-glass thermometers belies the fact that they are extraordinarily difficult to use well. The use of the thermometric fluid as both sensor and indicator compromises the performance, as does the involvement of a human in the reading. Figure 7.5 summarises all the most significant sources of uncertainty in the use of liquid-in-glass thermometers.

7.3.1   Time constant effects

Time constant and thermal lag errors for thermometers are discussed in Sections 4.4.3 and 4.4.4. For a mercury-in-glass thermometer, the time constant is determined almost entirely by the diameter of the bulb since heat must be conducted from its outside to its centre. Commonly the bulb has a small diameter compared with its length to help keep the time constant short.

Table 7.3 gives the $1/e$ time constants in various media for a 5 mm diameter bulb. Time constants for other diameters can be estimated by scaling the time in proportion to the diameter. The table clearly indicates that the thermometer is best used with flowing or stirred liquids.
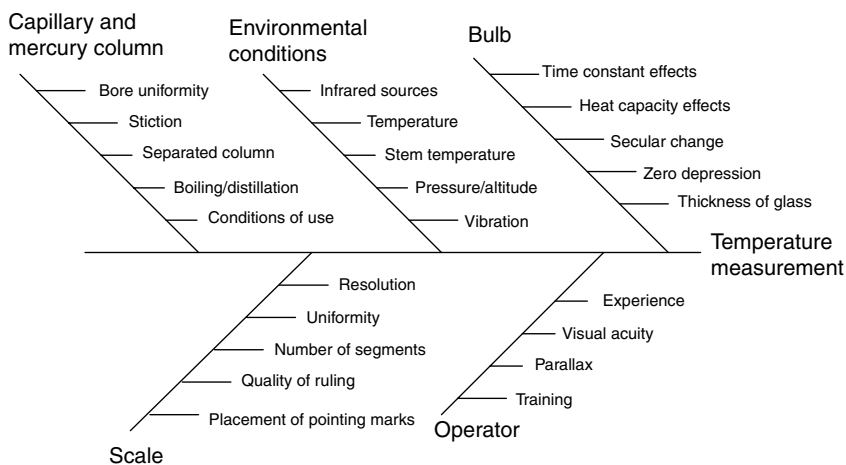
Figure 7.5   A cause and effect diagram for liquid-in glass-thermometers

Table 7.3 Time constants for a mercury-in-glass thermometer with a 5 mm diameter bulb

Medium	Still	0.5 m s⁻¹ flow	Infinite flow velocity
Water	10 s	2.4 s	2.2 s
Oil	40 s	4.8 s	2.2 s
Air	190 s	71 s	2.2 s

Lag effects are potentially a problem during calibration for the rising-temperature calibration method (see Sections 5.5.3 and 4.4.4) if the reference thermometer and the thermometer under calibration have different diameters.

7.3.2 Heat capacity effects

Glass thermometers are bulkier and have a larger thermal mass than other thermometers so heat capacity effects are worse than in other thermometers. They are also more likely to be used in situations where the temperature is not controlled; for example, to measure the temperature of small vessels, which can also lead to large static errors rather than transient errors from which the system will recover, given time. Pre-heating the thermometer can alleviate the worst of the problems, but it is generally better to choose an alternative type of thermometer with a smaller thermal mass, such as a thermistor (see Section 6.8.1).

Simple estimates of the heat requirements are made by measuring the volume of thermometer immersed, and assuming 2 J are required to raise 1 cm^3 of the thermometer volume (glass or mercury) by 1 °C. Section 4.4.2 covers methods for estimating the heat capacity error.

7.3.3 Pressure effects

The volume of the bulb is very sensitive to pressure because the envelope is so thin. The typical pressure coefficient for a liquid-in-glass thermometer is about 0.1 °C per atmosphere. There are at least four possible sources of pressure that may affect performance in use.

One atmosphere of pressure corresponds to a 760 mm high column of mercury; thus the column of mercury itself is one source of pressure. Thermometers are usually calibrated in the vertical position so measurements made in the horizontal plane can be in error by several hundredths of a degree. Figure 7.6 shows an example of the change in reading with orientation for a large high-precision thermometer.

In high-precision thermometers, particularly those near room temperature, the bulbs are very thin making them sensitive to quite small pressure variations. Pressure fluctuations associated with turbulence in a stirred bath are often visible, as are ice-point shifts due to large changes in altitude.

Pressure variations may also be due to external mechanical forces, such as caused by resting the thermometer on its bulb or immersion at high pressures. In fact, this can give rise to long-term problems if mechanical stress is introduced into the bulb. This becomes evident from inexplicable increases in the standard deviations from

(a)

(b)
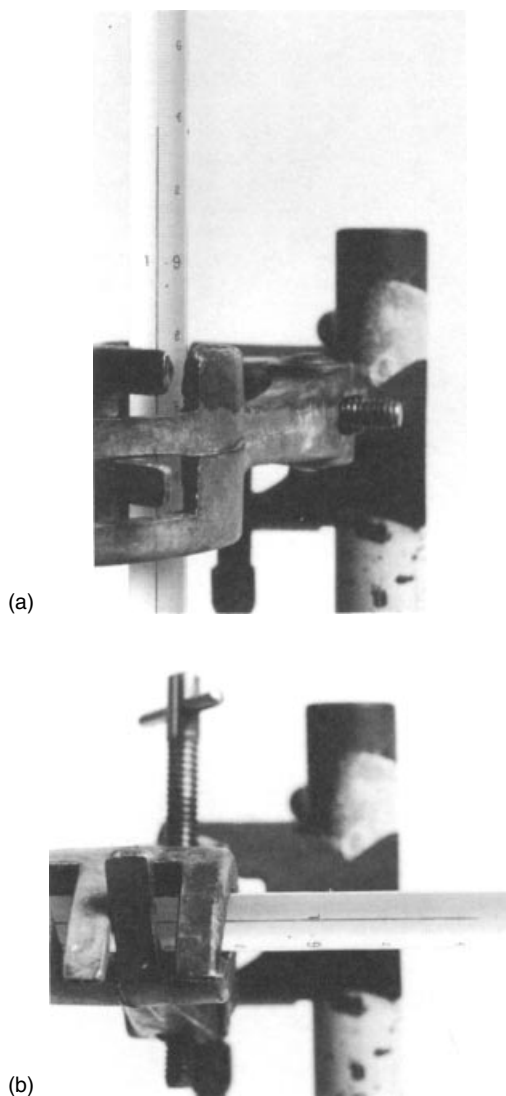
Figure 7.6 The pressure effect of the mercury column can be quite large for a long thermometer. Shown here is a bomb calorimeter thermometer with a mercury column about 400 mm long. The vertical reading at the top (as usual in calibration and use) is $19.374\,^{\circ}\mathrm{C}$. The horizontal reading (bottom) is $19.451\,^{\circ}\mathrm{C}$. The difference of $0.077\,^{\circ}\mathrm{C}$ is mostly due to the internal pressure change in the bulb

calibrations or erratic shifts in the ice-point record. For this reason, thermometer stems and not the bulbs should be used to support liquid-in-glass thermometers. Because thermometers appear to be ideal stirring rods, some lower-quality thermometers are made with thick bulbs to allow their use as stirring rods, but stirring should not be done with a precision thermometer. Points of stress in the bulb can be detected by inspecting the glass under polarised light.

The fourth pressure source is within the thermometer itself, and is due to the pressure of the gas in the capillary above the mercury column. Mercury boils at approximately 356 °C, so thermometers used at high temperature may be subjected to high internal pressures as the vapour pressure of the mercury increases exponentially with temperature. For this reason, the tops of mercury thermometers should be kept cool to keep the filling gas at low pressure. High-temperature thermometers are usually filled with an inert gas, commonly nitrogen, at low pressures to inhibit the diffusion of the mercury vapour. Gas-filled thermometers designed for use at low temperatures can also be subject to high internal pressures if they are overheated and the mercury column is allowed to compress the gas into a small volume at the top of the capillary. Gas-filled thermometers commonly have a large expansion chamber to mitigate this problem.

7.3.4   Bulb hysteresis and drift

A liquid-in-glass thermometer has two moving parts: the thermometric liquid and the glass bulb. The liquid expands and follows temperature changes rapidly, but the glass does not. The non-crystalline nature of glass means that the most stable atomic arrangement of its constituents varies almost continuously with temperature. As a result the bulb volume, and hence the thermometer reading, depends on its thermal history. Since an accuracy of 0.05 °C implies reproducibility in bulb volume of better than 1 part in 100 000, this is one of the major sources of error in liquid-in-glass thermometry. There are two main effects to be considered: bulb contraction with time and hysteresis.

Glass is not crystalline but behaves more like a very viscous liquid, and even the best annealed glass bulb will steadily shrink in volume with time. This volume change is called a *secular change*. Thermometers are sometimes made with an initial ice-point reading just below the zero mark to allow for this rise over the lifetime of the thermometer. Since almost all of the mercury is in the bulb, a contraction of the bulb simply introduces an offset into the scale. Because all readings are affected similarly by the volume change, any change in the ice-point reading after calibration is a measure of the secular change and should be applied as a correction.

When heated, the bulb expands with the temperature, in small part owing to changes in the structure of the glass. As the temperature falls the bulb contracts and the internal structure returns to its low-temperature state. Because the kinetic energy of atoms increases with temperature, the structure of the glass comes to equilibrium more quickly at higher temperatures than at lower temperatures. While much of the recovery from high-temperature exposure occurs over a few days, the effects are often measurable for many weeks or months. Indeed, the recovery from use is one of the factors distinguishing good thermometer glasses from poor. A good glass exhibits a hysteresis effect of no more than 0.1 °C change for each 100 °C rise in temperature, or equivalently about 0.1% hysteresis (which is worse than the worst PRTs).

The hysteresis effect is worst if the thermometer is subject to rapid cooling so the structural change in the glass is 'frozen' in, and can be greatly reduced by cooling the thermometer slowly. Historically, when liquid-in-glass thermometers were used as the main repository for temperature scales, elaborate procedures and storage conditions were required to get the best accuracy. The simplest method of reducing the effects of hysteresis is to use liquid-in-glass thermometers for measuring increasing temperatures

only; that is, immediately after use at a high temperature the calibration will not apply to subsequent lower temperatures. A variety of methods have been developed to help overcome this limitation, for example taking ice points immediately after each reading and adjusting the calibration value according to the shift in the zero. Alternatively, you could use a PRT.

7.3.5   Bore non-uniformity effects

The bore of the capillary must be smooth and uniform, with the cross-sectional area not varying by more than a few per cent for high-precision applications such as with calorimetric thermometers. During production, the bore is checked by introducing a small amount of mercury and measuring the length of the mercury column at various positions along the capillary. Changes in the bore can be recognised by a change in the length of the column. After manufacture thermometer bore errors cannot be assessed so directly and instead possible errors are controlled by visual inspection. If irregularities in the bore smoothness or uniformity, such as in Figure 7.7, are noticeable then the thermometer should be discarded.

Where an expansion or contraction chamber is added, it must be sufficiently distant from the scale to ensure that the bore is uniform over the scale region. Expansion chambers are safety devices to prevent permanent damage occurring if the thermometer is accidentally overheated. Contraction chambers, on the other hand, transmit the signal to allow a shorter length for high-temperature thermometers. They must be well shaped to avoid breaks or bubbles occurring in the liquid column. In use, the contraction chamber must be at the same temperature as the bulb.

7.3.6   Stiction

The choice of the bore diameter is a compromise involving several effects. A larger-diameter bore requires a larger-volume bulb to achieve a given resolution, thus increasing the thermal capacity. A small-diameter bore not only becomes difficult to read but also suffers from *stiction*, the mercury moving in fits and starts due to the surface tension between the mercury and the bore wall. Thermometers with large thin-walled bulbs are more susceptible because the bulb will accommodate larger-volume changes before the internal pressure forces the mercury to move. Stiction can be reduced substantially by tapping the thermometer lightly before it is read. Small-bore diameters also cause the mercury column to break readily and to be difficult to rejoin (see Section 7.3.7).

7.3.7   Separated columns

A common problem is for a part of the thermometric liquid in the capillary to become separated from the main volume in the bulb. While this can be recognised as an ice-point shift it is still important to make a simple visual check when using the thermometer at other temperatures.

With organic liquids, the problem is harder to identify because liquid adheres to the surface of the capillary and may not be visible. Spirit thermometers must be held
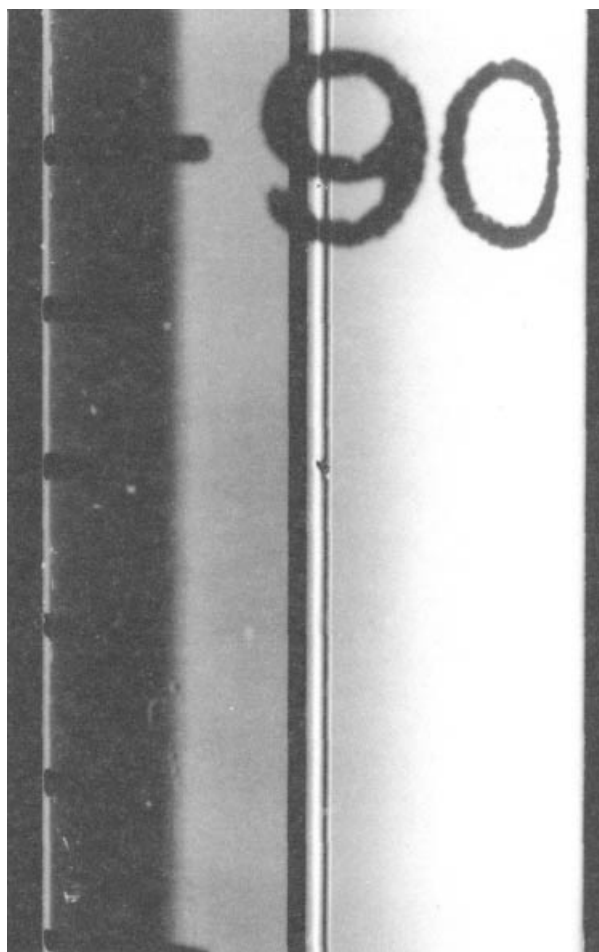
Figure 7.7 Capillary distortion in an inexpensive thermometer. A small piece of foreign material appears to be embedded into the glass. To locate such faults requires careful visual examination

vertically to allow the thermometric liquid to drain. Allow approximately 3 minutes per centimetre that the column falls. Spirit thermometers should be stored with the top of the thermometer warmer than the bottom to prevent condensation of any vapour in the expansion chamber.

With mercury thermometers, the separation is usually visible. Two causes can be identified: boil-off (Figure 7.8) and mechanical separation (Figure 7.9).

To help retard the evaporation of mercury vapour at high temperatures (e.g. above 150 °C) the capillary is filled with an inert gas, often nitrogen. The gas is inert to prevent the oxidation of the mercury, which can lead to deposits within the capillary and large errors due to stiction.

Mechanical separation of the liquid column is, unfortunately, a common occurrence, particularly during shipment. A gas filling helps prevent this separation but, conversely,
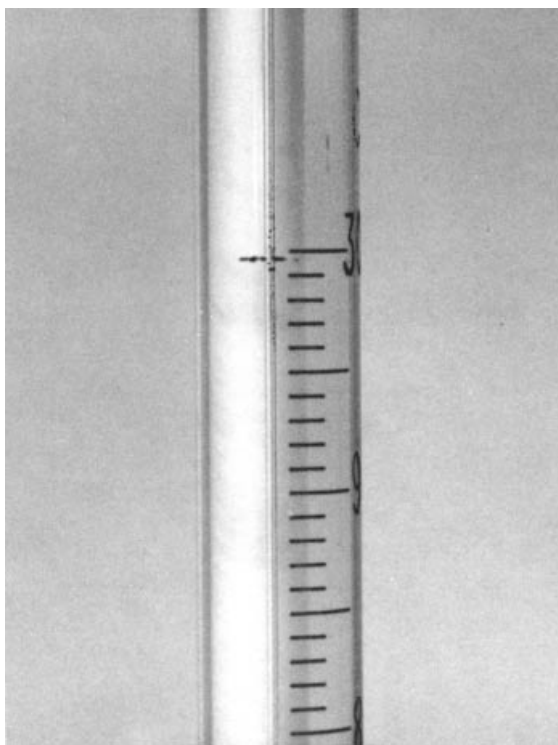
Figure 7.8   A 300 °C thermometer showing small globules of mercury in the bore around the 300 °C mark. These have evaporated off the mercury column at 250 °C and condensed up the capillary tube; this is a common problem with high-temperature thermometers. Note too that the pointing mark at 300 °C is one-third of a scale division lower than the 300 °C mark

the gas makes the column more difficult to rejoin. There is also a risk of trapped gas bubbles forming in the bulb or chambers and careful inspection is needed to locate them. Evacuated capillary tubes tend to result in more breaks but they are easily rejoined.

With care, it is quite practical to rejoin the column and still have a viable thermometer. However, it must be realised that attempts to join a broken column could also result in the thermometer needing to be discarded if the procedure is not successful. Breaks that occur only when the thermometer is heated often indicate that the thermometer should be discarded.

The procedures given below for joining a broken mercury column are given in order of preference.

- Lightly tap the thermometer while holding it vertically. This may work for a vacuous thermometer.
- Apply centrifugal force, but avoid a flicking action, and be careful to avoid striking anything. This is best done by holding the thermometer parallel to the arm with the bulb alongside the thumb protected by the fingers, and with the stem along the arm. Raise the arm above the head and bring it down quickly alongside the leg.
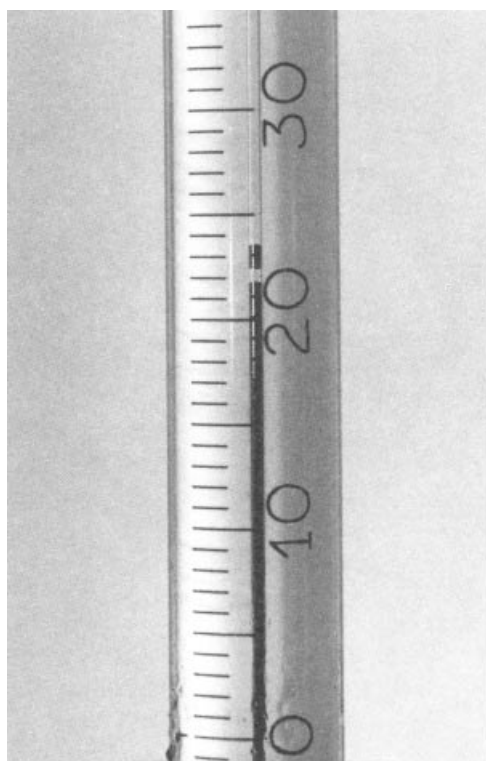
Figure 7.9   A typical break in the mercury column of a thermometer

- If both of the above methods are unsuccessful, a cooling method can be tried. This method requires sufficient cooling of the bulb for all the mercury to contract into the bulb or contraction chamber, leaving none in the stem. Tapping or centrifugal action may be applied to assist movement of the mercury. The column should then be rejoined when it has warmed to room temperature. Carry out the warming slowly so that all the mercury is at the same temperature and no bubbles are trapped in the bulb. More than one attempt may be needed. There are three readily available refrigerants that can be used: a mixture of salt, ice and water (to $-18\,°C$), 'dry ice', that is solid CO_2 ($-78\,°C$), and liquid nitrogen ($-196\,°C$). Dry ice and liquid nitrogen require more care as they will freeze mercury, can cause high levels of thermal stress in the glass, and will cause cold burns on human skin.

- A more drastic method of rejoining is to apply heat to the bulb and allow the rejoining to occur in the expansion chamber at the top of the thermometer. This method should be one of last resort. Of all the methods, it is the one most likely to damage a thermometer and render it useless. The great risk of damage arises because of the high internal pressures with the high vapour pressure of mercury and the compression of any gas fill. This will stress the bulb making it unstable, or in the worst case, burst the bulb. Do not use it on high-temperature thermometers in case the bulb breaks releasing mercury vapour. Much care is needed to avoid overheating, so a temperature-controlled bath should be used.

If the broken column has been successfully rejoined, then an ice-point check or a verification with a second thermometer should be made. If the reading is the same as obtained previously, then the join can be considered completely successful and the thermometer ready for use. However, a significant ice-point shift indicates that the join was not successful and the thermometer should be discarded. If a small ice-point shift has occurred then treat the thermometer with suspicion until there is evidence of long-term stability, that is no further significant ice-point changes after use.

7.3.8   Errors in reading

Liquid-in-glass thermometers have an analogue display that requires some care in reading. The indication of the temperature is provided by the flat portion of the meniscus. That is, for mercury thermometers, which have a convex meniscus, the reading is taken at the top of the meniscus. For spirit thermometers, which have a concave meniscus, the reading is taken at the bottom of the meniscus.

Parallax errors, due to the apparent displacement of the meniscus and scale when the position of the eye is changed, are the main problem with reading. For a solid-stem thermometer, with the scale located 2 mm to 4 mm in front of the meniscus, parallax errors of more than one scale division are possible. To avoid the error the eye should always be at right angles to the scale. The most convenient way to do this is to keep the thermometer vertical and use a horizontally mounted telescope. The telescope is also an optical aid to reading the scale and to interpolate between scale marks. It should have magnification in the range $5\times$ to $10\times$.

There are two disadvantages with the use of telescopes. Although a little counter-intuitive, optical magnification with a large-aperture lens increases the parallax effect. Placing a horizontal slot in front of the telescope will help reduce the parallax error (see Figure 7.10). Secondly, the small field of view in a telescope means that it can be difficult to identify correctly the position on the scale of the thermometer — for example, whether the 2 mark corresponds to 22 °C or 32 °C.

Many general-purpose thermometers have coarse markings and variable bores so there is often little benefit from interpolating between scale markings; instead estimates to half a scale division are more appropriate. This is often the best policy for the general user, so if readings to 0.1 °C are needed, then a thermometer divided to 0.1 °C or 0.2 °C should be used.

For precision thermometers, such as those used for calibration, the scale markings are fine and the bore is uniform (see Figure 7.11), so interpolating readings between scale divisions usually gives an improvement in accuracy. Estimates to one-twentieth of a scale division can be made repeatably with practice, although the accuracy will not be as great as this. The limiting factors are due to perceptual difficulties that even skilled observers cannot overcome entirely. The human eye does some unconscious image processing that makes it very sensitive to boundaries and edges in a scene. Consequently, there is a very strong tendency to interpolate between the edges of the scale markings rather than the centres (see Figure 7.12). Secondly, most people have a subconscious tendency to select some digits and avoid others. In the authors' experience, a 95% level of confidence of about one-fifth of a scale division is readily achieved with a little practice.

Figure 7.10   A simple monocular telescope with a close-up lens being used to read the ice point on a mercury-in-glass thermometer. The telescope is on a heavy stand to free the user's hands, and its height is set on the same level as the top of the mercury to avoid parallax errors. The distance is about an arm's length, allowing the user to adjust the thermometer for position, clear any fogging or obstacle away from the scale and to be able to tap the thermometer just before the reading is made

7.3.9   Immersion errors

We have already mentioned that problems are expected if the liquid in the stem of a liquid-in-glass thermometer is not at the same temperature as the bulb. Yet, this must happen in practice because the scale has to be read visually. In addition, some liquid in
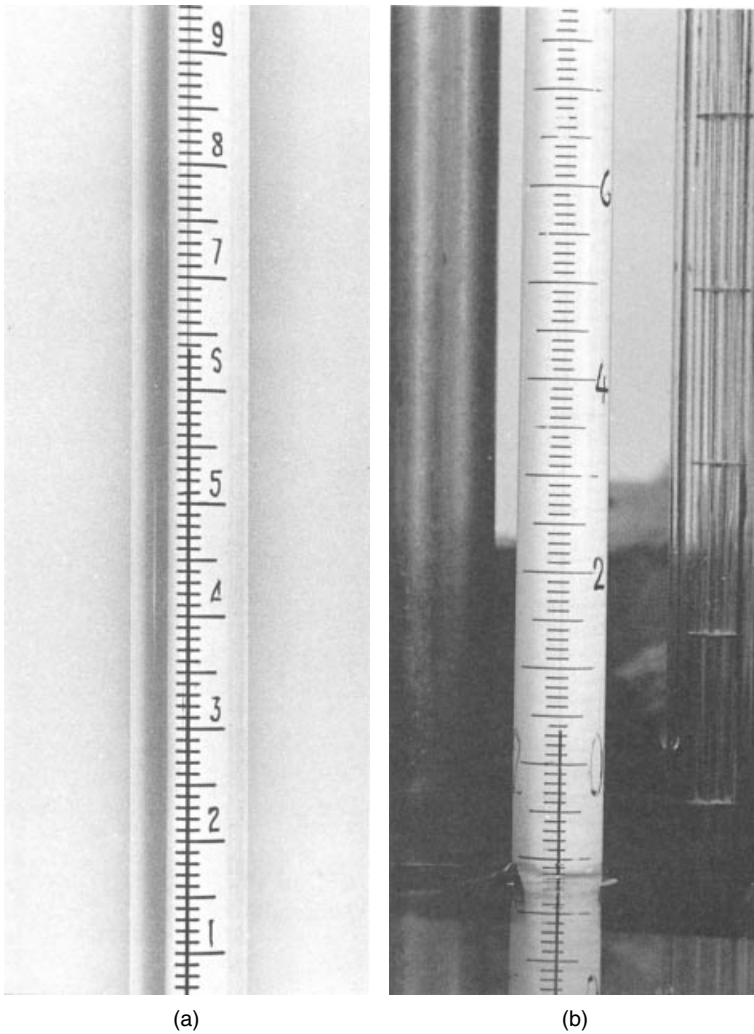
Figure 7.11   The difference in quality between two thermometers marked to 0.1 °C. Both were purchased to allow readings to be interpolated to a few hundredths of a degree. Note that on both thermometers the numbers are not complete; for example, the 2 displayed in the photograph on the right corresponds to 22 °C. On the thermometer on the left the markings are thick (about one-fifth of a scale division) and uneven. The 25.1 °C marking is on a slope and is an indicator that the thermometer is not suitable for the purpose it was bought. A second indicator is that some of the numbers are not well formed; there appear to be two 5 s and no 6. On the thermometer on the right the markings are fine (one-tenth of a scale division) and appear even

glass thermometers are used at fixed immersion depths, which also results in different parts of the thermometric liquid being at different temperatures.

Three distinct immersion conditions are recognised for liquid-in-glass thermometers and each requires a different error treatment. Figure 7.13 illustrates the three conditions.
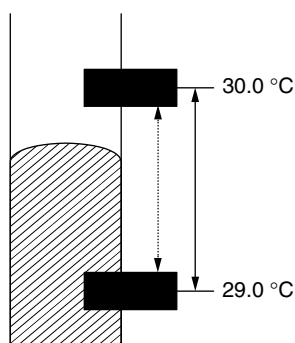
Figure 7.12   Diagram of a mercury meniscus in a bore and the scale markings. The tendency is for an observer to subdivide the interval between the inside edges of the scale markings (the dotted line). The interval should be divided between the centres of the marks (solid line). In this instance, the first method would give 29.9 °C whereas the correct method gives 29.8 °C
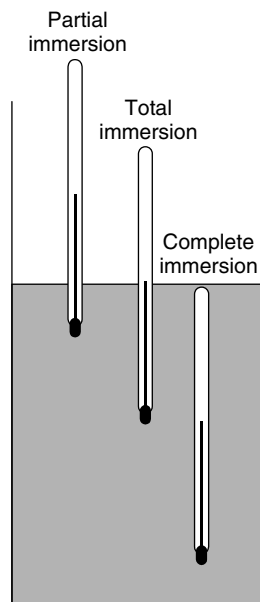
Figure 7.13   The three immersion conditions used for liquid-in-glass thermometers. The preferred immersion condition is often determined by the application, and for partial-immersion thermometers is usually marked as a line or distance on the stem

Complete immersion

If the bulb and the entire stem are immersed at the same temperature, the thermometer is said to be completely immersed. Thermometers designed for complete immersion are rare. The pressure build-up in the thermometer may cause it to rupture spreading deadly mercury vapour throughout the laboratory. In particular, **DO NOT** put mercury thermometers completely inside drying ovens to measure the temperature. Special calibration procedures are also needed to handle pressure changes.

Total immersion

Total immersion applies to the situation where all the thermometric liquid, that is all the mercury in the bulb, any contraction chambers and the stem, is at the temperature of interest. The remaining portion of the stem is not immersed and so will have a temperature gradient to room temperature (approximately). The expansion chamber should be kept close to room temperature, especially at high temperatures. A very small part of the mercury column may be outside the region of interest, to allow visual readings to be made. At very high temperatures, the error introduced by this might be significant and can be estimated by the procedures given below for partial-immersion thermometers. Obviously, the thermometer must be able to be moved if a range of temperatures is to be measured. Total-immersion thermometers are generally calibrated at total immersion and therefore do not need additional corrections.

Partial immersion

One way around the problem of scale visibility and the need to move the thermometer is to immerse the thermometer to some fixed depth so that most, but not all, of the mercury is at the temperature of interest. The part of the mercury column not immersed is referred to as the *emergent column*, and the average temperature of the emergent column is called the *stem temperature*. Corrections must be made to compensate for the error arising from the emergent column not being at the same temperature as the bulb. Many thermometers are designed and calibrated for partial immersion and are marked accordingly with an immersion depth or an immersion line.

A partial-immersion thermometer is not properly defined unless the temperature profile of the emergent column is also specified. The thermometer specifications may define the expected stem temperature for a set of test temperatures but they do not usually define stem temperatures for all possible readings. For this reason, partial-immersion thermometers are exclusively used as working thermometers, and should only be used in tests that specify their use. Many ASTM and IP thermometers are of this nature.

Occasionally in use, and always during calibration, it is necessary to determine the stem temperature. The traditional way to measure the stem temperature is with a *Faden thermometer*. These are mercury-in-glass thermometers with very long bulbs, and come in sets with various bulb lengths. In use, the bulb of the Faden thermometer is mounted alongside the emergent column of the partial-immersion thermometer with the bottom of the bulb just in the fluid. The average stem temperature is obtained as indicated by the Faden thermometer. Other ways of measuring the stem temperature are to use thermocouples along the length of the thermometer or even several small mercury-in-glass thermometers. The stem temperature is calculated as a simple average, but strictly it should be a length-weighted average.

When the measured stem temperature is not the same as that given on the calibration certificate it is necessary to make a correction for the difference. For partial-immersion thermometers the true temperature reading, t, is given by

$$t = t_i + N(t_2 - t_1)\kappa, \tag{7.2}$$

where:
t_i is the indicated temperature;

N is the length of the emergent column expressed in degrees, as determined by the thermometer's scale;

t_2 is the mean temperature of the emergent column when calibrated (i.e. the stem temperature on a certificate for partial immersion or the thermometer reading for a total-immersion certificate);

t_1 is the mean temperature of the emergent column in use;

κ is the coefficient of expansion of the thermometric liquid used, in the glass of which the thermometer stem is made (see Table 7.1 for suitable values to use for normal temperature ranges).

The use of Equation (7.2) with typical κ values from Table 7.1 is estimated to give a correction with an uncertainty of about 10% (95% level of confidence). The correction is a major source of uncertainty for large temperature differences.

Figure 7.14 is a chart derived from Equation (7.2) that enables the stem correction for mercury thermometers to be determined graphically. You should become familiar enough with the chart to make quick estimates in order to determine whether the immersion error is significant and therefore requires correction.

Using the stem-temperature correction chart

Total-immersion thermometer used in partial immersion   Measure the total length of the emergent column in degrees Celsius. If part of the stem is unmarked, its length in degrees is estimated by comparison with the divided scale. From the length of the emergent column at the top or bottom of the chart, follow a line vertically until it reaches the diagonal line corresponding to the difference between the thermometer reading and the mean temperature of the emergent column. The height of this intersection, measured on the vertical scale, gives the correction to be applied. It is positive when the stem temperature is lower than the thermometer reading and negative when it is higher.

> **Example 7.1   Stem correction for total-immersion thermometer used in partial immersion**
>
> A high-temperature total-immersion thermometer is used in partial immersion to measure the temperature of an oil bath. The reading is $375.0\,°C$ after applying certificate corrections and allowing for any ice-point shift. The mean temperature of the emergent column is $75\,°C$ and the length of the emergent column is $150\,°C$.
>
> *Using Equation (7.2)*
>
> $$t = 375.0 + 150 \times (375 - 75) \times 1.6 \times 10^{-4}\,°C$$
>
> $$= 375.0 + 7.2\,°C$$
>
> $$= 382.2\,°C.$$
>
> This is the temperature that the thermometer would indicate if it were used in total immersion.

Using the chart (Figure 7.14)   Find the vertical line corresponding to an emergent-column length of 150 °C. Move up the line until it intersects with the angled line corresponding to the 300 °C temperature difference (375 − 75 °C = 300 °C). Now move horizontally from the intercept to the vertical scale and read the correction to be close to 7 °C. Since the mercury in the column is cooler than it was in calibration, the thermometer will be reading low. Hence 7 °C must be added to the reading.

Change in stem temperature of a partial-immersion thermometer   When a partial-immersion thermometer is used at the immersion for which it has been calibrated, but with a different stem temperature, follow the same procedure as above, but in evaluating the temperature difference use the stem temperature given on the calibration certificate instead of the thermometer reading.

Example 7.2   Stem correction for partial-immersion thermometer

A partial-immersion thermometer indicates a temperature of 375 °C after the certificate corrections have been applied. In calibration the stem temperature was 70 °C and in use it is 85 °C. The emergent column length is 150 °C.

Using Equation (7.2)

$$t = 375.0 + 150 \times (70 - 85) \times 1.6 \times 10^{-4} \,°C$$

$$= 375.0 - 0.36 \,°C$$

$$= 374.6 \,°C.$$

Using the chart (Figure 7.14)   Find the vertical line corresponding to 150 °C emergent-column length. Move up the line until it intersects the 15 °C temperature-difference line. Now move horizontally to read 0.36 °C off the horizontal scale. Since the stem of the thermometer is hotter in use than it was in calibration, the thermometer reading is high. Hence the correction is −0.36 °C.

It is instructive to compare the results of Examples 7.1 and 7.2. The stem correction for the total-immersion thermometer used in partial immersion is about 20 times that for the partial-immersion thermometer. It is important that thermometers are used in immersion conditions as close as possible to their calibration conditions so that the stem corrections and the accompanying ∼10% uncertainty are kept small. Example 2.18 in Section 2.9 discusses the uncertainty in stem corrections.

Change in both temperature and length of emergent column   To convert from one condition of partial immersion to another, when both the lengths and temperatures of the emergent columns are different, it is best to find the correction to total immersion for each condition. The difference between the two corrections then gives the correction to apply to convert from one condition of partial immersion to the other.
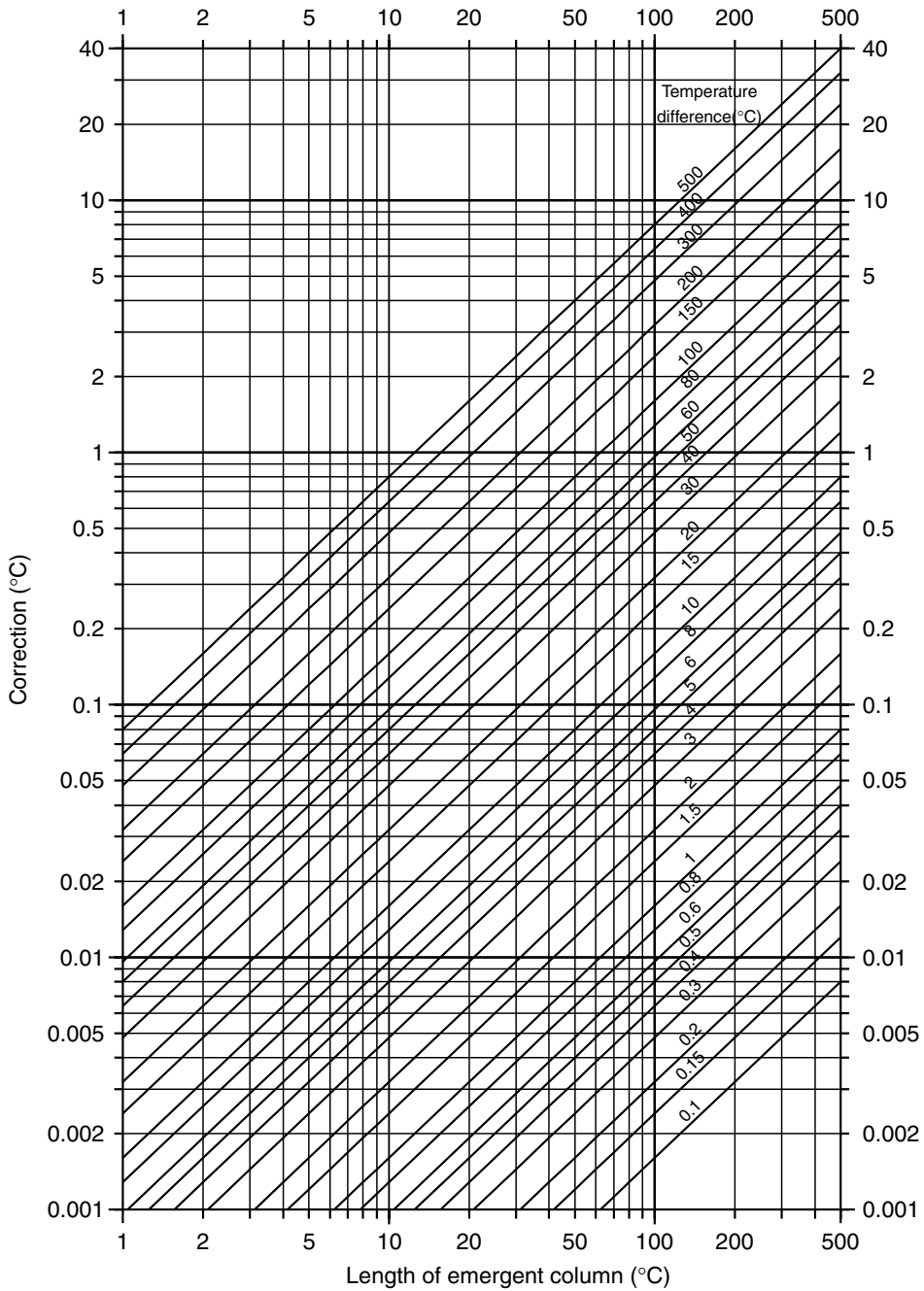
Figure 7.14   Chart of stem exposure corrections for mercury-in-glass thermometers with $\kappa = 0.000\,16\,°\text{C}^{-1}$

Example 7.3   A difficult stem-correction calculation

A partial-immersion thermometer indicates a temperature of 200.0 °C after the certificate corrections have been applied. In use, it has an emergent-column length of 100 °C with a mean stem temperature of 70 °C. In calibration it had an emergent-column length of 50 °C and a mean stem temperature of 90 °C. Calculate the true temperature.

Correction to total immersion for calibration

$$\Delta t = 50 \times (200 - 90) \times 1.6 \times 10^{-4} \, °C$$

$$= +0.88 \, °C.$$

Correction to total immersion for use

$$\Delta t = 100 \times (200 - 70) \times 1.6 \times 10^{-4} °C$$

$$= 2.08 \, °C.$$

Since the correction in use is greater than when calibrated the thermometer is reading low. Hence the correction must be positive, that is

$$\Delta t = 2.08 - 0.88 = +1.2 \, °C.$$

Hence the true temperature is 201.2 °C.

When performing these calculations it is very easy to get the sign wrong. To check the calculation get a colleague to go over the calculation independently. As a guide, if the thermometer is in a hot medium, the average temperature of the emergent mercury is lower, and so a positive correction is needed.

Exercise 7.1

A total-immersion thermometer is used in partial immersion to measure the temperature of a cold bath. The indicated temperature is −31.50 °C after all certificate corrections have been applied. The emergent column length is 10 °C, and the mean stem temperature is 15 °C. Calculate the true temperature.
    [Ans: −31.57 °C.]

Exercise 7.2

A partial-immersion thermometer indicates a temperature of −31.50 °C after the certificate corrections have been applied. In calibration the stem temperature was 20 °C and in use it is 15 °C. The emergent-column length is 10 °C. Calculate the true temperature.
   [Ans: −31.49 °C.]

7.3.10   Scale errors

The scale on a liquid-in-glass thermometer serves not only to indicate the temperature but also to linearise the temperature response of the mercury and glass. Errors arising from the placement and ruling of the scale are a major source of uncertainty in liquid-in-glass thermometry and have a significant impact on the design of calibrations. A common feature of the various types of scale error is that they introduce rapid changes in the thermometer error that typically occur within one scale division, but possibly over several scale divisions. Their non-smooth nature makes calibrations using equations impractical and imposes constraints on the choice of calibration points. Four types of scale error can be distinguished.

Linearisation errors

A main function of multi-segment thermometer scales is to compensate for the non-linearity in the expansion of the liquid and the glass. This was highlighted in Figure 7.3, which shows the length non-linearity of a five-segment thermometer scale. With enough segments, the effects of the non-linearity of mercury can be made arbitrarily small. Example 2.22 evaluated the effect for a PRT, but the problem is the same for a liquid-in-glass thermometer. The interpolation error is approximately

$$\Delta t = \frac{B \, (t - t_1) \, (t - t_2)}{A + B \, (t_1 + t_2)}, \tag{7.3}$$

where A and B are the combined first-order and second-order expansion coefficients for mercury and glass, and t_1 and t_2 are the temperatures defining the interpolation (at each end of a segment). By using this formula and Figure 7.3 we can estimate the values of the coefficients and approximate the maximum interpolation error as

$$\Delta t \approx 0.6 \left(\frac{t_1 - t_2}{100} \right)^2 {}^{\circ}\text{C}. \tag{7.4}$$

The error is less than $6\,\text{mK}$ if the length of each segment is $10\,^{\circ}\text{C}$ or less.

   If too few segments are used for the scale, the scale error has a very jagged shape consisting of a sequence of intersecting parabolas, similar in appearance to laundry hanging on a washing line (see Figure 5.2). This not only makes interpolation difficult, but also introduces a systematic error to the scale. If the scale is ruled properly only the ends of each scale segment near the pointing marks have no error. Everywhere else on the thermometer scale there will be errors, all with the same sign. Thus, all the readings on the thermometer are subject to a systematic error. Some manufacturers use non-linear ruling machines to overcome this problem. More commonly precision thermometers have multi-segment scales. Equation (7.4) provides a guide to how close the points must be. For the interpolation error to be less than about one-tenth of a scale division, the calibration points must be no more than about 50, 100 and 200 scale divisions apart for a scale marked to $1\,^{\circ}\text{C}$, $0.1\,^{\circ}\text{C}$ and $0.01\,^{\circ}\text{C}$ respectively.

Misplacement of pointing marks

Figure 7.2 shows the pointing marks on the stems of two thermometers. The manufacturer uses these scratches to locate the start and end positions for the ruling machine. If, on a multi-segment scale, one scratch is misplaced then one neighbouring scale segment will be compressed, and the other scale segment will be stretched. Figure 7.15 shows the measured correction curve for a precision thermometer with a scale ruled in five segments. The graph shows that a significant part of the structure in the curve is due to the misplacement of the pointing marks. The two marks at 30 °C and 40 °C in particular are misplaced by more than 0.03 °C, which would be accounted for by the scratches being misplaced by only 0.2 mm on the stem.

Misalignment errors

If the ruling machine is not aligned to the pointing marks then a step-shaped error occurs. These are normally visible on multi-segment thermometers as a single unusually large or small division next to the pointing mark. Where they occur on the ends of a thermometer's scale or on single-segment thermometers, they have the effect of simply stretching or compressing the scale, so no discontinuity occurs.

Ruling errors

Ideally, the ruling machine should evenly subdivide the interval between the pointing marks. Figure 7.16 shows the scale of a thermometer ruled by a poor ruling machine. The curve suggests that the scale was ruled in 12 segments of 50 scale divisions each. However, there was no sign of the pointing marks on the thermometer (although they may have been covered by the scale markings), and scale segments of 1 °C length
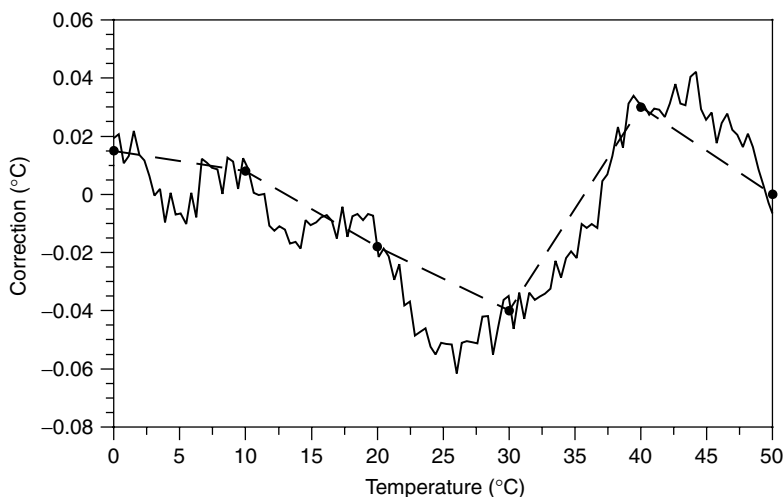
Figure 7.15   The measured correction curve for a −1 °C to 51 °C reference thermometer divided to 0.1 °C and marked in five segments. The overlaid dashed lines indicate the value of the corrections that would be interpolated from calibrations at the manufacturer's pointing marks
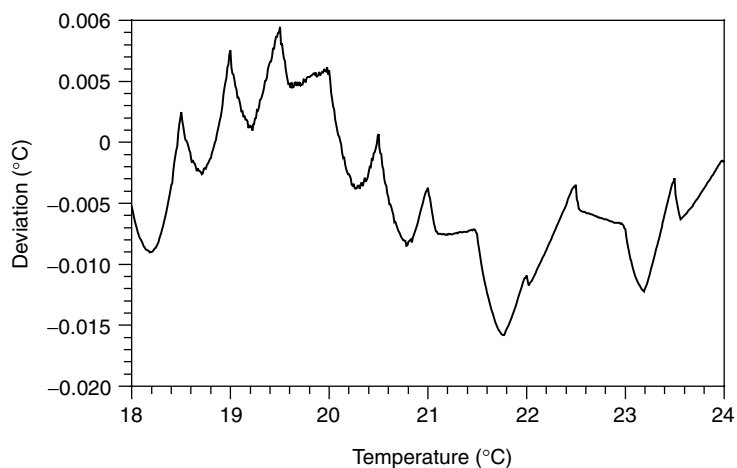
Figure 7.16   The deviations from length linearity of a calorimeter thermometer scale. The scale appears to have been ruled in 12 segments, but in fact the ruling machine has created the distortions. The positions of the scale markings were measured with an automatic laser length-bench as though the thermometer was a rule. The length of the scale and deviations from linearity are expressed in equivalent temperatures

would be unnecessarily small (a single $6\,°C$ segment has interpolation error of less than $2\,mK$). Thus, the ruling machine caused the distortions in this scale. The resulting error curve includes periodic components that may be symptomatic of a bent shaft or gears in the machine.

7.4 Choice and Use of Liquid-in-glass Thermometers

In many cases the choice and use of liquid-in-glass thermometers is completely covered by the documentary standards for test methods; for example, many ASTM and IP tests are of this nature. In such a situation, follow the documentary standard and use this book as an aid to understanding the requirements. Many of the tests are for situations where it is difficult to measure the true temperature of the physical system of interest. Therefore, careful adherence to the test specification is needed for repeatability and consistency between different laboratories (see also the discussion in Section 1.4.2).

   In general, liquid-in-glass thermometers have a high cost of ownership. Their fragility means that two must be held for any one application, and the nature of the errors makes calibration costs very high. This is especially true for high-temperature and high-precision applications. In most cases PRTs are better suited and less expensive. Liquid-in-glass thermometers do, however, have some advantages. For narrow temperature ranges of, say, $50\,°C$ or so the cost of ownership is not so high. The main advantages of liquid-in-glass thermometers are that they are fully self-contained and have lower initial cost, immunity to chemical attack, low susceptibility to electrical interference, and low thermal conductivity. Some of the negative aspects include their fragile nature, the risk of mercury and glass contamination, and the need to view at line of sight.

A bewildering number of types of liquid-in-glass thermometers are available. Where possible, choose those made to a recognised specification. In particular, determine what dimensional tolerances are appropriate for your application. Thermometers with controlled dimensions will be more expensive to purchase.

7.4.1   Range and type

For best performance, mercury-in-glass thermometers should be restricted to operation over a maximum range of $-38\,°\text{C}$ to $250\,°\text{C}$. Outside of this range choose a different type of thermometer, for example a PRT, which may allow you to do away with glass thermometry altogether. The purchase should be guided by a specification as published by a recognised standards body, such as ASTM, BSI, IP or ISO. Thermometers made to such specifications are subject to better quality control and the standard provides a basis for negotiation with suppliers if they fail to meet specifications. Beware that some type numbers are the same yet refer to different thermometers, and so make sure the specification body is referred to. This confusion occurs, for example, with IP and ASTM; an order for a 16C thermometer could result in either an ASTM 10C, the equivalent of IP 16C, or an IP 61C, the equivalent of ASTM 16C.

Always choose thermometers with an ice point on the scale. Regular checks at the ice point determine the stability of the thermometer and enable longer recalibration intervals.

Your choice of thermometer will most probably be a compromise between the best range, scale division and length for your purpose. If you need good precision then the thermometer range will be constrained to avoid extremely long and unwieldy thermometers. Table 7.4 gives the ASTM specifications for precision thermometers. The best resolution (one scale division) for ASTM liquid-in-glass thermometers is around $0.1\,°\text{C}$ with the thermometers supplied being accurate to one scale division. If a resolution better than $0.1\,°\text{C}$ is required (e.g. reference thermometers with a resolution of $0.01\,°\text{C}$), then the maximum error rises to several scale divisions. Table 7.5 shows the compromises reached by the BSI. As a rule, choose thermometers subdivided at intervals close to the accuracy you wish to achieve and do not rely heavily on visual interpolation to increase the accuracy. Tables 7.4 and 7.5 both list mainly thermometers with an ice point either in the main scale or as an auxiliary scale.

Table 7.4   Summary of requirements for ASTM precision thermometers

ASTM thermometer number	Range (°C)	Maximum length (mm)	Graduations (°C)	Maximum error (°C)
62C	−38 to +2	384	0.1	0.1
63C	−8 to +32	384	0.1	0.1
64C	−0.5 to +0.5 and 25 to 55	384	0.1	0.1
65C	−0.5 to +0.5 and 50 to 80	384	0.1	0.1
66C	−0.5 to +0.5 and 75 to 105	384	0.1	0.1
67C	−0.5 to +0.5 and 95 to 155	384	0.2	0.2
68C	−0.5 to +0.5 and 145 to 205	384	0.2	0.2
69C	−0.5 to +0.5 and 195 to 305	384	0.5	0.5
70C	−0.5 to +0.5 and 295 to 405	384	0.5	0.5

Table 7.5 Details of BS secondary reference thermometers (reproduced from BS1900 by permission of BSI)

Designation mark	Range (°C)	Maximum overall length (mm)	Graduation (°C)	Maximum error at any point (°C)	Maximum permitted interval error in an interval* (°C)
SR1/30C	−80 to +30	405	0.5	1.0	1.0/2.0
SR2/2C	−40 to +2	455	0.1	0.3	0.3/5
SR3/20C	−20 to +20	405	0.1	0.2	0.2/5
SR4/1C	−11 to +1	485	0.02	0.1	0.1/2
SR4/11C	−1 to +11	485	0.02	0.1	0.1/2
SR5/20C	−0.5 to +0.5 and 9.5 to 20.5	485	0.02	0.1	0.1/2
SR5/30C	−0.5 to +0.5 and 19.5 to 30.5	485	0.02	0.1	0.1/2
SR5/40C	−0.5 to +0.5 and 29.5 to 40.5	485	0.02	0.1	0.1/2
SR5/50C	−0.5 to +0.5 and 39.5 to 50.5	485	0.02	0.1	0.1/2
SR5/60C	−0.5 to +0.5 and 49.5 to 60.5	485	0.02	0.1	0.1/2
SR5/70C	−0.5 to +0.5 and 59.5 to 70.5	485	0.02	0.15	0.15/2
SR5/80C	−0.5 to +0.5 and 69.5 to 80.5	485	0.02	0.15	0.15/2
SR5/90C	−0.5 to +0.5 and 79.5 to 90.5	485	0.02	0.15	0.15/2
SR5/100C	−0.5 to +0.5 and 89.5 to 100.5	485	0.02	0.15	0.15/2
SR6/18C	−1 to +18	485	0.05	0.1	0.1/3
SR6/34C	−0.5 to +0.5 and 16 to 34	485	0.05	0.1	0.1/3
SRC/51C	−0.5 to +0.5 and 33 to 51	485	0.05	0.1	0.1/3
SR6/68C	−0.5 to +0.5 and 50 to 68	485	0.05	0.15	0.15/3
SR6/85C	−0.5 to +0.5 and 67 to 85	485	0.05	0.15	0.15/3
SR6/102C	−0.5 to +0.5 and 84 to 102	485	0.05	0.15	0.15/3
SR7/51C	−1 to +51 and 99 to 101	505	0.1	0.2	0.2/10
SR7/101C	−1 to +1 and 49 to 101	505	0.1	0.2	0.2/10
SR8/151C	−1 to +1 and 99 to 151	540	0.1	0.2	0.2/10
SR8/201C	−1 to +1 and 149 to 201	540	0.1	0.3	0.3/10
SR8/251C	−1 to +1 and 199 to 251	540	0.1	0.5	0.5/10
SR9/202C	−2 to +2 and 98 to 202	540	0.2	0.4	0.4/20
SR10/302C	98 to 102 and 198 to 302	540	0.2	1.0	1.0/20
SR11/452C	98 to 102 and 198 to 452	590	0.5	1.5	1.5/25
SR12A/505C	95 to 505	590	1.0	2.0	2.0/50

*Expressed in the form maximum permitted interval error/interval, the interval error being the algebraic difference between the errors at opposite ends of the interval. For example, 0.2 °C/5 °C is written as 0.2/5 and means that the change of error in any interval of 5 °C does not exceed 0.2 °C.

7.4.2 Acceptance

Once a thermometer has been received from a supplier, you should subject it to a thorough visual inspection, preferably under magnification up to 20×. Figure 7.17 gives an example checklist of the main physical dimensions to be checked. In principle, the supplier should have carried out this inspection but unless it was written into the purchase contract, with evidence supplied, then it is unlikely. Suppliers may request a premium for carrying out such an inspection, but the cost will usually repay itself in reducing the time wasted on a bad thermometer and the cost of a calibration.
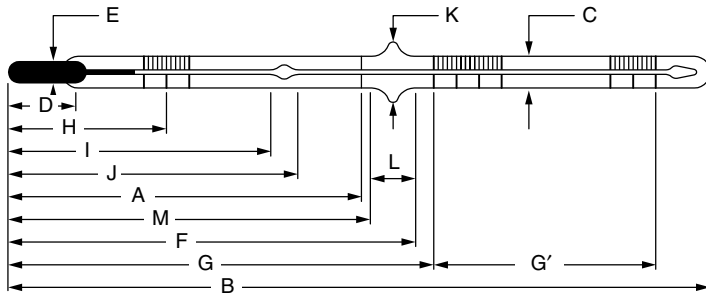
Thermometer ID:	Type:	Name:	No:

General observations:		Gas bubbles	
		Globules of liquid	
		Foreign matter	
Scale specifications:		Temperature range	
		Scale divisions	
		Long lines at	
		Numerals at	
		Max scale error	
	A	Immersion	
Expansion chamber:		Permits heating to	
Dimensional specifications:		**(in mm)**	
	B	Total length	
	C	Stem outer diameter	
	D	Bulb length	
	E	Bulb diameter	
Scale:	F	Length to bottom of scale	
	G	Length to top of scale	
	G′	Scale length	
Ice point:		Range	
	H	Bottom of bulb to ice point	
Contraction chamber:	I	distance to bottom, min	
	J	Distance to top, max	
Stem enlargement:	K	Outer diameter	
	L	Length	
	M	Distance to bottom	

Figure 7.17 A checklist to record the result of the visual and dimensional inspection of a thermometer when first obtained. This is important for ASTM and IP thermometers, where the correct physical size is essential for insertion into a test apparatus

The points to watch for are:

- breaks and bubbles in the mercury which may be repairable (Section 7.3.7);
- any foreign matter in the capillary;
- distortions in the capillary or scale;
- the presence of fine scale markings, less than one-fifth of a division;
- the scale markings to be at multiples of one, two or five;
- the dimensions to match the specifications;
- the required markings to be on the stem; for example, possible markings include:
    — temperature scale;
    — immersion condition;
    — immersion line;
    — gas fill or vacuum;
    — bulb glass;
    — serial number;
    — vendor's name;
    — specification body;
    — type number.

See Section 7.4.3 for adding your own markings or serial number.

If the thermometer is mechanically sound then an ice-point check should be made and recorded. Check this value with any value supplied by the supplier. Any large difference, for example greater than one-fifth of a scale division, indicates a potential fault or mishandling of the thermometer.

Any special-purpose thermometer not purchased to a recognised specification should undergo a thermal cycling test. This will also apply to specified thermometers used over 300 °C, and those you are suspicious about. Warm the thermometer to the maximum temperature at which it will be used. Leave it for an appropriate period, for example the expected time in use, and let it cool to room temperature. An ice point taken straight away should not be out by more than about 0.1% of the temperature excursion. After three days the ice point should have relaxed back to within one-fifth of a scale division of its original value. Reject the thermometer if it does not stabilise, or subject it to more thermal cycling tests. Note that this test is designed to eliminate bad thermometers and does not give an assurance of good behaviour in the future.

7.4.3   Etching and engraving

Manufacturers usually supply thermometers with serial numbers on them. If there is no serial number or identification markings, it is necessary to put one on the thermometer so that an accurate record of the thermometer may be kept. Our preferred option is to use a marking tool with a tungsten carbide tip to scratch markings directly on to the thermometer stem. While this may endanger the thermometer if not done carefully, it is the preferred method for personal safety.

The alternative method is to etch the glass stem with hydrofluoric acid.

WARNING! Hydrofluoric acid is very dangerous. Small spills on bare skin can be fatal. This procedure should NOT be attempted if your laboratory does not have specific safety procedures and facilities for handling hydrofluoric acid. In some countries users of hydrofluoric acid must be licensed.

If hydrofluoric acid is used, the following procedure should be carried out. The thermometer is first degreased with a solvent such as white spirit. The top 50 mm of the thermometer is then dipped in a bath of melted microcrystalline wax, which is maintained at such a temperature that a thin transparent layer of wax is left on the thermometer. When the wax has set, the required marking is made on the thermometer stem by cutting through the layer of wax with a stylus. The wax chips produced are brushed off the stem with a soft brush. The hydrofluoric acid is then painted on the wax-covered stem and left for 4 minutes. The acid is removed by washing with water and the wax removed by remelting and wiping off. The etched markings can then be filled with black engraving filler while the thermometer is still hot.

7.4.4   Use of the thermometer

Any apparatus employing a liquid-in-glass thermometer must be designed to allow it to be read visually, with the main variable available to the designer being the depth of immersion. Methods to cope with different immersion conditions are given in Section 7.3.9. If you find you have to move the thermometer away from its proper position in order to read it then you should use a different type of thermometer or redesign the apparatus.

Some general points on the use of the thermometer are as follows:

- Do not drop the thermometer; it causes irreversible changes!
- Hold the thermometer vertically by the stem and do not let it rest on its bulb.
- Keep the bulb protected and free from knocks.
- Keep the thermometer below its maximum indicated temperature.

For the best accuracy care should be exercised when reading the thermometer, as follows:

- Read the thermometer on increasing temperatures only.
- Tap the thermometer lightly before reading to prevent stiction. A small artist's brush is useful as it can also serve to clear any frosting or fog on the scale.
- Use a telescope or other optical aid to read the scale.
- For each reading recheck the scale markings to ensure they have been interpreted correctly; for example, is the scale divided to $0.1\,°C$ or $0.2\,°C$?
- Remember to divide the interval from the centres of the graduation lines, not their edges.

7.4.5   Organic liquids

Thermometers with organic liquids have three possible uses:

(1)   for measuring temperatures below $-38\,°C$;

(2)   for situations where mercury must be avoided; and

(3)   for inexpensive thermometers.

The utility of spirit thermometers is limited because of the high non-linearities, the volatile nature of the liquids, and the lower achievable accuracy. Organic liquid thermometers are also difficult to read because of the very clear liquid and concave meniscus. The use of a suitable dye and wide bore can give them a readability as good as mercury. Follow the recommendations of Section 7.3.7 on separated columns and Section 7.4.6 on storage in order to get the best results from organic liquid thermometers.

7.4.6 Storage

Mercury-in-glass thermometers should be stored horizontally on trays in cabinets, with care being taken to avoid any weight or pressure on the bulbs (one reason for the horizontal position). Avoid vibration. Corrugated cardboard, or similar material, can be used as a liner for a tray to prevent the thermometers rolling.

Thermometers employing organic thermometric liquids are better stored vertically, bulb down, in a cool place, but do not rest the thermometer on its bulb. Organic liquid thermometers should also be shielded from light sources because ultraviolet radiation can often degrade the liquid or the pigment. If the top of the bore of a spirit thermometer is kept at a slightly higher temperature than the rest of the thermometer, then the volatile liquid will not condense in the expansion chamber.

7.4.7 Transport

Periodically, it may be necessary to send your thermometer away for calibration. Remember that there is a considerable investment in a good thermometer, not just in the purchase price but in the calibration and a recorded history of its good behaviour. Therefore, it is important that it survives shipment. Remember to carry out an ice-point or similar reference-point check before and after shipment to check that it has survived.

The preferred method of transport of thermometers is by safe hand; otherwise use the most reliable delivery service. Regardless of the method of despatch, thermometers should be adequately packed to ensure their safe arrival. The following procedure has been found to be highly reliable (see Figure 7.18).

- Use a wooden box with a lid secured by screws.
- Line the inside of the box with flexible foam. The thickness and density of the foam must be sufficient to prevent the thermometer from coming into contact with the inside of the box while in transit.
- Support the thermometer firmly throughout its length to prevent vibration and sliding of the thermometer. The use of expanded polystyrene with slots cut by the hot-wire method is satisfactory. If thermometers are to be transported inside their protective tubes then it is essential that they are packed firmly into the tubes, supported from end to end and unable to move inside the protective tube. Firmly packed cotton wool is suitable.
- Keep the thermometers separated within the box. Lengths of wooden dowelling may be used to fill up unused spaces in a multi-thermometer box.
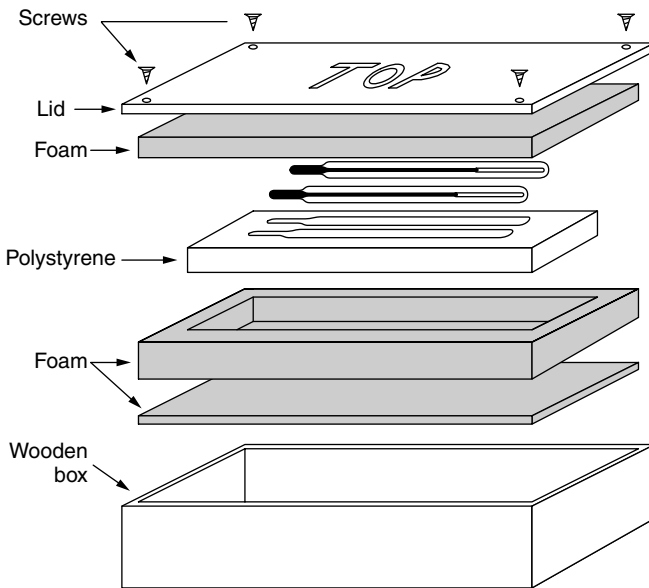
Figure 7.18 Outline diagram of a box suitable for transporting liquid-in-glass thermometers

● Thermometer bulbs should all be at the same end of the box, and the box clearly labelled as to which side is the top.

As air cargo is the most common means of transport for thermometers, a few aspects need to be noted. The transport of goods by air is covered by the International Air Transport Association (IATA) and its regulations need to be observed, especially those concerning restricted articles for which special documents have to be prepared. Mercury is a restricted article and the regulations require mercury to be properly sealed inside a non-breakable container. Clearly glass is not; therefore some form of sealing is required. If thermometer tubes are used, and properly packed, they can be sealed with a suitable tape. Otherwise it will be necessary to wrap the wooden box or its insert in a strong plastic bag and seal it.

Spilt mercury inside an aircraft can be a direct danger to the aircraft itself because aluminium is used in its construction. Mercury removes the oxide coating off aluminium and thus allows the aluminium to burn slowly in air. Such damage is difficult to locate without a complete scan of the aircraft. A number of airlines refuse to ship mercury.

Two extracts from the IATA regulations are also of interest:

Vibrations in commercial aircraft to which packages are exposed range from 5 mm amplitude at 7 cycles/sec (corresponding to 1 g acceleration), to 0.05 mm amplitude at 200 cycles/sec (corresponding to 8 g acceleration).

Except as otherwise specified in these regulations, completed and filled packages shall be capable of withstanding one 1.2 m drop test on solid concrete or other equally hard surface in the position most likely to cause damage.

7.5 Calibration

Traditionally calibration procedures for liquid-in-glass thermometers have not used statistical techniques to evaluate the uncertainty of the calibration. Instead, a variety of tests are carried out to verify that the thermometer conforms to the standard specification. There are several reasons for this.

- Some of the tests are necessary because many liquid-in-glass thermometers have highly specific applications that impose dimensional and structural constraints, besides the accuracy of the temperature measurements.

- Other tests were, in effect, the basis of Type B assessments of uncertainty that were used to classify the performance of thermometers.

- At the time, liquid-in-glass thermometers were the most cost-effective way of maintaining temperature scales and some of the practices had developed to obtain the very best performance from them.

- Until relatively recently, there was no universally accepted uncertainty treatment on which to base an alternative approach.

Nowadays, since we have the required uncertainty treatment and PRTs for maintaining the temperature scale, we can adopt a simpler and more systematic approach to the calibration of liquid-in-glass thermometers.

7.5.1 Short-range calibrations

Working thermometers are often associated with specific test apparatus and are nearly always used at well-defined temperatures; for example, with medical testing at 37 °C. In these cases, the client is only interested in a calibration at a few specific points on the thermometer's scale.

As we discussed in Section 5.3.3 the comparison can be performed at several points over a few scale divisions either side of the nominal calibration point. The comparison data is used to calculate the mean error in the thermometer reading and a standard deviation. The mean reflects the systematic error in the thermometer readings so is used as the correction, while the standard deviation measures the dispersion of readings caused by variations in the bore diameter and quality of the scale markings. To keep the coverage factors for the expanded uncertainty reasonable (Section 2.6) we recommend making six or more comparison measurements. The procedure is repeated for each calibration point and is the simplest approach for working thermometers used at a few specific temperatures. The results are most simply presented as a correction for each calibrated point and an uncertainty.

Investigation of thermometer performance at a single point does not provide sufficient evidence of reliability to satisfy our definition of a calibration. In addition, the calibration laboratory must make a close visual inspection of the thermometer, and check the short-term stability by carrying out ice-point checks before and after the comparison. If the thermometer is to be used in a special test apparatus, the laboratory may also be asked to check its dimensional characteristics (see Figure 7.17).

7.5.2 Calibration of reference and general-purpose thermometers

A sequence of short-range comparisons is also useful for calibrating reference liquid-in-glass thermometers or general-purpose liquid-in-glass thermometers. Because the temperatures of interest are not known in advance for these thermometers, the calibration must provide the client with the means to determine a correction for any reading from the thermometer.

As we discussed in Section 7.3.10, the fact that liquid-in-glass thermometer scales are ruled in segments greatly complicates their calibration as compared with other thermometers. The variety of discontinuities introduced by the various stages of the ruling process means that the error curve for a liquid-in-glass thermometer is not well modelled by a simple equation. For thermometers ruled with more than one scale segment, the calibration is best carried out by calibrating at carefully chosen points on the scale and interpolating between those points.

For thermometers that suffer from errors caused by misplaced scales the best choice of calibration points is the same points as those used by the manufacturer to locate the scale. In this way the linear interpolation between pointing marks will closely follow the interpolation carried out by the scale markings (see Figure 7.15). For thermometers that exhibit the 'hanging laundry' shape of interpolation error due to an insufficient number of segments, an additional point between each of the pointing marks helps correct for a lot of the error. For a good reference thermometer, this typically corresponds to one point for every 50 scale divisions.

General-purpose thermometers have relaxed accuracy specifications so they are often ruled with a single scale segment. Only in these cases is a least-squares fit practical. The equation should be cubic (Equation (5.6)) and should be based on single measurements at about every 25 scale divisions.

All liquid-in-glass thermometers should be subjected to a close visual inspection. Possible checks include:

- Visual examination for defects in the bore.

- Visual examination for scale clarity.

- Dimensional inspection of the thermometer.

- Thermal cycling to establish ice-point stability.

- Restrictions on the maximum error observed.

- Restrictions on the maximum rate of change of error.

The last two constraints are particularly important for reference thermometers, since the maximum error and maximum rate of change of error are measures of the uniformity of bore diameter. If the bore is not uniform then linear interpolation between pointing marks will not be as accurate as expected, and the reported uncertainty will probably be optimistic. Tables 7.4 and 7.5 illustrate typical error restrictions. The dimensional and other physical constraints can be checked by following checklists similar to Figure 7.17.

7.5.3 Outline of a liquid-in-glass calibration procedure

A procedure for calibrating a liquid-in-glass thermometer is outlined here. The outline follows the step-by-step calibration procedure of Section 5.5.2 and includes the extra requirements for liquid-in-glass thermometers.

Step 1: Start record keeping

Include in the records any information as to why and how this liquid-in-glass thermometer is being used as this may point to documentary standard specifications that the thermometer must satisfy.

Step 2: General visual inspection

Besides checking for any broken glass or loose mercury, examine the column for any breaks. Rejoin any breaks found as per Section 7.3.7. Consult with the client if you are likely to risk the integrity of the thermometer in the process of rejoining the column (especially if heating is found to be necessary). Check that the thermometer has a serial number; if not then engrave a suitable number or identifying mark (Section 7.4.3). This will be used to identify the thermometer in the calibration certificate.

Step 3: Conditioning and adjustment

Adjustments are not possible with the liquid-in-glass thermometers described here.

Thermally cycle any thermometer that is to be used over $300\,^{\circ}\text{C}$ and check for stability at the ice point. Also thermally cycle brand-new thermometers as a small percentage are commonly not annealed properly. This will show as a very unstable ice-point reading. In extreme cases, the ice-point reading may move several scale divisions.

Give the thermometers at least three days at room temperature before remeasuring the ice point. Store them carefully (see Section 7.4.6). Organic liquid thermometers should be stored vertically with the top slightly warmer than the bulb to ensure that all the liquid drains before making measurements.

Very high-precision reference thermometers may need additional conditioning if required by the client; for example, keeping the thermometer below $0\,^{\circ}\text{C}$ before the ice-point reading.

Step 4: Generic checks

Carry out a detailed visual check at $20\times$ magnification. Reject any thermometer with bore or scale irregularities. The scale markings need to be clear and marked according to their documentary standard. Check that the quality is consistent with the client's requirements.

Ensure that any dimensional requirements are met. Figure 7.17 gives the more common dimensions that need to be controlled. Ideally, these should have been checked before submission for calibration, as incorrect dimensions are a common reason for non-compliance with the standard specification.

Step 5: The comparison

There are two essential features for a liquid-in-glass comparison:

(1)   use increasing temperatures for measurements; and
(2)   ensure visual access to the scale.

An overflow bath is ideal for total-immersion thermometers as it allows viewing across the liquid surface and hence a very short emergent column. Otherwise, a window is required to view the thermometer. Provide a means to lower the thermometers physically during the calibration in order to keep the meniscus at the same height as the viewing telescope. A firm clip will be needed to prevent the thermometer dropping into the bath, but not so firm as to stress the glass.

Fix a partial-immersion thermometer so that the telescope can be moved up and down without any blockage in the line of sight. Arrange for a stem-temperature measurement. Alternatively, the partial-immersion thermometer could be calibrated as a total-immersion thermometer and the stem corrections applied later. This can only be done where the 10% uncertainty in the stem correction (Equation (7.2)) will not be the dominant contribution to the total uncertainty.

To keep the k factor for the expanded uncertainty low, choose a minimum of six measurements for each calibration point, with the measurements dispersed over plus or minus three scale divisions. For a least-squares fit, a minimum of 12 points distributed evenly over the range of interest is satisfactory. If the number of scale segments on the thermometer can be identified then try to choose a minimum of two points per segment, with points at the end and middle of each segment. If the thermometer has few segments, more points should be chosen.

Step 6: Analysis

Make any necessary corrections arising from the stem temperature not being at its designated value. This may apply to a total-immersion thermometer if the column was too far above the bath liquid.

Step 7: Uncertainty

If a fitting procedure was used, obtain the uncertainty from the standard deviation of the fit (Section 2.12.1). Otherwise, use the standard deviation of the residuals from the calculation of all of the corrections.

The hysteresis uncertainty can be estimated from the change in ice-point values before and after the calibration (see Example 2.10).

Include an assessment of the uncertainty in any immersion corrections (see Example 2.18).

Step 8: Complete records

Decide if the thermometer's performance warrants issue of a calibration certificate. If it does, prepare the certificate. Report the ice-point value on the certificate. The ice point may be on an auxiliary scale and not the main scale.

A table of correction terms can be drawn up for the thermometer.

A completed certificate for the short-range style of calibration is shown in Figure 5.8. A certificate for the deviation function style will look more like that in Figure 5.10.

Further Reading

ASTM in its standards on Temperature Measurement Vol 14.03 includes two standards related to liquid-in-glass thermometers:
  E 1-91 *Specification for ASTM Thermometers*.
  E 77-89 *Test Method for Inspection and Verification of Liquid-in-Glass Thermometers*.
BSI publishes a series of documentary specifications for thermometers including:
  BS 593 *Laboratory Thermometers*.
  BS 791 *Thermometers for Bomb Calorimeters*.
  BS 1704 *General Thermometers*.
  BS 1900 *Secondary Reference Thermometers*.
Calibration practice for liquid-in-glass thermometers is covered in:
  J A Wise (September 1988) *Liquid-in-glass thermometer calibration service*, NIST Spec. Publ. 250-23, US Department of commerce.
ISO issues documentary standards related to the liquid-in-glass thermometers:
  ISO 386-1977 *Liquid-in-Glass Laboratory Thermometer–Principles of Design, Construction and Use*.
  ISO 651-1975 *Solid-Stem Calorimeter Thermometers*.
  ISO 653-1980 *Long Solid-Stem Thermometers for Precision Use*.
  ISO 654-1980 *Short Solid-Stem Thermometers for Precision Use*.
  ISO 1770-1981 *Solid-Stem General Purpose Thermometers*.
R E Bentley (1998) Handbook of Temperature Measurement, Vols 1, 2 and 3, Springer Verlag, Singapore.

8

Thermocouple Thermometry

8.1 Introduction

Thermocouples are the most widely used of all temperature sensors. Their basic simplicity and reliability have an obvious appeal for many industrial applications. However, when accuracies greater than normal industrial requirements are called for, their simplicity in use is lost and their reliability cannot be assumed.

For example, a major manufacturer of Type K thermocouple wire advises: 'Once a thermocouple has been used at a high temperature, it is not good practice to use it later at a lower temperature'. Yet commercial hand-held electronic thermometers using Type K thermocouples are sold for use over the range $-200\,°C$ to $1400\,°C$ and at an accuracy far exceeding that claimed by the wire manufacturer!

Such misuse of thermocouples arises in large part from a lack of understanding of how thermocouples work. Thermocouple literature often mistakenly states that the thermocouple junction is the source of the voltage, whereas in a well-designed measurement the junction does not contribute to the signal at all! Instead, the signal is generated along the length of the thermocouple wire. This small piece of knowledge tells us that conventional calibration techniques applied to thermocouples are often futile, and has a profound effect on the way traceability must be established.

William Thomson (Lord Kelvin) outlined the principles of thermocouple thermometry in the 1850s. He explained the relationship between the thermoelectric effects discovered by Seebeck in 1821 and Peltier in 1834, and predicted and verified the effect now known as the Thomson effect. Unfortunately, in most manufacturers' literature and texts this understanding has been replaced by three empirical observations that have come to be known as the 'Three Laws of Thermoelectricity'. These laws have the appeal of simplicity but give a working model that completely obscures the physical source of the thermoelectric potential. The model is both unhelpful and misleading for anyone analysing thermocouples or trying to avoid the common errors in thermocouple practice. Periodically the basic principles are rediscovered, most often when large errors result from the use of thermocouples in new and unusual applications, or when some large industry loses millions of dollars because of the misunderstanding.

In this chapter, we will cover the construction of thermocouples, the errors that occur in use, and calibration methods for thermocouples that do work in practice. Before we do, however, we shall spend some time developing a clear description (hopefully) of the operating principles of thermocouples.

8.2 The Thermoelectric Effects

Quite frequently, the authors have had colleagues asking for thermocouple wire, which we gladly give them. This is nearly always followed by the question, 'How should we make the junction?' In these days of semiconductor junctions, thermistors and PRTs, we expect the tip of a thermometer to be the sensor, so the question is reasonable. But reason should also tell us that a junction, damaged by heat treatment, mechanical work and contamination with solder or braising, could not possibly be the sensor. Despite reason, this conclusion is so counterintuitive that it cannot normally be accepted without an explanation. Also, without the same explanation it is almost impossible to fix a thermocouple circuit that is behaving strangely.

Metals owe almost all of their properties to electrons. Their high electrical conductivity and thermal conductivity in particular are due to the free movement of the electrons within the metal. Because the electrons are responsible for both properties, they give rise to some interesting interactions between the electrical and thermal behaviour. These are known as the thermoelectric effects.

Perhaps surprisingly, electrons in metals also owe many of their properties to the lattice of metal ions. This may sound weird, but consider the way a small bubble rises in water. While the air is rising, a small drop of water is also falling, but because the water is confined, it cannot fall freely, like a raindrop for example. In the same way, the confinement of the electrons and their interactions with the metal lattice affect their properties; in some situations they even appear to have a negative mass!

Electrons in metals carry two types of energy: kinetic energy and chemical potential energy. As we discussed in Chapter 1, temperature is a measure of the kinetic energy. As metals get warmer, the average kinetic energy of the electrons increases and they move about more violently, as do the atoms. The chemical potential energy, which is energy stored against the forces of attraction between the electrons and the positively charged metal ions in the lattice, is similar to the energy stored in stretched rubber bands.

The thermoelectric effects are due to one single phenomenon: the properties of the electrons depend on their interaction with the lattice. The interaction means that the total energy carried by the electrons changes with the metal as well as temperature.

8.2.1   The Peltier effect

Figure 8.1 shows a simple thermocouple circuit made from two dissimilar wires, all at the same temperature. Now consider what happens when an electric current flows around the circuit. At one junction (in this case, the left-hand junction), the electrons move from a metal where they carry a lot of chemical potential energy to one where they carry less (at the same temperature). So the electrons carry that energy across the junction and then must come to thermal equilibrium with the different metal. In doing so they give some of their spare energy to the lattice and we see this as heat.

At the right-hand junction, the opposite happens. The electrons move across the junction and find that they suddenly have a shortage of energy, so come to thermal equilibrium with the lattice by taking up energy from the lattice, which we see as
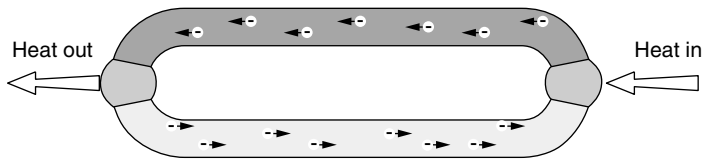
Figure 8.1 The Peltier effect. Electrons moving from one conductor to another change state and may take in heat or release heat. The effect is reversible; changing the direction of the current moves heat in the other direction

cooling. In effect, the electric current has carried heat from one junction to the other; this is the Peltier effect. It is a junction effect and occurs only with the flow of current.

The heat-pumping mechanism of the Peltier effect is similar to that in household refrigerators. The refrigerant is evaporated in the cooling plates inside the refrigerator to take in latent heat, and condensed under pressure to release the latent heat on the outside of the refrigerator. Instead of the change of state from solid to liquid, the electrons undergo the equivalent of the phase transition, complete with change in total energy, when they move from one metal to another.

8.2.2 The Thomson effect

Figure 8.2 shows a single conductor exposed to a temperature gradient, with an electric current carrying electrons from lower temperatures to higher temperatures. As the cool electrons move into hotter parts of the lattice and come to thermal equilibrium by taking up kinetic energy from the lattice, so the conductor cools with the flow of current. The effect is entirely reversible so electrons flowing from parts of a conductor at a high temperature will release heat and warm cooler parts of the conductor. The phenomenon is very much like the exchange of heat that occurs when water flows in a heat exchanger. The Thomson effect is a temperature gradient effect and only occurs when an electric current flows.

8.2.3 The Seebeck effect

Figure 8.3 shows a single conductor exposed to a temperature gradient, but with no current flowing. The electrons within the conductor behave much like a gas. At the hot end of the conductor, the electrons have a high kinetic energy so move around violently and diffuse towards the cold end of the conductor. Similarly cold electrons
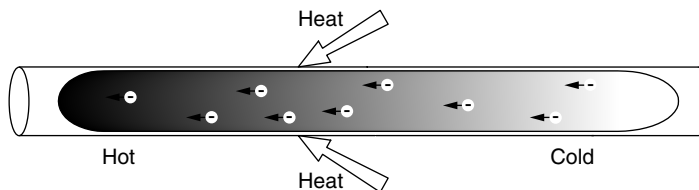
Figure 8.2 The Thomson effect. Electrons moving from cold parts of a conductor into hotter parts take up heat and cool the conductor. The effect is reversible; heat is released as electrons move from hotter parts to cooler parts
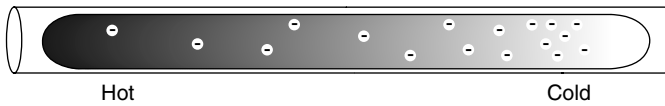
Figure 8.3 The Seebeck effect. The electrons in a conductor behave like a gas and expand under the influence of temperature. We observe the redistribution of electrons as a change in voltage along the length of the conductor. This occurs only where there is heat flowing; that is, only where there is a temperature gradient

diffuse towards the hot end, but not so vigorously. The hot electrons carry heat to the cool parts of the conductor, while cool electrons take up heat from the hot parts of the conductor. The diffusion of free electrons is the main reason that metals have a high thermal conductivity.

However, in the process of conducting heat, the electrons are involved in a balancing act. If the hot electrons exert a greater pressure than the cold electrons, the conductor will develop a surplus of electrons at the cold end of the wire. An electrostatic force, due to the displacement of the negatively charged electrons, provides the balancing pressure. The change in the electric potential (voltage) along the wire accompanying the redistribution of the electrons is the Seebeck effect. It happens only where there is heat flow, so is strictly a temperature gradient effect. It does not depend on a flow of electric current, and has nothing to do with any junction.

A simple analogy will help to explain the effect in more detail. Figure 8.4 shows a hose lying on uneven ground and filled with water. Consider the internal water pressure at various parts of the hose. Along that part of the hose lying flat on the top of the hill, the pressure is constant. As we follow the hose downhill the pressure increases because of the extra weight of water above the point where we measure. Once we reach that part of the hose lying flat on the lower ground, the pressure is constant again. The internal pressure change occurs only where there is a gradient, with the rate of change of pressure proportional to the gradient.

In the same way, the change in Seebeck voltage, E_s, occurs only where there is a temperature gradient and in proportion to the temperature gradient:

$$dE_s = s(T)dT, \tag{8.1}$$
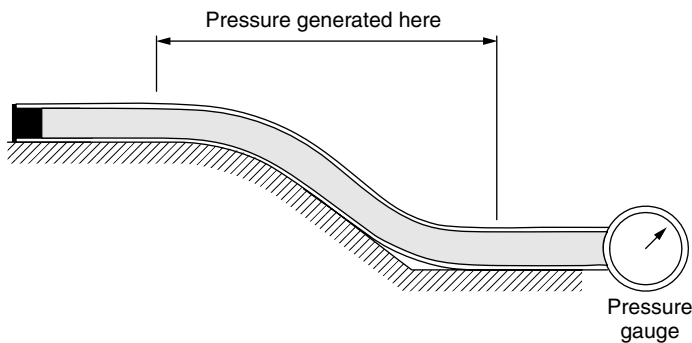
Figure 8.4 The siphon analogy of the Seebeck effect. The change in pressure in the fluid-filled hose occurs only where there is a gradient
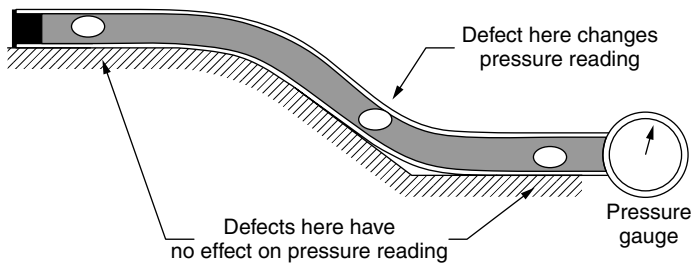
Figure 8.5   A defect (bubble) that occurs at a gradient has an effect on the pressure in the siphon, whereas a defect in an area where there is no gradient has no effect

where $s(T)$ is called the Seebeck coefficient of the conductor, and dE_s and dT are small changes in Seebeck voltage and temperature respectively. The *Seebeck coefficient* depends on the electronic properties of the conductor so is different for every metal and alloy, and varies with defect or contaminant concentration.

We can take the hose analogy further. Figure 8.5 shows a section of hose with three bubbles in the water. Consider first the bubble in the sloping part of the hose. Because it displaces water that would otherwise contribute to the weight pressing down on the water below, this bubble affects the pressure measurement. On the other hand, the two bubbles in the horizontal parts of the hose occur where the downward force from the weight of the water is at right angles to the direction of the hose. Therefore, these bubbles have no effect on the pressure measurement.

In a thermocouple, damaged wire occurring in an area where there is a temperature gradient will affect the measured voltage. Because wire in an isothermal (same temperature) area contributes nothing to the voltage, defects in isothermal conditions have no effect. This conclusion is also apparent from Equation (8.1); if the temperature change $dT = 0$ then the change in voltage is also zero, independent of the value of $s(T)$.

Thermocouple wire that is free of defects and contaminants, so that it has the same Seebeck coefficient $s(T)$ for all parts of the wire, is said to be homogeneous. *Inhomogeneities* commonly arise in a single piece of wire from mechanical damage due to bending and twisting, changes in the diameter of the wire, chemical changes due to oxidation, reduction and contamination, changes in internal structure due to heat treatment, and changes in composition due to radiation damage.

Figure 8.6 shows yet another hose. In this case, it is lying on very uneven ground. However, it is free of any bubbles that might affect the pressure measurement. Given this condition we can very easily calculate the pressure difference between the two ends of the hose. It is simply the difference in height between the two ends times a constant that depends on the water density and the earth's gravity. That is, we do not need to measure all of the variations in slope and add up all of the little pressure differences. Similarly, so long as thermocouple wire is free of defects that might upset the value of the Seebeck coefficient, the total change in Seebeck voltage between one end of a wire and the other depends only on the two end temperatures. Note that, if the Seebeck coefficient were constant with temperature, $s(T) = s$, the Seebeck voltage would depend only on the temperature difference.
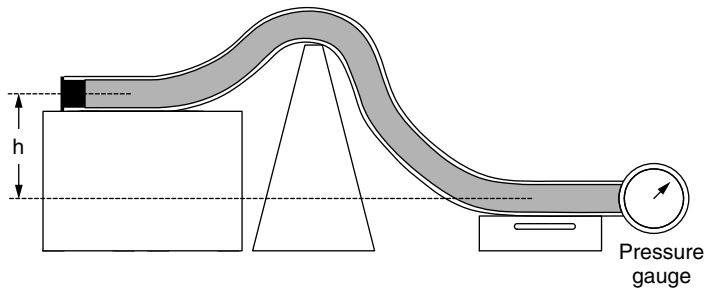
Figure 8.6   Although the pressure difference is generated at the gradients, the total pressure drop across a defect-free siphon depends only on the difference in height between the two ends

8.2.4   Exploiting the Seebeck effect to measure temperature

The preceding sections have given us the two key facts we must exploit to measure temperature accurately with a thermocouple:

(1)   The Seebeck voltage is generated only at temperature gradients, and if the gradient is zero (the wire is isothermal) the voltage generated is zero.

(2)   If the wire is homogeneous then the voltage generated along a length of wire depends only on the end temperatures.

Now let us apply these two facts to the thermocouple circuit in Figure 8.7, where A and B are wires of different metals or metal alloys, and the voltmeter measures the voltage across the two wires of material C, probably copper.

As we noted earlier, both wires near the measurement junction have been severely damaged by the making of the junction, and any voltage generated by damaged material will be unpredictable. However, we can eliminate the junction from consideration by making it isothermal; if there is no temperature gradient at the junction, there can be no voltage. Thus, in a well-designed thermocouple installation

the junction generates no voltage!

This same treatment, of making parts of the circuit isothermal, can be used wherever we find circuit components of unknown or uncontrolled thermoelectric properties. In particular, the area around the reference junction and the voltmeter should be
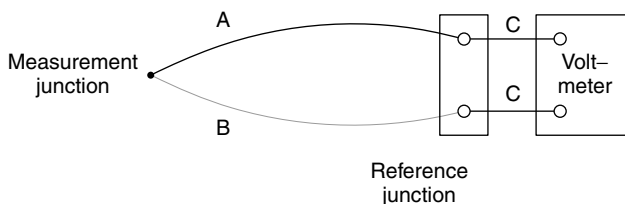
Figure 8.7   The thermocouple, a circuit that uses the Seebeck effect to measure temperature

isothermal. The voltmeter is the most complex part of the circuit, and thermoelectric effects in and around the connections to voltmeters are a major source of error. These are usually managed by making most of the circuit through the meter out of one material (copper), so that the circuit through the voltmeter is as homogeneous as practical. Then, since the two connections at the reference junction are at the same temperature, the net voltage generated in the meter circuit is zero. In practice, of course, not all of the meter circuit is copper; the connecting terminals, amplifiers, switches, etc., are often made from different materials. Therefore, it is also essential that these parts of the voltmeter are isothermal, and meter designers take care to avoid placing heat sources near critical components.

Analysis of the circuit in Figure 8.7 now reduces to determining the thermoelectric effects for three wires: the thermocouple pair A and B, and the instrument leads C. Since each of the three wires is homogeneous, we can calculate the measured voltage simply from the end temperatures:

$$E_{\text{meas}} = E_{\text{A}}(T_{\text{M}}) - E_{\text{A}}(T_{\text{R}}) + E_{\text{C}}(T_{\text{R}}) - E_{\text{C}}(T_{\text{R}}) + E_{\text{B}}(T_{\text{R}}) - E_{\text{B}}(T_{\text{M}}), \qquad (8.2)$$

where for the wires A, B and C, E_{A}, E_{B} and E_{C} are the voltages for the endpoint temperatures T_{M} and T_{R}, which are the measurement- and reference-junction temperatures respectively. Note that the endpoint is not the position of the junctions but the temperature of the isothermal region that includes the junctions.

From Equation (8.2), it can be seen that the net contribution of the instrument lead wire, C, is zero, and hence under the above conditions the instrumentation for measuring a thermocouple sensor can be considered independent of the sensor.

In addition, from Equation (8.2) the voltage output from the pair of wires, A and B, is related to the difference between the thermoelectric effect for the wires A and B. It is common to consider only a *relative Seebeck voltage*, E_{AB}, and *relative Seebeck coefficient*, S_{AB}, and thus Equation (8.2) becomes

$$E_{\text{meas}} = E_{\text{AB}}(T_{\text{M}}) - E_{\text{AB}}(T_{\text{R}}). \qquad (8.3)$$

A further simplification is made by choosing a single reference temperature for all thermocouples and setting $E_{\text{AB}}(T_{\text{R}}) = 0$. By convention the reference temperature is the ice point, namely $T_{\text{R}} = 0\,°\text{C}$, and the measured temperature is similarly expressed as a Celsius temperature. Then

$$E_{\text{meas}} = E_{\text{AB}}(t_{\text{M}}). \qquad (8.4)$$

Equation (8.4), which relates the measured voltage to the temperature, is the thermocouple relationship presented in tables and equations for thermocouple-type definitions. However, unlike the corresponding equations for thermistors and other temperature sensors, the equation is based on several critical assumptions that may not apply in practice. Any error analysis must use the more fundamental sensor equation, Equation (8.1). The critical assumptions are:

- the reference junction is at $0\,°\text{C}$;
- the pair of thermocouple wires exposed to temperature gradients are homogeneous;
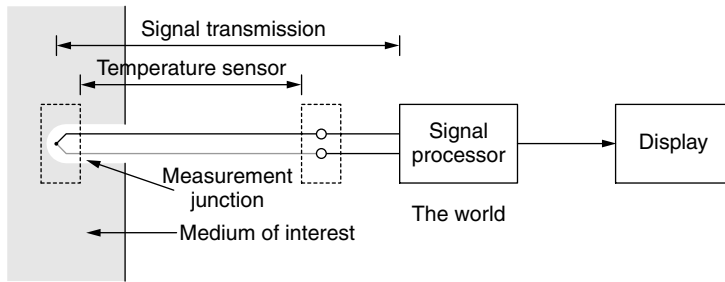
Figure 8.8   A model of a thermocouple measurement. The two boxes around the junctions indicate that they are isothermal and that no voltage is produced there

- the relative Seebeck voltage for the pair of wires is given by Equation (8.4);
- any instruments and connecting wires are isothermal or homogeneous; and
- the measurement and reference junctions are isothermal.

We shall find that the assumption of homogeneity is the most difficult to satisfy.

8.2.5   A model of a thermocouple measurement

It is instructive to compare a simple model of a thermocouple measurement in Figure 8.8 with the general measurement model we gave in Figure 2.10. In Figure 2.10, the sensor is immersed in the medium of interest, at a sufficient depth to ensure that the sensor is isothermal and giving a signal related only to the temperature of interest. With a thermocouple, the junction is immersed at a sufficient depth and made isothermal to be sure that it does not produce a signal. The sensing part of the thermocouple is everywhere between the measurement junction and the reference junction, the exact opposite of a conventional sensor. In a thermocouple, the active sensor comprises all of the wire protruding through the furnace wall or slammed in the oven door, the plugs, sockets and joins at any point along the length, and the extension cables lying over the floor where they can be damaged by traffic.

We can now see why it is so difficult to make a reliable and accurate thermocouple measurement. To do so, it is necessary to exploit repeatedly the two facts from the thermocouple theory:

(1)   Wherever the wire is exposed to temperature gradients, it must be homogeneous. We cannot allow mechanical, chemical or thermal damage.

(2)   Where the wire is suspect or damaged, it must be made isothermal. This means that we must avoid placing connections, joins, plugs, sockets, etc., in an environment where there is heat flow, drafts or infrared radiation.

8.3 Thermocouple Types

Three categories of thermocouple types are considered: *rare-metal* standard thermocouples, *base-metal* standard thermocouples and *non-standard* thermocouples. The

distinction between 'base' and 'rare' is that the rare metals contain platinum and the base metals contain nickel. Consequently, the rare-metal thermocouples are some 200 times more expensive than base-metal thermocouples, at current prices.

8.3.1   Standard thermocouple types

While Equation (8.4) applies to virtually any pair of wires, there are few metals and alloys with the required high output voltage, ability to withstand harsh chemical and thermal environments, and proven reliability that make them useful for temperature measurement. Standard tables of the relative Seebeck voltage, $E_{AB}(t)$, have been approved internationally for a number of different wire pairs. The type designations for these pairs are listed in Table 8.1, and Appendix D gives the mathematical definition for their response versus temperature (ITS-90).

Table 8.1 The compositions, trade names and letter designations for standardised thermocouples

Type	Materials
B	Platinum 30% rhodium/platinum 6% rhodium
E	Nickel chromium alloy/a copper nickel alloy
J	Iron/another slightly different copper nickel alloy
K	Nickel chromium alloy/nickel aluminium alloy
N	Nickel chromium alloy/nickel silicon alloy
R	Platinum 13% rhodium/platinum
S	Platinum 10% rhodium/platinum
T	Copper/a copper nickel alloy
	Single-leg thermoelements
BN	Platinum nominal 6% rhodium
BP	Platinum nominal 30% rhodium
EN or TN	A copper nickel alloy, constantan: Cupron[a], Advance[c], ThermoKanthal JN[b], nominally 55% Cu, 45% Ni
EP or KP	A nickel chromium alloy: Chromel[d], Tophel[a], T-1[c], ThermoKanthal KP[b], nominally 90% Ni, 10% Cr
JN	A copper nickel alloy similar to but usually not interchangeable with EN and TN
JP	Iron: ThermoKanthal JP[b], nominally 99.5% Fe
KN	A nickel aluminium alloy: Alumel[d], Nial[a], T-2[c], ThermoKanthal KN[b], nominally 95% Ni, 2% Al, 2% Mn, 1% Si
NN	Nickel silicon alloy: nominally 95.5% Ni, 4.4% Si, 0.15% Mg, Nisil, HAI-NP[e]
NP	Nickel chromium alloy: nominally 84.4% Ni, 14.2% Cr, 1.4% Si, HAI-NN[e], Nicrosil
RN, SN	High-purity platinum
RP	Platinum 13% rhodium
SP	Platinum 10% rhodium
TP	Copper, usually electrolytic tough pitch

All compositions are expressed in percentages by weight.

The use of trade names does not constitute an endorsement of any manufacturer's products. All materials manufactured in compliance with the established thermoelectric voltage standards are equally acceptable.

Registered trade marks: [a]Wilbur B Driver Co.; [b]Kanthal Corp.; [c]Driver-Harris Co.; [d]Hoskins Manufacturing Co. [e]Harrison Alloys Ltd.

...N denotes the negative thermoelement of a given thermocouple type.

...P denotes the positive thermoelement of a given thermocouple type.

The various letter-designated thermocouple types were originally based on the composition of the alloys for each 'leg' of the pair. Now they are based on mathematical functions that closely describe the thermoelectric behaviour of the original alloys. Manufacturers found problems conforming to an alloy definition because trace impurities in raw materials vary and change the Seebeck coefficient. Now manufacturers can adjust the alloys to make thermocouple wires match these tables within a close tolerance (see Table 8.2). A manufacturer may also vary the alloy composition in order to make a superior wire, for example, one more resistant to chemical attack.

Table 8.1 lists the letter designation for pairs of thermocouple wires as well as for single thermoelements or 'legs', which can be combined in pairs to form thermocouples. The classification is based on the polarity of the separate legs; for example, a negative leg EN and a positive leg EP can be combined to form a Type E thermocouple. However, caution must be observed when 'mixing and matching' thermocouple elements. In particular, it is very unwise to break up a pair supplied by a manufacturer and then attempt to recombine these legs with those from another pair. Normally the manufacturer ensures that the pair conforms to the type definition by adjusting the composition of one of the legs. Mixing legs from different manufacturers, or even the same manufacturer, could result in a thermocouple not conforming to the standard. For example, one well-known manufacturer makes seven different versions of Type K thermocouples to suit different applications, and mixing of legs from these pairs will result in departures from the standard.

Table 8.2 Tolerance classes* for thermocouples (reference junction at 0 °C)

	Class 1	**Class 2**	**Class 3**[‡]
Tolerance values[†] (±)	0.5 °C or 0.4%	1 °C or 0.75%	1 °C or 1.5%
	Temperature limits for validity of tolerances		
Type T	−40 °C to 350 °C	−40 °C to 350 °C	−200 °C to 40 °C
Tolerance values[†] (±)	1.5 °C or 0.4%	2.5 °C or 0.75%	2.5 °C or 1.5%
	Temperature limits for validity of tolerances		
Type E	−40 °C to 800 °C	−40 °C to 900 °C	−200 °C to 40 °C
Type J	−40 °C to 750 °C	−40 °C to 750 °C	—
Type K	−40 °C to 1000 °C	−40 °C to 1200 °C	−200 °C to 40 °C
Type N	−40 °C to 1000 °C	−40 °C to 1200 °C	−200 °C to 40 °C
Tolerance values[†] (±)	1 °C plus 0.3% of ($t − 1100$) °C	1.5 °C or 0.25%	4 °C or 0.5%
	Temperature limits for validity of tolerances		
Type R or S	0 °C to 1600 °C	0 °C to 1600 °C	—
Type B	—	600 °C to 1700 °C	600 °C to 1700 °C

*These tolerances follow IEC584-2.
[†]The tolerance is expressed either as a deviation in degrees Celsius or as a percentage of the actual temperature. The greater value applies.
[‡]Thermocouple materials are normally supplied to meet the manufacturing tolerances specified in the table for temperatures above −40 °C. However, these materials may not fall within the manufacturing tolerances for low temperatures given under Class 3 for Types T, E, K and N thermocouples if thermocouples are required to meet limits of Class 3, as well as those of Class 1 and Class 2. The purchaser shall state this, and selection of materials is usually required.

Table 8.3   Uses for thermocouple types

Type	Allowable environment	Comment	Maximum temperature (°C)*
B	Oxidising, inert, vacuum for short periods	Avoid metal contact. Most suitable for high temperature. Has low voltage at room temperature	1700
E	Oxidising, inert	Good for sub-zero temperature. Highest voltage output of common thermocouples	870
J	Oxidising, inert, reducing in partial vacuum	Iron rusts or oxidises quickly	760
K	Oxidising, inert	Subject to 'green rot' in some atmospheres	1260
N	Oxidising, inert	More stable than Type K at high temperatures	1300
R and S	Oxidising, inert	Avoid metal contact	1400
T	Oxidising, inert, reducing in partial vacuum	Sub-zero temperatures. Can tolerate moisture	370

*See Table 8.4.

Table 8.4   Upper temperature limits in °C for the various wires with continuous operation

	Wire diameter (mm)				
Type	3.25	1.53	0.81	0.51	0.33
B				1705	
E	871	649	538	427	427
J	760	593	482	371	371
K	1260	1093	982	871	871
R and S				1482	
T		371	260	204	204

Note: The limits apply to thermocouples in normal protective ceramic sheathing. Life will depend on the type of atmosphere etc. Operation at higher temperatures for shorter periods may be possible.

The thermocouple types in Table 8.1 have been developed to satisfy most needs in temperature measurement. However, they do not meet all needs and there is continuing development of new types. In order to make an informed selection of a thermocouple type the user may need to acquire detailed knowledge about the properties of the materials involved. This section gives some of the basic starting information required, and Table 8.3 and Table 8.4 summarise the information.

8.3.2   Rare-metal thermocouples

There are three standard types of rare-metal thermocouples, B, R and S, as shown in Table 8.1. The main advantage of these types is that they do not readily undergo chemical reactions. Rare-metal alloys also tend to be simple and do not undergo significant metallurgical changes at high temperatures. Therefore, the inhomogeneities in these

thermocouples arise mainly from mechanical effects, which can be reversed by careful annealing, and from contamination.

Pure platinum suffers from excessive crystal grain growth above 1100 °C making the wire very fragile. The grains become large enough to give a jagged edge to the wire, and under a microscope the wire has a bamboo-like appearance. Because the Type B wires are both alloys this effect is much reduced and they give better behaviour at temperatures above 1100 °C. Type B is also less sensitive to contamination than either Type R or S.

Rhodium has a relatively high vapour pressure so it tends to migrate to the pure platinum legs of Types R and S, which are sensitive to rhodium contamination. Ideally, the insulation should be a single piece to prevent the migration. High-purity insulation must be used and metal sheaths should be avoided unless they are made out of platinum. Platinum thermocouples normally work well in an oxygen atmosphere but not in a reducing atmosphere, especially if hydrogen is present.

The main disadvantage of the rare-metal thermocouples is their cost. This may be considerable: a reference thermocouple should be continuous from the measurement junction to the reference junction, and may require over 2 metres of wire costing as much as US$1000 at current prices. Many high-temperature applications need the rare-metal thermocouple for stability but do not need high accuracy. In these cases, a cheaper compensating extension cable can be used for the portion of the thermocouple at or near room temperature; such cables are discussed in Section 8.4.3.

Types R and S are very similar and at one time were nominally the same material, but early troubles in obtaining pure platinum and rhodium caused a divergence. Type R has about 10% more voltage output than Type S. The Type S is thought to be slightly more stable so was used as the reference thermocouple for the earlier temperature scales. Consequently, Type S has a better history of proven performance and is therefore preferred as a reference thermocouple for the calibration of other thermocouple types. With care, errors can be kept to a few tenths of a degree up to 1000 °C.

Type B thermocouples were designed solely for high-temperature applications. Around room temperature, the Seebeck coefficient is sufficiently low (see Figure 8.9) that quite large errors in the reference-junction temperature do not cause a significant error in the observed voltage. As a result, Type B thermocouple instrumentation is often supplied with no input from a reference-junction temperature, and instead a fixed offset is applied to the voltage output to account for a typical room temperature. However, for the thermocouple to function properly the two connections at the reference junction must be at the same temperature; therefore a proper reference junction should always be used.

8.3.3   Base-metal thermocouples

Base-metal thermocouples are the standard types T, J, K, E and N, all of which use nickel in some form (see Table 8.1). Because they all oxidise easily, they are not easily annealed to remove mechanically induced inhomogeneities. In addition, at higher temperatures the more complex alloys undergo microscopic metallurgical changes that may not be reversible. Overall, base-metal thermocouples do not make as good thermometers as rare-metal thermocouples. However, their lower cost can offset this, especially for harsh environments where frequent replacement is required.
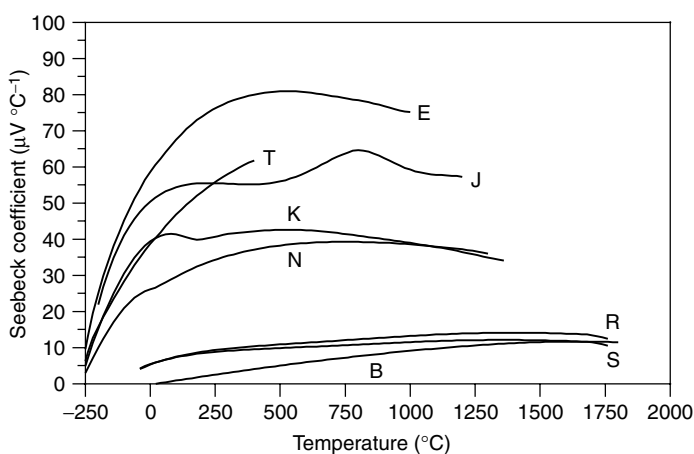
Figure 8.9   The Seebeck coefficient for various thermocouples. The letters refer to the thermocouple types of Table 8.1

As a rule, do not use base-metal thermocouples as all-purpose wide-range thermometers (see Tables 8.3 and 8.4) unless errors of over $10\,°C$ are of no concern. They are best used in fixed locations to measure temperatures over a limited temperature range. This is especially true for higher temperatures. Otherwise, great care is needed to ensure that the wires have not been subjected to mechanical forces or to higher temperatures between uses. The proper use of a wide-range thermocouple instrument is to connect it to different thermocouples reserved for special purposes and *not* to use a single thermocouple probe as a general-purpose thermometer.

Each thermocouple has its particular niche but some of these are being taken over by PRTs or thermistors. In general, base-metal thermocouples have two advantages: they can be made very small, and they can be made to withstand harsh environments.

Type T, being made out of copper and a simple copper nickel alloy, often withstands more handling and is useful for temperature surveys in applications such as performance tests on electrical appliances. It is also the preferred thermocouple for low-temperature work, that is to $-200\,°C$. However, the copper is a good conductor of heat so thin wire may be needed to reduce the heat flow to and from junctions to ensure they remain isothermal. Thermal anchoring of the wire, that is attaching the wire to a point at a known temperature near that of the isothermal environment, will also help reduce the heat flow. Copper should not be used above $200\,°C$, not only because of oxidation but also because increasing metal migration can cause contamination. Some manufacturers provide Type T wire made to very tight tolerances. Unfortunately, the German (DIN) Type T was once different from the Type T defined by other standards bodies. Now the DIN defines two standards, one with a letter designation of T that is the same as the internationally recognised Type T thermocouples, and one with a letter designation of U that is used for the older German Type T standard. With older European-made equipment, the user should be aware that the replacement wire may be Type U and not Type T as indicated on the instrument.

Type J is the only standard thermocouple suitable for use in a reducing atmosphere at high temperatures and as such finds wide use. In other applications, the iron wire can

oxidise rapidly if not protected. The German (DIN) Type J was once different from the Type J defined by other standards bodies. Now the DIN defines two standards, one with a letter designation of Type J that is the same as the internationally recognised Type J thermocouples and one with a letter designation of Type L for the older German Type J standard. As the difference is about 8 °C at 200 °C care is necessary when obtaining replacement wire. Type J instruments should be checked to find out which standard they require and they should then be marked accordingly.

Type K was the first successful low-cost thermocouple developed for high-temperature use but it also gives useful output down to −200 °C. It is therefore tempting to use Type K as a general-purpose thermocouple. However, because of the complex alloys used it is the worst of the thermocouples in preserving its homogeneity. Therefore, other thermocouple types should always be used where they are suitable. There are at least three main problems occurring with Type K and they are given here as examples of the complex processes that can occur inside a piece of wire and affect its performance:

(1)   Steady drift occurs above 500 °C, and more markedly above 1000 °C. Oxidation, particularly internal oxidation, changes the wire composition to cause the output voltage to increase with time (see Figure 8.10). The typical drift rate is about 1% per 1000 hours at 1000 °C.

(2)   Short-term cyclic changes, as much as 8 °C, occur on heating and cooling in the range 250 °C to 500 °C. This is caused by metallurgical changes in the positive thermoelement, which produce structural inhomogeneities.

(3)   Reversible changes, due to a magnetic/non-magnetic transformation in the negative thermoelement, make the thermocouple output vary by ±1.5 °C over the range 50 °C to 250 °C.

Note that above 500 °C all these effects contribute to the error since at least one part of the thermocouple will be at the lower temperatures.
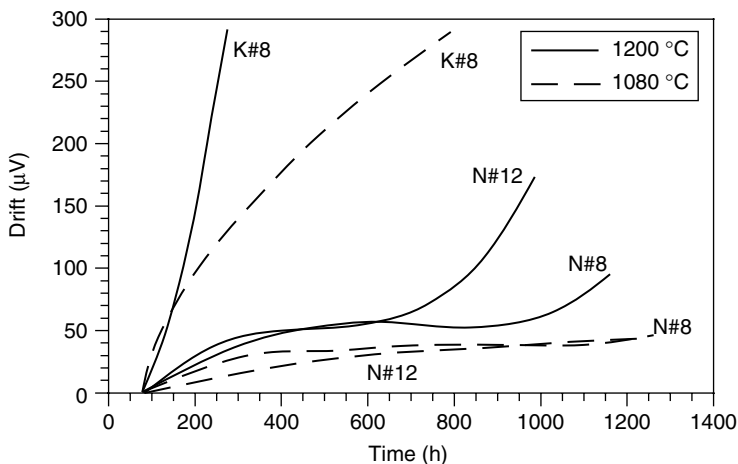
Figure 8.10   High-temperature drift for bare Type K and Type N thermocouple wires of two different gauges

Type E has the highest Seebeck coefficient of the standard thermocouples and uses the positive thermoelement of Type K with the negative thermoelement of Type T. This gives a much better short-term performance than Type K, so it should be more frequently used than it is. Type E can be used for high-temperature surveys above the reach of Type T.

Type N was developed to improve on and remove the known problems in Type K. A better performance is obtained for the bare wire, and very much better performance when used in a sheath made from material similar to the positive leg of the Type N. In particular, the stability approaches that of rare-metal thermocouples for temperatures below 700 °C. The sheathed material is available under the trade name Nicrobel® in several variations optimised for different conditions. Figure 8.10 illustrates the typical drift that can be expected for these two types of thermocouples. The drift is that expected under good conditions; in more hostile environments the drift will be much faster. While many problems are reduced by using Type N, this has been achieved by moving some of the problems with alloy composition to higher temperatures. Overall, Type N is a significantly better thermocouple than Type K, and is now widely available.

8.3.4   Non-standard thermocouples

As a result of investigations into more suitable materials for difficult situations, the performance of over 200 different thermocouples has been studied and reported. Two areas of industrial importance are the measurement of temperatures up to 3000 °C and temperatures of highly reactive gases, especially those rich in hydrogen and carbon monoxide. Both molecules are highly reducing so they cause major chemical changes in some wires. Hydrogen is a small molecule that passes easily through hot metals, including sheaths, so it damages many thermocouples.

Tungsten–rhenium alloys are suitable for higher temperatures, up to 2400 °C, and are not overly affected by hydrogen, but have a poor oxidation resistance and are very brittle. Suitable sheaths are needed to prevent oxidation and to protect the wire from mechanical stress. The Seebeck coefficient is low at low temperature so they are not normally used below 400 °C. Large drifts can occur around 2000 °C due to boron in the commonly used boron nitride sheath. Alumina sheaths cause considerably less drift but restrict the upper temperature to 1800 °C. Low drift is found for clean atmospheres up to 1500 °C. Table 8.5 lists the more common tungsten rhenium pairs. The one with the pure tungsten is particularly brittle so is not often used.

An alternative high-temperature thermocouple is boron carbide/graphite (B_4C/C) for temperatures up to 2200 °C. The output of these thermocouples is very high, around

Table 8.5   Available tungsten-rhenium alloys for thermocouples

Type designation*	Alloy	Range	Tolerance
G	W/W 26%Re	300 °C to 2400 °C	±5 °C ±1%
C	W 3%Re/W 25%Re	0 °C to 2400 °C	±5 °C ±1%
D	W 5%Re/W 26%Re	0 °C to 2400 °C	±5 °C ±1%

*The letter type designations are those commonly given by manufacturers but are not currently recognised by documentary standards.

$290\,\mu V\,K^{-1}$. While there is a large variation in Seebeck coefficient with production, the resulting temperature error is only of the same order as that resulting from their use in hostile environments. Comparison against high-temperature noise thermometers shows drift or variability up to 10% when such a thermocouple is operated around $2000\,°C$. Overall, the performance in terms of stability is better than for tungsten–rhenium thermocouples.

Making a thermocouple out of pure metals rather than alloys avoids alloy variation as a source of inhomogeneity, and this has been proved for the platinum–gold thermocouple. Investigations of this thermocouple reveal that uncertainties as low as a few hundredths of a degree are possible if care is taken to avoid strain from the differential expansion of the two metals. It is hoped that this thermocouple will be a practical transfer standard that can utilise the increased accuracy of ITS-90 above $630\,°C$. Modern instruments can handle the lower output of this thermocouple with reasonable accuracy.

In recent years, the platinum–palladium thermocouple has been investigated. Like the platinum–gold thermocouple, it is a pure-element thermocouple pair so is capable of accuracies approaching $10\,mK$ at $1000\,°C$ and $0.1\,°C$ at temperatures up to $1500\,°C$. Stability and repeatability are, however, dependent on the use of high-purity palladium ($>99.997\%$), which is difficult to obtain.
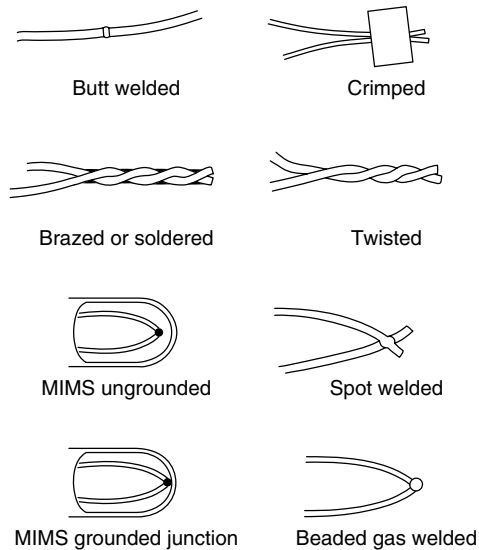
8.4 Construction

There is no standard way to construct a thermocouple thermometer, as they have been adapted to a wide variety of situations. Where possible a thermocouple assembly should be obtained from a well-known supplier because specialised materials and techniques can be involved for some applications. The main steps involved in construction are covered here primarily to help the user specify the thermocouple when purchasing. They will also provide general guidance for the construction of thermocouples.

8.4.1 Junctions

The sole purpose of a thermocouple junction is to provide electrical continuity. Whereas twisting and soft solder may well be suitable at low temperatures, for reliable high-temperature exposure the junction should be welded.

The size of the junction can be an important consideration. The upper limit on the size is determined by the requirement that the junction should always be immersed in an isothermal environment. If a small junction is required then some methods of construction are precluded (see Figure 8.11), as are large wire diameters. Limits on the wire diameter may also depend on the amount of immersion error tolerated (see Section 4.4.1).

Before joining the wires, make sure that they are clean. For the smallest-size junction, the two wires can be butt welded. For the best mechanical strength, twist the wire pair together so that thermocouple metal is in contact with thermocouple metal (see Figure 8.11). The wires can be held together more permanently with soft solder for lower temperatures, and silver solder, brazing, arc, gas and spot welding for higher

Figure 8.11 Construction of thermocouple junctions — a representation of a variety of methods that have been found satisfactory. MIMS thermocouples are covered in Section 8.4.5

temperatures; or crimping for speed of operation. Avoid excessive acid or flux, if used, as it may contaminate the wire near the junction, and do not subject the wires beyond the junction area to undue force. If flames are used, keep them small and avoid contact with any other part of the thermocouple wire. All the operations should be done in a neat and tidy manner so that the position of the junction is well defined and the wire near the junction is undamaged, especially if the bare junction is to be exposed.

8.4.2 Joins

The first rule with joins is: don't unless it is absolutely necessary! They are a major source of difficulty because of the inhomogeneity introduced. The first choice should always be to have the same single continuous wire from the measurement junction to the reference junction, for each thermoelement.

There is only one good reason for a join: to connect a specialised thermocouple assembly to more flexible leads. Specialised assemblies include high-temperature thermocouples with very heavy-gauge wires, totally sealed units with protection against corrosive atmospheres, very fine wires to prevent thermal loading, and very expensive thermocouple wires such as the rare metals. Note that in all these cases the lead wire being connected is unlikely to be identical to that in the thermocouple assembly. In any case, the specialised assembly should be sufficiently long that all joins and connections will be below 50 °C. If you cannot handle a join or a head assembly with bare hands, it is too hot.

A partially acceptable reason for a join is for convenience; for example, in a test rig where many tests are made and the thermocouples must be replaced frequently. Procedures must be in place to check the integrity of the thermocouple circuit after any changes have been made.

A poor reason for a join is to repair a break in the wire. Replace the whole wire, and if this is not immediately feasible, make sure that the repair is recorded so that the wire will be replaced later. This also allows checking if problems arise.

Another poor reason for joins is to switch many thermocouples to one reference junction and instrument. This was common practice in early thermocouple thermometry, but is prone to difficulties because the switches are not of the same material as the thermoelements and are difficult to keep isothermal. Each measurement junction should be connected to its own reference junction, that is an isothermal region whose temperature is known. Any switching should be made after the reference junction so that only copper wires are being switched. Even so, remember that the switch assembly is still part of a thermoelectric circuit and ensure that it is as near isothermal as practical.

The same principles that apply to junctions apply to joins: they must be electrically continuous, mechanically strong, clean and in an isothermal environment. Unlike a junction, however, a join should never be at high (or low) temperatures and instead should be at a temperature near room temperature, for example between $10\,^{\circ}\mathrm{C}$ and $50\,^{\circ}\mathrm{C}$.

Joins should be made with thermocouple metal to thermocouple metal and held in a mechanically stable manner. Special plugs, sockets and connectors made out of mechanical grades of the thermocouple alloys are readily available commercially and should always be used for making quick connections (see Figure 8.12). The plugs and sockets should conform to the appropriate standard. While the plug and socket connections for base-metal thermocouples are to a very similar alloy, it is best to
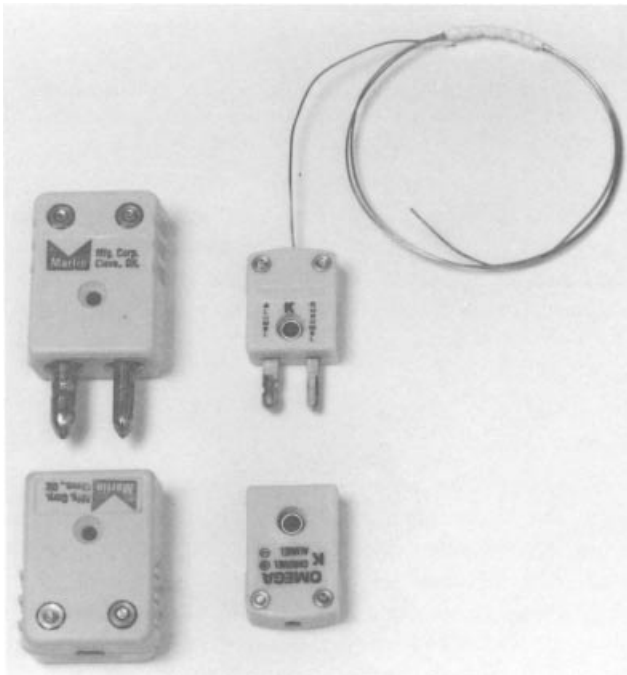
Figure 8.12 Examples of two types of plugs and sockets for connecting thermocouples. The plug and socket contacts are made from the appropriate thermocouple materials

ensure there are no temperature gradients across the connector. For the rare-metal thermocouples, this is essential. The two metals used in these connectors are usually a pair of copper alloys rather than the Type R or Type S platinum–rhodium alloys. As a pair, they mimic the required Seebeck coefficient but individually the Seebeck coefficients are much different to the platinum and platinum–rhodium legs. Therefore, if the two pairs of junctions associated with the connectors are not at the same temperature, large errors can occur. Note too that the same connectors are used for Type R and Type S thermocouples.

If joins are held by a screw thread, soldering or welding should not be necessary, because at low temperatures there should be very little thermal expansion to loosen the mechanical joint. Ensure that the joins for the pair of wires are as close to each other as possible. Suitable thermocouple connection boxes or heads made out of cast metal are available commercially, and can be used to house the joins in order to keep them isothermal. Keep the location of the join free from draughts and away from hot or cold objects.

8.4.3 Extension leads and compensating leads

In spite of the fact that joins are undesirable, many practical thermocouple circuits use flexible wires to connect a specialised assembly to the reference junction. Generally, this connecting wire differs from the wire in the thermocouple assembly in both diameter and composition. Thus, the thermocouple circuit has a long length of distributed inhomogeneity. If it were possible to keep the connecting wire isothermal then there would be no Seebeck voltage from the connecting wire, and hence no error. As it is not feasible to ensure isothermal conditions along a long length of wire, an alternative approach is needed to reduce the likelihood of error.

A thermocouple extension lead is a connecting wire or cable that has been selected not only to keep the error low but also to provide convenience in use, for example, flexibility. The basis for the selection can be seen by considering Equation (8.1). If the temperature gradient along the extension lead can be kept small, perhaps zero (i.e. the isothermal condition), then the Seebeck voltage produced by the extension lead is small. If in addition the Seebeck coefficient for the extension lead is similar in value to the Seebeck coefficient for the thermocouple wire in the assembly, then the additional error contribution due to the use of the extension lead can be kept small and probably insignificant. The Seebeck coefficients need only match over a limited temperature range if the use of extension leads is restricted. For standard thermocouple types, the range should be restricted to $10\,°C$ to $50\,°C$ in line with that for joins.

Two types of extension leads are usually distinguished: *extension leads* and *compensating extension leads*.

Extension leads are made from the same alloys as the thermocouple wires but may have small differences in Seebeck coefficient due to the smaller diameter of the wire. Some manufacturers make the leads to the same tolerance as the single thermocouple wire, but generally they are made to twice the tolerance. They are usually supplied as flexible multi-strand cable.

Compensating extension leads are made from different alloys but match the Seebeck coefficient of the required thermocouple over a limited temperature range. In the case

of the platinum-based thermocouples, Types R and S, the leads are made of copper and a copper alloy in a multi-strand cable to give both flexibility and lower cost. The considerations for the use of the compensating leads are the same as that for joins, but because the materials only match the Seebeck coefficient as a pair, and only over a small temperature range, special care must be taken to ensure that the pairs of connections are isothermal.

From Figure 8.9 it can be seen that Types T and K match quite closely ($\pm 0.2\,°C$) over the room-temperature range, and sometimes Type T extension wire is used as a compensating extension lead for Type K thermocouples. However, this penny-pinching is misguided. The difference in cost between the Type K and Type T wires is small compared with the cost of the rest of an installation, and the cost of the extra care required to avoid an increased uncertainty of several degrees Celsius arising from increased sensitivity to temperature gradients at the joins. Therefore, use compensating extension leads only for the expensive rare-metal thermocouples and then only if long wires are needed.

8.4.4 Sheaths and thermowells

While completely bare wire is sometimes used, especially in applications requiring the heavier gauges, it is more common to cover the wire to provide electrical insulation and environmental protection. A wide variety of insulating materials are available to suit many purposes and the user is advised to consult a catalogue to select an appropriate covering material. See Table 8.6 for a short list of possibilities. For higher temperatures, thermocouples are commonly hand assembled from bare wire and ceramic beads. Cleanliness is essential for this operation. Avoid work hardening the wire during handling. Bare junctions can be used to achieve a low mass or small size. If there is a risk of contamination the wire may need to be replaced frequently or if an increase in size and mass can be tolerated, a sheath can be used to provide protection.

Dimensional constraints on the sheath should be established first in order to select the length and diameter of the sheath. The minimum length will be determined by two thermometric factors: the immersion depth and the temperature gradients. The immersion depth should be at least five times the diameter of the sheath, and preferably

Table 8.6 Insulating materials for thermocouples

Material	Range of maximum temperatures*
PVC	65 °C to 85 °C
Polyurethane	65 °C to 85 °C
PTFE	190 °C to 260 °C
Polymer/glass laminate	200 °C to 280 °C
Glass fibre	400 °C to 480 °C
Ceramic fibre	800 °C to 1200 °C
Ceramic beads	1100 °C to 1950 °C
Magnesia/stainless steel sheath	600 °C to 900 °C
Magnesia/Inconel® sheath	800 °C to 1050 °C
Magnesia/Nicrobel® or Magnesia/Nicrosil®	1100 °C to 1200 °C

*The maximum temperature depends on a number of factors including the manufacturer, the duration of exposure, the environment and the detailed composition of the material.
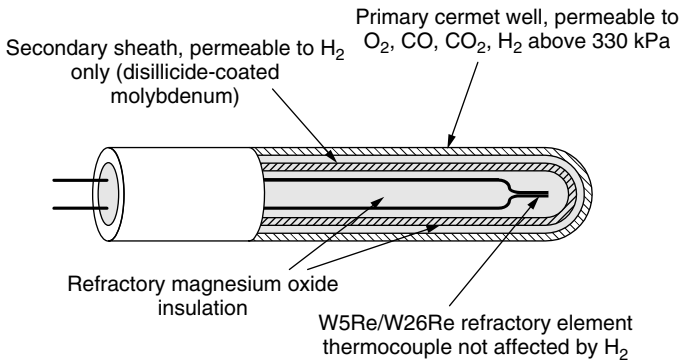
Figure 8.13   A multi-layer protective sheath required for a high-temperature thermocouple used in a hostile environment

10 times (see Figure 4.4 and accompanying discussion). As the output of the thermocouple is largely determined by the region of maximum temperature gradient, it is important that the wire has good protection over this region. Therefore, the sheath should extend beyond the medium of interest until its temperature is close to room temperature. This can lead to unsightly assemblies protruding well out from furnace walls, but it is necessary for the best accuracy. The choice of diameter is likely to be a compromise between the time constant and the thickness to achieve adequate protection. Other physical constraints may be imposed by the size and nature of the system of interest.

For particularly harsh environments, it is unlikely that a single sheath will provide all the protection required, and several layers may be needed. An example is given in Figure 8.13 for tungsten–rhenium wire. Another example is where a ceramic sheath is used in a metal thermowell to prevent contamination of a platinum thermocouple by the metal. Suppliers of sheathing material provide extensive lists recommending cost-effective materials for particular environments.

Over their lifetime thermocouples need regular checking or calibration and will eventually need replacing. Sheaths and thermowells should be designed to allow this to be done relatively easily and without a major disruption to an ongoing process. One way is to have two thermowells close together so that a calibration can be done in one without disturbing the other. Alternatively, provide enough space in one thermowell so that a thin calibrated probe can be inserted alongside.

Complete removal of a thermocouple for calibration is not desirable. Not only will the calibration process assess the output from a different section of wire (see Section 8.8), but it may also heat treat the wire so that it performs differently when it is put back into service. The thermocouple must also be reinstalled at exactly the same position to ensure that the temperature profile and the output voltage are the same.

8.4.5   Mineral-insulated metal sheaths

MIMS (mineral-insulated, metal-sheathed) thermocouples are a very convenient form of thermocouple cable (see Figure 8.14). They offer the same protection as a metal
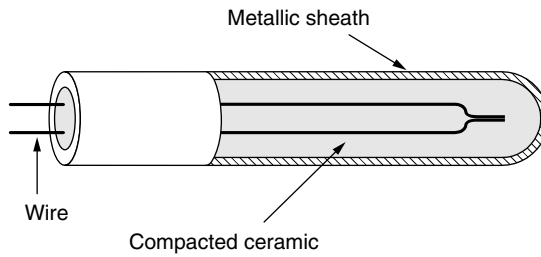
Figure 8.14   Compacted ceramic-insulated MIMS thermocouple showing its composition

sheath while retaining a reasonable amount of flexibility. Various sizes from 0.25 mm to 6 mm diameter are often available from stock with special diameters up to 24 mm made to order. The smaller diameters make it possible to preserve the size and mass advantage of thermocouples in a protective sheath.

There are, of course, compromises that must be made in return for the convenience:

- The force required to produce the cable produces strain in the wire and gives rise to inhomogeneities. MIMS cable is therefore more likely to exhibit variability in output with changes in immersion and heat treatment than bare-wire thermocouples.

- Although the cables are flexible, bends in the cable put strain on the thermocouple's wires inside the sheath. Bends in the cable should never be positioned at a temperature gradient. A single bend placed at a sharp gradient can produce errors of several degrees.

- Magnesium oxide, the most commonly used insulation material, can absorb moisture and provide an electrical shunt along the length of the cable. It is very difficult to assemble a fully sealed cable; a full seal may not even be desirable as a pressure build-up in the cable may occur on heating. If the cable is used frequently above room temperature then the cable insulation will remain dry. Prolonged storage of the cable will give time for water to be absorbed and an insulation check should be made before use. The insulation resistance should be over $1\,M\Omega$. If necessary, dry the cable in an oven until the insulation resistance is restored.

- In the compact MIMS structure, migration of metal atoms from the metal sheath to the thermocouple wire can occur more easily at higher temperatures and thus contaminate the thermocouple. This will happen long before the sheath fails. Therefore stainless steel sheathed cable should not be used above $600\,°C$ for permanent installations, and similarly Inconel® should not be used above $800\,°C$ for permanent installations. As a rule, choose sheath material whose composition is as close as possible to the thermocouple material, providing that there is still adequate chemical protection. For platinum thermocouple types, a platinum sheath is best. For Type N thermocouples, the best practice is to use an alloy closely related to the Type N wire, either Nicrosil® or Nicrobell®. Nicrosil® or Nicrobell® sheathing is now available for heavy-gauge Type K assemblies for high-temperature use, and is far superior to stainless steel or Inconel®. As several variants are available, the user will need to exercise care in selecting the best one for the particular application.

- The MIMS sheath, while convenient, provides only limited protection, and, being flexible, may not provide the best mechanical stability. Use other protection besides

that offered by the sheath material, especially where the cable goes through a temperature gradient. Where there is a harsh chemical environment, use additional sheath material.

- Electrical effects may interfere with the thermocouple's performance. Long cables will lower the insulation resistance even without moisture. The metal sheath may need to be electrically grounded, depending on the environment. MIMS cable also allows the junction to be grounded to the sheath.

- Electrical safety must be considered where the thermocouple is used near bare electrical heaters, for example. In particular, electrically ground any metal sheaths but avoid any ground loops. Most modern voltmeters work best with differential inputs and hence there is no need to ground electrically any of the thermocouple wires.

8.5 Instrumentation

8.5.1 Reference junctions

A small rearrangement of Equation (8.3) gives the measurement equation that must be implemented in any thermocouple temperature measurement:

$$E(t_M) = E_{meas} + E(t_R). \tag{8.5}$$

In order to claim traceability for a thermocouple measurement, two measurements are needed: the output voltage of the thermocouple, E_{meas}, and the temperature of the reference junction, t_R.

Reference junctions at 0 °C

The use of an ice point to enclose the reference junction has the advantage of simplicity in the calculation of the temperature, since by definition, $E(0\,°C) = 0$. With the reference junction at $0\,°C$, one only has to measure the voltage from the thermocouple and convert the reading to temperature using tables or an equation (see Appendix D for the tables and equations for standard letter-designated thermocouples).

In the laboratory, the ice-point procedure (Section 3.2.4) makes a reference-junction environment of known temperature and uniformity suitable for a small number of thermocouples. If heavy wires or numerous thermocouples are involved then an ice–water mixture of sufficient capacity may be better. The mixture should be kept well stirred and the temperature monitored with a reference thermometer. Sealed reference junctions can be used to protect the wire, or an oil-filled thermowell can be placed in the ice–water mixture. While in the short term pure water may not affect a bare junction, there is the risk of corrosion in the longer term. With some insulation materials, there is the risk of contaminating the water and changing its electrical conductivity.

The main difficulty with ice is the need to keep it replenished and stirred. For many industrial surveys, an automatic ice point is suitable. Automatic ice points use the expansion of ice on freezing to serve as a control mechanism for a thermowell holding the reference junctions (Figure 8.15). While the general accuracy may not be as good
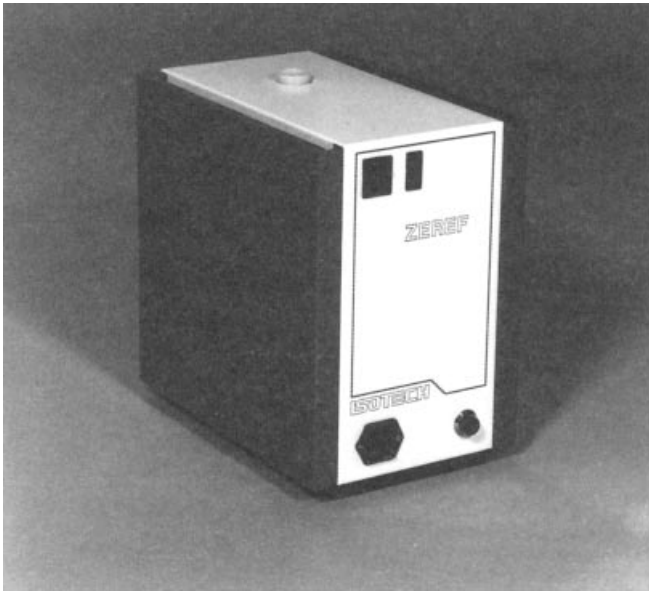
Figure 8.15   An automatic ice point for thermocouples

as that of a well-made ice point, the automatic ice point will work over longer periods and avoid gross errors due to lack of attention.

The use of an ice point usually results in an extra temperature gradient of 20 °C (or thereabouts) over a short length of the thermocouple wire as well as over the leads to the voltmeter. The extra wire and gradients are a potential source of spurious voltages if the wires are not homogeneous.

Reference junctions at other than 0 °C

When the reference junction is not at 0 °C, we must make a correction to the measured voltage to account for the voltage that would be produced by the length of thermocouple exposed to a temperature gradient between t_R and 0 °C. This process is often called *cold-junction compensation*. To ensure confidence in a thermocouple measurement the following procedures must be carried out either by the user or by automatic functions of the instrument:

- establish an isothermal reference junction;
- know the temperature of the reference junction;
- use the standard tables or reference functions to determine the Seebeck voltage at the reference-junction temperature;
- make an accurate measurement of the Seebeck voltage from the thermocouple;
- add the two voltages together; and
- use the standard tables or reference functions to determine the measured temperature.

In principle, a fully automatic approach to the reference-junction compensation gives the highest reliability by removing the chance of human error. However, in practice the user may find that the traceability requirement imposed by standard test methods is to have the process directly under human control and properly documented to allow an audit to be made. This is especially true when higher than normal accuracy or reliability is called for.

When making corrections to measurements for a reference junction not at $0\,°C$, the calculations should always be carried out in terms of voltage, since according to Equation (8.5) it is the voltages that add around a thermocouple circuit. Failure to add voltages can give rise to significant error, as illustrated in the following example.

Example 8.1

A Type N thermocouple is used to measure a temperature. A voltage reading of $2050\,\mu V$ is obtained. The isothermal reference junction is at $18\,°C$ at the time of the reading. What is the measured temperature?

Firstly, we must apply a correction for the reference-junction temperature. From the Type N thermocouple tables we find $E_N(18\,°C) = 472\,\mu V$. Thus

$$E_N(t) = (2050 + 472)\,\mu V = 2522\,\mu V.$$

Using the table again we can now find the temperature: $t = 91.5\,°C$.

A common error is to use the table only once to find an apparent temperature difference and add this to the reference-junction temperature. In that case, inferring that $2050\,\mu V$ were equivalent to a $75.2\,°C$ temperature difference would lead to an incorrect temperature reading of $93.2\,°C$. With this example, the resulting error is less than $2\,°C$; unfortunately few thermocouple types are as linear as Type N and much larger errors are more common (see Exercise 8.1).

In an instrument implementing Equation (8.5) properly, the temperature of the reference-junction is measured using an independent thermometer, perhaps a thermistor or a PRT. The microprocessor in the instrument converts the reference-junction temperature to a voltage, which is added to the measured voltage, and the sum is then converted back to temperature. While this approach is well suited to digital instruments, it is not easily implemented directly in analogue instruments. Consequently, a variety of analogue techniques have been developed that make various compromises between accuracy and cost.

One common approximation is based on solid-state temperature sensors (diodes or transistors), which produce a voltage or current that is proportional to temperature. The reference-junction compensation is carried out by using the sensor to inject a voltage proportional to the reference-junction temperature into the measurement circuit. This technique provides a linear approximation to $E(t_R)$. This is suitable for instruments used close to the nominal reference-junction temperature, typically $20\,°C$. The technique introduces errors due to the errors in the reference-junction temperature measurement and in the fraction of the voltage injected. In good instruments, the errors

are typically less than $0.2\,°C$ for reference junctions near $20\,°C$, but increase rapidly with temperatures much higher or lower than $20\,°C$ according to the non-linearity in the thermocouple response. An additional error arises because the temperature sensor may not follow the reference-junction temperature after rapid changes in ambient temperature, for example with movement of the meter into very hot or cold environments. In many instruments, the fraction of the voltage injected is programmed using a single resistor chosen according to the type of thermocouple. Since a change in thermocouple type requires a change in the resistor, the technique is suited to instruments designed for a single thermocouple type. The technique is very common in hand-held instruments.

A coarser approximation is to assume a fixed temperature for the reference-junction and add a fixed compensating voltage to the measured voltage. This technique produces a large error as the reference-junction temperature changes away from the nominal temperature, except for thermocouples where the Seebeck coefficient is zero at the nominal reference-junction temperature. For this reason, Type B thermocouples are the only standard types that should employ this technique. For the other standard thermocouple types, the errors can be many degrees.

In principle, digital equipment should be more capable than most analogue equipment of following good practice for the reference-junction and data conversion. Unfortunately, electronic reference junctions can present traceability problems to the user. Many digital circuits are blind copies of analogue methods, which were designed for convenience and low cost rather than good thermometry. The compromises involved are seldom documented in user manuals so the user should check that the instrument functions correctly. This can be done by checking that the instrument reads $0\,°C$ with the thermocouple in an ice point, for a range of different ambient temperatures. In most cases, the errors arising in the thermocouple due to inhomogeneity effects will be greater than the errors introduced by the instrument, typically $±1\%$.

Exercise 8.1

Using thermocouple tables repeat Example 8.1 assuming that a Type B thermocouple was used. How large is the error if the temperature is incorrectly calculated assuming $2050\,\mu V$ correspond to a temperature difference?

8.5.2   Instrument types

There are two broad categories of instrument: instruments with external reference junctions and those with internal reference junctions. Recorders can fall into both categories.

Instruments with external reference junctions

The best accuracy with thermocouple measurement is obtained with an ice-point reference-junction. The ice point is made according to the guide in Section 3.2.4. Typically, a $5\frac{1}{2}$-digit instrument with a resolution to $1\,\mu V$ is used.

A lower-precision measurement can be made with an electronic compensating reference-junction. These small battery-powered electronic devices amplify and linearise the thermocouple signal, and compensate for the reference-junction temperature. They provide an output voltage proportional to temperature, typically $10\,\text{mV}\,^\circ\text{C}^{-1}$.

In either case, the voltmeter should have its own calibration as a voltmeter. As most meters have an input impedance over $1\,\text{M}\Omega$ compared with the maximum $1\,\text{k}\Omega$ impedance for a thermocouple, there is negligible electrical loading on the thermocouple. The voltmeter should be kept reasonably isothermal inside its specified temperature range and not subjected to rapid temperature changes. Reverse the leads to the voltmeter to check for thermal stability, as the reading should change only its sign and not its numerical value.

Instruments with internal reference junctions

As discussed in the previous section, reference or cold-junction compensation takes several forms offering various compromises between accuracy and cost. Digital equipment is available with a wide range of accuracies, depending largely on the quality of the reference junction. Obtaining good isothermal conditions for the instrument is more important than for the voltmeter because of the included reference-junction. In this respect, plug-in cards for computers may not always be in suitable environments to provide accurate reference junctions.

A feature of a good thermocouple meter is the ability to monitor the impedance of the thermocouple. A $1\,\text{kHz}$ signal can be used to avoid thermoelectric voltages interfering with the a.c. resistance measurement. If, say, the impedance is over $1\,\text{k}\Omega$ then the display can be blanked out to indicate a likely open circuit. A more useful feature is to have a record of the changes in impedance with time to compare with the temperature record. Ageing of the thermocouple can then be followed, as well as any sudden changes that may indicate a fault, for example crushing of a thermocouple cable.

Connection to the meter may be by direct wiring or through plugs. Direct wiring to the reference junction will usually be found in cases where the meter can cope with several thermocouple types. Plugs will be used where the meter is intended for one thermocouple type. As the materials in the thermocouple plugs and sockets will be the correct type for the thermocouple wire, it is important not to mix them with other types. Similarly, for a multi-thermocouple meter it is important to select the correct thermocouple type. Meters usually cover a wide range but this does not mean that a single thermocouple probe can be used over that range; several different probes may be required. In general, thermocouples cannot be used as general-purpose thermometers unless they are used at greater immersion or higher temperature than previously. In this way, it is always new wire that is exposed to the temperature gradient.

Chart recorders

A chart recorder includes all the features of the thermocouple meter along with a record-keeping function. As such, it should be considered as two separate instruments: firstly as a meter, and secondly as a recorder.

Calibration of a chart recorder should firstly be in terms of its indicating device and not the paper record. It is the operator's responsibility to ensure that pen, ink and paper make an accurate recording of the output of the chart recorder.

Several factors can influence the accuracy of the record. The pen and ink need regular checking to ensure that the record is actually being written. Paper size varies with humidity and temperature at a different rate than the metal of the chart recorder. Sprocket holes on the chart paper can be distorted or mis-punched. The printed scale on the chart may be displaced and usually the chart recorder has a small adjustment to ensure that the pen is indicating the same value on the chart paper as the instrument indicator. Daily procedures may be needed to ensure that the chart records are as accurate as the instrumentation allows. Uncertainties in the recording process are typically half a scale division, that is wider than the pen thickness.

Both analogue and digital chart recorders are available. An analogue recorder may use a non-linear scale on the chart paper to convert its output to temperature. Digital recorders often print the reading as well, and hence are easier to check. Where colour coding is used for multiple channels, it is essential not to allow confusion by poor lighting or colour blindness.
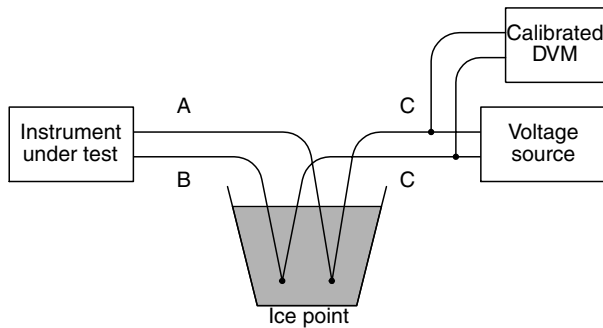
8.5.3   Thermocouple calibrators

Many manufacturers make devices called calibrators for checking thermocouple instruments. They are normally portable devices used to check thermocouple equipment throughout an industrial plant. A calibrator is essentially a thermocouple meter in reverse. When a temperature is dialled on the front panel of the calibrator, a voltage is produced at the output which, when connected by thermocouple wire to a thermocouple meter, should cause the meter to give the same temperature reading. A very important point is that even though calibrators give temperature readings they cannot provide a temperature calibration. A thermocouple temperature measurement relies on a meter and the thermocouple. The calibrator checks only the meter, and not the thermocouple. Unfortunately, the biggest problems occur with the thermocouple.

Meter readings made with the calibrator should be taken going both up and down the scale, especially in the case of chart recorders, which often have a considerable deadspan (mechanical hysteresis). For a meter resolution of $1\,°C$ the calibration steps should be every $50\,°C$ or so. Any differences can be used to correct readings made with the meter, or the meter may be adjusted to give the same reading as the calibrator.

Both the meter and the calibrator can be designed for multiple thermocouple types. Therefore, it is essential to use the correct thermocouple wire to connect the instruments and to ensure that both are set to the same thermocouple type. Again, isothermal connections to both instruments are important. Many calibrators have exposed terminals and these should be protected and allowed to stabilise after the thermocouple wire has been connected. If the wrong wire is used then an error will result depending on the temperature difference between the calibrator reference junction and that of the thermocouple meter.

The output impedance of the calibrator should be low, that is below $10\,\Omega$. Thermocouple circuits have a very low electrical resistance and therefore thermocouple meters do not require high input impedance. Some older instruments have low input impedance so, for example, injecting a voltage from a potentiometer with a $10\,k\Omega$

Figure 8.16 Calibration of a thermocouple instrument. The thermocouple instrument is connected by thermocouple wire, of the same type as programmed in the instrument undergoing the test, to the reference junction, immersed in an ice point. Instrument wires, typically copper, connect the reference junction to a stable voltage source and a calibrated voltmeter to provide traceability

output impedance will cause errors. Modern digital thermocouple meters should not be prone to this problem.

The general accuracy of calibrators is around $\pm 0.5\,°C$ to $\pm 2\,°C$. While this accuracy is sufficient for many thermocouple instruments, a higher precision is sometimes required. Figure 8.16 shows a method of calibrating thermocouple meters with a voltage source and a digital voltmeter (DVM). This circuit can also be used with calibrators when higher accuracy is required, by disabling the internal reference-junction compensation in the calibrator. Note that the user must supply a short length of thermocouple wire between the ice point and the instrument under test. This wire should be in good condition to prevent the introduction of inhomogeneity errors into subsequent measurements.

8.5.4 Alternative thermocouple circuits

The basic measurement circuit of Figure 8.7 will generally be used with most instruments. However, there are several variations that solve or simplify some measurement problems.

Differential thermocouples

In general, thermocouples are not good thermometers for measuring temperature differences. The uncertainties arising from inhomogeneities tend to be several tenths of a degree unless great care is taken over the condition of the wire. However, those thermocouple types with pure elements on one leg lend themselves to higher-accuracy measurements of temperature difference. An example is shown in Figure 8.17. In this case, a Type T (copper–constantan) thermocouple is used to measure the temperature gradient in an oven. Note that the constantan is contained entirely within the oven so is not subjected to large temperature gradients. Instead, the two copper leads carry the signal to the meter. The copper leads are normally pure so are not afflicted with the
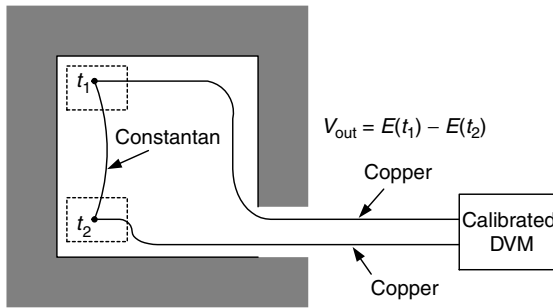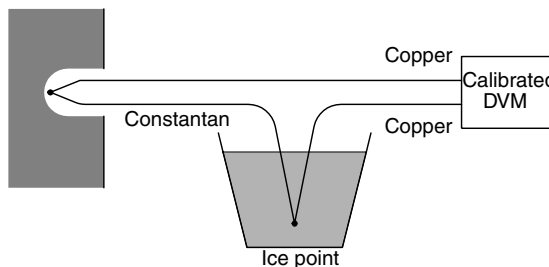
Figure 8.17   A differential thermocouple using Type T thermocouple wire. Note that the alloy leg of the thermocouple is not exposed to large temperature gradients. The two pure copper legs are less susceptible to inhomogeneities so are used to connect the thermocouple to the meter

same inhomogeneity problems as alloy wires. This same technique can be employed with Type R and Type S thermocouples since they have a pure platinum leg, and Type J thermocouples since they have a nearly pure iron leg. Type T is generally the first choice for a differential thermocouple because the copper leads can go directly to a meter. With the other thermocouple types, a proper reference junction should be used to control the temperatures of the two connections between the platinum or iron legs and the copper instrument leads. Remember that the output of the thermocouple is the voltage difference $E(t_1) - E(t_2)$, but we want to measure temperature difference. If accurate measures of temperature difference are required, an independent measure of the temperature of the oven is required to determine the Seebeck coefficient at the oven temperature.

In the case of Type T thermocouples, the alternative circuit of Figure 8.18 is sometimes used to measure temperature. For other thermocouples, this circuit arrangement is not suitable because of the higher relative Seebeck coefficient with respect to the copper alloy terminals of the voltmeter.
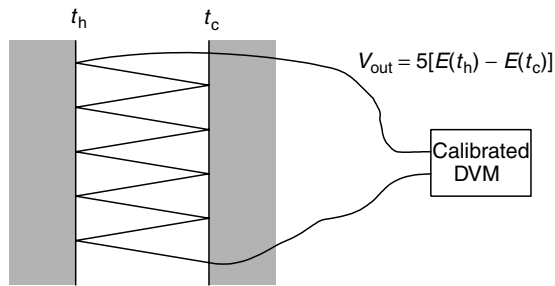
Series thermocouple circuits

The main practical problem with the differential circuit of Figure 8.17 is the very low signal voltage for small temperature differences, typically a few microvolts if a

Figure 8.18   Alternative measurement circuit for Type T thermocouples, based on the differential thermocouple

**Figure 8.19** Thermocouples combined in series as a thermopile

temperature difference of less than $0.1\,°C$ must be detected. Higher sensitivity can be obtained by combining differential circuits in series as in Figure 8.19, to form a *thermopile*. Note that only two of the leads are subject to major temperature gradients, so the relative effect of inhomogeneities is reduced. Two disadvantages result: firstly, the thermopile covers a wider area and hence it is more difficult to keep the junctions isothermal; and secondly, error arises from increased heat conduction through the wires unless they are very fine.

Parallel thermocouple circuits

An apparently simple way to average the results of several thermocouples is to join them in parallel, and a number of standard test methods employ this technique. The output of the circuit is a voltage average, with the voltages weighted by the electrical resistance of each thermocouple circuit. Therefore it represents a true temperature average only when the electrical resistance in each circuit is equal and the $E(t)$ relationship for the thermocouple is linear over the range of temperatures in the average. Parallel circuits sometimes use a resistor of about $500\,\Omega$ in one leg of each thermocouple to balance the currents, but this introduces a major inhomogeneity into the thermocouple wire. The method is only suitable as a monitor of wide temperature fluctuations or variations, and hence only a very low accuracy is expected. With the ready availability of multi-channel meters and recorders, an average of actual readings from the thermocouples should be the preferred option. This would also provide the means to calculate the uncertainty or to measure the spread of temperatures.

8.6 Errors in Thermocouples

Reconsider Figure 8.8, which shows a measurement model for a thermocouple thermometer. Unlike other temperature sensors, the active part of the thermocouple is distributed over a long length and is thus exposed to a wide variation in environmental conditions, making an error assessment very difficult. Figure 8.20 summarises the various error effects that must be considered.
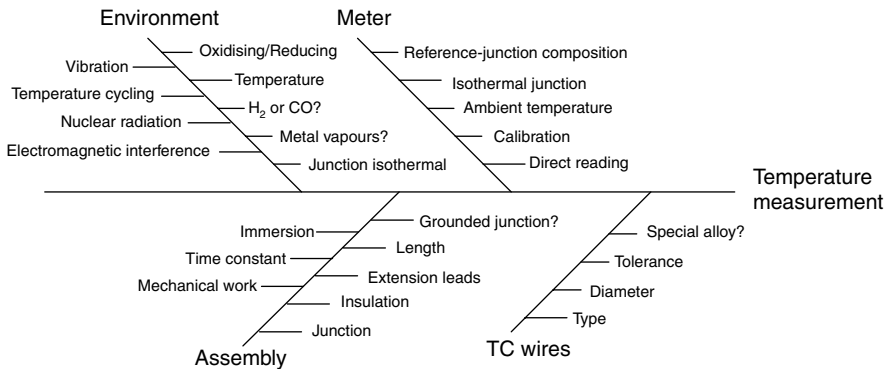
Figure 8.20 A summary of the sources of error in a thermocouple temperature measurement

8.6.1 Thermal effects

The four main thermal effects are the same factors affecting other contact thermometers: immersion, thermal lag, heat capacity and the influence of radiation. The nature of these effects is covered in detail in Section 4.4. Because of the wide diversity of constructions of thermocouple assemblies, the magnitude of the various effects is best determined experimentally. However, we can make some useful observations.

Most thermowells compromise immersion for mechanical reliability. For example, a thermowell in a pipeline may be short in length and thick in diameter to ensure it does not fatigue and snap off with vibration induced by turbulence that accompanies high flow rates. Typical thermowells have a length-to-diameter ratio of five or less, which means that they are designed to make measurements of an accuracy no better than 1%. In some cases it may be possible to improve the effective immersion depth by surrounding the thermowell with thermal insulation.

With multi-layer assemblies involving thermowells and mineral-insulated sheath assemblies, it is very easy to introduce several time constants into a thermocouple installation. The cumulative effect is that thermocouples initially appear to settle quickly, but after the initial response they continue to settle slowly for some time. In most control situations, multiple time constants severely limit the effectiveness of the temperature controller.

8.6.2 Inhomogeneity errors

The discussion on the origin of the thermoelectric effects has already emphasised the inhomogeneity problem, which is the major source of error. The big problem with thermocouples is that inhomogeneities can be introduced in any number of different ways yet can be very difficult to detect and recognise. The most important factor is an awareness of potential problems at the time of installation.

The following examples highlight some of the potential problems. Additional problems also occur with exposure to magnetic fields and ionising radiation, which are not discussed here.

Cold work

Most thermocouples are susceptible to mechanical damage. Unfortunately damage tends to occur in the very worst place on the wire: the point of entry into the furnace or oven where the temperature gradient is greatest. Alloy legs tend to be the most prone to damage. For Type K wire, measurements of the effect of cold work (bending, twisting, etc.) have been shown to cause changes in the Seebeck coefficient of up to 4% for temperatures below 400 °C. Inhomogeneities in new wire due to cold work, which occurs during the drawing of the wire and in mineral-insulated cables, can push wire outside the manufacturer's specifications. In principle, the manufacturer should anneal the wire before sale, but residual effects often persist, and may take the wire outside the manufacturer's specifications.

Chemical

Most thermocouples are fussy about their chemical environment. In particular, very few thermocouples tolerate reducing atmospheres. Often the problem lies not with the thermocouple itself but with insulating structures around the thermocouple. Magnesia, silica, boron nitride and alumina all tend to break down in a reducing environment and in the process free metal ions that migrate and contaminate the thermocouple.

With long exposure to any high-temperature environment the composition of alloys will change. Examples include the evaporation of rhodium that occurs in the platinum–rhodium alloys, and the preferential oxidation of one component of the alloy in most base-metal thermocouples. In Type K thermocouples, oxidation induces an increase in voltage of about 1% per 1000 hours at 1000 °C.

With some alloy thermocouples, a low level of oxygen is a problem. Preferential oxidation of some components of the alloy substantially changes the Seebeck coefficient. The most notable example is the 'green rot' that occurs in Type K thermocouples as the chromium is preferentially oxidised, causing a 30% drop in the Seebeck coefficient. This often happens where the wire is clamped at the wall of a furnace, right where the temperature gradient is greatest.

Heat treatment

Alloy thermocouples are also amongst those most affected by heat treatment. Alloys quite commonly have several different crystal structures or phases. As the temperature changes, the alloy will slowly change structure, sometimes permanently, to the one that offers the lowest energy state at that temperature. Typically, the different phases have different Seebeck coefficients so the phase changes give rise to hysteresis effects (where the reading depends on previous temperature exposure). Again, Type K thermocouples are the worst affected with a magnetic transformation in the range 50 °C to 250 °C giving rise to a ±1.5 °C change in output, and a short-range ordering phenomenon causing shifts of up to 8 °C between 250 °C and 500 °C. The higher-temperature transition is a difficult problem because it can take several weeks to stabilise and gives rise to sufficient hysteresis to cause the thermocouple to be out of specification after having been used just once.

Example 8.2

A Type K thermocouple instrument is used to monitor a low-temperature bath at $-20\,°\text{C}$ but the thermocouple wires have to go over a heating pipe at $90\,°\text{C}$ to reach the bath. What is the likely uncertainty in the measured temperature due to inhomogeneities?

The class 3 percentage tolerance for the Type K thermocouple is, from Table 8.2, 0.75%. The maximum temperature difference along the length of wire is $110\,°\text{C}$. The uncertainty due to inhomogeneities is estimated as 0.75% of $110\,°\text{C} = \pm0.8\,°\text{C}$. If the high-temperature excursion is reduced to $20\,°\text{C}$ then the uncertainty is reduced to $\pm0.3\,°\text{C}$.

8.6.3 Isothermal errors

Several parts of the thermocouple circuit require good isothermal conditions to ensure that any introduced inhomogeneity does not give rise to a significant error; for example, joins, junctions and terminals, and circuits in instrumentation. Experimental estimation of the likely error may be inferred by the application of a hot-air blower to the suspected parts; less than a $0.2\,°\text{C}$ change should be observed for wire in good condition.

Commonly, problems occur when compensating extension leads are used. It is important that the joins between each thermoelement and its extension lead are at the same temperature. In Type R or Type S compensating leads, a difference in the two temperatures introduces errors of about $0.6\,°\text{C}$ per degree Celsius difference in temperature, due to the difference in Seebeck coefficient between the platinum legs and the copper alloy used to simulate the platinum.

8.6.4 Reference-junction errors

Inadequate knowledge of the reference-junction temperature is probably the second most significant error for thermocouples after the ones caused by inhomogeneity. The use of a well-constructed ice point can remove this error.

Compensating reference junctions will normally have their uncertainty quoted in their specifications; $\pm1\,°\text{C}$ over the ambient temperature range is typical. The value is likely to be the isothermal value; that is, the junction needs time to settle down if, say, the temperature changes from $20\,°\text{C}$ to $15\,°\text{C}$. Some instruments can take up to half an hour to settle. This is a problem with hand-held instruments used intermittently or carried in pockets.

When switching between thermocouples on a single meter, each thermocouple should have its own reference junction so that the switching occurs along copper leads.

8.6.5 Interference errors

Even though thermocouples are low-impedance devices, they will pick up electromagnetic interference. Long lengths of thermocouple wire, for example $50\,\text{m}$ or so, make

good radio aerials! They also increase the risk of errors from unknown temperature profiles and accidental damage. Therefore, avoid long lengths of wire by using signal transmission devices that are immune to interference, such as 4 mA to 20 mA current loops. It is essential that the instrumentation used can cope with any changes in the ambient temperature.

The recommendations of Section 6.5.12 for controlling electromagnetic interference in PRTs apply here. However, some of the recommendations are not possible with thermocouple wires; for example, twisting the wire pair may create large inhomogeneity errors.

8.6.6   Wire resistance errors

As the signal to be measured is the Seebeck voltage (i.e. open circuit, as in Figure 8.7), the wire resistance should have no effect if a potentiometer or good digital voltmeter is used. Analogue voltmeters should not be used as they may draw too high a current and the reading becomes dependent on the circuit resistance.

An increase in the thermocouple resistance of three or four times indicates that a thermocouple is nearing the end of its life, and a circuit resistance of over 1 kΩ should be considered an open circuit. Monitoring the circuit resistance is useful to check for possible wire damage from chemical or mechanical sources.

Ungrounded thermocouple circuits should be tested before use to ensure that there are no short circuits to ground, which may be caused by loose connections in plugs, sockets and connecting blocks. Because the thermocouple has very low electrical impedance, short circuits will not normally prevent a thermocouple from working. Instead, a short circuit will allow a percentage of the signal to pass, and cause the thermocouple to read low. In combination with temperature controllers this leads to overheating and possible plant failure.

8.6.7   Linearisation errors

All thermocouples have a non-linear response with temperature, so some form of linearisation is necessary to convert the measured voltage to temperature. The different techniques, which are discussed in Section 5.3.1, all give rise to different errors. The defining tables for the thermocouple types (Appendix D) are usually given to a resolution of 0.01 °C to allow practical linearisation schemes to be developed to match the tables to better than 0.1 °C. Modern digital equipment should easily meet this requirement. More rough forms of linearisation may be found which are accurate to only 1 °C.

8.7 Choice and Use of Thermocouples

Thermocouples are not failsafe. Major inhomogeneities can give rise to voltage errors of 30% or more, yet in every other respect the thermocouple appears to be in perfect condition. Other temperature sensors would fail completely before errors reach a few

per cent. Therefore, thermocouples require checking while in service if they are in difficult environments.

As a rule, thermocouples are not high-precision temperature sensors; their main use is in low-accuracy or high-temperature industrial measurements, and for some unusual environmental conditions. In general, a thermocouple should not be considered more accurate than about $\pm 1\%$; for example, $\pm 1\,^\circ$C for normal temperatures and $\pm 10\,^\circ$C at $1000\,^\circ$C. Rare-metal thermocouples can give accuracies better than 0.1% with care. Because thermocouples have such a wide range of applications, it is difficult to generalise on their use and the guidelines given here are designed merely as a starting point to find the best thermocouple for your application.

8.7.1   Selection of thermocouple type

Firstly, check your test specification to see if the thermocouple type is specified. Often test methods are designed around the properties of a particular thermocouple and substituting another type can give invalid results.

Otherwise, the maximum temperature to be measured will be the deciding factor. Tables 8.3 and 8.4 give some of the details for selecting bare-wire thermocouples. Table 8.4 assumes a long life, and if a short operating life is acceptable then the range may be extended, or thinner wire may be used. With suitable sealed sheathing, the range may be extended, but in some cases, because of contamination from the sheath, the sheathing may limit the range.

Above $1700\,^\circ$C none of the standard thermocouple types are suitable and one of the special types will have to be used, for example, tungsten–rhenium or boron carbide/graphite. Consult the manufacturer's recommendations for the best use. With appropriate protective sheaths, these types may also be useful at lower temperatures in chemically hostile or reducing environments.

From $1100\,^\circ$C to $1700\,^\circ$C a Type B thermocouple would be preferred for a clean environment. From $1200\,^\circ$C to $1500\,^\circ$C a Type R or Type S thermocouple could also be used in a clean environment, but because of possible grain growth in the platinum leg they may become fragile after long exposure. The advantages of Type R or Type S are that their use can be extended down to $200\,^\circ$C and their accuracy is better. The main disadvantages of all three rare-metal thermocouples are the cost of the wire, the more sensitive instrumentation required, and the extra care needed in installation. Over time, there will be a drift in the output even in a clean environment. If most of the change is due to thermal and mechanical stress, then cleaning and annealing as per Section 8.8.3 will help restore the output.

Below $1200\,^\circ$C where a less expensive solution can be used if high precision is not required, then there is a choice between Types K and N. Type N should always be the first choice, but the decision may often be predetermined by specified test methods. In general, these thermocouples are sufficiently low priced that a frequent replacement scheme can be considered to keep the thermocouple in good condition in a hostile environment.

Below $700\,^\circ$C, Types J and E can be considered. Type E performs better than Type K and hence is used in survey work, but it is not so commonly used as it should be. Type J is the only standard type that will tolerate a reducing atmosphere.

Below 200 °C and down to −200 °C, Type T is a suitable thermocouple wire. The wires are flexible and can be obtained with very fine diameter to reduce the thermal loading on small objects.

Where possible, select thermocouples in the most complete state of assembly that is consistent with your application. In particular, wires should be bought as matching pairs, that is as MIMS cable, or as Teflon®-coated or fibreglass-covered duplex cable. If single wires are required then they should be obtained to specification so that when paired they will match standard tables. In general, do not mix wires from different manufacturers. For example, the copper wire used in Type T thermocouples may be less pure than the copper used in modern electrical wire because the manufacturer has the option of varying either the constantan alloy or the copper purity in order to match the tables.

8.7.2   Acceptance

Ensure that the wire supplied is of the type ordered and that it is in the continuous lengths required. The length is easily checked but the wire type is not because wires are generally not labelled in any consistent fashion.

While colour coding is often used to denote individual wire, wire pairs and extension wire, unfortunately each country of manufacture has a different colour-coding system. There is currently no agreed international colour-coding for thermocouple wire. Colour coding of plugs, sockets and extension cables is more consistent. Unless you are very sure of the thermocouple's origin the colour coding may not be helpful. Keep wires on the original reels, if supplied that way, until used and ensure that any identification labelling will remain attached.

A check can be made on the output voltage of the thermocouple. If the check is made at 50 °C to 100 °C, say, then it is not likely to degrade the wire. This should enable most types to be distinguished (see tables in Appendix D), except possibly for Types T and K, or Types R and S. Type T can usually be distinguished by its copper thermoelement and for Type K the negative thermoelement is magnetic so that a small magnet can be used to check. Because of the small difference between Types R and S a full calibration is often the only way to tell them apart. Use only one of these types throughout your laboratory or plant, Type S if possible, to avoid confusion.

Acceptance tests can be made close to the temperature of use, if required. In some cases, an inhomogeneity test may be called for (see Section 8.7.4).

8.7.3   Assembly

Many of the factors for the successful assembly of a thermocouple and its measurement circuit have been covered in the discussion in previous sections. Correct assembly is important for the traceability of a thermocouple measurement because the errors resulting from mistakes or failures can give false readings not easily discernible from real readings. Here are the main points to note:

- Ensure that assembly is done by skilled personnel.
- Ensure that materials used are clean, particularly for high temperatures.

- Ensure that the materials will withstand the temperature of use.

  — Most materials lose considerable strength well before they collapse at high temperatures. The upper rating on a material may be its collapse temperature and there may be very little mechanical strength below it.

  — Many of the materials look similar but can have very different temperature ratings. Test that they withstand the temperature first.

- Use matched pairs of wires.

- Immerse both junctions in isothermal environments.

- Use sufficient length of wire to enable connector heads to be mounted away from temperature gradients and sources of heat.

- Do not reverse the polarity of the thermoelements.

  — Test by applying hand heat to any joins and see if the temperature reading changes.

- Check that the insulation resistance is adequate.

  — Dry out slowly if moisture causes a low insulation resistance value.

  — Provide an electrical ground if necessary.

- Use proper thermocouple connectors throughout.

- Check the reading at the ice point, if possible.

- Finally, check the circuit with a hot-air blower.

  — Hold the measurement junction at a fixed temperature; the ice point is ideal.

  — Apply the hot air to all other parts of the circuit and connectors.

  — Any movement in the indicated temperature exposes a problem that needs solving. The main causes of problems are reversed connections, wrong wire or lack of thermal insulation to keep a join isothermal.

8.7.4   Inhomogeneity tests

In applications where high confidence is required, an assessment of the inhomogeneities in the thermocouple should be carried out. Such cases include the use of all reference thermocouples (ideally Types R, S or B), and where working thermocouples are used in high-value or high-accuracy applications.

There are four methods for checking for gross inhomogeneities. All may be used at different times to confirm the integrity of a thermocouple circuit. Remember that the methods will eliminate the worst of the problems but do not guarantee good performance.

Applying corrections for inhomogeneities is a major undertaking and is beyond the scope of this text. A very careful measurement of the inhomogeneity is needed to ensure that only the inhomogeneity is being assessed and not other electrical effects. The main limitation of a test is that the test conditions could change the nature of the inhomogeneity.

Type approval for new wire

Take at least two samples of wire from the reel, usually from the beginning and the end, and subject them to a compliance test as in Section 8.8.1. Any significant differences in the test results for the samples indicate an inhomogeneity problem; for example, the manufacturer did not anneal the wire after it was drawn or the alloy composition was not well controlled during manufacture. The variation in performance throughout the reel should be much smaller than the tolerances of Table 8.2.

Apply local heating

If the thermocouple is homogeneous then the reading is independent of the position and magnitude of temperature gradients. Conversely, a change in reading when a gradient is applied will expose inhomogeneities. A completed circuit can be tested by applying local heating to its various parts while the measurement junction is held at a constant temperature. The use of a hot-air blower is a convenient way to do this, as indicated in Section 8.7.3. More concentrated heat sources may also be useful, for example, small flames or a soldering iron, if the insulation material can withstand the heat. Not only will the test indicate unsuspected inhomogeneities, such as a badly bent wire, but it will also check that any known inhomogeneity, such as a join, is properly installed in an isothermal environment. The test is not good at detecting a distributed inhomogeneity, such as a chemical change along an extensive length of the wire.

Staggered replacement schedules

Unlike many temperature sensors, thermocouples continue to provide a signal even when they are severely damaged. In industrial plants, where the damage occurs slowly as chemical or thermal effects accumulate, the damage can be difficult to detect. This is a particular problem where thermocouples are used as control probes. The action of the controller is to adjust the temperature until the thermocouple produces the correct voltage for the set-point temperature. In this way, the indicator on the front panel of the controller always indicates the correct temperature even though the thermocouple may be very badly damaged. A very simple and powerful test based on staggered replacements will expose this problem.

   All industrial thermocouples used in control loops should be installed in pairs. Typically, one is used for the controller, the other for a separate indicator or over-temperature protection system. To prevent excessive accumulated damage the two thermocouples should be replaced regularly, but never at the same time. By replacing only one at a time, we can assess the damage in the replaced thermocouple by comparing the readings of the two thermocouples before and after replacement. The replacement schedule can be adjusted to ensure that the damage is kept within specified tolerances.

Immersion profile

As a quality control measure for platinum thermocouples and a general diagnostic tool, an inhomogeneity test is essential for a calibration laboratory. A straightforward

method is to use a two-zone furnace with a sharp transition between the two isothermal
zones or a liquid bath, as shown in Figure 8.21. The second zone needs to be long
enough for the required immersion conditions. For Type K wire the furnace or bath
should be below 150 °C to avoid altering the wire. Type S thermocouples, however,
can be tested at temperatures up to 1000 °C.

Figure 8.22 shows the output of a thermocouple as it is passed slowly through the
bath. Because the temperature gradient is highly localised the temperature reading at
any immersion is a measure of the Seebeck coefficient at the gradient. Departures of the
thermocouple reading from the true bath temperature are evidence of inhomogeneities.

The profile shown in Figure 8.22 is for a Type K thermocouple previously exposed
to 870 °C. As expected, there is a large deviation as the measurement junction is
immersed and affected by heat leaks up the wires. At slightly greater immersion in
Zone A, the wire has been altered by heat and oxidation, and shows the steady increase
in Seebeck coefficient with apparently random deviations typical of old Type K ther-
mocouples. In Zone B there is a large deviation of around 30 °C due to the formation
of green rot and the accompanying depletion of chromium. Zone C exhibits the same
features as Zone A. Finally, on the far right, Zone D, we encounter undamaged wire
that has not been exposed to any adverse effects, so there is no deviation and the reading
is 150 °C, the actual bath temperature. Such immersion profiles give a good indica-
tion of the damage suffered by thermocouples and can be used to plan a replacement
schedule.

The results of inhomogeneity tests such as that shown in Figures 8.21 and 8.22
depend on the thickness of the thermocouple, the speed of movement, and the sharpness
of the transition. However, when these are well controlled, guidelines can be established
as to acceptable levels for reference thermometers.
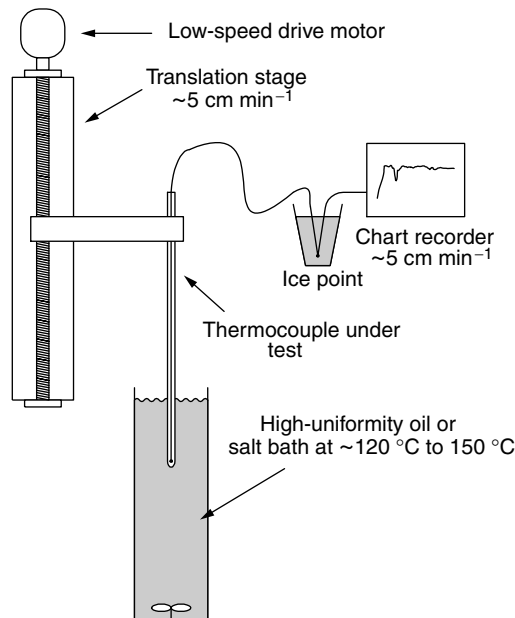
Figure 8.21   A bath for measuring thermocouple inhomogeneity
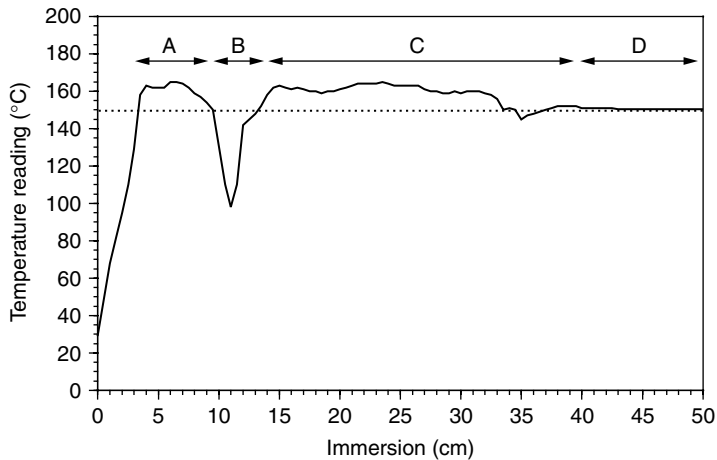
Figure 8.22   The thermocouple reading as it is inserted into the calibration bath. The errors due to inhomogeneities vary between $+10\%$ and -30%

8.8 Calibration

In Section 5.2, we discussed the meaning of the word 'calibration'. In the context of thermocouples, a further confusion arises. Frequently 'calibration' is used to refer to the various thermocouple types. Even more confusing, the term 'de-calibration' is applied to the growth of inhomogeneities in the wire. While it may be a confusing term it certainly highlights a fundamental problem with formal thermocouple calibrations.

Suppose the thermocouple that was given the immersion profile test in Figure 8.22 is sent to a laboratory for calibration. The chances are the laboratory would ensure that the thermocouple has sufficient immersion to avoid errors due to heat leaks up the sheath, and would immerse the thermocouple to at least 50 cm. That is, in calibration, the Seebeck voltage would be generated entirely within that part of the wire we have labelled Zone D. The laboratory would conclude that the thermocouple is in 'as new condition'. In use, however, the thermocouple would not be so well immersed. The voltage would then be generated along those parts of the wire indicated as Zones A, B and C. Depending on where the temperature gradients fall, any reading within $+10\%$ and -30% of that obtained during calibration is possible. That is, the calibration is a complete waste of time.

From this discussion, we can see that the calibration procedures of Section 5.5.2 may not be suitable for thermocouples. A conventional calibration applied to thermocouples will only work under two conditions:

(1)   The wire is homogeneous. This condition tends to preclude calibration of base-metal thermocouples since they are made inhomogeneous simply by the act of using them.

(2)   The temperature profile in calibration is identical to the temperature profile in use. That is, the calibration must be performed *in situ*.

Three possible methods for establishing traceability with thermocouple calibrations are given here. The first method is a simple conformance check. The second method is to calibrate the thermocouples *in situ*. Not all applications will allow this but it is a better method. A detailed example of an oven survey illustrates the method. The third method follows the step-by-step procedure of Section 5.5.2 for rare-metal thermocouples, for they should have sufficient homogeneity and stability to warrant it.

8.8.1 Conformance or type approval

Base-metal thermocouples, because of the complex alloys used, tend to become inhomogeneous simply because they are used, especially when they are used at high temperatures. In these situations, conformity testing is an important step in achieving traceability. Effectively, a batch of thermocouples is sampled and tested against the type definition. Traceability can then be claimed on the remaining thermocouples in the batch on a 'use once and throw away' basis.

If thermocouples are made up from wire off a reel then sample thermocouples made from different sections along the wire length can be submitted for calibration. As new, the wire should be reasonably homogeneous, so the sample of thermocouples should all have the same temperature response and be within the manufacturer's specifications, or comply with standard tables.

A replacement regime for the thermocouples should be established based on experience or recommendations; for example, thermocouples may need to be replaced after every 8 hours of use in high-temperature corrosive atmospheres, or may need replacement every 6 months under less harsh conditions. Once installed, the thermocouples should be fixed in place to ensure that their immersion cannot change, and that they are never used at a lower temperature having been exposed to a high temperature. The utility of the conformity approach is highly dependent on the application, the type of thermocouple used, and the temperature range covered. It also relies on the ease with which a thermocouple can be replaced. The design of the thermowells should allow for the removal of thermocouples while the plant is operating.

The uncertainty in the thermocouple calibration includes a term due to the variability observed in the samples (few samples implies a high coverage factor and a high uncertainty). Note that it is the user's responsibility to determine the rate of degradation of the thermocouple in use, usually by carrying out one or more of the inhomogeneity tests given in Section 8.7.4. In many cases, the conformity test is simply used as verification that the thermocouples comply with the standard, and that the uncertainties in the thermocouple readings are no greater than the manufacturer's tolerances.

8.8.2 *In situ* calibration

The only reliable method of reducing errors in thermocouple readings is to calibrate *in situ*. This ensures that the immersion conditions in use are the same as those during calibration. For base-metal thermocouples an *in situ* calibration may give a 10-fold improvement in accuracy over the conformity assessment, that is ~0.1% of temperature.

The design of the installation should make provision for *in situ* calibration with either two adjacent thermowells or a thermowell of sufficient diameter to accommodate a thin reference rare-metal thermocouple alongside the working thermocouple. For a single thermocouple, the calibration procedure then follows the outline in Section 5.5.2. Some experimental effort may be required to quantify the uncertainty due to poor immersion of the reference thermocouple.

Furnace survey procedure

The following example shows how the *in situ* calibration principle can be applied to a temperature uniformity survey of a heat treatment furnace or oven. This is a common problem requiring many, sometimes very long, thermocouples, so it precludes the use of rare-metal thermocouples because of cost. Yet, somehow we must survey the furnace with accuracy far better than the normal capability of base-metal thermocouples.

Preliminary   Before starting a survey, ensure that the controller and indicator are working properly. Poor control will result in poor spatial and temporal uniformity. The controller should be set to the temperature of the test and any recording meter should read within 1 °C of the setting. The controller should always be set to the temperature required and not subsequently adjusted to obtain the 'correct' temperature.

Tuning of the controller may be needed. Ensure that both the controller and recorder instrumentation are functioning correctly and are calibrated.

Equipment   A multi-channel thermocouple recorder or logger with good reference junctions is required. The number of channels will depend on the extent of the survey Typically, a minimum of 12 channels are required, comprising:

- Nine survey positions in the furnace, one in each corner of the furnace plus one in the centre (more may be required in large installations);
- one adjacent to each of the furnace controller and indicator thermocouples;
- one to monitor the ambient temperature.

Flexible thermocouple wire or cable of a type to match the temperature range is needed. For best accuracies select from Types T, E and N.

Access   Obtaining access for the survey thermocouples can be a problem if the furnace designer has not provided for it. Any hole through to the internal space of the furnace may need to be covered subsequently to prevent heat loss through convection or radiation. The most critical factor is that there should be a means of mechanically anchoring the thermocouple cables as they enter the furnace so that they do not move during the calibration. This ensures that the temperature profile along the wire remains constant.

Avoid going in through the door, as closing the door on thermocouples can cause a significant inhomogeneity at the point of maximum temperature gradient. It is also difficult to reproduce the placement of the thermocouples at the door. The reference thermometer will also need a means of entry and this thermometer is generally rigid and more fragile. The entry hole for the reference thermometer should be of adequate size and positioned for easy use.

Wire length   The thermocouple wire inside the furnace should be sufficiently long to reach two sites, namely the centre of the furnace and the survey site. Outside of the

furnace, there should be sufficient length so that any joins can be made at ambient temperature.

Calibration   All the survey thermocouples should be brought together in the centre of the furnace and thermally anchored to the reference thermometer. The centre is used because it tends to have the best temperature uniformity, but other sites can be used if there are physical restrictions, in which case more care may be needed to ensure an isothermal connection between the thermocouples and the reference thermometer. The reference thermometer may be either a PRT or a platinum thermocouple suitably calibrated. Once the thermocouples are tied to the reference thermometer, carry out comparisons at the required temperatures beginning at the highest temperature and working down.

Survey   When the furnace is cool move the thermocouples to their survey sites. Note that in moving the thermocouples the effective immersion depth in the furnace will stay the same if the bundle of wires is well anchored as it enters the furnace space. This ensures that the same length of wire is at the maximum temperature gradient for both the calibration and survey.

Surveys may be made with or without loading in the furnace according to requirements. Often the nominal workspace of the furnace must be specified in advance of the survey; usually the space at least 5 cm from any wall is a good guide. Mounting of the survey thermocouples can be facilitated by using a rigid wire frame to hold the thermocouples close to their sites. A survey probe should be mounted alongside both the recorder and controller probes. The recorder probe should be inside the designated workspace.

The temperature survey is then carried out at the required temperatures in order of rising temperature. Record the temperature rise and its settling response for each step. Often a uniformity specification may require that the overshoot should not be excessive and that the furnace comes to a stable condition over a few control cycles.

Note on the measurement sequence   The best accuracy is achieved by commencing calibrations at the highest temperatures first, and carrying out the survey at the lowest temperatures first. This ensures that the wire is not subject to heat treatment at higher temperatures between the calibration and survey phases.

Reporting   Usually furnace surveys are carried out to test the furnace against a specification. Specifications vary greatly and may specify:

- the number of thermocouples required;

- the type of survey and reference thermocouples required;

- the definition of non-uniformity;

- definitions of response times and overshoots;

- whether the furnace should be loaded or not;

- whether the survey thermocouples must be lagged by covering the measurement junction with a slug of metal to ensure a consistent response time for the thermocouples.

The report of the survey may be required to address all of these concerns. If required, a calibration certificate may be issued for the recorder and perhaps the controller. A calibration certificate is not normally required for the survey thermocouples because of

the short-term nature of the calibration. If a formal statement of compliance is required for the furnace, a certificate may be issued for the furnace.

8.8.3 Rare-metal thermocouple calibration

The third calibration method is based on the assumption that the thermocouple is homogeneous, so the method is similar to that for other thermometers. It is usually only appropriate for the platinum thermocouples, Types S, R and B, the platinum–gold thermocouple and the platinum–palladium thermocouple. It can also be applied to base-metal thermocouples where they are used at low temperatures so are not exposed to heat treatment that may make them inhomogeneous.

The procedures for calibrating rare-metal thermocouples require a higher level of expertise than for other thermocouples. This is in part because of the experience required to disassemble and reassemble the thermocouples reliably, and in part because the reproducibility of the thermocouples depends in detail on the annealing procedure. For these reasons few users would have the competence to calibrate the thermocouples in-house, particularly if accuracies of better than $\pm 1\,°C$ are required.

The procedure we give here is based on the outline given in Section 5.5.2 and is primarily for calibrating rare-metal thermocouples used as working thermometers. If you are involved in the calibration of reference thermocouples, consult the references at the end of the chapter, which explain the procedures in more detail.

Step 1: Start record keeping

As for Section 5.5.2.

Step 2: General visual inspection

As for Section 5.5.2.

Step 3: Conditioning and adjustment

There are five main tasks to perform at this stage:
Disassembly   The thermocouple should be removed from its sheath, which usually comprises one or more sections of twin-bore alumina tubing or beads.
Cleaning   Reference thermocouples and working thermocouples in good, bright condition should be cleaned with ethanol. Working thermometers that are not visually bright should be cleaned by boiling for 10 minutes in each of distilled water, 20% nitric acid, distilled water, 20% hydrochloric acid and distilled water. Three cycles may be required before the wire is clean.
Electric anneal   The thermocouple is then annealed by passing an a.c. electric current through each leg. The pure platinum leg should be annealed at $1100\,°C$ and the platinum–rhodium leg at $1450\,°C$. The anneal removes strain due to work hardening, oxidises residual impurities, and restores the wire to a uniform state of oxidation. For $0.5\,mm$ diameter wires about 12 to 13 amps is required.

Reassembly   The thermocouple is then carefully reassembled in its sheath. If the old sheath is not clean, it should be replaced by a new sheath that has been baked at 1100 °C for a minimum of 2 hours to drive off potential contaminants.

Furnace anneal   After the thermocouple has been reassembled, that part of the thermocouple that will be exposed to temperature gradients is furnace annealed at 1100 °C. For reference thermocouples, the correct annealing and cooling procedures are critical for best performance (see references).

Step 4: Generic checks

There are two basic checks that should be carried out with rare-metal thermocouples: a visual inspection and an inhomogeneity test.

Detailed visual inspection   This is carried out at the first stages of the cleaning and annealing phase above. The inspection is primarily to determine the suitability of the thermometer for its purpose. Reference thermocouples are assembled in a single 300 mm to 1000 mm length of twin-bore alumina, are clean and bright, and do not have any breaks, joins or extension leads attached to them. Thermocouples that are not in this condition are not suitable as reference thermocouples. Working thermocouples may be assembled in a variety of sheaths, should be reasonably clean, and not have any breaks or joins. Thermocouples that do not satisfy these requirements have been abused and should not be calibrated.

Inhomogeneity test   This is carried out according to the procedure in Section 8.7.4, which is illustrated in Figures 8.21 and 8.22. The variation in the Seebeck coefficient is assessed to determine the likely uncertainty in use due to inhomogeneities in the wires. For reference thermocouples, the maximum observed variation must be less than 0.05% (0.5 °C at 1000 °C). This test is carried out after the reassembly and furnace anneal. An inhomogeneity test may also be carried out prior to the disassembly to assess the user's treatment of the thermocouple.

Step 5: Comparison

In most cases, the reference thermometer for the comparison will be a rare-metal thermocouple. In some instances where the highest accuracy is required, the reference thermometer may be a high-temperature SPRT (Chapters 3 and 6), or a transfer standard radiometer (Chapters 3 and 9), or several of the defined fixed points (Chapter 3). Whatever the calibration medium, care must be taken to avoid contaminating the thermocouple. In particular, there should be no metals, other than platinum and rhodium, in the immediate vicinity of the calibrating furnace.

In all cases, the most convenient representation of the determined ITS-90 relationship is a deviation from the reference function. For reference thermocouples working over a narrow range (e.g. 600 °C to 1100 °C), a linear or quadratic deviation function will suffice, and therefore not as many points are required in the comparison. For thermometers working over a wider range, or working thermometers not conforming so closely to the generic history, a cubic deviation function is more appropriate.

Step 6: Analysis

The analysis of the comparison data proceeds as described in Section 5.5.2 with a least-squares fit used to determine the best values of the coefficients in the deviation function. For reference thermocouples the deviations from the reference function should be less than $\pm 1.5\,^{\circ}$C for Types R and S, and less than $\pm 2.5\,^{\circ}$C for Type B.

Step 7: Uncertainties

The contributing factors to the uncertainty are as follows.
Uncertainty in reference thermometer readings   As for Section 5.5.2.
Variations in the stability and uniformity of the calibration medium   As for Section 5.5.2. This is a difficult assessment when the reference thermometer is a transfer standard radiometer.
Departure from the determined ITS-90 relationship   As for Section 5.5.2.
Uncertainty due to hysteresis   As with all thermocouples, rare-metal thermocouples suffer from hysteresis. This is particularly true in the $500\,^{\circ}$C to $900\,^{\circ}$C range where the platinum is subject to changes in the state of oxidation. Where the thermal history of the thermocouples is not controlled, the uncertainty is about 0.1% (95% confidence level). Where the annealing and use are controlled, the uncertainty is typically between 0.02% and 0.05%, depending on the detail of the procedures (see references).
Uncertainty due to inhomogeneities   This uncertainty is assessed as the maximum observed variation in the Seebeck coefficient as determined from the inhomogeneity test, normally expressed as a 95% confidence interval. For reference thermocouples, this must be less than 0.05%.
Total uncertainty   This is calculated as the quadrature sum of the contributing uncertainties. Since the most significant uncertainties due to hysteresis and inhomogeneities are approximately proportional to the output voltage, the uncertainty should be reported as a percentage. For example:

> The uncertainty in the corrected thermocouple readings is estimated as 0.1% of the output voltage at the 95% confidence level.

Step 8: Complete records

As for Section 5.5.2.

Further Reading

Thermocouple theory

H B Callen (1948) The application of Osager's reciprocal relations to thermoelectric, thermo-magnetic and galvanometric effects, *Phys. Rev.* **73**, 1349–1358.

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R P Reed (1982) *Thermoelectric thermometry: a functional method,* in *Temperature, its Measurement and Control in Science and Industry*, Vol 5, American Institute of Physics, New York, 915–922.

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P A Kinzie (1973) *Thermocouple Temperature Measurement*, John Wiley, New York.

Manual on the Use of Thermocouples (1993) ASTM STP 470B, 4th Edition, American Society for Testing and Materials, Philadelphia.

Calibration

G W Burns and M G Scroger (1989) The Calibration of Thermocouples and Thermocouple Materials, NIST *Spec. Pub.* 250–35, US Department of Commerce. Techniques for Approximating the International Temperature Scale of 1990 (1990) BIPM, Services.

9

Radiation Thermometry

9.1 Introduction

We are all familiar with the dull red glow of embers in a fire and the bright white glow of incandescent lamps. We know that the brighter and whiter a glowing object, the hotter it is. This is the simplest form of radiation thermometry. Although it is simple, temperature discrimination on the basis of colour can be remarkably accurate. Those who work in high-temperature processing industries, such as a steel works, can often estimate the temperature to better than $\pm 50\,°C$ simply on the basis of colour.

Because our eyes cannot detect the radiation from bodies cooler than about $500\,°C$, most of us associate thermal radiation only with objects that are hot and often dangerous. However, everything around us radiates electromagnetic energy in quite large quantities. By understanding how this radiation depends on temperature we can make accurate measurements of temperature over a very wide range.

For many radiation thermometry applications, absolute accuracy is not important. As a diagnostic tool radiation thermometers are very good for identifying hot spots, for example, in buildings, switchyards and even people. Increasingly, however, radiation thermometers are being used in applications where hard decisions are made and traceable measurement is necessary. Such applications include medicine, food storage and process control. Much of this has been made possible by rapid advances in infrared sensors and the accompanying electronics.

Radiation thermometers have three main features that distinguish them from the other thermometers discussed in this book. Firstly, they are thermodynamic; they are based on a universal physical law that is known to describe real objects to very high accuracy. Radiation thermometers can be, and have been, built with reference only to the triple point of water. Secondly, they are non-contact thermometers and can be used to measure the temperatures of remote or moving objects. This makes it possible to measure the temperature inside furnaces, fires and even the sun and stars, places too hostile or remote for any contact thermometer.

The third feature is that radiation thermometers use the surface of the object of interest as the sensor. This is both a blessing and a bane. While the use of the object as a sensor overcomes a lot of the difficult questions about immersion and thermal contact that affect other thermometers, it raises even more difficult questions about traceability. How can we make measurements traceable if they involve different sensors every time the instrument is used?

9.2 Blackbodies and Blackbody Radiation

Hot objects emit radiation over a wide range of the electromagnetic spectrum. For objects at temperatures of practical interest, most of the radiation is in the infrared and visible portions of the spectrum. A graphical description of the distribution of thermal radiation is shown in Figure 9.1.

The spectral radiance, plotted on the vertical axis of Figure 9.1 on a logarithmic scale, is a measure of the amount of energy emitted by an object in a given wavelength range. The horizontal scale describes the wavelengths at which the radiation is emitted. The visible portion of the spectrum is also marked, with the violet end of the visible spectrum at $0.4\,\mu\text{m}$ and the red end at $0.7\,\mu\text{m}$. Radiation at wavelengths shorter than $0.4\,\mu\text{m}$ is described as ultraviolet (above violet) or UV, while radiation at wavelengths longer than $0.7\,\mu\text{m}$ is described as infrared (below red) or IR.

We can see from Figure 9.1 that for objects below about $500\,^\circ\text{C}$ ($\sim 800\,\text{K}$) all of the radiation is in the invisible infrared region. As the temperature increases and the radiance curves of Figure 9.1 begin to edge into the red end of the visible spectrum, we see objects as red hot. As the temperature increases further the emission spectrum moves further into the visible and we see objects with the perceived colours shown in Table 9.1. At temperatures above $1500\,^\circ\text{C}$ to $1800\,^\circ\text{C}$, objects become so bright that our eyes have difficulty accurately and comfortably discerning the colour.

In order to give the mathematical description of the radiation distribution shown in Figure 9.1 we need to introduce the concept of spectral radiance and define the term blackbody.
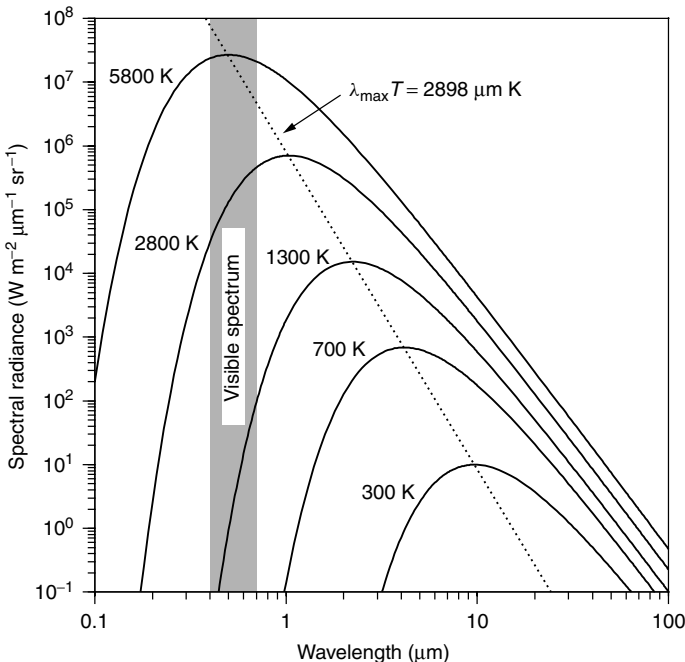
Figure 9.1   Planck's law: the spectral radiance of a blackbody as a function of temperature

Table 9.1   Temperature versus perceived colour

Temperature (°C)	Colour
500	Red, just visible
700	Dull red
900	Cerise
1000	Bright cerise
1100	Dull orange red
1250	Bright orange yellow
1500	White
1800	Dazzling white

Spectral radiance, measured as the energy emitted by a surface per unit area, per unit wavelength, per unit solid angle, is the technical term for the optical brightness of a surface. The advantage of using radiance, rather than other optical quantities, is that radiance is independent of the distance to the surface and the size of the surface. Also, in an ideal optical system of lenses and mirrors, the radiance of an object is constant. Instruments that measure radiance allow us to infer temperatures at a distance and, if necessary, to use close-up or telephoto lenses.

A *blackbody* is simply a perfectly black surface: a perfect emitter and absorber of radiation. Those who first encounter the blackbody concept may find it paradoxical; our everyday experience is that bright objects are white, not black. The apparent paradox arises because no visible blackbody radiation is emitted at room temperature. At room temperature, the brightest objects are bright because they reflect, not because they emit. For any object, the ability to absorb (absorptivity) is the same as its ability to emit (emissivity). If not we could find situations where heat would flow from cooler temperatures to hotter temperatures, in contradiction to the basic laws of thermodynamics.

Objects have three basic optical properties: *emissivity*, *reflectivity* and *transmissivity*. Since any light falling on a surface must be either absorbed, reflected or transmitted,

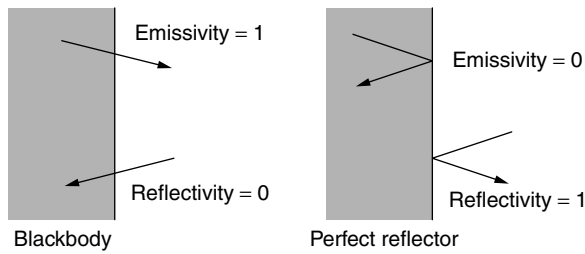$$\text{reflectivity} + \text{emissivity} + \text{transmissivity} = 1, \tag{9.1}$$

or using the appropriate symbols,

$$\rho + \varepsilon + \tau = 1. \tag{9.2}$$

Most of the objects encountered in radiation thermometry are opaque so the transmissivity is zero. In that case, the reflectivity and emissivity are complementary properties. Figure 9.2 gives a simple pictorial explanation of the relationship between reflectivity and emissivity for two different opaque surfaces. We shall see later (Section 9.6) that we can exploit this relationship to make good approximations to ideal blackbodies by making cavities that are designed to trap and not reflect light.

In 1900, Planck derived the mathematical description of the distribution of blackbody radiation shown in Figure 9.1:

$$L_b(\lambda, T) = \frac{c_1}{\lambda^5} \left[\exp\left(\frac{c_2}{\lambda T}\right) - 1 \right]^{-1}, \tag{9.3}$$

Figure 9.2 The complementary properties of emissivity and reflectivity

where L is the radiance, the subscript b indicates that the radiance is that of a blackbody, λ is the wavelength of the radiation and T is the temperature of the blackbody in kelvins.

The two constants c_1 and c_2 are known as the *first* and *second radiation constants*, and their best measured values are currently

$$c_1 = 1.191\,044 \times 10^{-16}\,\mathrm{W\,m^2}$$

and

$$c_2 = 0.014\,387\,69\,\mathrm{m\,K}.$$

Equation (9.3), *Planck's law*, is used to define the ITS-90 temperature scale above the silver point, $961.78\,^{\circ}\mathrm{C}$ (see Section 3.3.6). To do this only the second radiation constant is required, and it is assigned the value

$$c_2 = 0.014\,388\,\mathrm{m\,K}.$$

By assigning a value to c_2 the temperature-scale definition becomes fixed and cannot change simply because research determines a 'better' value. At many points in this chapter we make the approximation $c_2 = 0.0144\,\mathrm{m\,K} = (120)^2\,\mathrm{\mu m\,K}$. This enables the development of simple formulae that serve as aids to memory.

In practice, real objects are not blackbodies, but emit less radiation than predicted by Planck's law by the factor ε, the emissivity of the surface. The spectral radiance of a real object is

$$L(\lambda, T) = \varepsilon(\lambda)L_{\mathrm{b}}(\lambda, T), \tag{9.4}$$

where $\varepsilon(\lambda)$ indicates that the emissivity may vary with wavelength.

Planck's law (Equation (9.3)) is not a simple law, and provides no obvious assistance in the development of an intuitive understanding for how radiation thermometers work. We give here some simpler results that are easier to remember and to work with.

All of the curves in Figure 9.1 are characterised by a maximum that occurs at shorter and shorter wavelengths as the temperature increases. The wavelength at which the maximum occurs is

$$\lambda_{\max} = \frac{2989}{T}\mathrm{\mu m}. \tag{9.5}$$

At room temperature ($T = 300\,\mathrm{K}$), for example, the maximum spectral radiance is near $10\,\mathrm{\mu m}$, and at $3000\,\mathrm{K}$, the temperature of an incandescent lamp filament, the peak

occurs at $1\,\mu m$. For objects of practical interest most of the radiation is emitted in the infrared portion of the spectrum. It is interesting to note that the response of the human eye has evolved to match the peak in the solar spectrum near 500 nm ($T = 5800\,K$).

For several practical reasons, most radiation thermometry is carried out at wavelengths in the $0.5\,\mu m$ to $20\,\mu m$ portion of the spectrum, depending mostly on the temperature of interest. In the normal operating regime, λ is less than λ_{max}, and Planck's law is approximated to 1% or better by *Wien's law*:

$$L_b(\lambda, T) = \frac{c_1}{\lambda^5} \exp\left(\frac{-c_2}{\lambda T}\right). \tag{9.6}$$

Although it is less exact because of the minor simplification, this is a much more 'user-friendly' function than Planck's law for estimating the errors and uncertainties in measurements.

The total radiance of a blackbody, $L_b(T)$, is found by integrating Planck's law to determine the area under the curves of Figure 9.1:

$$L_b(T) = \frac{\sigma}{\pi} T^4, \tag{9.7}$$

where σ is the Stefan–Boltzmann constant, $\sigma = 5.670\,51 \times 10^{-8}\,W\,m^{-2}\,K^{-4}$. The total energy emitted by the blackbody in all directions is π times this value; hence energy ($W\,m^{-2}$) is emitted by a real surface at the rate of

$$M = \varepsilon \sigma T^4, \tag{9.8}$$

where ε is the total emissivity. Some examples of the energy emitted by blackbodies are given in Table 9.2. Both the table and the fourth-power law in Equation (9.8) show that the total radiance increases very rapidly with temperature. At the short-wavelength end of the Planck spectrum the spectral radiance increases spectacularly. For $\lambda < \lambda_{max}$ the spectral radiance follows an approximate power law given by

$$L \propto T^x, \tag{9.9}$$

where, using the approximation for c_2,

$$x = \frac{12}{\lambda} \frac{1200}{T},$$

where λ is in micrometres.

Table 9.2   The rate of emission of blackbodies at a range of temperatures

| Temperature (°C)	Rate of emission (per square metre)
25 (room temperature)	470 W
230 (melting point of solder)	3.6 kW
500 (a hot stove element)	20 kW
1000 (yellow flame)	150 kW
2500 (lamp filament)	3.4 MW
5800 (sun)	77 MW

At a temperature of 1200 K and a wavelength of 1 μm the spectral radiance changes as T^{12}. This high-order power law is typical of the operating regime of many radiation thermometers. One of the earliest radiation thermometers, the disappearing-filament thermometer, operated at 655 nm and at temperatures as low as 600 °C; here the power law is T^{25}.

This rapid change of radiance with temperature has a bad side and a good side. Over the operating range of a thermometer the measured radiance may vary by a factor of 100 000. It is quite difficult to design instruments that operate accurately over such a dynamic range. The high power law does, however, make for an extremely sensitive instrument, which is just as well because optical measurements are amongst the most difficult. Even in laboratory conditions it is difficult to measure radiance to better than 1%. A more serious problem is that we are rarely able to determine the emissivity to better than 5%. Were it not for the high power law, radiation thermometry measurements would have such high uncertainties as to render them useless.

9.3 Spectral Band Thermometers

Most radiation thermometers are of the type known as *spectral band thermometers*. They measure the radiance over a relatively narrow band of wavelengths somewhere within the range 0.5 μm to 25 μm. The choice of wavelength depends on, amongst other factors, the temperature range, the environment, and the type of surface under investigation. Discussion of the operating principles, use, errors and calibration of spectral band thermometers will form the basis of this chapter. The spectral band grouping includes most industrial radiation thermometers and all primary and transfer standard thermometers.

Figure 9.3 shows a simplified diagram of a spectral band thermometer. We have deliberately included the radiant target, the surface of interest, as part of the thermometer since the surface is the sensor. It may seem absurd to treat the target as the sensor, but it is the surface that converts the temperature into a measurable signal. The basic operating principle is to collect radiation from the surface, filter it to select the radiation at the wavelengths of interest, and then measure it with a detector and signal processing system. The two apertures in the system define the target area or field of
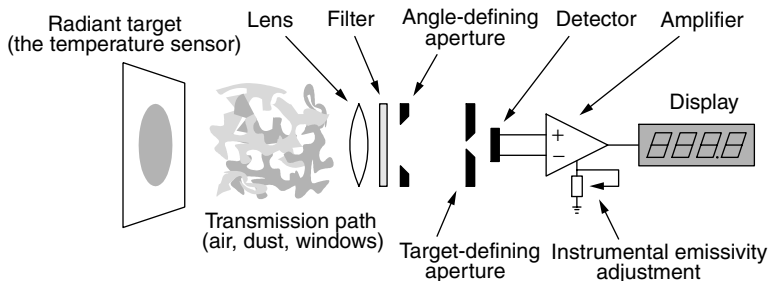
Figure 9.3 Simplified schematic drawing of a spectral band radiation thermometer showing the basic elements of its construction and operation

view, and the acceptance angle of the thermometer (similar to the f-stop in a camera). The lens is used to focus an image of the target area onto the target-defining aperture. Without the lens, or with the lens not properly focused, the boundary of the target area is not well defined.

The signal at the output of the detector is a complex function of the dimensions of the apertures, the transmission of the various optical components, and the detector responsivity. For simplicity, we assume that the filter has a sufficiently narrow pass-band to ensure that the output of the detector is proportional to Planck's law. We will look more closely at the actual responsivity later when we consider calibration equations.

The spectral radiance measured by the thermometer in the absence of reflections is

$$L_m = \varepsilon(\lambda)L_b(\lambda, T_s) - L_b(\lambda, T_d), \tag{9.10}$$

where $\varepsilon(\lambda)$ is the spectral emissivity of the surface at the operating wavelength, T_s is the true temperature of the surface, and T_d is the temperature of the detector. Note that it is assumed that the emissivity of the detector is equal to 1.0; in practice this is a good approximation because it is enclosed in a cavity at the same temperature (see Section 9.6).

For thermometers used to measure temperatures above 150 °C to 200 °C the term in Equation (9.10) due to the detector radiance is negligible (because the target radiance rises as T^{12}), so no correction need be applied. For thermometers measuring lower temperatures, the thermometer must compensate for the detector radiance, or equivalently the detector temperature.

To determine the target temperature we must also measure or estimate a value for the surface emissivity. Many radiation thermometers have a built-in adjustment called the *instrumental emissivity*, ε_i, which may be used to compensate the measured radiance for the surface emissivity. The temperature is calculated by solving

$$L_b(\lambda, T_m) = \frac{\varepsilon(\lambda)L_b(\lambda, T_s)}{\varepsilon_i}. \tag{9.11}$$

Ideally ε_i is set to $\varepsilon(\lambda)$ so that the measured temperature T_m is equal to the true surface temperature T_s. A typical radiation thermometer of this kind is shown in Figure 9.4.

A measurement made using $\varepsilon_i = 1$, that is assuming that the surface is a blackbody, is called the *radiance temperature*, and gives the temperature of a blackbody with the same spectral radiance. The true surface temperature, T_s, can be estimated from a radiance temperature, T_λ, according to

$$\frac{1}{T_s} = \frac{1}{T_\lambda} + \frac{\lambda}{c_2} \ln[\varepsilon(\lambda)], \tag{9.12}$$

which is an approximation based on Wien's law. Note that the radiance temperature is wavelength dependent, so that thermometers operating at different wavelengths measure different radiance temperatures when aimed at the same target, even if the emissivity of the target is the same at each wavelength.

Figure 9.4   An example of a hand-held spectral band radiation thermometer

9.4 Errors in Spectral Band Thermometry

Comparison of Figure 9.3 with the general measurement model of Figure 2.10 shows that two crucial components of the thermometer, namely the sensor and transmission path, change with each new measurement. Every measurement made with a radiation thermometer involves the characterisation of these important and often inaccessible parts of the thermometer.

That part of the thermometer that we normally describe as the radiation thermometer is, strictly speaking, only a *radiometer*. The radiometer, which measures radiance, is analogous to the potentiometer or voltmeter in a thermocouple circuit; only when the potentiometer is attached to the thermocouple do the two, together, form a thermometer.

The errors in radiation thermometry fall into three main groups:

(1)   errors relating to the characterisation of the target surface (sensor): emissivity, reflections and fluorescence;

(2)   errors due to variations in the transmission path: absorption and emission, scattering, size-of-source effects and vignetting; and

(3)   signal processing errors due to variations in ambient temperature, linearisation and the instrumental emissivity.

The radiometric measurement of the temperature of a real object requires knowledge of two, sometimes three, quantities: the surface emissivity, the spectral radiance of the surface and, if a low-temperature thermometer is being used, the detector temperature. Many of the dominant errors that occur in spectral band thermometry can be interpreted as errors in either the measured radiance or the estimated emissivity.

The temperature error caused by errors in the measured radiance and emissivity is estimated as

$$\Delta T_{\mathrm{m}} = \frac{\lambda T^2}{c_2} \left(\frac{\Delta L_{\mathrm{m}}}{L_{\mathrm{m}}} - \frac{\Delta \varepsilon(\lambda)}{\varepsilon(\lambda)} \right). \tag{9.13}$$

Here ΔL_{m} represents the difference between the measured and true values of spectral radiance, and $\Delta \varepsilon(\lambda)$ represents the difference between the value of the instrumental emissivity and the true value of the emissivity, $\varepsilon_{\mathrm{i}} - \varepsilon(\lambda)$.

Equation (9.13) is appropriate when the errors are known, but if the errors are unknown, then their relationship to the measurement error is properly expressed in terms of uncertainty:

$$\sigma_{T_{\mathrm{m}}} = \frac{\lambda T^2}{c_2} \left(\frac{\sigma_{L_{\mathrm{m}}}^2}{L_{\mathrm{m}}^2} + \frac{\sigma_{\varepsilon(\lambda)}^2}{\varepsilon^2(\lambda)} \right)^{1/2}. \tag{9.14}$$

This equation is conveniently expressed as

$$\sigma_{T_{\mathrm{m}}} = \lambda \left(\frac{T}{1200} \right)^2 \left(\rho_{L_{\mathrm{m}}}^2 + \rho_{\varepsilon(\lambda)}^2 \right)^{1/2}, \tag{9.15}$$

where λ is in micrometres (microns) and the relative uncertainties, ρ, are in per cent. For all three of these equations we can make the following observations:

- The errors and uncertainties increase with operating wavelength; therefore, as a general rule, choose thermometers with a short operating wavelength.
- The errors and uncertainties increase as the square of the temperature.
- The errors and uncertainties due to the emissivity increase as $1/\varepsilon(\lambda)$. In general, the errors are very large for low-emissivity materials, such as metals.

The wavelength dependence of errors can cause confusion when thermometers of differing operating wavelengths are used to measure the same temperature. Indeed, a difference in readings between two thermometers would normally indicate that both are probably in error, since nearly all of the major sources of error are wavelength dependent and affect all spectral band thermometers.

In the following sections, we treat each source of error in detail. Figure 9.5 summarises all of the errors discussed. In some cases, the errors are beyond the capability of the user to deal with. However, an understanding of the sources of error leads to an understanding of the need for proper care and maintenance of the thermometer. The
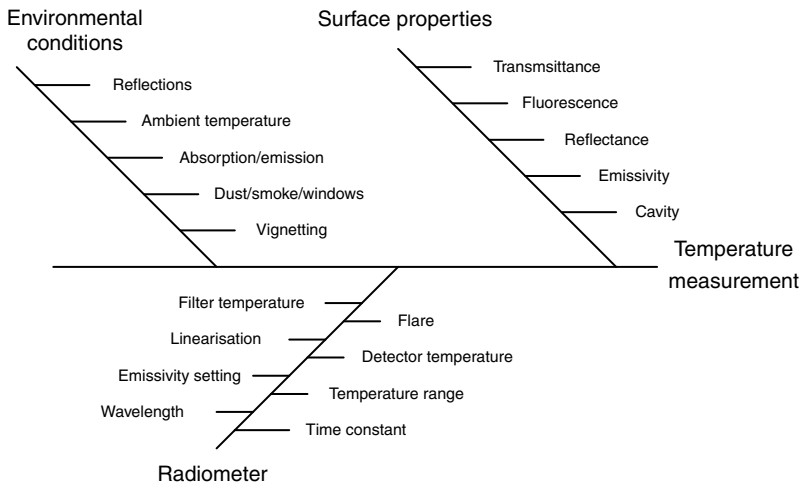
Figure 9.5 A summary of the errors in radiation thermometry
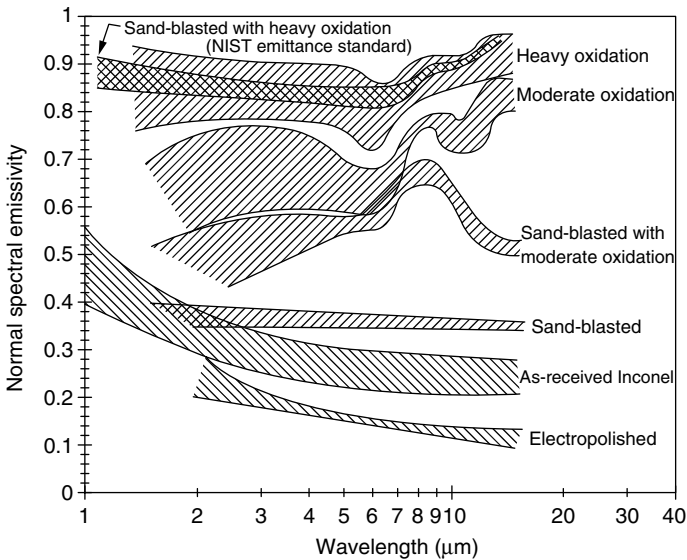
Figure 9.6 The spectral emissivity of Inconel®. There is a wide range of emissivities depending on the surface finish

two most significant errors are those associated with emissivity and reflections, and are dealt with first.

9.4.1 Errors in emissivity

In almost all areas of radiation thermometry the largest source of error is the lack of knowledge about the surface emissivity. Figure 9.6, which shows the spectral emissivity

of various samples of Inconel®, gives an indication of the problem. Depending on the degree of oxidation, roughness and wavelength, the emissivity varies between 0.1 and 0.95. And this is a material that is used as an emissivity standard!

For many materials, especially rough and amorphous materials, the practical problems are not as bad as implied by Figure 9.6. It is reasonably easy to identify the material, decide whether it is rough or polished, oxidised or not, and make an estimate of the emissivity. However, to make a good estimate of the emissivity some serious homework is necessary. It is important to know what wavelength the thermometer operates at, and what the material is, and to have access to reliable information on the surface properties of the material. Most manufacturers of radiation thermometers supply a list of the emissivities of a wide variety of materials, each measured at the operating wavelength of their thermometer. If all of this information is available, it is usually possible to make an estimate to about ±0.05.

Example 9.1

Estimate the uncertainty in the measurement of the temperature of steel in a rolling mill where the temperature is approximately $1000\,^\circ$C and the emissivity of the highly oxidised steel at $1\,\mu$m is estimated to be 0.80 ± 0.1 (95% CL). Assume the uncertainty in the measured radiance is zero.

Direct substitution into Equation (9.15) yields

$$U_{T_\mathrm{m}} = \pm 1 \times \left(\frac{1273}{1200}\right)^2 \times \frac{100 \times 0.1}{0.80} = \pm 14\,^\circ\text{C}.$$

Example 9.2

Estimate the uncertainty in the measurement of the temperature of freshly galvanised steel in a galvanising plant where the temperature of the plated steel is about $450\,^\circ$C and the emissivity of molten zinc at $4\,\mu$m is estimated to be 0.15 ± 0.05 (95% CL). Assume the uncertainty in the measured radiance is zero.

Direct substitution into Equation (9.15) yields

$$U_{T_\mathrm{m}} = \pm 4 \times \left(\frac{723}{1200}\right)^2 \times \frac{100 \times 0.05}{0.15} = \pm 50\,^\circ\text{C}.$$

The examples above illustrate the importance of knowing the emissivity. At moderately high temperatures, where short-wavelength thermometers operate and the emissivity of materials is usually high, measurements can be made with reasonable accuracy. At lower temperatures, where the longer-wavelength thermometers must be used and some materials have very low emissivities, the uncertainties can be so large as to make the measurements almost useless.

Without information on the spectral emissivity of the material, it is almost impossible to make a reasonable estimate of the emissivity from visual assessment alone. Surfaces that are black in the visible portion of the spectrum may well have a low emissivity in the infrared and vice versa. Two common examples will illustrate this point.

Nowadays, most paints use titanium dioxide as the base pigment. While the pigment is extremely white (i.e. has a low emissivity) in the visible part of the spectrum, it is also very black in the infrared. Thus the appropriate emissivity setting for a $10\,\mu m$ thermometer looking at any painted surface is about 0.95. As a general rule most organic materials, for example wood, skin and organic fibres, exhibit this type of behaviour.

The opposite effect occurs with metals coated with thin layers of oxide. At short and visible wavelengths the surface can be quite black. At longer wavelengths the oxide layer becomes transparent so that the surface behaves as the pure metal and has a very low emissivity. Figure 9.7 shows some examples. The curves in Figure 9.7 also exhibit some wiggles. These are caused by interference due to thin layers of metal oxide, the same phenomenon seen with oil films on water. These interference phenomena lead to emissivities that are extremely sensitive to the film thickness, viewing angle and operating wavelength. Under these conditions, radiation thermometers are almost useless.

For most surfaces the emissivity is also dependent on the angle of view. This is shown in Figure 9.8. The drop in emissivity at high angles, that is for views near grazing incidence, is a feature in common with all surfaces. As a general rule the emissivities that are published are for normal incidence, that is viewing at right angles to the surface, so radiation thermometers should always be used at or near normal incidence.

To obtain the most accurate information, the spectral emissivity must be measured. The simplest method is to measure the temperature of a sample of the material using
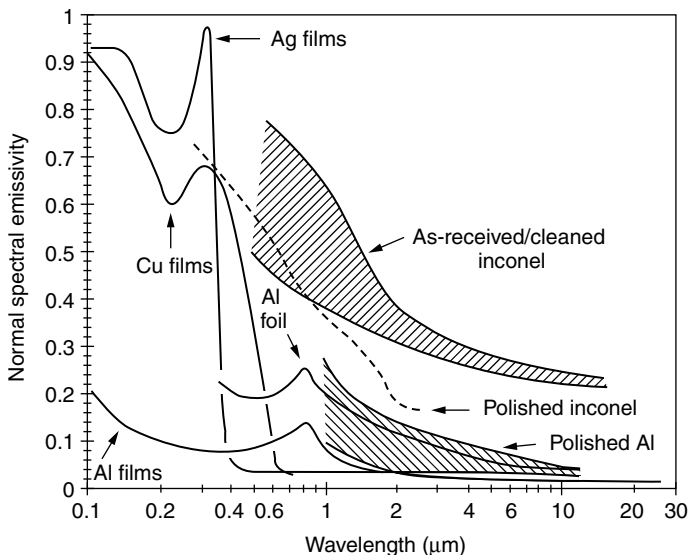
Figure 9.7   The normal spectral emissivity for a number of metals
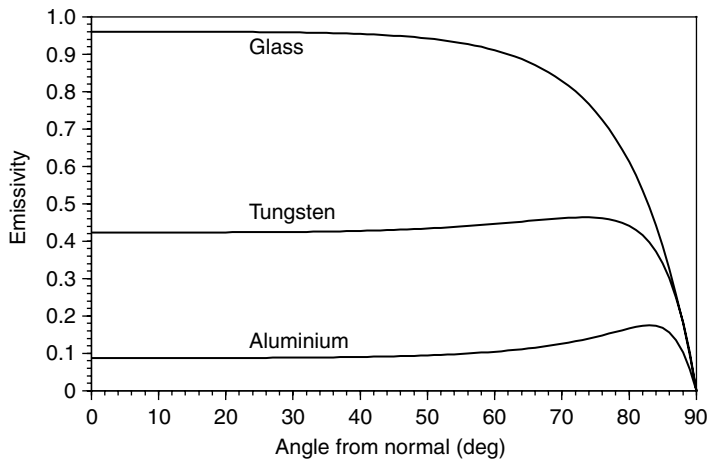
Figure 9.8 The emissivity of glass, aluminium and tungsten as a function of the angle of view

an alternative thermometer, such as a calibrated thermocouple, and then to adjust the instrumental emissivity setting on the radiation thermometer to give the same reading as the thermocouple. If there are no other errors and the emissivity is the same for all samples of the material, then this technique results in temperature measurements of a similar accuracy to that of the alternative thermometer. Measurements of the emissivity made in this way may be accurate to better than ±0.05 depending on the wavelength.

A second method of measuring emissivity is to make a blackbody to operate at exactly the same temperature as the material. Then adjust the instrumental emissivity setting on the thermometer so that the temperature is the same as the reading for the blackbody with the instrumental emissivity set to 1.0. The main difficulty with this technique is getting the required uniformity of the blackbody while keeping the surface of the sample free of reflections. The simplest version of the technique is to coat a sample of the surface with black paint or soot, both of which have emissivities in the range 0.9 to 0.95. With this method ±0.05 is about the best accuracy that can be expected.

A third, less practical, technique, which is the most accurate, is to measure the spectral reflectance of the surface. This is, however, a job for a specialist with specialised equipment. Accuracies of ±0.02 or better are possible this way. If the measurements are carried out at room temperature they will be in error at high temperatures if the emissivity is temperature dependent.

In recent years a number of radiation thermometers have emerged on the market that use an infrared laser to measure the emissivity of the surface *in situ*. Their operation is based on the relationship between the emissivity and hemispherical reflectance (Equation (9.2)). In practice these thermometers measure the retro-reflectance of the surface. Estimating the hemispherical reflectance from the retro-reflectance is analogous to estimating the volume of soil in a hill from one measurement of the height. The measurement is quite good for highly diffusing surfaces, such as those with a fine powdery texture, or for very rough surfaces. But for other surfaces the measurements can be very poor, certainly worse than a well-informed estimate.

In general, the emissivity of surfaces can rarely be determined with the accuracy desired for accurate radiation thermometry. The exception is for objects that behave as blackbodies. While it may seem unlikely, there are quite a number of situations where this occurs. As a general guide, the thermometer manufacturer's list of emissivity versus material will enable estimates to within ± 0.05 for rough or diffuse surfaces, and to within ± 0.1 for surfaces with any gloss, polish or film associated with them.

Exercise 9.1

Use Equation (9.15) to calculate the uncertainty in a radiation thermometry measurement made near $130\,^{\circ}\mathrm{C}$ (400 K) and $10\,\mu\mathrm{m}$. The uncertainties in the measured radiance and emissivity are 3% and 4% respectively.

9.4.2   Reflection errors

Because radiation thermometers infer temperature from measured radiance, anything that adds to the surface radiance will cause the thermometer to be in error. The most important source of additional radiance is radiation reflected from other objects in the vicinity. Radiation thermometers are most useful in high-temperature processing industries where, unfortunately, there are invariably reflections from flames, electric heaters, furnace walls, etc. At low temperatures, the problem is even worse because the whole environment behaves as a very large blackbody at 300 K. In fact it is quite hard to find an application where reflections are not a problem.

The most difficult aspect of the reflection problem is that we do not naturally associate other hot objects, which may be some distance from the surface of interest, with the surface itself. It is a matter of discipline to be aware of all objects in the space above a surface and methodically assess the likelihood of a reflection error caused by that object.

The most effective way of eliminating reflection errors is to eliminate the source of extraneous radiation. One of the most important sources of radiation in measurements made outdoors is the sun. If a radiation thermometer is being used to detect hot spots, such as thermal leaks in buildings, then the measurements should be made when the surface is shaded, or at night. In many cases, it is possible to shade the surface artificially. This technique can also be used inside furnaces to shade heaters or flames that are in close proximity to a surface.

More often than not, the interfering source is too large or too hot to shade. This occurs in many high-temperature processing industries where a product is pre-heated in a large firebox, and radiation thermometers are used to determine when the product has reached the required temperature. Fortunately, in these cases it is relatively easy to estimate the magnitude of the errors.

If we assume that the firebox walls are at a uniform temperature, T_{w}, then the firebox behaves as a blackbody cavity with an emissivity of 1.0 (see also Exercise 9.2 and Section 9.6.1). The radiance of a small object within the firebox then comprises two parts:

$$L_{\mathrm{m}} = \varepsilon(\lambda) L_{\mathrm{b}}(\lambda, T_{\mathrm{s}}) + [1 - \varepsilon(\lambda)] L_{\mathrm{b}}(\lambda, T_{\mathrm{w}}). \qquad (9.16)$$

The first part of the equation represents the thermal emission from the surface (Equation (9.4)), and the second is the radiance due to reflections originating from the firebox walls. Now, depending on the wall temperature, T_w, there are four strategies for handling the reflection.

Strategy 1: For $T_w \ll T_s$ assume negligible error and set $\varepsilon_i = \varepsilon(\lambda)$

This is the strategy employed during normal use of a radiation thermometer when measuring objects at temperatures well above ambient temperatures. It is the appropriate strategy for situations where the firebox temperature (or that of any other interfering source) is much less than that of the object, or the source of extraneous radiation is small. Figure 9.9 shows the errors that occur for this situation, with the object at 900 °C and various firebox wall temperatures. A simple approximation of Equation (9.16), based on Wien's law, shows that the error in the measured temperature, when T_w is near T_s, is

$$\Delta T = T_m - T_s = \left(\frac{1 - \varepsilon(\lambda)}{\varepsilon(\lambda)} \right) \left(\frac{\lambda T_s^2}{c_2} + T_w - T_s \right). \qquad (9.17)$$

Both Figure 9.9 and the approximation show that the errors increase with wavelength and the square of the temperature. The error also decreases with increasing emissivity.

Strategy 2: For $T_w \approx T_s$ assume blackbody conditions and set $\varepsilon_i = 1.0$

In many applications the object and the firebox have very similar temperatures. Under these conditions the object/firebox system behaves as a blackbody. Indeed, if we
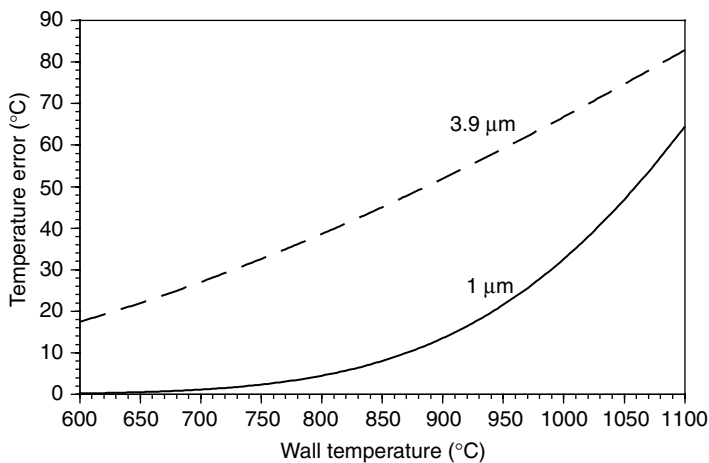
Figure 9.9   Temperature errors due to reflections versus firebox wall temperature for thermometers using the $\varepsilon_i = \varepsilon(\lambda)$ strategy. The surface of interest has an emissivity of 0.85 and a temperature of 900 °C. For wall temperatures less than the surface temperature short-wavelength thermometers have less error

substitute $T_w = T_s$ in Equation (9.16), then

$$L_m = L_b(\lambda, T_s), \tag{9.18}$$

so that the effective emissivity of the object is 1.0. Setting $\varepsilon_i = 1.0$, that is measuring the radiance temperature, is therefore a good strategy when the firebox and the object are at similar temperatures.

Figure 9.10 shows the same situation as in Figure 9.9, except that $\varepsilon_i = 1.0$. The central region of the graph near $T_w = 900\,°C$ shows that the strategy is quite effective and that the errors are almost independent of wavelength. A good approximation for the error in this region is

$$\Delta T = [1 - \varepsilon(\lambda)](T_w - T_s). \tag{9.19}$$

This is the equation of the dotted line in Figure 9.10. This measurement strategy also has the advantages of eliminating the uncertainties in the emissivity, and operating the thermometer under the same conditions as those under which it is calibrated (namely, $\varepsilon_i = 1$).

It might be thought that the situations where this strategy can be employed with confidence are rare. However, measurements in any closed temperature-controlled environment, such as cool-stores, furnaces and kilns, are candidates for this strategy. Nearly all measurements made indoors near room temperature also fall into this category, although there is a more effective and common strategy for this situation (see Strategy 4).

Strategy 3: For $T_w \gg T_s$ apply corrections for the reflections (high temperatures)

There are now a number of thermometers on the market, both hand-held and fixed installation types, that measure the firebox wall radiance and the radiance of the surface,
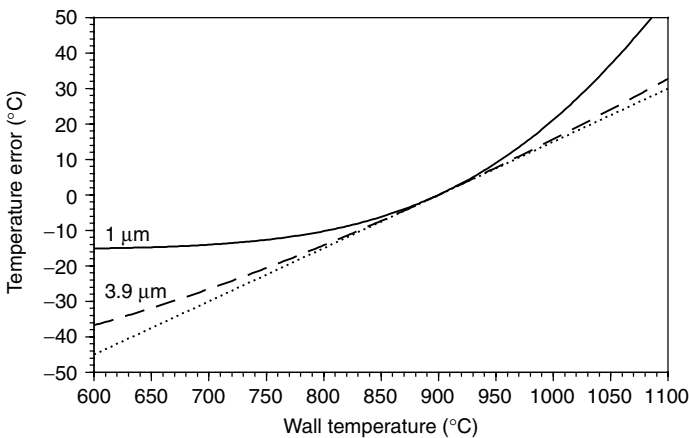
Figure 9.10   Temperature errors for radiation thermometers employing the $\varepsilon_i = 1.0$ strategy. The errors are almost independent of wavelength when $T_w \approx T_s$. At very long wavelengths the error approaches the dotted line (Equation (9.19))

and apply corrections for the reflected radiation. However, for $T_w > T_s$ this strategy is very sensitive to the operating wavelength and the uncertainties in both the emissivity of the surface and the wall radiance, particularly as the wall is rarely uniform. For these systems there is an optimum operating wavelength that minimises the uncertainty in the corrected result. For $T_w > T_s$ this wavelength, λ_{opt}, is near

$$\lambda_{opt} \approx \frac{c_2(T_w - T_s)}{T_w T_s} = \left(\frac{1200}{T_s}\right)\left(\frac{1200}{T_w}\right)\left(\frac{T_w - T_s}{100}\right). \tag{9.20}$$

At wavelengths shorter than this, the uncertainty in the corrected measurements increases exponentially. At longer wavelengths the uncertainty tends to increase more slowly, usually linearly. For $T_w \leq T_s$ the previous two strategies apply and the shortest practical wavelength should be chosen.

For applications where the temperature difference between the wall and object is less than 200 K the optimum wavelength is well within the normal range of operating wavelengths for that temperature. As the temperature difference $T_w - T_s$ increases, the optimum operating wavelength also increases. Usually the optimum operating wavelength is within the range of commercially available instruments.

Strategy 4: For $T_w \approx T_d$ apply corrections for reflections (low temperatures)

Low-temperature thermometers are used very often indoors where walls at room temperature surround them. Almost all low-temperature measurements are therefore corrupted by the reflected radiation from the walls. The measured radiance in the presence of reflections for low temperature thermometers is

$$L_m = \varepsilon(\lambda)L_b(\lambda, T_s) + [1 - \varepsilon(\lambda)]L_b(\lambda, T_w) - L_b(\lambda, T_d). \tag{9.21}$$

Now in principle we should first correct for the detector radiance, then the reflection error, and finally the emissivity. However, if we correct for the emissivity first and then for the detector radiance we obtain

$$L_m = L_b(\lambda, T_s) + \frac{[1 - \varepsilon(\lambda)][L_b(\lambda, T_w) - L_b(\lambda, T_d)]}{\varepsilon(\lambda)}. \tag{9.22}$$

Thus the reflection error is zero if the detector and the surroundings are at the same temperature. This requirement is very nearly satisfied for measurements made indoors since our rooms behave very much like a blackbody at the same temperature as the thermometer.

This strategy is implemented directly in many hand-held low-temperature radiation thermometers. However, while the thermometers work very well in most indoor situations, there are occasions in cool-stores, outdoors, or when the thermometer has been carried in clothing next to the body, when errors occur. Further, if the correction method is not understood, the behaviour of the residual reflection errors can be very puzzling. If the background temperature is not the same as that of the detector then the error is

$$\Delta T_m \approx \frac{1 - \varepsilon(\lambda)}{\varepsilon(\lambda)}(T_w - T_d). \tag{9.23}$$

The error in practice with this strategy is often quite low. Many low-temperature measurements are made of organic materials or painted surfaces so the emissivity is high, perhaps as high as 0.95, and the wall temperature is usually quite close to the detector temperature. The combination of these two factors ensures that the residual error is typically less than a few tenths of a degree. In cases where the detector temperature and the temperature of the surroundings are not the same, the error can be several degrees.

In use, these thermometers should be allowed to come to thermal equilibrium with the surroundings before a measurement is taken. If the measurements are made below $0\,°C$, care should be taken to purchase a thermometer that will operate below $0\,°C$. If the measurement error, Equation (9.23), is large then Strategy 2 ($\varepsilon_i = 1$) is often a better choice. However, some cheaper thermometers are manufactured with a fixed instrumental emissivity setting (often $\varepsilon_i = 0.95$), so for these instruments Strategy 2 cannot be applied.

Exercise 9.2

By considering the total radiance of a closed isothermal (i.e. with a uniform temperature) cavity as the sum of emitted and reflected parts (Equation (9.16)), show that the effective emissivity is 1.0.

Exercise 9.3

Compare the accuracy of measurements of the temperature of a hotplate using the $\varepsilon_i = \varepsilon(\lambda)$ and $\varepsilon_i = 1.0$ strategies. The temperature of the hotplate is expected to be $37\,°C$ and has an emissivity of 0.3. The operating wavelength of the radiation thermometer is $12\,\mu m$. Room temperature is $300\,K$.

9.4.3 Absorption errors

One of the great advantages of radiation thermometers is that they can measure temperature at a distance. However, this involves using the intervening space between the object and the thermometer as the transmission path for the radiation, and unfortunately most gases, including air, are not completely transparent. Most of the absorption in air (Figure 9.11) is due to water vapour and carbon dioxide.

Nearly all spectral band thermometers are designed to avoid the worst of the absorption bands, and in most practical situations the absorption effects can be neglected. However, most of the thermometers operate over a broad band of wavelengths that overlaps the tails of the absorption lines and will not be completely immune to these effects. When they are used in environments with very high concentrations of carbon dioxide and water, such as inside oil- or gas-fired furnaces, they are sensitive to absorption effects. Where the gas is hotter than the target the thermometer will read high, and vice versa. The worst cases are in the exhausts of flames where there are high concentrations of water and carbon dioxide at high temperatures. Errors approaching $10\,°C$ per metre of path length have been observed. Absorption errors are also a problem for
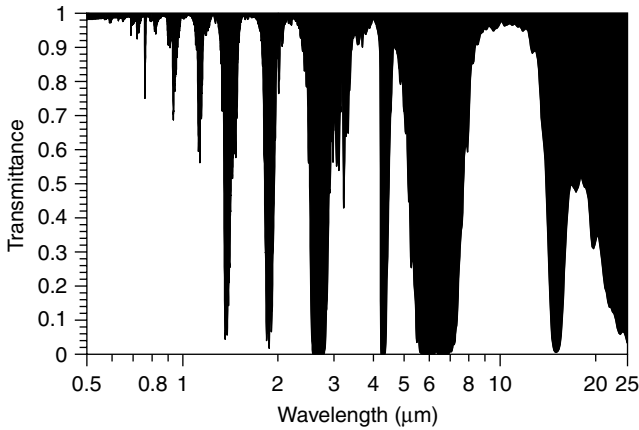
Figure 9.11   The transmittance of 300 m of air at sea level. The area above the transmittance curve is shaded to emphasise wavelengths for which the atmosphere is opaque. Those parts of the spectrum for which the atmosphere is transparent (unshaded) are known as *windows*. Some of the most useful windows for spectral band radiation thermometry are near $0.65\,\mu m$, $0.9\,\mu m$, $1.05\,\mu m$, $1.35\,\mu m$ $1.6\,\mu m$, $2.2\,\mu m$, $4\,\mu m$ and $10\,\mu m$

some general-purpose low-temperature thermometers because they employ very wide bandwidths, such as from $8\,\mu m$ to $20\,\mu m$, which includes water absorption lines.

   When absorption errors occur they can be modelled by an equation of the same form as that for the reflection errors:

$$L_{m,a} = \alpha(\lambda)dL_b(\lambda, T_g) + [1 - \alpha(\lambda)d]L_m, \tag{9.24}$$

where $\alpha(\lambda)$ is the absorption coefficient of the gas, d is the path length through the gas, T_g is the gas temperature, and L_m is the radiance of the surface that would be measured in the absence of the gas (Equation (9.21) or (9.16)). The effect of the gas absorption is almost identical to reflection errors (except that it varies with path length, d), so there are three similar measurement strategies:

(1) $T_g \ll T_s$: the absorption in the gas appears to reduce the emissivity of the target.
(2) $T_g \approx T_s$: the gas and target behave much like a blackbody.
(3) $T_g \gg T_s$: the emission from the gas appears to increase the emissivity of the target.

   In principle, we could use Equation (9.24) to calculate corrections for the absorption. In practice, however, there are large uncertainties associated with the values of the absorption coefficient and gas temperature. In addition, the effect often occurs in combination with reflection errors, with the result that the uncertainties in the corrections are impractically large.

   A key factor in Equation (9.24) is that the absorption effect increases with distance. Thus the error can be detected, and the magnitude of the error estimated, by observing the same target through different distances, thereby changing the path length through the interfering gas.

9.4.4   Transmission errors

With transparent objects, radiation from behind the target can find its way to the radiometer. This situation arises most commonly with glass and plastics. Models of the situation are almost identical to those for reflection and absorption, and as expected the strategies for avoiding the errors are similar. If the object behind is sufficiently cool, there is no error. If the object behind is at a similar temperature, it enhances the effective emissivity of the object to a value near 1.0. If the object behind is hotter then it can cause large errors. The error can be detected by changing the temperature of the background, perhaps by placing a different object behind the object of interest. For situations in the glass and plastics industries there are radiation thermometers specially designed to avoid these errors (see Section 9.8.5).

9.4.5   Non-thermal emission

Another, less frequent, source of error is *fluorescence*, which arises because thermal energy excites impurities in the object that then emit radiation in a very narrow band of wavelengths. This can happen with some types of glass, for example. Figure 9.12 shows the phenomenon for diamond.

   If this type of non-blackbody emission occurs within the pass-band of the radiation thermometer, then the measured radiance will be high. The problem is most likely to occur in relatively pure materials that are partially transparent in the pass-band of the thermometer.

   Avoiding errors due to fluorescence is difficult unless equipment is available to measure the whole spectrum. The best strategy is to use well-established procedures and operating wavelengths. This relies heavily on the fact that others have found such procedures reliable.
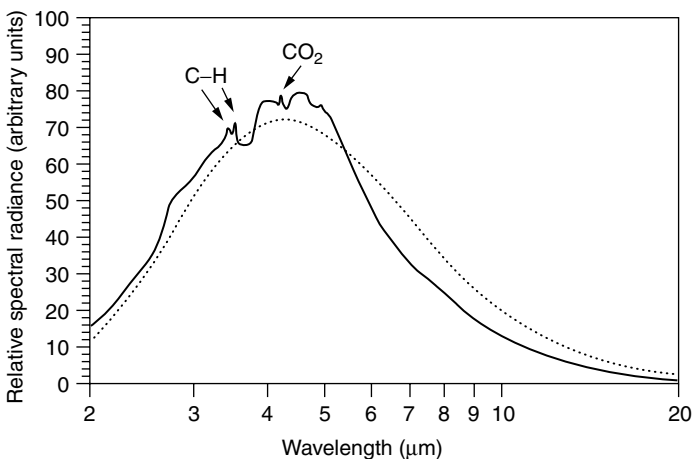
Figure 9.12   The emission spectrum of a sample of diamond. The dotted curve shows the emission spectrum for an object with constant spectral emissivity and a temperature of $400\,°C$. As well as the blackbody radiation there is additional radiation due to fluorescence. The C–H emission is at the same wavelength as the C–H absorption band in plastics (see Section 9.8.5)

9.4.6   Scattering errors

Dust in the transmission path of a radiation thermometer has three detrimental effects. Firstly, it scatters radiation out of the transmission path. This causes a decrease in the measured radiance of the object of interest, and therefore a decrease in the temperature reading. Secondly, it scatters radiation from other sources into the transmission path and increases the temperature reading. Thirdly, the dust may itself emit blackbody radiation, so that the dust temperature will affect the thermometer reading. Examples of dust include smoke, luminous flames, water fog, carbon, metal ore and silica. The 2% to 3% loss in transmission in the windows in Figure 9.11 is due to atmospheric scattering.

The general problem of the scattering of radiation from small particles is extremely complicated and depends on the size of the particles, on whether they transmit or absorb, and on the wavelength of the radiation. The only useful general principle is that the problem can often, but not always, be reduced by using thermometers that operate at longer wavelengths.

9.4.7   Size-of-source effects

All radiation thermometers collect the radiation from a well-defined conical zone in front of the thermometer (see Figure 9.13). The size of the zone is defined by the two defining apertures and is known as the field of view. Ideally, the zone has a sharp boundary so that radiation from outside the cone has no effect on the reading. In addition, the field of view must be completely filled to give an accurate reading. In practice, there are three effects, as shown in Figure 9.13, which contribute to the blurring of the field of view boundary. These three effects are discussed below.

Flare

Flare is the most serious of the size-of-source effects. It is caused by scattering of radiation within the radiation thermometer; in particular, by dust, scratches and density imperfections on, or in, the front lens of the thermometer. An analogous problem is the glare caused by dust on the windscreen of a car when driving towards the sun. When driving away from the sun, so that the windscreen is shaded from the sun, there is usually no problem. As the analogy suggests, flare is a serious problem when there
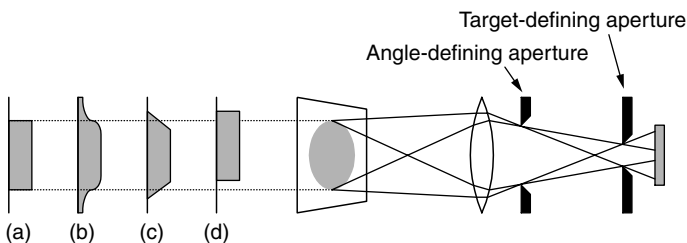
Figure 9.13   Size-of-source effects: (a) an ideal target profile, (b) a target profile broadened by flare, (c) a target profile due to poor focus, and (d) misalignment

are other bright radiation sources near the field of view of the thermometer. In many cases flare is difficult to distinguish from a reflection error.

Flare is usually prevalent in long-wavelength thermometers operating at 4 μm or more. In these thermometers, the increased effect is due to density variations in the lenses that scatter the radiation, and the increased sensitivity is due to the longer wavelength (Equation (9.13)). It is also more prevalent in systems with narrow fields of view or high magnification. As a guide the errors for a short-wavelength (∼1 μm) industrial thermometer operating at 1000 °C are typically 2 °C to 5 °C, and for long-wavelength thermometers (∼5 μm) about 10 °C to 25 °C.

Usually the only way to minimise flare is to use *sight tubes*. These are tubes which are black on the inside, and mounted on the front of the thermometer to restrict the radiation falling on the lens to that within the field of view. The lens hoods on cameras and car windscreen visors perform the same function. When employing sight tubes it is important that the tube does not impinge on the field of view, as this will cause vignetting (see below).

Because scratches and dust also cause flare, it is essential that radiation thermometers are maintained with due care. In particular, the front lens should be cleaned regularly with an airbrush or high-quality lens tissue. On no account should abrasive materials be used to clean a lens. Permanently-installed radiation thermometers may require an air purge facility, which supplies cool filtered air over the front of the lens both to cool the lens and to prevent dust from settling.

Poor focus

Lenses and mirrors in radiation thermometers are used to focus an image of the object of interest onto the target-defining aperture. Radiation from the portion of the image over the aperture then passes on to the detector. If the thermometer is not well focused then the boundaries of the target area are not well defined. This is shown in the poor-focus target profile in Figure 9.13(c). For systems with a fixed focus or no lenses, the field of view must be well overfilled in order to get an accurate reading.

Optical aberrations and misalignment

A radiation thermometer with the ideal target profile shown in Figure 9.13(a) is not realisable. In practice, imperfections in the optical components, interelement reflections, and slight misalignment of the optical components all lead to very slight blurring of the target image.

Usually these effects are negligible for practical purposes. However, there are two examples of misalignment that lead to large size-of-source problems. The first occurs if, for example, the thermometer is dropped or knocked, so that some of the components become seriously misaligned. Of course, serious misalignments of this kind usually invalidate the calibration as well.

The second problem occurs in long-wavelength thermometers where a separate visual telescope or sighting laser is provided to sight the target. If the two optical paths are not exactly aligned, or not in focus at the same time, then the field of view may have to be overfilled considerably to get an accurate reading.

To minimise size-of-source effects, always overfill the field of view as much as possible with neighbouring objects at the same or a similar temperature as the object of interest. In particular, avoid having objects at a much higher temperature than the object of interest near the field of view.

9.4.8   Ambient temperature dependence

All radiation thermometers suffer some sensitivity to the ambient temperature due to any one of three causes. The one cause that affects all radiation thermometers is the change in the detector sensitivity with temperature. In most radiation thermometers, there is an electronic means of compensating the change in sensitivity. However, if the ambient temperature changes quickly the compensation is unlikely to track the change in detector temperature exactly. For this reason thermometers should be allowed to settle in a new environment for up to an hour to ensure that the whole instrument has come to equilibrium. This is a more serious problem for low-temperature instruments, in part because of the longer wavelength used, in part because of the types of detectors used, but mostly because of the reflection correction strategy employed (see Strategy 4, Section 9.4.2).

In instruments with very narrow bandwidths, the wavelength response is determined by the pass-bands of interference filters, which are extremely sensitive to temperature. Examples of instruments that include interference filters are laboratory instruments, which often have their own temperature control, ratio thermometers, and special thermometers for the glass and plastics industries.

Low-temperature and long-wavelength radiation thermometers are probably the most susceptible to ambient temperature changes. This is because the signal from a detector in a radiation thermometer is actually a measure of the difference between the radiance of the target and the radiance of the detector (Equation (9.10)). For high-temperature applications, the detector radiance is negligible and is ignored. However, for thermometers working below 200 °C, and especially those working near 20 °C or lower, the detector radiance is significant and may be greater than that of the object of interest. In these instruments it is necessary to measure or compensate for the detector radiance in order to achieve an accurate measurement. Again, these instruments are susceptible to rapid changes in the ambient temperature.

9.4.9   Vignetting

In all radiation thermometers the acceptance angle and the target area are defined by the two apertures (see Figure 9.13). Anything that further restricts the cone of radiation accepted by the thermometer will cause the thermometer to read low, since there will be less radiation falling on the detector. In particular, all parts of the front lens of the thermometer must have an unobstructed view of the entire target. Obstruction of the field of view, known as *vignetting*, occurs often in high-temperature applications where the thermometer is sighted through small peepholes in furnace walls. Vignetting also occurs when sight tubes are misaligned.

9.4.10 Linearisation

All direct-reading radiation thermometers include some form of linearisation in their electronic systems. This is necessary to convert the signal from the detector, which is an extremely non-linear function of temperature, into a signal that is proportional to temperature. As with other direct-reading thermometers (Section 5.3.1), this linearisation is at best an approximation. For most industrial thermometers, the residual errors of 1 °C to 5 °C are negligible in comparison with the errors introduced through reflections, flare, and uncertainty in the emissivity.

9.4.11 Instrumental emissivity

Most spectral band thermometers include an emissivity adjustment to compensate for the emissivity of the surface of interest. In its simplest form the adjustment is a dial on the side of the thermometer with a scale marked typically from 0.2 to 1.0. For analogue dials the accuracy of the dial and scale limits the precision in the setting to about ±0.02. This uncertainty is additional to the uncertainty in the knowledge of the emissivity (Section 9.4.1).

In higher-accuracy applications, thermometers with a digital emissivity setting are preferred since the uncertainty in the setting is reduced to ±0.005. This applies particularly to long-wavelength thermometers, which are more susceptible to the error.

Quite a number of fixed-installation thermometers have the instrumental emissivity set at the time of manufacture, often to $\varepsilon_i = 0.95$. For these instruments, the uncertainty is probably negligible. There will be, however, an error if the factory setting is different from what is required.

9.5 Use and Care of Radiation Thermometers

9.5.1 Choosing a radiation thermometer

Probably the first question asked should be: is a radiation thermometer the best option? Generally, if a good contact thermometer can be used for the application it is almost certainly capable of higher accuracy than a radiation thermometer in the same situation. However, there are situations where radiation thermometers are appropriate:

- where the target object is moving;
- where, because of vibration or corrosion, the environment is too hostile for a contact thermometer;
- where the temperature is very high, especially above 1500 °C, or 1100 °C if the installation is long term;
- where a fast response is required;
- where remote measurement is required;
- where a contact thermometer would disturb the heat balance around the object.

Where several of these factors are involved, the radiation thermometer may be the only choice.

Once it has been decided that a radiation thermometer is required, a suitable thermometer must be chosen from the literally hundreds available. This is a bewildering problem for those unfamiliar with the variety of operating wavelengths, applications and options. Some suggestions are made here as a guide.

In the first instance determine the specifications required of the instrument.

Temperature range   The temperature range should be chosen conservatively. The accuracy of wide-range instruments is generally less than that of narrower-range instruments.

Accuracy   When determining the accuracy required, some thought should be given to the likelihood of errors due to reflections, uncertainty in the surface emissivity and flare. If the likelihood of error is high then short-wavelength, high-quality instruments are to be preferred. Instruments with digital rather than analogue adjustments for the emissivity compensation are also preferred, especially for long-wavelength thermometers.

Operating wavelength   In choosing the operating wavelength, the shortest wavelength is usually best. However, there are three situations where longer wavelengths may prove advantageous. Firstly, if there are reflections from large distributed sources and the thermometer is to be used in the $\varepsilon_i = 1.0$ mode (Section 9.4.2) then the operating wavelength should be chosen according to Equation (9.20). Long-wavelength thermometers also reduce the reflection errors caused by very hot sources such as the sun. Secondly, if there is fine dust, smoke or visible flames in the vicinity (indicating that carbon dust is present), then a slightly longer-wavelength thermometer may be less susceptible to scattering errors. Thirdly, if the thermometer is to be used in the plastics or glass industry then it should operate at wavelengths where the glass or plastic is opaque (see Section 9.8.5).

Field of view   The field of view is determined by the size of the target and the distance to it from the most convenient observation or mounting point. Some attention may need to be given to the choice of observation point if there are other radiation sources and flames about.

Response time   The response time of radiation thermometers varies from about 0.001 to 10 seconds, with most industrial thermometers in the range 0.1 to 10 seconds. Some manufacturers are prepared to set the response time according to the client's requirements.

Mode of readout   Some manufacturers provide voltage outputs that simulate thermocouples as well as the usual analogue, digital, current and voltage output modes.

Special environmental considerations   One of the most important factors is the environment of the thermometer: if the thermometer is exposed to dust then air purge systems may be required; if it is exposed to high ambient temperatures then water cooling and a high ambient temperature rating will be required. Other possible options include explosion-proofing and radiation shields.

Application/manufacturer   Often the best advice on the choice of thermometer can be obtained from a manufacturer. Many of the larger manufacturers have links with, or cater for, particular industries, for example the glass, petrochemical, plastics and steel industries. If you are working in an industry that is a heavy user of radiation thermometers, it is likely that one of the larger manufacturers has specialised in supplying

your industry. In this case you should first determine which is the manufacturer with
the strongest association with your industry. This manufacturer will be able to advise
on environmental concerns and on choice of wavelength if, for example, scattering due
to dust is a problem.

Calibration   Thought should also be given to the calibration of the instrument. If
this is the only radiation thermometer you have, then the calibration overheads may
be quite high. The thermometer should be calibrated when new, when one year old,
then when necessary (judged by the observed drift in regular single-point checks) up
to a maximum of five years. Unlike other thermometers, high-temperature radiation
thermometers are not easily checked at the ice point, so additional equipment may be
required for traceability. There are available commercially a number of relatively low-
cost blackbodies which are suitable for both regular verification checks and calibrations.
In addition, a number of manufacturers offer an annual calibration service.

9.5.2   Care and maintenance

The physical care and maintenance of radiation thermometers is straightforward: they
should be treated as you would treat a very expensive camera. Usually the manufacturer
makes quite strong recommendations in the manual for cleaning and general care. The
lens should be cleaned periodically with high-quality lens tissue or an airbrush to
remove dust. If absolutely necessary, ethanol and lens tissue can be used to remove
grease.

9.5.3   Using the thermometer

When using a radiation thermometer it is useful to go through a simple checklist to
make sure that none of the possible sources of error are overlooked, and that everything
practical is done to minimise errors.

Emissivity

Know the emissivity of the surface. Spend some time in advance of the measurement
looking at the thermometer manufacturer's guide and samples of the material so that
you have a good estimate of the emissivity. The choice of emissivity may well be
controlled by a QA system so that there is uniform practice within the company.

   If the thermometer is used for diagnostic purposes, be wary of changes in surface
emissivity that create the illusion of hot or cold spots. Changes in emissivity on hot
materials can make hot spots appear cold and vice versa. Because a surface with a
high emissivity radiates more energy than a low-emissivity surface, a spot with a high
emissivity is often cooler than the rest of the material. Yet because it is radiating more
strongly it will appear hotter to the radiation thermometer unless the emissivity is
adjusted.

   Look out for and use cavities in the target. Cavities behave as blackbodies so they
have an emissivity close to 1.0 (see Section 9.6 for an explanation). Examples include
the insides of pots or glass jars in kilns, gaps or cracks in between boxes of frozen

goods, and blind bolt holes in metal structures. If such cavities are available always use them with the instrumental emissivity set to 1.0 rather than using a flat surface and a guess at the emissivity.

Reflections

Systematically look about the space in the hemisphere above the surface for bright objects that may be sources of additional radiation, for example the sun, flames, heaters, furnace walls and incandescent lamps. If possible, shield the sources. If the object is in near-blackbody conditions the $\varepsilon_i = 1$ strategy will minimise the errors (see Section 9.4.2).

Environment

Avoid taking a thermometer into areas where there is a lot of dust or the ambient temperature is high. Remember that lenses are prone to fracture if they are exposed to too high a temperature too quickly. If you cannot keep your hand on the thermometer in use then it is too hot. This is true particularly where a manufacturer has supplied a radiation shield to help keep the thermometer body (but not the lens) cool.

Absorption

Make sure there are no windows, smoke, dust or haze in the field of view of the thermometer. If there are visible flames nearby there may be some carbon dust in the field of view. If working near flames or large bodies of water try observing the target from different distances to test for gas absorption.

Flare

Check that there are no objects brighter than the object of interest near the field of view of the thermometer. If the flare risk is high a sight tube may be necessary. It may also be possible to use a cool object in the foreground to shield the thermometer from hot objects outside the field of view.

Field of view

Ensure that the field of view is completely filled, preferably well overfilled, and as uniform as possible.

Safety and exposure to bright sources

Never sight a radiation thermometer on the sun. Quite apart from the potential damage to the instrument, it is also likely that your eye could be permanently damaged.

With most radiation thermometers exposure to very bright sources, particularly sources like the sun, that contain a lot of ultraviolet radiation, may cause permanent damage to the thermometer. The thermal stress resulting from exposure may be sufficient to break any of the optical components. In addition, ultraviolet radiation has sufficient energy to photo-degrade many detector materials, and change the detector characteristics.

Record keeping

More than most thermometers, radiation thermometers are affected by the manner in which they are used. For a measurement to be traceable it must be repeatable: that is, documented in sufficient detail for a similarly competent person to be able to verify and, if necessary, modify the results of the measurement. The documentation may be casual, as in a lab book, or more formal, as required by a QA system. The record should identify the instrument used, include the choice of emissivity setting and the rationale for that choice, state who took the measurement, the position from where the measurement was taken, and any significant features in the environment that are of concern, such as dust and bright objects.

9.6 Practical Blackbodies

9.6.1 Blackbody principles

The principles underlying the design of practical blackbodies are useful for several reasons. The most important application is, of course, the manufacture of blackbodies used for calibrating radiation thermometers. Additionally, reflection errors can be more easily understood or eliminated by invoking blackbody concepts. We can also make a blackbody ice point, which is useful for checking low-temperature thermometers.

Practical blackbodies are not surfaces, but cavities. Because cavities trap and absorb rather than reflect light, they have a much higher emissivity than any real surface. Figure 9.14 shows a simple example. An upper limit on the cavity emissivity can be very easily determined by considering its reflectance. Consider a ray of light that enters the cavity and strikes the back surface. The amount of light reflected back out of the aperture depends on two factors: firstly, the reflectance of the surface; and secondly, the size of the aperture relative to the hemisphere above the back surface. By considering only the rays that undergo a single reflection, the effective reflectance of the cavity, ρ_{eff}, (i.e. the fraction of light escaping), is estimated as

$$\rho_{\text{eff}} = \rho_{\text{s}} \frac{r^2}{R^2}, \tag{9.25}$$

where ρ_{s} is the reflectance of the cavity material, r is the radius of the aperture and R is the distance between the back of the cavity and the aperture. Since the emissivity and reflectance of the cavity are related (by Equation (9.2)), we estimate the emissivity as

$$\varepsilon_{\text{eff}} = 1 - (1 - \varepsilon_{\text{s}}) \frac{r^2}{R^2}. \tag{9.26}$$
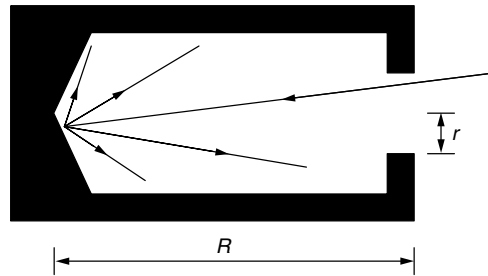
Figure 9.14   A simple representation of a blackbody cavity

This formula is an upper limit for the emissivity since the light escaping via two or more reflections is assumed not to have escaped. We can see from the equation that three of the factors affecting the quality of a blackbody are:

(1)   the emissivity of the surface (ε_s);

(2)   the size of the aperture (r);

(3)   the size of the cavity (R).

Example 9.3   Estimating the emissivity of a blackbody cavity

Estimate the emissivity of an Inconel® cavity that has a 1 cm diameter aperture and is 10 cm long. The emissivity of rough and heavily oxidised Inconel® is about 0.9.

From the information supplied $\varepsilon_s = 0.9$, $r = 0.5$ cm and $R = 10$ cm. Hence

$$\varepsilon_{\text{eff}} = 1 - 0.1 \times 0.5^2 / 10^2 = 0.999\,75.$$

Remember that this is an optimistic estimate based on geometry only. In practice, the extra reflections might double the reflectance of the cavity. There is also a requirement for the cavity to be isothermal.

Exercise 9.4

Calculate the effective emissivity of the cavity formed by a glass jar 200 mm deep and 100 mm wide at the mouth. Assume the emissivity of glass at 8 μm is 0.85.

9.6.2   Ice-point blackbody

In Section 3.2.4 we described how to manufacture an ice point to check and calibrate contact and immersion thermometers. The method we describe here is more suited to long-wavelength (low-temperature) radiation thermometers.

For wavelengths beyond about 4 μm ice has a high emissivity, typically greater than 0.95, which makes it an ideal material for a blackbody cavity. The cavity is made very
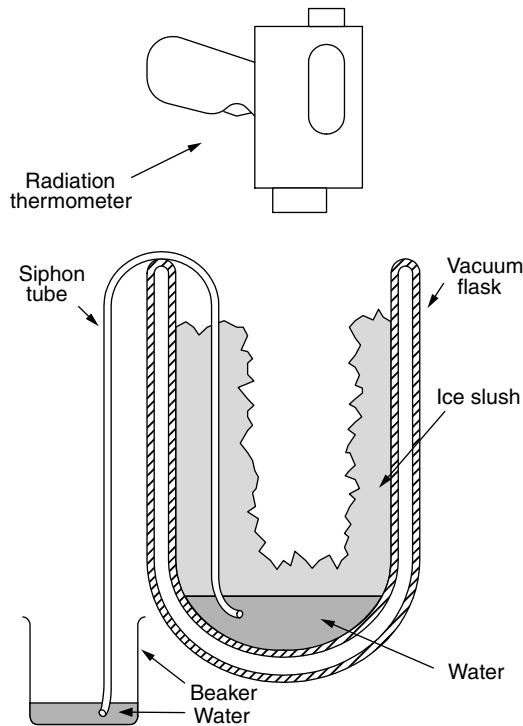
Figure 9.15 An ice-point blackbody

simply, as shown in Figure 9.15, using a wide-mouthed flask. The flask is first filled with crushed or shaved ice. The ice is then drained of any excess water and a cavity is carved or pressed into the remaining ice. The cavity should be wide enough at the back to accommodate the field of view of the thermometer, and deeper than about five times the diameter. This will ensure that the radiance temperature of the cavity is within about $0.1\,°C$ of $0\,°C$.

In the band between $1.4\,\mu m$ and $4\,\mu m$ ice has very similar optical properties to water. Therefore, the chances are that the ice is partially transparent at the operating wavelength of the thermometer and the radiation thermometer will be able to 'see' the walls of the flask. For wavelengths shorter than $4\,\mu m$, the flask should be opaque, have a high emissivity to eliminate room reflections, and be a good insulator so that the flask wall is also at the ice-point temperature.

9.6.3 Errors in blackbodies

To be a good blackbody, a cavity must also be uniform in temperature. We can see this by considering the cavity radiance due to the surface emission and the first reflection. Using Equation (9.16) for reflection errors we estimate the total radiance of the rear of the cavity as

$$L_{\text{tot}} = \varepsilon_{\text{s}} L_{\text{b}}(\lambda, T_{\text{c}}) + (1 - \varepsilon_{\text{s}}) L_{\text{b}}(\lambda, T_{\text{w}}), \qquad (9.27)$$

where T_c is the nominal cavity temperature (the rear wall temperature), and T_w is the cavity side wall temperature. We can relate this radiance (see Exercise 9.6) to the radiance temperature, T_λ, of the cavity:

$$T_\lambda \approx T_c + (1 - \varepsilon_s)(T_w - T_c). \tag{9.28}$$

This tells us what a radiation thermometer with an emissivity setting of 1.0 will read when viewing the blackbody. We can also determine the uncertainty in the radiance temperature in terms of the uncertainty in the cavity wall temperature.

Example 9.4 Uncertainty in radiance temperature due to non-uniformity of the cavity wall temperature

A blackbody's temperature is monitored with a thermocouple mounted in the rear wall of the cavity. Experiments with a fine rare-metal differential thermocouple show that the temperature gradient is such that the front of the cavity is $6\,°C$ cooler than the rear of the cavity. Calculate the uncertainty in the cavity temperature if the emissivity of the cavity material is 0.9.

The easiest way of characterising the radiance temperature is to estimate the two extremes of the likely range of values.

Maximum temperature   Since those portions of the cavity closest to the rear wall are at a temperature very near to that of the rear wall, the maximum radiance temperature is

$$T_{\lambda,max} = T_c.$$

Minimum temperature   The average wall temperature is $3.0\,°C$ lower than the rear wall temperature so we could expect, from Equation (9.28), that the minimum radiance temperature is

$$T_{\lambda,min} = T_c - (1 - 0.9) \times 3.0 = T_c - 0.3.$$

Treating these two values as the limits of a rectangular distribution we estimate that the radiance temperature is

$$T_\lambda = T_c - 0.15 \pm 0.15\,°C,$$

where the uncertainty is expressed as a 95% confidence interval.

Non-uniformity is a serious problem in most blackbodies, in part because of the difficulty obtaining uniform heating over the object containing the cavity, and in part because of the convection currents in the air near the aperture of the cavity. The currents cause a cool stream of air to enter the cavity, which disturbs the heat balance, generating a gradient in the cavity walls.

The last factor to consider in the evaluation of the performance of a blackbody is the effect of the loss of energy that is radiated by the aperture. Since heaters around the cavity must continuously replace the energy, there must be a temperature gradient through the walls of the cavity. If the cavity uses a reference thermocouple mounted in the cavity wall to determine the cavity temperature then it will be in error due to

the gradient. If it is assumed that the energy is lost uniformly by all parts of the cavity then the wall temperature gradient can be estimated from Equation (4.1) as

$$\frac{dT}{dx} = \sigma(T_c^4 - T_a^4)\frac{a}{Ak},\qquad(9.29)$$

where σ is the Stefan–Boltzmann constant, T_a is the ambient temperature around the cavity, a is the aperture area, A is the internal area of the cavity, and k is the thermal conductivity of the blackbody material.

In high-temperature blackbodies, this effect is the most significant source of error. Not only does it contribute to the non-uniformity of the cavity, but also it makes accurate measurement of the cavity temperature difficult by any means other than a transfer standard radiation thermometer. For the highest-precision work, the aperture must be as small as practical to reduce the radiation loss to a minimum.

Example 9.5   Blackbody wall gradient due to aperture loss

Estimate the temperature gradient in the wall of a spherical blackbody 20 cm in diameter with a 5 cm diameter aperture. The cavity is made from Inconel® (thermal conductivity = 25 W K^{-1} m^{-1}) and must operate at 1100 °C.

At 1100 °C the radiation received by the cavity is negligible compared with that radiated, and therefore the T_a term can be ignored. Substitution of the values for the other variables into Equation (9.29) leads to

$$\frac{dT}{dx} = 5.7 \times 10^{-8} \times (1100 + 273)^4 \times \frac{\pi(0.025)^2}{25 \times 4\pi(0.1)^2}.$$

Hence

$$\frac{dT}{dx} = 1.27 \,°\text{C cm}^{-1}.$$

This effect imposes a severe limitation on the accuracy of thermocouples and PRTs as reference thermometers in blackbody cavities.

Overall we have identified three main factors contributing to errors in blackbody cavities. In order of significance they are: temperature gradients due to energy loss, errors in radiance temperature or emissivity due to temperature non-uniformity, and the reduction in effective emissivity due to the cavity reflectance. Collectively this limits the accuracy of radiance temperatures of blackbodies as measured by a contact thermometer to about ±0.5%.

Exercise 9.5

Consider the blackbody cavity of Figure 9.14.

(a)   By assuming that radiation falling on the rear surface is scattered equally in all directions, show that the reflectance of the cavity is $\rho_s r^2/2R^2$.

(b) In practice the radiation is not scattered equally in all directions but is scattered according to the projected area of the rear surface; that is the scattered flux is proportional to $\cos\theta$, where θ is the angle from the normal (this is _Lambert's law_). Hence show that the reflectance of the cavity is $\rho_s r^2/R^2$ (Equation (9.25)), which is twice that calculated in (a). [Note: part (b) is difficult.]

Exercise 9.6

Using the definition of radiance temperature, $L_b(\lambda, T_\lambda) = L_{tot}$, derive Equation (9.28). [Hint: Expand $L_b(\lambda, T)$ as a Taylor series around T.]

Exercise 9.7

A small fixed-point blackbody at the silver point uses a graphite cavity 10 mm in diameter and 80 mm long, within a 5 mm diameter aperture. Estimate the temperature gradient across the 5 mm thick graphite wall. The thermal resistivity of graphite is approximately $1\,^\circ\text{C}\,\text{cm}\,\text{W}^{-1}$.

9.7 Calibration of Radiation Thermometers

9.7.1 Calibration methods

Historically radiation thermometers have been used mainly for monitoring industrial processes rather than for making accurate quantitative measurements. With the trend towards more accurate and traceable measurements, the calibration procedures for radiation thermometers are evolving rapidly. In particular, calibrations of direct-reading thermometers must establish the accuracy of the emissivity compensation adjustment as well as determining the radiance–temperature relationship.

The traceability of radiation thermometers to ITS-90 may be obtained through three chains as shown in Figure 9.16.

Via a tungsten strip lamp

This is the traditional means of disseminating the radiation thermometry scale. The lamp is calibrated by the national standards laboratory against a fixed-point blackbody with the aid of a transfer standard thermometer. The lamp can then be used as the radiance source for calibrating other radiation thermometers, particularly disappearing-filament thermometers, which operate near 655 nm and use tungsten filaments.

The lamp may also be used in conjunction with a transfer standard radiometer (operating at 655 nm) to establish the temperature of a blackbody. This is the best method for calibrating thermometers operating at wavelengths much longer than 655 nm
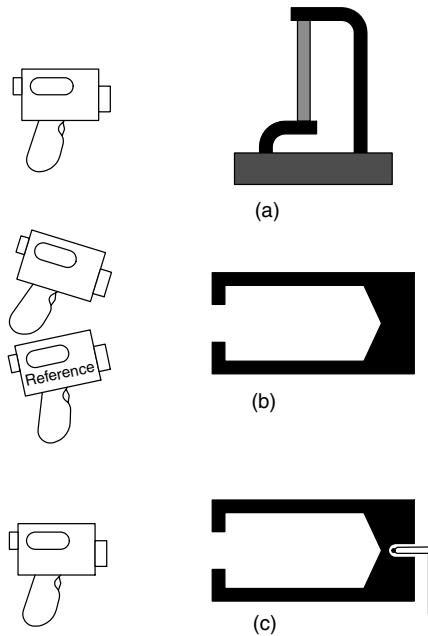
Figure 9.16 The three basic traceability chains for the calibration of radiation thermometers: (a) via a tungsten strip lamp, (b) via a transfer standard radiometer, (c) via a thermocouple or resistance thermometer

or with fields of view much greater than 2 mm. If the two thermometers operate at different wavelengths corrections must be applied for the wavelength dependence of the radiance temperature of the lamp.

Via a transfer standard radiometer

With the improvement in the stability of transfer standard radiometers, it is no longer necessary to use strip lamps to maintain the temperature scale, and this is now the preferred method of calibrating radiation thermometers. Once calibrated against a fixed-point blackbody and fully characterised, the thermometer can be used to establish the radiance temperature of a blackbody, which is used to calibrate thermometers operating at any wavelength.

Via a thermocouple or resistance thermometer

At temperatures below 960 °C, where ITS-90 is defined in terms of PRTs, the temperature of a blackbody can be determined by using a calibrated thermocouple or resistance thermometer. This is a very convenient and cost-effective way of measuring blackbody temperature, but it is subject to significant errors and uncertainty due to temperature gradients in the cavity.

This method may also be used above 960 °C and up to 1700 °C with rare-metal thermocouples. However, this involves an extra step in the calibration chain that may increase the uncertainty further.

9.7.2   Calibration equations

Above the silver point ($\sim$962 °C) ITS-90 defines temperature in terms of Planck's radiation law (Equation (9.3)). The primary thermometer, which compares the unknown radiance with the radiance of a fixed-point blackbody at the silver, gold ($\sim$1064 °C) or copper point ($\sim$1085 °C), is known as a *transfer standard radiometer*. The thermometer may be used to transfer the scale to a tungsten strip lamp or, if sufficiently stable, it may be used directly to determine the temperature of a blackbody. A fuller description of the realisation of the ITS-90 radiation scale is given in Chapter 3.

So far, we have assumed that the measured radiance is proportional to Planck's law for all spectral band radiometers. In practice, the finite bandwidth of the filter leads to significant departures from Planck's law. For transfer standard thermometers, the departure is usually characterised by an effective operating wavelength, which is temperature dependent. For narrow-band thermometers the effective wavelength is very closely described by the simple relationship

$$\lambda_{\text{eff}} = A + B/T, \tag{9.30}$$

where A and B are constants. For primary thermometers this relationship is calculated from measurements of the responsivity of the filters and detector. However, a further simplification is to use this in conjunction with Wien's law. This leads to a simple calibration equation that is useful for many narrow-band (50 nm to 100 nm) radiation thermometers:

$$V(T) = C \exp\left(\frac{-c_2}{AT + B}\right), \tag{9.31}$$

where $V(T)$ is the measured output signal (voltage) of the thermometer, and C is a constant. This equation is used for many radiation thermometers including some transfer standard thermometers. For thermometers with bandwidths of 50 nm or less, Equation (9.31) will fit the thermometer response to within a few tenths of a degree, and the three coefficients can be determined by comparison with three fixed-point blackbodies. For long-wavelength or high-temperature thermometers the Planck version of Equation (9.31),

$$V(T) = C \left[\exp\left(\frac{c_2}{AT + B}\right) - 1\right]^{-1}, \tag{9.32}$$

is a significant improvement. For wide-band thermometers an extension to Equation (9.31), which includes higher-order terms to account for the greater departures from Wien's law, is used:

$$\log[V(T)] = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3}. \tag{9.33}$$

This equation is more amenable to least-squares fitting than Equation (9.32), and will fit most broadband responses to a degree or better. An equation less frequently used is

$$\frac{1}{T} = A + B \log[V(T)] + C \log^2[V(T)] + D \log^3[V(T)], \tag{9.34}$$

which has the advantage of giving the temperature in terms of the signal. These two equations are used either directly or as the basis for look-up tables in direct-reading radiation thermometers. Equation (9.34) is also used for thermistors (see Section 6.8.1).

For direct-reading radiation thermometers the equation

$$\Delta T = a + bt + ct^2 + dt^3, \tag{9.35}$$

which was developed in Chapter 5 for direct-reading thermometers, should be used. Note that the t^2 term will usually be significant since most errors in radiation thermometry have a quadratic dependence (see Section 9.4).

9.7.3 Tungsten strip lamps

Tungsten strip or ribbon lamps have been used for many years to maintain the radiation thermometry portion of the temperature scale. They are also a convenient and often lower-cost source of spectral radiance than the equivalent blackbody.

Strip lamps consist of a tungsten ribbon up to 5 mm wide and 50 mm long supported in a pyrex or silica envelope (see Figure 9.17). They are usually mounted on a substantial base that is cooled to minimise the influence of the ambient temperature on

Figure 9.17 A tungsten strip lamp
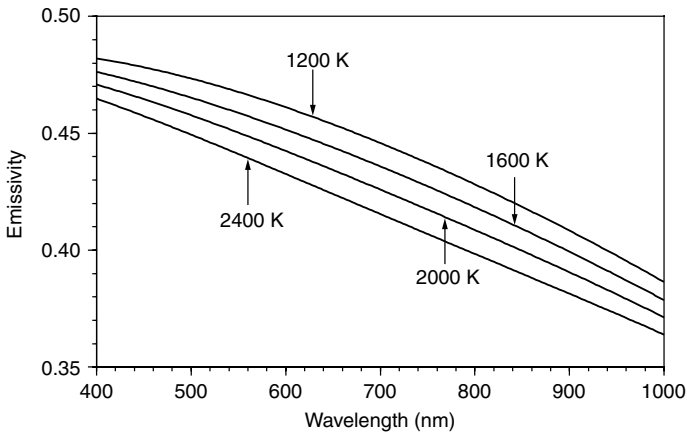
Figure 9.18   The emissivity of tungsten filament versus temperature and wavelength

the lamp. The envelope may be filled with an inert gas to prevent oxidation and contamination of the filament. Vacuum lamps are suitable for operation between $700\,°C$ and $1700\,°C$ while gas-filled lamps are suitable from $1500\,°C$ to $2300\,°C$.

The lamps are calibrated in terms of the filament current required to achieve a specified radiance temperature at a specific wavelength (often $655\,nm$). The radiance temperature is the temperature of a blackbody that would have the same spectral radiance as the lamp. The radiance temperature of a lamp is strongly wavelength dependent and corrections must be applied if the lamp is used at other wavelengths. Lamps may also be calibrated at several wavelengths. Since the emissivity of the tungsten filament is about 0.4, the radiance temperature of the lamp is typically $40\,°C$ to $300\,°C$ less than the true temperature of the filament.

The difference between the true temperature of the tungsten filament and the radiance temperature is approximately (see Equation (9.12))

$$T - T_\lambda = \frac{\lambda T^2}{c_2}[1 - \varepsilon(\lambda)]. \tag{9.36}$$

Hence the difference in radiance temperature for thermometers operating at different wavelengths is

$$T_{\lambda_2} - T_{\lambda_1} = \frac{T^2}{c_2}\{\lambda_1[1 - \varepsilon(\lambda_1)] - \lambda_2[1 - \varepsilon(\lambda_2)]\}. \tag{9.37}$$

This is the correction that must be applied when a tungsten lamp has been calibrated at one wavelength and is used at another wavelength. Figure 9.18 shows the variation of the emissivity of tungsten with temperature and wavelength.

Example 9.6   Radiance temperature correction for a tungsten strip lamp

A tungsten strip lamp calibrated at $655\,nm$ is used to calibrate a radiation thermometer operating at $900\,nm$. Calculate the radiance temperature correction for the lamp at $1200\,K$.

By applying Equation (9.37) directly, using the approximation for c_2, we obtain

$$\Delta T_\lambda = 100 \left(\frac{T}{1200} \right)^2 [0.655(1 - \varepsilon_{0.655}) - 0.9(1 - \varepsilon_{0.9})].$$

Now substituting values of 0.46 and 0.41 for the spectral emissivity of tungsten at 655 nm and 900 nm respectively, the correction is calculated as $\Delta T_\lambda = -17.7\,°C$.

The typical uncertainty in radiance temperature corrections is 2% to 3% owing to the uncertainty in the emissivity. The uncertainty in the correction is much larger at longer wavelengths and where the operating wavelength of the thermometer is not known to high accuracy.

The spectral radiance calibration for a lamp applies to a small area of the filament marked by a notch in one edge midway along its length. Since the radiance of the tungsten filament depends slightly on the angle of view (Figure 9.8), there is a second mark on the envelope behind the filament to aid the alignment of the thermometer. Current for the lamp should be provided by a high-stability current source capable of supplying several tens of amps (depending on the lamp design). Note that the lamps are sensitive to the polarity of the d.c. current, and the required polarity is usually marked on the base. Connecting the lamp with the wrong polarity will change the emissivity of the lamp and invalidate the calibration. Equilibrium is reached within 30 minutes of turning the lamp on, with shorter settling times of several minutes for small changes in filament current.

Good-quality lamps, properly annealed, are capable of reproducing spectral radiance to better than 0.1% for several hundred hours. This corresponds to reproducibility in radiance temperatures of better than $0.1\,°C$ around $1000\,°C$.

Exercise 9.8

(a) By following Example 9.6, calculate the radiance temperature correction for the lamp at 1600 K and 2000 K.

(b) Estimate the uncertainty in each of the corrections at 1200 K, 1600 K and 2000 K.

9.7.4 Calibrating a radiation thermometer

The calibration of radiation thermometers follows the basic guide in Chapter 5. Here we give a simple procedure that highlights the additional elements relevant to radiation thermometers.

Step 1: Start record keeping

As for Section 5.5.2.

Step 2: General visual inspection

As for Section 5.5.2.

Step 3: Conditioning and adjustment

Only if necessary and according to the manufacturer's manual.

Step 4: Generic checks

Before the comparison, there are a number of checks that should be carried out on the thermometer. The results of the checks can be expected to be similar for all thermometers of the same make and model number. Departure from the typical behaviour is a departure from the generic history and may be indicative of faults or damage.

Detailed visual inspection   Remember that a radiation thermometer is an instrument that should be treated like an expensive camera. Check the lens for dust, grease and scratches, and if necessary clean it. If the thermometer is battery powered, check that the battery is charged. Check that the thermometer radiance measurement and emissivity compensation both work. This can be done by viewing a desk lamp with a frosted bulb.

Stability and settling   Over the first hour of settling after exposure to a blackbody, monitor the reading of the thermometer to ensure that the thermometer is stable. If possible, also change the ambient temperature to determine the sensitivity to ambient temperature. These checks are particularly important for long-wavelength and very narrow-band thermometers.

If the thermometer's sensitivity to ambient temperature changes is large, then it may be necessary to assess the resulting uncertainty in use for inclusion in the total uncertainty of calibration. Extreme sensitivity may be indicative of faulty ambient temperature compensation.

Size-of-source effects   With the blackbody set to the highest temperature of the calibration range, adjust a variable aperture between the thermometer and the blackbody to a diameter a little greater than the specified field of view for the thermometer. Ensure that the thermometer is properly focused. Record the reading. Now open the aperture to at least two times the specified field of view and record this reading. The difference between the two readings is a measure of the uncertainty due to size-of-source effects.

This test is impossible to carry out effectively unless the environment around the blackbody is cool relative to the blackbody; hence the test is carried out at the highest calibration temperature. A laboratory (a closed cavity) behaves as a blackbody at room temperature so the variable aperture and surrounds will have a similar radiance to a room-temperature blackbody. To be sure that the size of the source is well defined, the reference blackbody should be about 200 °C hotter than ambient temperature. This test should be carried out before the comparison so that the comparison can be carried out with apertures large enough to avoid significant size-of-source effects.

With most radiation thermometers the field of view must be overfilled by two to three times before the reading is independent of the size of the blackbody aperture. This may be the most significant contributor to the total uncertainty for long-wavelength

thermometers. Large flare effects may be indicative of lens damage or misalignment. For example, damage to the protective film on the lens of a 10 μm thermometer has been observed to cause errors of more than 10 °C at 140 °C.

Emissivity calibration (if appropriate) Traditionally, radiation thermometers are calibrated only against blackbodies, yet in almost all applications they are used with emissivity compensation on surfaces that are not blackbodies. Clearly those measurements cannot be traceable unless the accuracy of the emissivity compensation is confirmed. The accuracy of the compensation mechanism can be checked by two methods, as follows.

Set the blackbody to the highest calibration temperature and record the reading of the thermometer with the emissivity compensation set to 1.0. Now place a calibrated neutral density filter between the thermometer and the blackbody so that the filter overfills the field of view by at least a factor of 2. Now adjust the emissivity compensation to obtain the same reading as without the filter. Record the emissivity setting. Ideally the emissivity setting is the same as the transmittance of the filter. Use a range of neutral density filters with transmittances in the range 0.2 to 1.0. Suitable filters include absorbing glass for short-wavelength thermometers and rotating sectored discs for longer-wavelength thermometers. Calibrated wire mesh may also be used. Care should be taken to ensure that the filters are cool relative to the blackbody and that there are no reflections (e.g. from room lighting) from the filter surface.

A second approach is to record the measured temperature versus emissivity setting with a blackbody at one temperature. The indicated temperature and the various measured temperatures should follow Equation (9.12). This test should be carried out at the middle of the temperature range to avoid reflections and allow for the increase in reading as the instrumental emissivity is reduced.

Step 5: Comparison

This portion of the calibration compares the temperatures measured by the thermometer with those measured by a calibrated radiance source. As discussed in Section 9.7.1, there are three basic ways to carry out the comparison: tungsten strip lamp (with or without transfer standard radiometer); blackbody plus transfer standard radiometer; or blackbody plus calibrated contact thermometer.

The radiation thermometer must be mounted to view the blackbody with the specified field of view overfilled by at least a factor of 2. This ensures that size-of-source effects have the least effect on the readings. Throughout the calibration, care should be taken to ensure that the front lens of the thermometer is not exposed to direct radiation from sources other than the blackbody. Radiation from other lamps or room lighting may cause additional error in thermometers that are prone to flare. As with all optical measurements, the calibration should be carried out in a darkened laboratory. With tungsten strip lamps a darkened laboratory is essential because of reflections from the lamp filament.

Two of the calibration equations for radiation thermometers (Equations (9.33) and (9.34)) require four constants to be fitted to calibration data. The calibration could be done with four fixed points for a transfer standard thermometer, or by least squares with a minimum of 12 comparison points for a general-purpose thermometer. Unlike other thermometers, radiation thermometers do not normally exhibit hysteresis

so it does not matter whether the temperature range is covered in an ascending or descending sequence. Blackbody furnaces often settle faster through an ascending sequence, making this the preferred option.

The achievable accuracy in the comparison depends strongly on the traceability chain chosen. When a blackbody and contact thermometer are used to provide the reference radiance, the uncertainties are quite large because of the temperature gradients in the blackbody cavity and radiation losses (see Section 9.6.3).

When a transfer standard radiometer or a tungsten strip lamp is used for the calibration the uncertainty can be either very small or large, depending on the operating wavelength of the thermometer under test. Transfer standard thermometers and strip lamps are calibrated in terms of radiance temperature, that is an emissivity of 1.0 is assumed. If the emissivity of the radiance source is not 1.0 then the radiance temperature is wavelength dependent. This is a particular problem with strip lamps, which have an emissivity of about 0.4. When strip lamps are used a correction must be applied to correct for the wavelength dependence (Section 9.7.3).

Step 6: Analysis

The first part of the analysis is the least-squares fit that provides the following information:

- By showing that a thermometer fits the calibration equation well, a successful least-squares fit confirms that the thermometer is well behaved and conforms to the generic history for that type of thermometer. There should not be unexplained jumps in the errors or large consistent patterns in the residual errors in the fit. There should also be sensible values for the calculated coefficients.
- The variance of the residual errors in the fit measures both the random error in the comparison and the unpredictable departures of the thermometer from the calibration equation. This effectively measures the repeatability of the thermometer.
- By using a relatively large number of calibration points compared with the number of parameters in the fit and demonstrating that all the points fit the calibration function, we show that the fitted function is suitable for interpolation between calibration points.

Step 7: Uncertainties

The contributing factors to the calibration uncertainty are as follows.

Uncertainty in the reference thermometer readings   This uncertainty is easily assessed since it is reported on the reference thermometer's or tungsten strip lamp's certificate. The value may need to be adjusted to the required confidence limits.

Variations in the stability and uniformity of the calibration medium   This depends on which of the three traceability chains is employed:

(1)   With a transfer standard radiometer and tungsten strip lamp the uncertainty depends on the radiance temperature correction as shown in Example 9.6.
(2)   With a transfer standard radiometer and blackbody, the transfer standard radiometer measures the radiance as seen by the thermometer under test, so there is

minimal error in the comparison. If the emissivity of the blackbody is uncertain then there will be an uncertainty in the radiance temperature of the cavity. This leads to an additional uncertainty in the calibration of

$$\sigma_{T_\lambda} = \frac{|\lambda_1 - \lambda_2|T^2}{c_2}\sigma_\varepsilon, \tag{9.38}$$

where λ_1 and λ_2 are the effective wavelengths of the transfer standard radiometer and the thermometer under test. This uncertainty is usually significant only for very long-wavelength thermometers and low-precision blackbodies.

(3)   With a contact thermometer and blackbody, the uncertainty in the radiance depends on two factors. Firstly, the degree of temperature uniformity within the cavity (Equation (9.28) and Example 9.4), and secondly, the combination of the proximity of the contact thermometer to the cavity and the energy radiated by the cavity (Equation (9.29) and Example 9.5). As a guide, it is usually difficult to reduce the uncertainty below 0.5% (e.g. $\pm 5\,°C$ at $1000\,°C$).

Departure from the determined ITS-90 relationship   This is the standard deviation of the residual errors from the calculation of the calibration equation.

Uncertainty due to drift   For thermometers employing interference filters the drift may be as large as 1% (in radiance) or more per year. Otherwise the drift is negligible for most broadband thermometers so long as the thermometer is well maintained. Therefore, assume that uncertainty due to drift is zero.

Uncertainty due to hysteresis   There should be no hysteresis effects in radiation thermometers other than those caused by the response time of the thermometer, which is usually less than a few seconds. Set this uncertainty to zero. If hysteresis is observed then the instrument is faulty.

Uncertainty due to flare   This is usually the largest source of calibration uncertainty in working thermometers. In use a thermometer will be used to measure the temperatures of a variety of objects of different sizes, and with surrounds both hotter and colder than the object of interest. The best approach is to calibrate the thermometer with the specified field of view overfilled by at least a factor of 2 (in diameter). Assess the uncertainty as the difference in reading between the situations when the field of view is filled exactly and when overfilled. Thus the fitted ITS-90 relationship corresponds to near-ideal use, and the uncertainty covers use in environments where the surrounds of the object are hotter or colder. For reference and transfer standard radiometers this uncertainty is set to zero since the thermometer is always used in ideal conditions to measure the temperature of a blackbody. There may be a small size-of-source effect so the blackbody aperture size should be reported on the certificate as a calibration condition. The user of the thermometer can then assess any uncertainty due to different usage.

Total uncertainty   The total uncertainty in the calibration is assessed as the quadrature sum of all the contributing uncertainties with confidence intervals of 95%. For all spectral band thermometers the uncertainty will have a predominantly T^2 dependence. For wide-range thermometers the uncertainty should be reported for one temperature within the calibration range with an indication of how to determine the uncertainty at other temperatures. For example, if all the uncertainties are evaluated at $200\,°C$ and the total uncertainty is $\pm 7\,°C$ (95% CL) then the uncertainty may be reported as

the uncertainty in the corrected readings of the thermometer at T kelvin is estimated as $\pm 7(T/473)^2$ K at a 95% confidence level.

Step 8: Complete records

As for Section 5.5.2.

9.8   Other Radiation Thermometers

9.8.1   The disappearing-filament thermometer

The disappearing-filament thermometer is one of the earliest examples of a spectral band radiation thermometer. It uses the observer's eye to compare the surface radiance against a known radiance — a hot tungsten filament. The temperature of the filament is adjusted until it has the same radiance as the surface in the background and disappears. The current through the filament is the indicator of the surface temperature.

The disappearing-filament thermometer uses very short wavelengths, about 650 nm, so that instrumental uncertainties, including the emissivity dependence, are minimised. The main difficulties lie with the observer. Firstly, it takes a good deal of practice before the measurements made by one observer are highly repeatable. Secondly, variations in the response of the eye from different observers and at different states of dark adaption also affect the accuracy. When used to view uniform objects, in a darkened room so that the eye is properly dark adapted, the thermometer is capable of accuracies of better than $\pm 5\,^{\circ}$C.

The third and most important factor affecting the accuracy is the uniformity of the field of view. Any non-uniformity in the surface radiance will betray the presence of the filament and give the eye sufficient information to reconstruct the filament outline so that it never quite disappears. This image processing done by the eye is unconscious and cannot be completely overcome by training. Errors of several hundred degrees can occur for small non-uniform objects.

The disappearing-filament thermometer is calibrated in terms of radiance temperature and has no emissivity adjustment. The error introduced when measuring the temperatures of non-blackbody surfaces is serious only when the emissivity is low. For example, for $\varepsilon = 0.6$ the error is about $-25\,^{\circ}$C at $900\,^{\circ}$C and $-100\,^{\circ}$C at $2000\,^{\circ}$C.

The temperature range of the disappearing-filament thermometer is determined by the sensitivity of the eye. The lowest operating temperature is about $600\,^{\circ}$C. The upper temperature range can be extended from $1400\,^{\circ}$C as far as $4000\,^{\circ}$C by using filters to reduce the radiance to a level where the eye is both comfortable and most sensitive.

9.8.2   The ratio thermometer

In some applications the uncertainty in the emissivity seriously limits the utility of spectral band thermometers. This is particularly true in some parts of the steel and aluminium industries where the emissivities are not only low but also extremely variable. One of the worst examples is in the manufacture of galvanised steel where the

emissivity varies from a little over 0.1 to 0.7 in a single process. Under these conditions ratio thermometers are a useful alternative to spectral band thermometers. They are also useful in some applications where smoke, dust or windows affect spectral band measurements.

Ratio thermometers, also known as dual-wavelength and two-colour thermometers, measure radiance at two wavelengths and determine the ratio

$$R = \frac{\alpha(\lambda_1)}{\alpha(\lambda_2)} \frac{\varepsilon(\lambda_1)}{\varepsilon(\lambda_2)} \frac{L_b(\lambda_1, T_s)}{L_b(\lambda_2, T_s)}. \tag{9.39}$$

If it is assumed that the absorption $\alpha(\lambda)$ and the emissivity $\varepsilon(\lambda)$ are constant over the wavelength range including λ_1 and λ_2, then the ratio R depends only on the temperature.

The independence from emissivity and absorption is obtained at the expense of sensitivity. This can be seen firstly from Wien's law approximation for R,

$$R = \left(\frac{\lambda_2}{\lambda_1}\right)^5 \exp\left[\frac{c_2}{T}\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)\right], \tag{9.40}$$

and secondly from the propagation-of-uncertainty formula which gives the uncertainty in temperature versus the uncertainty in R:

$$\sigma_{T_m} = \frac{\lambda_1\lambda_2}{\lambda_1 - \lambda_2} \frac{T^2}{c_2} \frac{\sigma_R}{R}. \tag{9.41}$$

The similarity of these equations to those for the single-wavelength spectral band thermometers suggests that the performance of the ratio thermometer would be similar to that of a spectral band thermometer with an operating wavelength of

$$\lambda_e = \frac{\lambda_1\lambda_2}{\lambda_1 - \lambda_2}. \tag{9.42}$$

However, this is misleading. While the sensitivity is 10 to 20 times worse than a good spectral band thermometer, some of the most significant errors are also much less. Firstly, the most significant error in spectral band thermometry, the uncertainty in the emissivity, has been eliminated. And secondly, many of the instrumental errors that affect the radiance measurement in spectral band thermometers are common to both channels of the ratio thermometer and so do not affect the ratio (see Exercise 9.9).

Overall the performance of ratio thermometers on surfaces that have a high emissivity and are grey (i.e. constant emissivity with wavelength) is perhaps two to three times worse than good spectral band measurements. On the other hand, if the surface is grey and has a low or highly variable emissivity (with time or temperature) then the ratio thermometer is clearly better. Ratio thermometers also find application where the object is too small to fill the field of view and a spectral band thermometer would be susceptible to size-of-source effects. Such objects include hot wires and molten-glass streams.

Example 9.7 Comparison of spectral band and ratio thermometers

A steel galvanising plant is monitoring temperatures near 450 °C. The emissivity of the freshly plated steel varies from about 0.15 to 0.7 as molten zinc forms the protective alloy surface. Compare the performance of a spectral band thermometer operating at 2.2 µm with a ratio thermometer operating at wavelengths of 2.2 µm and 2.4 µm.

Spectral band thermometer   Based on Equation (9.15) and a nominal value of emissivity of 0.4, the variation of the reading error is estimated to be

$$U_T = \pm 2.2 \times \frac{(273 + 450)^2}{1200^2} \times 100 \times \frac{0.3}{0.4} \,°\text{C} = \pm 60 \,°\text{C}.$$

Ratio thermometer   Based on Equation (9.41) and a variation of spectral emissivity of 1% between 2.2 µm and 2.4 µm, the variation in the temperature error is estimated to be

$$U_T = \pm \frac{2.2 \times 2.4}{2.4 - 2.2} \times \frac{(273 + 450)^2}{1200^2} \times 1 = \pm 9.5 \,°\text{C}.$$

Thus the ratio thermometer can accommodate quite large changes in emissivity so long as the spectral emissivities at the two wavelengths are the same. In practice the emissivity variations are often larger than 1%.

Exercise 9.9

Consider a temperature measured with a ratio thermometer. Estimate the uncertainty in temperature due to the uncertainty in the measured radiances $L_b(\lambda_1, T_s)$, $L_b(\lambda_2, T_s)$. Assume that the relative uncertainty σ_L/L is the same in both measurements and that the correlation coefficient of the errors in the measured radiances is r.

$$\text{Ans: } \sigma_{T_m} = \frac{\lambda_1 \lambda_2}{\lambda_1 - \lambda_2} \frac{T^2}{c_2} \left[2(1 - r)\frac{\sigma_L^2}{L^2} + \frac{\sigma_\varepsilon^2}{\varepsilon^2} \right]^{1/2}, \tag{9.43}$$

where σ_ε characterises the likely difference between the emissivities at the two wavelengths.

9.8.3 Multi-spectral radiation thermometers

One of the practical problems of radiation thermometry is that the emissivity of the surface is often difficult to determine with sufficient accuracy. Therefore the radiance temperature is sometimes measured at several wavelengths in order to assemble a model of the spectral emissivity and hence make a more accurate determination of

the true surface temperature. One of the simplest models employed approximates the logarithm of the emissivity by a series expansion in wavelength:

$$\ln[\varepsilon(\lambda)] = a + b\lambda + c\lambda^2 + \cdots . \tag{9.44}$$

This approximation is substituted into Equation (9.12) yielding a model for radiance temperature versus wavelength:

$$\frac{1}{T} = \frac{1}{T_\lambda} + \frac{\lambda}{c_2}(a + b\lambda + c\lambda^2 + \cdots), \tag{9.45}$$

where the parameters $a, b, c, \ldots$ are determined from measurements of radiance at several wavelengths. While the principle appears sound, the mathematics of the method effectively render it useless. Determining the temperature from Equation (9.45) is equivalent to a Lagrange interpolation (Section 2.11.1) with the value of interest, the radiance temperature at zero wavelength, determined by extrapolation. Consequently, the uncertainty increases exponentially as N, the number of parameters in the model:

$$\sigma_T \propto N\frac{\lambda T^2}{c_2}\left(\frac{\lambda}{\Delta\lambda}\right)^{N-1}\sigma_{T_\lambda}, \tag{9.46}$$

where $\Delta\lambda$ is the nominal spacing between the different wavelengths, and σ_{T_λ} is the uncertainty in each of the radiance temperature measurements. Note that spectral band and ratio thermometers conform to Equation (9.45) with $N = 1$ and $N = 2$ respectively.

We have here a paradoxical situation where the more measurements we make the greater the uncertainty. The problem is one of not using the information wisely. A great number of multi-wavelength thermometers have been built and some are sold commercially. Because most employ the mathematical equivalent of an extrapolation to zero wavelength, very few are successful. The only successful thermometers are those employing a priori constraints on the emissivity model, and fitting only one or two parameters from the measurements. As a rule the first choice should be a spectral band thermometer, and then, subject to necessity, a ratio thermometer.

9.8.4 Total radiation thermometers

Total radiation thermometers measure the total radiance of a surface. Because of the problems with atmospheric absorption they are capable of accurate operation only when used very close to the surface of interest. One of the best known examples is the *gold cup thermometer* shown schematically in Figure 9.19.

In use the gold-plated hemisphere is placed against the surface to form a blackbody cavity. This eliminates the need to know the surface emissivity. A small aperture in the hemisphere allows radiation to be exchanged between the cavity and the detector. The net response of the detector is

$$V(T) = g(T_s^4 - T_d^4), \tag{9.47}$$
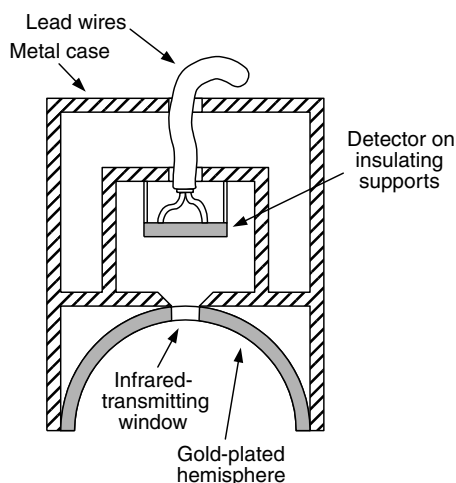
Figure 9.19   A simple schematic diagram of a gold cup thermometer

where T_s and T_d are the temperatures of the surface and detector respectively, and g is a constant. The dependence of the response on the detector temperature is common to all radiation thermometers (Equation (9.10)). In practice the thermometer is rarely used below 200 °C so that the uncertainty in the detector temperature is unimportant. When used below 200 °C considerable care is required to obtain accurate and repeatable results.

Errors may also arise because the detector responsivity (included in the constant g) is temperature dependent. This dependence is usually compensated by a simple thermistor circuit. However, the direct dependence on T_d cannot be compensated so easily.

In use the thermometer can suffer from large errors due to the surface heating. The surface of a hot object loses energy by radiation to cool surroundings. When the thermometer covers the surface, the heat loss is reduced almost to zero, so that the local temperature of the surface rises. The errors may be as large as 20 °C to 40 °C depending on the size of the thermometer and the properties of the surface.

There is a practical upper limit for the head temperature of the gold cup thermometer. Rubber and plastic components in the head and the temperature-compensation circuit limit the head temperature to the range −20 °C to 50 °C. Both of these factors, and the need to minimise the heating errors, limit the measurement period to 2 to 6 seconds. Thus, the thermometer is only for intermittent use, and is restricted to surfaces within arm's reach. Although strictly a contact thermometer it can be held a few millimetres off moving surfaces with minimal loss in accuracy.

One useful application of the gold cup pyrometer is the measurement of total emissivity. By replacing the gold hemisphere with a very black hemisphere the detector response becomes

$$V(T) = \varepsilon_s g(T_s^4 - T_d^4). \tag{9.48}$$

Thus the ratio of the two measurements gives the total emissivity of the surface. Knowledge of the total emissivity may be useful when estimating the spectral emissivity of surfaces.

Overall, the gold cup thermometer is capable of accuracies similar to those of a base-metal thermocouple, about 1%, and covers a range from 200 °C up to 1300 °C.

9.8.5 Special-purpose thermometers for plastic and glass

The plastics industry, and to a lesser extent the glass industry, present some interesting temperature measurement problems. How, for example, can we measure the temperature of a fast-moving plastic film less than 0.05 mm thick? Radiation thermometers would seem to be the obvious choice except that many plastics are transparent and most radiation thermometers would see straight through the film. Fortunately, organic materials such as plastics exhibit absorption lines in their spectra (see Figure 9.20). In these narrow regions of the spectra the plastics are opaque and have extremely high emissivities, typically 0.97. Therefore a spectral band thermometer with the pass-band centred on one of the absorption lines will make an accurate temperature measurement, indeed more accurate than most other radiation thermometry measurements because of the high emissivity of the plastic.

Table 9.3 shows the two most commonly used absorption lines and the plastics that absorb there. Thermometers that operate at the 3.43 µm band require filter bandwidths of 50 nm or less while those operating at the 7.95 µm band should have bandwidths of 100 nm or less. The narrow bandwidths are particularly important for very thin and visually transparent (non-pigmented) films. A simple check to make sure that the thermometer cannot see through the film is to move a highly polished metal sheet behind the film in the field of view of the thermometer. The metal mirror effectively doubles the thickness of the film seen by the thermometer. If the film is sufficiently thick the thermometer reading should not change.

Similar temperature measurement problems also occur in the glass industry except that the absorption bands in glass are very much broader. The most useful band for radiation thermometry is from about 5 µm to 8 µm. For relatively thick or pigmented
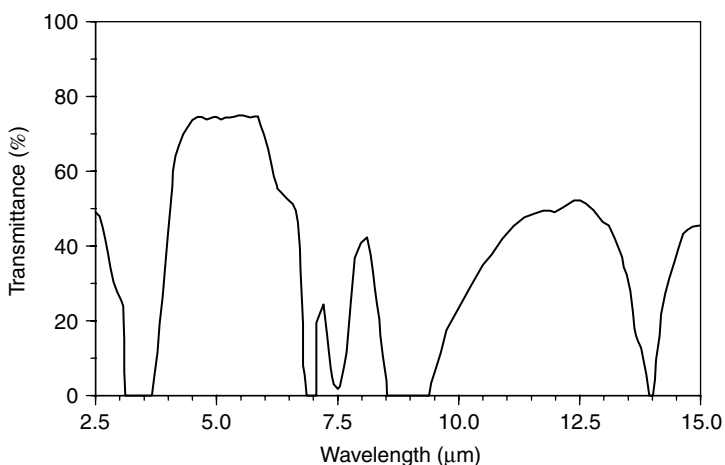
Figure 9.20 The spectral absorption of a sample of polyethylene film

Table 9.3   Infrared absorption for polymers

	C–H band 3.43 μm	Ester band 7.95 μm
Acrylic	X	X
Cellulose acetate	X*	X
Fluoroplastic (FEP)		X
Polyester (PET)	X*	X
Polyimide		X
Polyurethane	X	X
Polyvinyl chloride	X	X
Polycarbonate	X	X
Polyamide (nylon)	X	X
Polypropylene	X	
Polyethylene	X	
Polystyrene	X	
Ionomer	X	
Polybutylene	X	
Glassine	X	
Cellophane	X	
Paints	X	
Epoxy resins	X	

*For films ≥0.5 mm.

glasses, 5 μm thermometers are suitable; for thin transparent glasses the thermometer should operate nearer the 8 μm end of the band where the absorption is much stronger.

Radiation thermometers operating in narrow bandwidths must use interference filters to select the bandwidth. This makes them more susceptible than wider-band thermometers to drifts in calibration and changes in the ambient temperature. Drifts of 1% to 2% per year are not unusual. Narrow-band thermometers therefore have slightly higher maintenance and calibration demands.

9.8.6   Fibre-optic thermometers

In principle, radiation thermometers can exploit any temperature-dependent optical property, for example transmittance, reflectance, scattering and fluorescence, as well as radiance. The wide variety of fibre-optic thermometers is such that few of these techniques remain untried. However, the main attraction of fibre-optic thermometers lies not in the physical principles used, but in their ability to measure temperature in situations inaccessible to other thermometers. They are, for example, used increasingly in medical applications where the small sensor size and chemical immunity are important, and in the heavy electrical industries where their immunity to electromagnetic interference is important.

Other advantages over conventional radiation thermometers include confinement of the optical path, which eliminates scattering errors, and well-defined optical properties of the sensor. The main disadvantage of fibre-optic thermometers is the cost. Despite intensive efforts to reduce the cost of manufacture, the good performance of the thermometers invariably relies on a number of critical and often expensive components.

There are two types of fibre-optic thermometer that seem to be the most practical. The first uses fluorescence decay times to measure the temperature of a phosphor

located at the end of the fibre. It is extremely stable with time and immune to many environmental conditions, especially ambient radiation. The typical temperature range is from $-200\,°C$ to $250\,°C$ with accuracies of $\pm 1\,°C$.

The second type is essentially a radiance meter like conventional spectral band radiation thermometers except that the end of the fibre is covered to form a small blackbody cavity. With the use of sapphire fibres for the hot portion of the fibre these thermometers are useful from $250\,°C$ to $2000\,°C$. Typical accuracies are about 1% to 2%.

Further Reading

Radiation thermometry theory

D P DeWitt and G D Nutter (1988) *Theory and Practice of Radiation Thermometry*, Wiley Interscience, New York.

Radiation thermometry scales and calibration

Supplementary Information for the International Temperature Scale of 1990 (1990) BIPM.
Techniques for Approximating the International Temperature Scale of 1990 (1990) BIPM.

Fundamental measurements and blackbodies

T J Quinn (1990) *Temperature*, 2nd Edition, Academic Press, London.

Appendix A
Further Information for
Least-squares Fitting

A.1 Normal Equations for Calibration Equations

A.1.1 Deviation function for direct-reading thermometers

$$\Delta t = A + Bt + Ct^2 + Dt^3 \tag{5.2}$$

$$\begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = \begin{pmatrix} N & \Sigma t_i & \Sigma t_i^2 & \Sigma t_i^3 \\ \Sigma t_i & \Sigma t_i^2 & \Sigma t_i^3 & \Sigma t_i^4 \\ \Sigma t_i^2 & \Sigma t_i^3 & \Sigma t_i^4 & \Sigma t_i^5 \\ \Sigma t_i^3 & \Sigma t_i^4 & \Sigma t_i^5 & \Sigma t_i^6 \end{pmatrix}^{-1} \begin{pmatrix} \Sigma \Delta t_i \\ \Sigma t_i \Delta t_i \\ \Sigma t_i^2 \Delta t_i \\ \Sigma t_i^3 \Delta t_i \end{pmatrix}.$$

A.1.2 Extended Callendar equation for platinum resistance thermometers

$$W(t) = \frac{R(t)}{R(0\,°C)} = 1 + At + Bt^2 + Dt^3 \tag{6.47}$$

$$\begin{pmatrix} A \\ B \\ D \end{pmatrix} = \begin{pmatrix} \Sigma t_i^2 \Sigma t_i^3 \Sigma t_i^4 \\ \Sigma t_i^3 \Sigma t_i^4 \Sigma t_i^5 \\ \Sigma t_i^4 \Sigma t_i^5 \Sigma t_i^6 \end{pmatrix}^{-1} \begin{pmatrix} \Sigma t_i[W(t_i) - 1] \\ \Sigma t_i^2[W(t_i) - 1] \\ \Sigma t_i^3[W(t_i) - 1] \end{pmatrix}.$$

A.1.3 Callendar–van Dusen equation for platinum resistance thermometers

$$W(t) = 1 + At + Bt^2 + Ct^3(t - 100) \tag{6.46}$$

$C = 0$ above $0\,^\circ\text{C}$.

$$
\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} \Sigma t_i^2 & \Sigma t_i^3 & \sum_{t_i<0} t_i^4(t_i - 100) \\ \Sigma t_i^3 & \Sigma t_i^4 & \sum_{t_i<0} t_i^5(t_i - 100) \\ \sum_{t_i<0} t_i^4(t_i - 100) & \sum_{t_i<0} t_i^5(t_i - 100) & \sum_{t_i<0} t_i^6(t_i - 100)^2 \end{pmatrix}^{-1}
$$

$$
\times \begin{pmatrix} \Sigma t_i[W(t_i) - 1] \\ \Sigma t_i^2[W(t_i) - 1] \\ \sum_{t_i<0} t_i^3(t_i - 100)[W(t_i) - 1] \end{pmatrix}.
$$

A.1.4   The thermistor equation

$$\frac{1}{T} = a_0 + a_1 \log(R) + a_2 \log^2(R) + a_3 \log^3(R) \qquad\qquad (6.54),\ (9.34)$$

$$
\begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} N & \Sigma \log R_i & \Sigma \log^2 R_i & \Sigma \log^3 R_i \\ \Sigma \log R_i & \Sigma \log^2 R_i & \Sigma \log^3 R_i & \Sigma \log^4 R_i \\ \Sigma \log^2 R_i & \Sigma \log^3 R_i & \Sigma \log^4 R_i & \Sigma \log^5 R_i \\ \Sigma \log^3 R_i & \Sigma \log^4 R_i & \Sigma \log^5 R_i & \Sigma \log^6 R_i \end{pmatrix}^{-1} \begin{pmatrix} \Sigma \dfrac{1}{T_i} \\ \Sigma \dfrac{1}{T_i} \log R_i \\ \Sigma \dfrac{1}{T_i} \log^2 R_i \\ \Sigma \dfrac{1}{T_i} \log^3 R_i \end{pmatrix}.
$$

Appendix B
The Differences Between ITS-90 and IPTS-68

The numerical differences between the ITS-90 and the IPTS-68 scales up to 1064.18 °C have been fitted in three ranges by the following power-series polynomials. These polynomials, recommended by the CCT (1993), replace those recommended by BIPM (1990).

(1) From 13.8033 K to 83.8058 K
     (accuracy approximately ±0.001K)

$$(T_{90} - T_{68})\text{K} = \sum_{i=0}^{12} a_i [(T - 40)/40]^i.$$

(2) From −200 °C to 630.6 °C
     (accuracy approximately ±0.0015 °C up to 0 °C and ±0.001 °C above 0 °C)

$$(t_{90} - t_{68})\,°\text{C} = \sum_{i=1}^{8} b_i [t/630]^i.$$

(3) From 630.6 °C to 1064.18 °C
     (accuracy approximately ±0.01 °C)

$$(t_{90} - t_{68})\,°\text{C} = \sum_{i=0}^{5} c_i t^i.$$

The coefficients a_i, b_i and c_i, are as follows:

i	a_i	b_i	c_i
0	−0.005 903	—	$7.868\,720\,9 \times 10^1$
1	0.008 174	−0.148 759	$-4.713\,599\,1 \times 10^{-1}$
2	−0.061 924	−0.267 408	$1.095\,471\,5 \times 10^{-3}$
3	−0.193 388	1.080 760	$-1.235\,788\,4 \times 10^{-6}$
4	1.490 793	1.269 056	$6.773\,658\,3 \times 10^{-10}$
5	1.252 347	−4.089 591	$-1.445\,808\,1 \times 10^{-13}$
6	−9.835 868	−1.871 251	—
7	1.411 912	7.438 081	—
8	25.277 595	−3.536 296	—
9	−19.183 815	—	—
10	−18.437 089	—	—
11	27.000 895	—	—
12	−8.716 324	—	—

At temperatures above 1064.18 °C the differences are represented by

$$(t_{90} - t_{68})\,°C = -0.25[(t + 273.15)/1337.33]^2.$$

Wherever possible it is recommended that IPTS-68 calibrations should be converted to the ITS-90 scale directly, using the resistance ratios at the fixed points and the equations in the text of the scale.

Table of numerical differences, $T_{90} - T_{68}$, as recommended by the CCT (1993)

$(T_{90} - T_{68})\mathrm{K}$

$T_{90}\mathrm{K}$	0	1	2	3	4	5	6	7	8	9
10					−0.006	−0.003	−0.004	−0.006	−0.008	−0.009
20	−0.009	−0.008	−0.007	−0.007	−0.006	−0.005	−0.004	−0.004	−0.005	−0.006
30	−0.006	−0.007	−0.008	−0.008	−0.008	−0.007	−0.007	−0.007	−0.006	−0.006
40	−0.006	−0.006	−0.006	−0.006	−0.006	−0.007	−0.007	−0.007	−0.006	−0.006
50	−0.006	−0.005	−0.005	−0.004	−0.003	−0.002	−0.001	0.000	0.001	0.002
60	0.003	0.003	0.004	0.004	0.005	0.005	0.006	0.006	0.007	0.007
70	0.007	0.007	0.007	0.007	0.007	0.008	0.008	0.008	0.008	0.008
80	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008
90	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.009	0.009	0.009

$T_{90}\mathrm{K}$	0	10	20	30	40	50	60	70	80	90
100	0.009	0.011	0.013	0.014	0.014	0.014	0.014	0.013	0.012	0.012
200	0.011	0.010	0.009	0.008	0.007	0.005	0.003	0.001		

$(t_{90} - t_{68})\,°C$

$t_{90}\,°C$	0	−10	−20	−30	−40	−50	−60	−70	−80	−90
−100	0.013	0.013	0.014	0.014	0.014	0.013	0.012	0.010	0.008	0.008
0	0.000	0.002	0.004	0.006	0.008	0.009	0.010	0.011	0.012	0.012

$t_{90}\,°C$	0	10	20	30	40	50	60	70	80	90
0	0.000	−0.002	−0.005	−0.007	−0.010	−0.013	−0.016	−0.018	−0.021	−0.024
100	−0.026	−0.028	−0.030	−0.032	−0.034	−0.036	−0.037	−0.038	−0.039	−0.039
200	−0.040	−0.040	−0.040	−0.040	−0.040	−0.040	−0.040	−0.039	−0.039	−0.039
300	−0.039	−0.039	−0.039	−0.040	−0.040	−0.041	−0.042	−0.043	−0.045	−0.046
400	−0.048	−0.051	−0.053	−0.056	−0.059	−0.062	−0.065	−0.068	−0.072	−0.075
500	−0.079	−0.083	−0.087	−0.090	−0.094	−0.098	−0.101	−0.105	−0.108	−0.112
600	−0.115	−0.118	−0.122	−0.125	−0.11	−0.10	−0.09	−0.07	−0.05	−0.04
700	−0.02	−0.01	0.00	0.02	0.03	0.03	0.04	0.05	0.05	0.05
800	0.05	0.05	0.04	0.04	0.03	0.02	0.01	0.00	−0.02	−0.03
900	−0.05	−0.06	−0.08	−0.10	−0.11	−0.13	−0.15	−0.16	−0.18	−0.19
1000	−0.20	−0.22	−0.23	−0.23	−0.24	−0.25	−0.25	−0.25	−0.26	−0.26

$t_{90}\,°C$	0	100	200	300	400	500	600	700	800	900
1000		−0.26	−0.30	−0.35	−0.39	−0.44	−0.49	−0.54	−0.60	−0.66
2000	−0.72	−0.79	−0.85	−0.93	−1.00	−1.07	−1.15	−1.24	−1.32	−1.41
3000	−1.50	−1.59	−1.69	−1.78	−1.89	−1.99	−2.10	−2.21	−2.32	−2.43

Appendix C
Resistance Thermometer
Reference Tables

This reference function is that given by the following documentary standards: IEC-751-83 plus amendments A1:1986 and A2:1995, BS60751:1996, and EN 60751:1996. The values of temperature are on the International Temperature Scale of 1990 (ITS-90).

C.1 Reference Function

The reference function has the form

$$R(t) = R(0\,^\circ\text{C})[1 + At + Bt^2 + Ct^3(t - 100)]$$

where $R(t)$ is in ohms and t is in degrees Celsius,

$$R(0\,^\circ\text{C}) = 100\,\Omega$$
$$A = 3.9083 \times 10^{-3}\,^\circ\text{C}^{-1}$$
$$B = -5.775 \times 10^{-7}\,^\circ\text{C}^{-2}$$

where for $t \geq 0\,^\circ\text{C}$

$$C = 0.0$$

and for $t < 0\,^\circ\text{C}$

$$C = -4.183 \times 10^{-12}\,^\circ\text{C}^{-4}$$

Tolerances (in °C)

Class A: $0.15 + 0.2\%$
Class B: $0.3 + 0.5\%$

C.2 Reference Tables

T_{90} (°C)	−0.0	−5.0	−10.0	−15.0	−20.0
−200.0	18.52				
−175.0	29.22	27.10	24.97	22.83	20.68
−150.0	39.72	37.64	35.54	33.44	31.34
−125.0	50.06	48.00	45.94	43.88	41.80
−100.0	60.26	58.23	56.19	54.15	52.11
−75.0	70.33	68.33	66.31	64.30	62.28
−50.0	80.31	78.32	76.33	74.33	72.33
−25.0	90.19	88.22	86.25	84.27	82.29
0.0	100.00	98.04	96.09	94.12	92.16

T_{90} (°C)	0.0	5.0	10.0	15.0	20.0
0.0	100.00	101.95	103.90	105.85	107.79
25.0	109.73	111.67	113.61	115.54	117.47
50.0	119.40	121.32	123.24	125.16	127.08
75.0	128.99	130.90	132.80	134.71	136.61
100.0	138.51	140.40	142.29	144.18	146.07
125.0	147.95	149.83	151.71	153.58	155.46
150.0	157.33	159.19	161.05	162.91	164.77
175.0	166.63	168.48	170.33	172.17	174.02
200.0	175.86	177.69	179.53	181.36	183.19
225.0	185.01	186.84	188.66	190.47	192.29
250.0	194.10	195.91	197.71	199.51	201.31
275.0	203.11	204.90	206.70	208.48	210.27

T_{90} (°C)	0.0	5.0	10.0	15.0	20.0
300.0	212.05	213.83	215.61	217.38	219.15
325.0	220.92	222.68	224.45	226.21	227.96
350.0	229.72	231.47	233.21	234.96	236.70
375.0	238.44	240.18	241.91	243.64	245.37
400.0	247.09	248.81	250.53	252.25	253.96
425.0	255.67	257.38	259.08	260.78	262.48
450.0	264.18	265.87	267.56	269.25	270.93
475.0	272.61	274.29	275.97	277.64	279.31
500.0	280.98	282.64	284.30	285.96	287.62
525.0	289.27	290.92	292.56	294.21	295.85
550.0	297.49	299.12	300.75	302.38	304.01
575.0	305.63	307.25	308.87	310.49	312.10
600.0	313.71				

Appendix D
Thermocouple Reference Tables

D.1 Reference Functions

The coefficients for the reference functions for each of the IEC letter-designated thermocouple types is given on the following pages. The tables given have been formulated using these equations.

Except for the Type K thermocouple in the range $0\,°C$ to $1372\,°C$, the reference functions are of the form

$$E = \sum_{i=0}^{n} a_i t_{90}^i,$$

where t_{90} is in degrees Celsius and E is in the thermocouple output in microvolts. For Type K in the above range the reference function is of the form

$$E = \sum_{i=0}^{n} b_i t_{90}^i + c_1 \exp\left[-0.5\left(\frac{t_{90} - 126.9686}{65}\right)^2\right],$$

where t_{90} is in degrees Celsius and E is in microvolts.

D.2 Inverse Functions

The coefficients of inverse functions for each of the thermocouple types is also given. The inverse functions are of the form

$$t_{90} = \sum_{i=0}^{n} d_i E^i.$$

These inverse functions are approximate. The errors in temperatures calculated with these functions, relative to the reference functions, are less than $0.06\,°C$. The functions should not be extrapolated beyond the specified ranges.

D.3 Type B

Output in μV

$T_{90}(^\circ C)$	0	10	20	30	40
0	0	−2	−3	−2	−0
50	2	6	11	17	25
100	33	43	53	65	78
150	92	107	123	141	159
200	178	199	220	243	267
250	291	317	344	372	401
300	431	462	494	527	561
350	596	632	669	707	746
400	787	828	870	913	957
450	1002	1048	1095	1143	1192
500	1242	1293	1344	1397	1451
550	1505	1561	1617	1675	1733
600	1792	1852	1913	1975	2037
650	2101	2165	2230	2296	2363
700	2431	2499	2569	2639	2710
750	2782	2854	2928	3002	3078
800	3154	3230	3308	3386	3466
850	3546	3626	3708	3790	3873
900	3957	4041	4127	4213	4299
950	4387	4475	4564	4653	4743
1000	4834	4926	5018	5111	5205
1050	5299	5394	5489	5585	5682
1100	5780	5878	5976	6075	6175
1150	6276	6377	6478	6580	6683
1200	6786	6890	6995	7100	7205
1250	7311	7417	7524	7632	7740
1300	7848	7957	8066	8176	8286
1350	8397	8508	8620	8731	8844
1400	8956	9069	9182	9296	9410
1450	9524	9639	9753	9868	9984
1500	10 099	10 215	10 331	10 447	10 563
1550	10 679	10 796	10 913	11 029	11 146
1600	11 263	11 380	11 497	11 614	11 731
1650	11 848	11 965	12 082	12 199	12 316
1700	12 433	12 549	12 666	12 782	12 898
1750	13 014	13 130	13 246	13 361	13 476
1800	13 591	13 706	13 820		

Type B reference function coefficients

	0 °C to 630.615 °C		630.615 °C to 1820 °C
a_0	0	a_0	$-3.893\,816\,862\,1 \times 10^3$
a_1	$-2.465\,081\,834\,6 \times 10^{-1}$	a_1	$2.857\,174\,747\,0 \times 10^1$
a_2	$5.904\,042\,117\,1 \times 10^{-3}$	a_2	$-8.488\,510\,478\,5 \times 10^{-2}$
a_3	$-1.325\,793\,163\,6 \times 10^{-6}$	a_3	$1.578\,528\,016\,4 \times 10^{-4}$
a_4	$1.566\,829\,190\,1 \times 10^{-9}$	a_4	$-1.683\,534\,486\,4 \times 10^{-7}$
a_5	$-1.694\,452\,924\,0 \times 10^{-12}$	a_5	$1.110\,979\,401\,3 \times 10^{-10}$
a_6	$6.299\,034\,709\,4 \times 10^{-16}$	a_6	$-4.451\,543\,103\,3 \times 10^{-14}$
		a_7	$9.897\,564\,082\,1 \times 10^{-18}$
		a_8	$-9.379\,133\,028\,9 \times 10^{-22}$

Type B inverse function coefficients

	250 °C to 700 °C 291 µV to 2431 µV		700 °C to 1820 °C 2431 µV to 13 820 µV
d_0	$9.842\,332\,1 \times 10^1$	d_0	$2.131\,507\,1 \times 10^2$
d_1	$6.997\,150\,0 \times 10^{-1}$	d_1	$2.851\,050\,4 \times 10^{-1}$
d_2	$-8.476\,530\,4 \times 10^{-4}$	d_2	$-5.274\,288\,7 \times 10^{-5}$
d_3	$1.005\,264\,4 \times 10^{-6}$	d_3	$9.916\,080\,4 \times 10^{-9}$
d_4	$-8.334\,595\,2 \times 10^{-10}$	d_4	$-1.296\,530\,3 \times 10^{-12}$
d_5	$4.550\,854\,2 \times 10^{-13}$	d_5	$1.119\,587\,0 \times 10^{-16}$
d_6	$-1.552\,303\,7 \times 10^{-16}$	d_6	$-6.062\,519\,9 \times 10^{-21}$
d_7	$2.988\,675\,0 \times 10^{-20}$	d_7	$1.866\,169\,6 \times 10^{-25}$
d_8	$-2.474\,286\,0 \times 10^{-24}$	d_8	$-2.487\,858\,5 \times 10^{-30}$

Tolerances (whichever is greater)

Class 2:   1.5 °C or 0.25%   for 600 °C to 1700 °C
Class 3:   4 °C or 0.5%   for 600 °C to 1700 °C

Properties

Nominal composition: Platinum−30% rhodium versus platinum−6% rhodium

Type B is well suited for use in oxidising or inert atmospheres at high temperatures. It suffers less grain growth than either of Types R or S. Although it is slightly more immune to contamination than Types R or S it is still susceptible to contamination. In particular, Type B should not be exposed to metallic vapours or reducing environments.

Type B has very low output at low temperatures (< 200 °C). For low-accuracy applications no cold-junction compensation is necessary if the cold junction can be kept between 0 °C and 50 °C.

D.4 Type E

Output in μV

$T_{90}(°C)$	−0	−10	−20	−30	−40
−250	−9 718	−9 797	−9 835		
−200	−8 825	−9 063	−9 274	−9 455	−9 604
−150	−7 279	−7 632	−7 963	−8 273	−8 561
−100	−5 237	−5 681	−6 107	−6 516	−6 907
−50	−2 787	−3 306	−3 811	−4 302	−4 777
0	0	−582	−1 152	−1 709	−2 255

$T_{90}(°C)$	0	10	20	30	40
0	0	591	1192	1801	2420
50	3048	3685	4330	4985	5648
100	6319	6998	7685	8379	9081
150	9789	10 503	11 224	11 951	12 684
200	13 421	14 164	14 912	15 664	16 420
250	17 181	17 945	18 713	19 484	20 259
300	21 036	21 817	22 600	23 386	24 174
350	24 964	25 757	26 552	27 348	28 146
400	28 946	29 747	30 550	31 354	32 159
450	32 965	33 772	34 579	35 387	36 196
500	37 005	37 815	38 624	39 434	40 243
550	41 053	41 862	42 671	43 479	44 286
600	45 093	45 900	46 705	47 509	48 313
650	49 116	49 917	50 718	51 517	52 315
700	53 112	53 908	54 703	55 497	56 289
750	57 080	57 870	58 659	59 446	60 232
800	61 017	61 801	62 583	63 364	64 144
850	64 922	65 698	66 473	67 246	68 017
900	68 787	69 554	70 319	71 082	71 844
950	72 603	73 360	74 115	74 869	75 621
1000	76 373				

Tolerances (whichever is greater)

Class 1:	1.5 °C or 0.4%	for −40 °C to 800 °C
Class 2:	2.5 °C or 0.75%	for −40 °C to 900 °C
Class 3:	2.5 °C or 1.5%	for −200 °C to 40 °C

Type E reference function coefficients

	−270 °C to 0 °C		0 °C to 1000 °C
a_0	0	a_0	0
a_1	$5.866\,550\,870\,8 \times 10^{1}$	a_1	$5.866\,550\,871\,0 \times 10^{1}$
a_2	$4.541\,097\,712\,4 \times 10^{-2}$	a_2	$4.503\,227\,558\,2 \times 10^{-2}$
a_3	$-7.799\,804\,868\,6 \times 10^{-4}$	a_3	$2.890\,840\,721\,2 \times 10^{-5}$
a_4	$-2.580\,016\,084\,3 \times 10^{-5}$	a_4	$-3.305\,689\,665\,2 \times 10^{-7}$
a_5	$-5.945\,258\,305\,7 \times 10^{-7}$	a_5	$6.502\,440\,327\,0 \times 10^{-10}$
a_6	$-9.321\,405\,866\,7 \times 10^{-9}$	a_6	$-1.919\,749\,550\,4 \times 10^{-13}$
a_7	$-1.028\,760\,553\,4 \times 10^{-10}$	a_7	$-1.253\,660\,049\,7 \times 10^{-15}$
a_8	$-8.037\,012\,362\,1 \times 10^{-13}$	a_8	$2.148\,921\,756\,9 \times 10^{-18}$
a_9	$-4.397\,949\,739\,1 \times 10^{-15}$	a_9	$-1.438\,804\,178\,2 \times 10^{-21}$
a_{10}	$-1.641\,477\,635\,5 \times 10^{-17}$	a_{10}	$3.596\,089\,948\,1 \times 10^{-25}$
a_{11}	$-3.967\,361\,951\,6 \times 10^{-20}$		
a_{12}	$-5.582\,732\,872\,1 \times 10^{-23}$		
a_{13}	$-3.465\,784\,201\,3 \times 10^{-26}$		

Type E inverse function coefficients

	−200 °C to 0 °C −8825 μV to 0 μV		0 °C to 1000 °C 0 μV to 76 373 μV
d_0	0	d_0	0
d_1	$1.697\,728\,8 \times 10^{-2}$	d_1	$1.705\,703\,5 \times 10^{-2}$
d_2	$-4.351\,497\,0 \times 10^{-7}$	d_2	$-2.330\,175\,9 \times 10^{-7}$
d_3	$-1.585\,969\,7 \times 10^{-10}$	d_3	$6.543\,558\,5 \times 10^{-12}$
d_4	$-9.250\,287\,1 \times 10^{-14}$	d_4	$-7.356\,274\,9 \times 10^{-17}$
d_5	$-2.608\,431\,4 \times 10^{-17}$	d_5	$-1.789\,600\,1 \times 10^{-21}$
d_6	$-4.136\,019\,9 \times 10^{-21}$	d_6	$8.403\,616\,5 \times 10^{-26}$
d_7	$-3.403\,403\,0 \times 10^{-25}$	d_7	$-1.373\,587\,9 \times 10^{-30}$
d_8	$-1.156\,489\,0 \times 10^{-29}$	d_8	$1.062\,982\,3 \times 10^{-35}$
		d_9	$-3.244\,708\,7 \times 10^{-41}$

Properties

Nominal composition: Chromel-constantan, 90% nickel−10% chromium versus
55% copper−45% nickel

Type E has the highest output of all common thermocouples and is suited for use at low temperatures ($<0\,$°C). It is best used in strongly oxidising or inert atmospheres and will stand limited use in vacuum and reducing environments. It will not withstand prolonged use in marginally oxidising environments. In the medium temperature range ($<500\,$°C) it has a higher reproducibility than Type K.

D.5 Type J

	Output in μ V				
$T_{90}(^\circ C)$	−0	−10	−20	−30	−40
−200	−7890	−8095			
−150	−6500	−6821	−7123	−7403	−7659
−100	−4633	−5037	−5426	−5801	−6159
−50	−2431	−2893	−3344	−3786	−4215
0	0	−501	−995	−1482	−1961
$T_{90}(^\circ C)$	0	10	20	30	40
0	0	507	1019	1537	2059
50	2585	3116	3650	4187	4726
100	5269	5814	6360	6909	7459
150	8010	8562	9115	9669	10 224
200	10 779	11 334	11 889	12 445	13 000
250	13 555	14 110	14 665	15 219	15 773
300	16 327	16 881	17 434	17 986	18 538
350	19 090	19 642	20 194	20 745	21 297
400	21 848	22 400	22 952	23 504	24 057
450	24 610	25 164	25 720	26 276	26 834
500	27 393	27 953	28 516	29 080	29 647
550	30 216	30 788	31 362	31 939	32 519
600	33 102	33 689	34 279	34 873	35 470
650	36 071	36 675	37 284	37 896	38 512
700	39 132	39 755	40 382	41 012	41 645
750	42 281	42 919	43 559	44 203	44 848
800	45 494	46 141	46 786	47 431	48 074
850	48 715	49 353	49 989	50 622	51 251
900	51 877	52 500	53 119	53 735	54 347
950	54 956	55 561	56 164	56 763	57 360
1000	57 953	58 545	59 134	59 721	60 307
1050	60 890	61 473	62 054	62 634	63 214
1100	63 792	64 370	64 948	65 525	66 102
1150	66 679	67 255	67 831	68 406	68 980
1200	69 553				

Type J reference function coefficients

	−210 °C to 760 °C		760 °C to 1200 °C
a_0	0	a_0	$2.964\,562\,568\,1 \times 10^5$
a_1	$5.038\,118\,781\,5 \times 10^1$	a_1	$-1.497\,612\,778\,6 \times 10^3$
a_2	$3.047\,583\,693\,0 \times 10^{-2}$	a_2	$3.178\,710\,392\,4 \times 10^0$
a_3	$-8.568\,106\,572\,0 \times 10^{-5}$	a_3	$-3.184\,768\,670\,1 \times 10^{-3}$
a_4	$1.322\,819\,529\,5 \times 10^{-7}$	a_4	$1.572\,081\,900\,4 \times 10^{-6}$
a_5	$-1.705\,295\,833\,7 \times 10^{-10}$	a_5	$-3.069\,136\,905\,6 \times 10^{-10}$
a_6	$2.094\,809\,069\,7 \times 10^{-13}$		
a_7	$-1.253\,839\,533\,6 \times 10^{-16}$		
a_8	$1.563\,172\,569\,7 \times 10^{-20}$		

Type J inverse function coefficients

	−210 °C to 0 °C −8095 µV to 0 µV		0 °C to 760 ° 0 µV to 42 919 µV		760 °C to 1200 °C 42 919 µV to 69 553 µV
d_0	0	d_0	0	d_0	$-3.113\,581\,87 \times 10^3$
d_1	$1.952\,826\,8 \times 10^{-2}$	d_1	$1.978\,425 \times 10^{-2}$	d_1	$3.005\,436\,84 \times 10^{-1}$
d_2	$-1.228\,618\,5 \times 10^{-6}$	d_2	$-2.001\,204 \times 10^{-7}$	d_2	$-9.947\,732\,30 \times 10^{-6}$
d_3	$-1.075\,217\,8 \times 10^{-9}$	d_3	$1.036\,969 \times 10^{-11}$	d_3	$1.702\,766\,30 \times 10^{-10}$
d_4	$-5.908\,693\,3 \times 10^{-13}$	d_4	$-2.549\,687 \times 10^{-16}$	d_4	$-1.430\,334\,68 \times 10^{-15}$
d_5	$-1.725\,671\,3 \times 10^{-16}$	d_5	$3.585\,153 \times 10^{-21}$	d_5	$4.738\,860\,84 \times 10^{-21}$
d_6	$-2.813\,151\,3 \times 10^{-20}$	d_6	$-5.344\,285 \times 10^{-26}$		
d_7	$-2.396\,337\,0 \times 10^{-24}$	d_7	$5.099\,890 \times 10^{-31}$		
d_8	$-8.382\,332\,1 \times 10^{-29}$				

Tolerances (whichever is greater)

Class 1:	1.5 °C or 0.4%	for −40 °C to 750 °C
Class 2:	2.5 °C or 0.75%	for −40 °C to 750 °C

Properties

Nominal composition: Iron-constantan, iron versus 55% copper−45% nickel

Type J is one of the few common thermocouples that is suited for use in reducing environments. It is also suited for use in oxidising and inert atmospheres. In oxidising and sulphurous atmospheres above 500 °C the iron leg is prone to rapid corrosion. Type J is not recommended for use at low temperatures.

D.6 Type K

Output in μV

$T_{90}(^\circ C)$	-0	-10	-20	-30	-40
-250	-6404	-6441	-6458		
-200	-5891	-6035	-6158	-6262	-6344
-150	-4913	-5141	-5354	-5550	-5730
-100	-3554	-3852	-4138	-4411	-4669
-50	-1889	-2243	-2587	-2920	-3243
0	0	-392	-778	-1156	-1527

$T_{90}(^\circ C)$	0	10	20	30	40
0	0	397	798	1203	1612
50	2023	2436	2851	3267	3682
100	4096	4509	4920	5328	5735
150	6138	6540	6941	7340	7739
200	8138	8539	8940	9343	9747
250	10 153	10 561	10 971	11 382	11 795
300	12 209	12 624	13 040	13 457	13 874
350	14 293	14 713	15 133	15 554	15 975
400	16 397	16 820	17 243	17 667	18 091
450	18 516	18 941	19 366	19 792	20 218
500	20 644	21 071	21 497	21 924	22 350
550	22 776	23 203	23 629	24 055	24 480
600	24 905	25 330	25 755	26 179	26 602
650	27 025	27 447	27 869	28 289	28 710
700	29 129	29 548	29 965	30 382	30 798
750	31 213	31 628	32 041	32 453	32 865
800	33 275	33 685	34 093	34 501	34 908
850	35 313	35 718	36 121	36 524	36 925
900	37 326	37 725	38 124	38 522	38 918
950	39 314	39 708	40 101	40 494	40 885
1000	41 276	41 665	42 053	42 440	42 826
1050	43 211	43 595	43 978	44 359	44 740
1100	45 119	45 497	45 873	46 249	46 623
1150	46 995	47 367	47 737	48 105	48 473
1200	48 838	49 202	49 565	49 926	50 286
1250	50 644	51 000	51 355	51 708	52 060
1300	52 410	52 759	53 106	53 451	53 795
1350	54 138	54 479	54 819		

Tolerances (whichever is greater)

Class 1:	$1.5\,°C$ or 0.4%	for $-40\,°C$ to $1000\,°C$
Class 2:	$2.5\,°C$ or 0.75%	for $-40\,°C$ to $1200\,°C$
Class 3:	$2.5\,°C$ or 1.5%	for $-200\,°C$ to $40\,°C$

Type K reference function coefficients

	$-270\,°C$ to $0\,°C$		$0\,°C$ to $1372\,°C$
a_0	0	b_0	$-1.760\,041\,368\,6 \times 10^1$
a_1	$3.945\,012\,802\,5 \times 10^1$	b_1	$3.892\,120\,497\,5 \times 10^1$
a_2	$2.362\,237\,359\,8 \times 10^{-2}$	b_2	$1.855\,877\,003\,2 \times 10^{-2}$
a_3	$-3.285\,890\,678\,4 \times 10^{-4}$	b_3	$-9.945\,759\,287\,4 \times 10^{-5}$
a_4	$-4.990\,482\,877\,7 \times 10^{-6}$	b_4	$3.184\,094\,571\,9 \times 10^{-7}$
a_5	$-6.750\,905\,917\,3 \times 10^{-8}$	b_5	$-5.607\,284\,488\,9 \times 10^{-10}$
a_6	$-5.741\,032\,742\,8 \times 10^{-10}$	b_6	$5.607\,505\,905\,9 \times 10^{-13}$
a_7	$-3.108\,887\,289\,4 \times 10^{-12}$	b_7	$-3.202\,072\,000\,3 \times 10^{-16}$
a_8	$-1.045\,160\,936\,5 \times 10^{-14}$	b_8	$9.715\,114\,715\,2 \times 10^{-20}$
a_9	$-1.988\,926\,687\,8 \times 10^{-17}$	b_9	$-1.210\,472\,127\,5 \times 10^{-23}$
a_{10}	$-1.632\,269\,748\,6 \times 10^{-20}$		
		c_1	$1.185\,976 \times 10^2$

Type K inverse function coefficients

	$-200\,°C$ to $0\,°C$ $-5891\,\mu V$ to $0\,\mu V$		$0\,°C$ to $500\,°C$ $0\,\mu V$ to $20\,644\,\mu V$		$500\,°C$ to $1372\,°C$ $20\,644\,\mu V$ to $54\,886\,\mu V$
d_0	0	d_0	0	d_0	$-1.318\,058 \times 10^2$
d_1	$2.517\,346\,2 \times 10^{-2}$	d_1	$2.508\,355 \times 10^{-2}$	d_1	$4.830\,222 \times 10^{-2}$
d_2	$-1.166\,287\,8 \times 10^{-6}$	d_2	$7.860\,106 \times 10^{-8}$	d_2	$-1.646\,031 \times 10^{-6}$
d_3	$-1.083\,363\,8 \times 10^{-9}$	d_3	$-2.503\,131 \times 10^{-10}$	d_3	$5.464\,731 \times 10^{-11}$
d_4	$-8.977\,354\,0 \times 10^{-13}$	d_4	$8.315\,270 \times 10^{-14}$	d_4	$-9.650\,715 \times 10^{-16}$
d_5	$-3.734\,237\,7 \times 10^{-16}$	d_5	$-1.228\,034 \times 10^{-17}$	d_5	$8.802\,193 \times 10^{-21}$
d_6	$-8.663\,264\,3 \times 10^{-20}$	d_6	$9.804\,036 \times 10^{-22}$	d_6	$-3.110\,810 \times 10^{-26}$
d_7	$-1.045\,059\,8 \times 10^{-23}$	d_7	$-4.413\,030 \times 10^{-26}$		
d_8	$-5.192\,057\,7 \times 10^{-28}$	d_8	$1.057\,734 \times 10^{-30}$		
		d_9	$-1.052\,755 \times 10^{-35}$		

Properties

Nominal composition: Chromel–alumel, 90% nickel–10% chromium versus 95% nickel–2% aluminium–2% manganese–1% silicon

Type K is the most common thermocouple type and the most irreproducible, showing spurious errors of up to $8\,°C$ in the $300\,°C$ to $500\,°C$ range and steady drift above $700\,°C$. It is suited to oxidising and inert atmospheres but suffers from 'green rot' and embrittlement in marginally oxidising atmospheres. The main advantages of Type K are the wide range, the low cost and ready availability of instrumentation.

D.7 Type N

Output in μV

$T_{90}(\degree C)$	−0	−10	−20	−30	−40
−250	−4313	−4336	−4345		
−200	−3990	−4083	−4162	−4226	−4277
−150	−3336	−3491	−3634	−3766	−3884
−100	−2407	−2612	−2808	−2994	−3171
−50	−1269	−1509	−1744	−1972	−2193
0	0	−260	−518	−772	−1023

$T_{90}(\degree C)$	0	10	20	30	40
0	0	261	525	793	1065
50	1340	1619	1902	2189	2480
100	2774	3072	3374	3680	3989
150	4302	4618	4937	5259	5585
200	5913	6245	6579	6916	7255
250	7597	7941	8288	8637	8988
300	9341	9696	10054	10413	10774
350	11136	11501	11867	12234	12603
400	12974	13346	13719	14094	14469
450	14846	15225	15604	15984	16366
500	16748	17131	17515	17900	18286
550	18672	19059	19447	19835	20224
600	20613	21003	21393	21784	22175
650	22566	22958	23350	23742	24134
700	24527	24919	25312	25705	26098
750	26491	26883	27276	27669	28062
800	28455	28847	29239	29632	30024
850	30416	30807	31199	31590	31981
900	32371	32761	33151	33541	33930
950	34319	34707	35095	35482	35869
1000	36256	36641	37027	37411	37795
1050	38179	38562	38944	39326	39706
1100	40087	40466	40845	41223	41600
1150	41976	42352	42727	43101	43474
1200	43846	44218	44588	44958	45326
1250	45694	46060	46425	46789	47152
1300	47513				

Type N reference function coefficients

	−270 °C to 0 °C		0 °C to 1300 °C
a_0	0	a_0	0
a_1	$2.615\,910\,596\,2 \times 10^1$	a_1	$2.592\,939\,460\,1 \times 10^1$
a_2	$1.095\,748\,422\,8 \times 10^{-2}$	a_2	$1.571\,014\,188\,0 \times 10^{-2}$
a_3	$-9.384\,111\,155\,4 \times 10^{-5}$	a_3	$4.382\,562\,723\,7 \times 10^{-5}$
a_4	$-4.641\,203\,975\,9 \times 10^{-8}$	a_4	$-2.526\,116\,979\,4 \times 10^{-7}$
a_5	$-2.630\,335\,771\,6 \times 10^{-9}$	a_5	$6.431\,181\,933\,9 \times 10^{-10}$
a_6	$-2.265\,343\,800\,3 \times 10^{-11}$	a_6	$-1.006\,347\,151\,9 \times 10^{-12}$
a_7	$-7.608\,930\,079\,1 \times 10^{-14}$	a_7	$9.974\,533\,899\,2 \times 10^{-16}$
a_8	$-9.341\,966\,783\,5 \times 10^{-17}$	a_8	$-6.086\,324\,560\,7 \times 10^{-19}$
		a_9	$2.084\,922\,933\,9 \times 10^{-22}$
		a_{10}	$-3.068\,219\,615\,1 \times 10^{-26}$

Type N inverse function coefficients

	−200 °C to 0 °C −3990 µV to 0 µV		0 °C to 600 °C 0 µV to 20 613 µV		600 °C to 1300 °C 20 613 µV to 47 513 µV
d_0	0	d_0	0	d_0	$1.972\,485 \times 10^1$
d_1	$3.843\,684\,7 \times 10^{-2}$	d_1	$3.868\,96 \times 10^{-2}$	d_1	$3.300\,943 \times 10^{-2}$
d_2	$1.101\,048\,5 \times 10^{-6}$	d_2	$-1.082\,67 \times 10^{-6}$	d_2	$-3.915\,159 \times 10^{-7}$
d_3	$5.222\,931\,2 \times 10^{-9}$	d_3	$4.702\,05 \times 10^{-11}$	d_3	$9.855\,391 \times 10^{-12}$
d_4	$7.206\,052\,5 \times 10^{-12}$	d_4	$-2.121\,69 \times 10^{-18}$	d_4	$-1.274\,371 \times 10^{-16}$
d_5	$5.848\,858\,6 \times 10^{-15}$	d_5	$-1.172\,72 \times 10^{-19}$	d_5	$7.767\,022 \times 10^{-22}$
d_6	$2.775\,491\,6 \times 10^{-18}$	d_6	$5.392\,80 \times 10^{-24}$		
d_7	$7.707\,516\,6 \times 10^{-22}$	d_7	$-7.981\,56 \times 10^{-29}$		
d_8	$1.158\,266\,5 \times 10^{-25}$				
d_9	$7.313\,886\,8 \times 10^{-30}$				

Tolerances (whichever is greater)

Class 1:	1.5 °C or 0.4%	for −40 °C to 1000 °C
Class 2:	2.5 °C or 0.75%	for −40 °C to 1200 °C
Class 3:	2.5 °C or 1.5%	for −200 °C to 40 °C

Properties

Nominal composition: Nicrosil–Nisil, 84.4% nickel–14.2% chromium–1.4% silicon versus 95.5% nickel–4.4% silicon–0.1% magnesium

Type N is a nominal replacement for Type K with a very similar temperature range but much higher reproducibility. It is suited to oxidising and inert environments and limited exposure in vacuum and reducing environments. In MIMS form with Nicrosil® or Nicrobel® sheathing it is the most stable of the base-metal thermocouples for the 300 °C to 1200 °C range. The wire and instrumentation are becoming more available.

D.8 Type R

Output in μV

$T_{90}(°C)$	0	10	20	30	40
0	0	54	111	171	232
50	296	363	431	501	573
100	647	723	800	879	959
150	1041	1124	1208	1294	1381
200	1469	1558	1648	1739	1831
250	1923	2017	2112	2207	2304
300	2401	2498	2597	2696	2796
350	2896	2997	3099	3201	3304
400	3408	3512	3616	3721	3827
450	3933	4040	4147	4255	4363
500	4471	4580	4690	4800	4910
550	5021	5133	5245	5357	5470
600	5583	5697	5812	5926	6041
650	6157	6273	6390	6507	6625
700	6743	6861	6980	7100	7220
750	7340	7461	7583	7705	7827
800	7950	8073	8197	8321	8446
850	8571	8697	8823	8950	9077
900	9205	9333	9461	9590	9720
950	9850	9980	10 111	10 242	10 374
1000	10 506	10 638	10 771	10 905	11 039
1050	11 173	11 307	11 442	11 578	11 714
1100	11 850	11 986	12 123	12 260	12 397
1150	12 535	12 673	12 812	12 950	13 089
1200	13 228	13 367	13 507	13 646	13 786
1250	13 926	14 066	14 207	14 347	14 488
1300	14 629	14 770	14 911	15 052	15 193
1350	15 334	15 475	15 616	15 758	15 899
1400	16 040	16 181	16 323	16 464	16 605
1450	16 746	16 887	17 028	17 169	17 310
1500	17 451	17 591	17 732	17 872	18 012
1550	18 152	18 292	18 431	18 571	18 710
1600	18 849	18 988	19 126	19 264	19 402
1650	19 540	19 677	19 814	19 951	20 087
1700	20 222	20 356	20 488	20 620	20 749
1750	20 877	21 003			

Type R reference function coefficients

−50 °C to 1064.18 °C		1064.18 °C to 1664.5 °C		1664.5 °C to 1768.1 °C	
a_1	$5.289\,617\,297\,65 \times 10^0$	a_0	$2.951\,579\,253\,16 \times 10^3$	a_0	$1.522\,321\,182\,09 \times 10^5$
a_2	$1.391\,665\,897\,82 \times 10^{-2}$	a_1	$-2.520\,612\,513\,32 \times 10^0$	a_1	$-2.688\,198\,885\,45 \times 10^2$
a_3	$-2.388\,556\,930\,17 \times 10^{-5}$	a_2	$1.595\,645\,018\,65 \times 10^{-2}$	a_2	$1.712\,802\,804\,71 \times 10^{-1}$
a_4	$3.569\,160\,010\,63 \times 10^{-8}$	a_3	$-7.640\,859\,475\,76 \times 10^{-6}$	a_3	$-3.458\,957\,064\,53 \times 10^{-5}$
a_5	$-4.623\,476\,662\,98 \times 10^{-11}$	a_4	$2.053\,052\,910\,24 \times 10^{-9}$	a_4	$-9.346\,339\,710\,46 \times 10^{-12}$
a_6	$5.007\,774\,410\,34 \times 10^{-14}$	a_5	$-2.933\,596\,681\,73 \times 10^{-13}$		
a_7	$-3.731\,058\,861\,91 \times 10^{-17}$				
a_8	$1.577\,164\,823\,67 \times 10^{-20}$				
a_9	$-2.810\,386\,252\,51 \times 10^{-24}$				

Type R inverse function coefficients

−50 °C to 250 °C −226 µV to 1923 µV		250 °C to 1064 °C 1923 µV to 11 361 µV	
d_0	0	d_0	$1.334\,584\,505 \times 10^1$
d_1	$1.889\,138\,0 \times 10^{-1}$	d_1	$1.472\,644\,573 \times 10^{-1}$
d_2	$-9.383\,529\,0 \times 10^{-5}$	d_2	$-1.844\,024\,844 \times 10^{-5}$
d_3	$1.306\,861\,9 \times 10^{-7}$	d_3	$4.031\,129\,726 \times 10^{-9}$
d_4	$-2.270\,358\,0 \times 10^{-10}$	d_4	$-6.249\,428\,360 \times 10^{-13}$
d_5	$3.514\,565\,9 \times 10^{-13}$	d_5	$6.468\,412\,046 \times 10^{-17}$
d_6	$-3.895\,390\,0 \times 10^{-16}$	d_6	$-4.458\,750\,426 \times 10^{-21}$
d_7	$2.823\,947\,1 \times 10^{-19}$	d_7	$1.994\,710\,149 \times 10^{-25}$
d_8	$-1.260\,728\,1 \times 10^{-22}$	d_8	$-5.313\,401\,790 \times 10^{-30}$
d_9	$3.135\,361\,1 \times 10^{-26}$	d_9	$6.481\,976\,217 \times 10^{-35}$
d_{10}	$-3.318\,776\,9 \times 10^{-30}$		

1064 °C to 1664.5 °C 11 361 µV to 19 739 µV		1664.5 °C to 1768.1 °C 19 739 µV to 21 103 µV	
d_0	$-8.199\,599\,416 \times 10^1$	d_0	$3.406\,177\,836 \times 10^4$
d_1	$1.553\,962\,042 \times 10^{-1}$	d_1	$-7.023\,729\,171 \times 10^0$
d_2	$-8.342\,197\,663 \times 10^{-6}$	d_2	$5.582\,903\,813 \times 10^{-4}$
d_3	$4.279\,433\,549 \times 10^{-10}$	d_3	$-1.952\,394\,635 \times 10^{-8}$
d_4	$-1.191\,577\,910 \times 10^{-14}$	d_4	$2.560\,740\,231 \times 10^{-13}$
d_5	$1.492\,290\,091 \times 10^{-19}$		

Tolerances (whichever is greater)

Class 1: 1.0 °C or $[1 + 0.3\%(t - 1100)]$ for 0 °C to 1600 °C
Class 2: 1.0 °C or 0.25% for 0 °C to 1600 °C

Properties

Nominal composition: Platinum−10% rhodium versus platinum

Type R is suited for use at high temperature in oxidising and inert atmospheres. It may also be used intermittently in vacuum. At temperatures above 1100 °C prolonged use results in grain growth in the platinum leg, making the thermocouple fragile. Type R is very prone to contamination, especially from metal vapours. Types R and S are the two most accurate of the designated thermocouples for high temperatures (200 °C to 1400 °C).

D.9 Type S

Output in μV

$T_{90}(°C)$	0	10	20	30	40
0	0	55	113	173	235
50	299	365	433	502	573
100	646	720	795	872	950
150	1029	1110	1191	1273	1357
200	1441	1526	1612	1698	1786
250	1874	1962	2052	2141	2232
300	2323	2415	2507	2599	2692
350	2786	2880	2974	3069	3164
400	3259	3355	3451	3548	3645
450	3742	3840	3938	4036	4134
500	4233	4332	4432	4532	4632
550	4732	4833	4934	5035	5137
600	5239	5341	5443	5546	5649
650	5753	5857	5961	6065	6170
700	6275	6381	6486	6593	6699
750	6806	6913	7020	7128	7236
800	7345	7454	7563	7673	7783
850	7893	8003	8114	8226	8337
900	8449	8562	8674	8787	8900
950	9014	9128	9242	9357	9472
1000	9587	9703	9819	9935	10 051
1050	10 168	10 285	10 403	10 520	10 638
1100	10 757	10 875	10 994	11 113	11 232
1150	11 351	11 471	11 590	11 710	11 830
1200	11 951	12 071	12 191	12 312	12 433
1250	12 554	12 675	12 796	12 917	13 038
1300	13 159	13 280	13 402	13 523	13 644
1350	13 766	13 887	14 009	14 130	14 251
1400	14 373	14 494	14 615	14 736	14 857
1450	14 978	15 099	15 220	15 341	15 461
1500	15 582	15 702	15 822	15 942	16 062
1550	16 182	16 301	16 420	16 539	16 658
1600	16 777	16 895	17 013	17 131	17 249
1650	17 366	17 483	17 600	17 717	17 832
1700	17 947	18 061	18 174	18 285	18 395
1750	18 503	18 609			

Type S reference function coefficients

−50 °C to 1064.18 °C		1064.18 °C to 1664.5 °C		1664.5 °C to 1768.1 °C	
a_1	$5.403\,133\,086\,31 \times 10^0$	a_0	$1.329\,004\,440\,85 \times 10^3$	a_0	$1.466\,282\,326\,36 \times 10^5$
a_2	$1.259\,342\,897\,40 \times 10^{-2}$	a_1	$3.345\,093\,113\,44 \times 10^0$	a_1	$-2.584\,305\,167\,52 \times 10^2$
a_3	$-2.324\,779\,686\,89 \times 10^{-5}$	a_2	$6.548\,051\,928\,18 \times 10^{-3}$	a_2	$1.636\,935\,746\,41 \times 10^{-1}$
a_4	$3.220\,288\,230\,36 \times 10^{-8}$	a_3	$-1.648\,562\,592\,09 \times 10^{-6}$	a_3	$-3.304\,390\,469\,87 \times 10^{-5}$
a_5	$-3.314\,651\,963\,89 \times 10^{-11}$	a_4	$1.299\,896\,051\,74 \times 10^{-11}$	a_4	$-9.432\,236\,906\,12 \times 10^{-12}$
a_6	$2.557\,442\,517\,86 \times 10^{-14}$				
a_7	$-1.250\,688\,713\,93 \times 10^{-17}$				
a_8	$2.714\,431\,761\,45 \times 10^{-21}$				

Type S inverse function coefficients

−50 °C to 250 °C −236 μV to 1874 μV		250 °C to 1064 °C 1874 μV to 10 332 μV	
d_0	0	d_0	$1.291\,507\,177 \times 10^1$
d_1	$1.849\,494\,60 \times 10^{-1}$	d_1	$1.466\,298\,863 \times 10^{-1}$
d_2	$-8.005\,040\,62 \times 10^{-5}$	d_2	$-1.534\,713\,402 \times 10^{-5}$
d_3	$1.022\,374\,30 \times 10^{-7}$	d_3	$3.145\,945\,973 \times 10^{-9}$
d_4	$-1.522\,485\,92 \times 10^{-10}$	d_4	$-4.163\,257\,839 \times 10^{-13}$
d_5	$1.888\,213\,43 \times 10^{-13}$	d_5	$3.187\,963\,771 \times 10^{-17}$
d_6	$-1.590\,859\,41 \times 10^{-16}$	d_6	$-1.291\,637\,500 \times 10^{-21}$
d_7	$8.230\,278\,80 \times 10^{-20}$	d_7	$2.183\,475\,087 \times 10^{-26}$
d_8	$-2.341\,819\,44 \times 10^{-23}$	d_8	$-1.447\,379\,511 \times 10^{-31}$
d_9	$2.797\,862\,60 \times 10^{-27}$	d_9	$8.211\,272\,125 \times 10^{-36}$
1064 °C to 1664.5 °C 10 332 μV to 17 536 μV		1664.5 °C to 1768.1 °C 17 536 μV to 18 694 μV	
d_0	$-8.087\,801\,117 \times 10^1$	d_0	$5.333\,875\,126 \times 10^4$
d_1	$1.621\,573\,104 \times 10^{-1}$	d_1	$-1.235\,892\,298 \times 10^1$
d_2	$-8.536\,869\,453 \times 10^{-6}$	d_2	$1.092\,657\,613 \times 10^{-3}$
d_3	$4.719\,686\,976 \times 10^{-10}$	d_3	$-4.265\,693\,686 \times 10^{-8}$
d_4	$-1.441\,693\,666 \times 10^{-14}$	d_4	$6.247\,205\,420 \times 10^{-13}$
d_5	$2.081\,618\,890 \times 10^{-19}$		

Tolerances (whichever is greater)

Class 1:	$1.0\,°C$ or $[1 + 0.3\%(t - 1100)]$	for $0\,°C$ to $1600\,°C$
Class 2:	$1.0\,°C$ or 0.25%	for $0\,°C$ to $1600\,°C$

Properties

Nominal composition : Platinum−10% rhodium versus platinum

Type S is suited for use at high temperature in oxidising and inert atmospheres. It may also be used intermittently in vacuum. At temperatures above 1100 °C prolonged use results in grain growth in the platinum leg, making the thermocouple fragile. Type S is very prone to contamination, especially from metal vapours. Types R and S are the two most accurate of the designated thermocouples for high temperatures (200 °C to 1400 °C).

D.10 Type T

Output in μV

$T_{90}(\,^{\circ}\mathrm{C})$	−0	−5	−10	−15	−20
−250	−6180	−6209	−6232	−6248	−6258
−225	−5950	−6007	−6059	−6105	−6146
−200	−5603	−5680	−5753	−5823	−5888
−175	−5167	−5261	−5351	−5439	−5523
−150	−4648	−4759	−4865	−4969	−5070
−125	−4052	−4177	−4300	−4419	−4535
−100	−3379	−3519	−3657	−3791	−3923
−75	−2633	−2788	−2940	−3089	−3235
−50	−1819	−1987	−2153	−2316	−2476
−25	−940	−1121	−1299	−1475	−1648
0	0	−193	−383	−571	−757

$T_{90}(\,^{\circ}\mathrm{C})$	0	5	10	15	20
0	0	195	391	589	790
25	992	1196	1403	1612	1823
50	2036	2251	2468	2687	2909
75	3132	3358	3585	3814	4046
100	4279	4513	4750	4988	5228
125	5470	5714	5959	6206	6454
150	6704	6956	7209	7463	7720
175	7977	8237	8497	8759	9023
200	9288	9555	9822	10092	10362
225	10634	10907	11182	11458	11735
250	12013	12293	12574	12856	13139
275	13423	13709	13995	14283	14572
300	14862	15153	15445	15738	16032
325	16327	16624	16921	17219	17518
350	17819	18120	18422	18725	19030
375	19335	19641	19947	20255	20563
400	20872				

Tolerances (whichever is greater)

Class 1:	1.5 °C or 0.4%	for −40 °C to 350 °C
Class 2:	1.0 °C or 0.75%	for −40 °C to 350 °C
Class 3:	1.0 °C or 1.5%	for −200 °C to 40 °C

Type T reference function coefficients

	−270 °C to 0 °C		0 °C to 400 °C
a_0	0	a_0	0
a_1	$3.874\,810\,636\,4 \times 10^{1}$	a_1	$3.874\,810\,636\,4 \times 10^{1}$
a_2	$4.419\,443\,434\,7 \times 10^{-2}$	a_2	$3.329\,222\,788\,0 \times 10^{-2}$
a_3	$1.184\,432\,310\,5 \times 10^{-4}$	a_3	$2.061\,824\,340\,4 \times 10^{-4}$
a_4	$2.003\,297\,355\,4 \times 10^{-5}$	a_4	$-2.188\,225\,684\,6 \times 10^{-6}$
a_5	$9.013\,801\,955\,9 \times 10^{-7}$	a_5	$1.099\,688\,092\,8 \times 10^{-8}$
a_6	$2.265\,115\,659\,3 \times 10^{-8}$	a_6	$-3.081\,575\,877\,2 \times 10^{-11}$
a_7	$3.607\,115\,420\,5 \times 10^{-10}$	a_7	$4.547\,913\,529\,0 \times 10^{-14}$
a_8	$3.849\,393\,988\,3 \times 10^{-12}$	a_8	$-2.751\,290\,167\,3 \times 10^{-17}$
a_9	$2.821\,352\,192\,5 \times 10^{-14}$		
a_{10}	$1.425\,159\,477\,9 \times 10^{-16}$		
a_{11}	$4.876\,866\,228\,6 \times 10^{-19}$		
a_{12}	$1.079\,553\,927\,0 \times 10^{-21}$		
a_{13}	$1.394\,502\,706\,2 \times 10^{-24}$		
a_{14}	$7.979\,515\,392\,7 \times 10^{-28}$		

Type T inverse function coefficients

	−200 °C to 0 °C −5603 µV to 0 µV		0 °C to 400 °C 0 µV to 20 872 µV
d_0	0	d_0	0
d_1	$2.594\,919\,2 \times 10^{-2}$	d_1	$2.592\,800 \times 10^{-2}$
d_2	$-2.131\,696\,7 \times 10^{-7}$	d_2	$-7.602\,961 \times 10^{-7}$
d_3	$7.901\,869\,2 \times 10^{-10}$	d_3	$4.637\,791 \times 10^{-11}$
d_4	$4.252\,777\,7 \times 10^{-13}$	d_4	$-2.165\,394 \times 10^{-15}$
d_5	$1.330\,447\,3 \times 10^{-16}$	d_5	$6.048\,144 \times 10^{-20}$
d_6	$2.024\,144\,6 \times 10^{-20}$	d_6	$-7.293\,422 \times 10^{-25}$
d_7	$1.266\,817\,1 \times 10^{-24}$		

Properties

Nominal composition: Copper–constantan, Copper versus 55% copper–45% nickel

Type T is a very useful low-temperature thermocouple having a high reproducibility and an ability to withstand reducing, inert, vacuum and mildly oxidising environments. It also has a moderate resistance to corrosion in the presence of moisture, making it suitable for use at sub-zero temperatures. If restricted to temperature ranges below 150 °C its reproducibility is very good. The wire and instrumentation are readily available.

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