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Guide to Secondary Thermometry

Thermocouple Thermometry: 1. General Usage

Consultative Committee for Thermometry
under the auspices of the
International Committee for Weights and Measures

Thermocouple Thermometry: 1. General Usage

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References

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Thermocouple Thermometry Part 1:

General Usage

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ABSTRACT

The Guides on Secondary Thermometry are prepared by the Consultative Committee for Thermometry to provide advice on good measurement practice and making temperature measurements traceable to the International Temperature Scale of 1990. This guide is the first of two guides collating information and advice on thermocouple thermometry. This first guide, Part I, focuses on aspects of general usage: the principles of operation, a summary of common thermocouple types, performance characteristics and service conditions, sources of error, and guidance on the construction, installation and maintenance of thermocouples. Part II discusses reference thermocouples and thermocouple calibration.

1. Introduction

Thermocouples are the most widely used temperature sensor for both industrial and scientific applications. The wide range of available thermocouple materials allows their use from temperatures as low as –270 °C to as high as 2700 °C, and their low cost and simplicity make them especially attractive for industrial applications. Documentary standards defining the characteristics of more than a dozen different standard thermocouple types ensure that for most applications, thermocouples of known quality and characteristics are readily available.

Thermocouples are also the most misunderstood temperature sensor. Much of the confusion arises from their peculiar mode of operation, compounded by the mistaken belief that the thermocouple voltage is generated at the junction. In fact, the voltage is generated along the length of the thermocouple where it is exposed to temperature gradients, so it is the wire outside the zone of interest that generates the voltage. In a well-designed thermocouple installation, there is no voltage generated at the junction. Confusion about the origin of the voltage underlies many of the difficulties experienced with thermocouples and with the diagnosis of measurement problems.

The peculiar mode of operation makes thermocouples sensitive to variations in the material properties along the length of the wires. Such variations arise from exposure to different thermal conditions, to different chemical environments, to mechanical treatment such as bending and flexing, to strong magnetic fields, and to ionising radiation. A failure to manage all these aspects of usage means that measurement uncertainties may be unexpectedly large, calibrations may be a waste of time, and faulty thermocouples may go unrecognised. One of the aims of this guide is to provide sufficient understanding of thermocouples to avoid these outcomes.

The guide provides users with a foundation in thermocouple thermometry. It covers the operating principles, a summary of the performance and attributes of the different standardised thermocouple types, advice on thermocouple assembly and instrumentation, sources of error in thermocouple measurements, and advice on installation and usage. For additional advice on calibration and the use of reference thermocouples, see the accompanying guide *Thermocouple Thermometry: Part 2 Reference Thermocouples and Calibration* (in preparation).

Further general advice on thermocouple thermometry can be found in Bentley (1998a), ASTM (1993), Kerlin and Johnson (2012), Reed (1992a, 1992b), and Nicholas and White (2001). Guides may also be available from regional metrology organisations and accrediting organisations, e.g., Euramet (2020). For a more detailed treatment of thermocouples, see Pollock (1991) and Quinn (1990). For the theory of the thermoelectric effects, see Pollock (1991). Shorter summaries of the theory can be found in Pollock (1995), Bentley (1998a), ASTM (1993), and Goupil (2011). Although now an old book, Kinzie (1973) provides the best review of the properties and performance of both standardised and non-standardised thermocouples.

2. Principles of operation

In metals, the free movement of electrons is responsible for the electrical conductivity and most of the thermal conductivity. Because the electrons are responsible for both properties, several electrical and thermal effects occur together. These thermoelectric effects include the Seebeck, Thomson, and Peltier effects.

The Seebeck effect is the sole basis for the thermocouple and arises from the redistribution of electric charge occurring when electrons diffuse throughout a conductor carrying heat. The effect causes a voltage to be generated wherever heat flows within a conductor. The voltage gradient induced by the Seebeck effect, at any position, x, along the conductor, is directly proportional to the temperature gradient there:

$$\frac{\mathrm{d}V}{\mathrm{d}x} = S(T,x)\frac{\mathrm{d}T}{\mathrm{d}x} \ , \qquad (1)$$

where V is the Seebeck voltage, T is the temperature, and the temperature-dependent scale factor relating the two gradients, $S(T, x)$, is the Seebeck coefficient at that position on the conductor. Most importantly, if the temperature gradient is zero, i.e., the conductor is isothermal, then the voltage generated is also zero. The Seebeck voltage is commonly described as an electromotive force, or emf, and different electrical conductors have different Seebeck coefficients.

The idea that the thermocouple voltage is generated along the length of the wire wherever there are temperature gradients may seem strange, but there is another more familiar effect like this. Figure 1 shows an analogue for a thermocouple wire in which a fluid-filled tube is exposed to different elevations. Changes in the pressure in the fluid occur only where the tube lies within a vertical gradient. Further, if the fluid within the tube has the same density throughout, then the total pressure generated between one end of the tube and the other depends only on the elevations of the two ends. Similarly, if the Seebeck coefficient, $S(T, x)$, is the same for all positions along a conductor, the total Seebeck voltage generated in the conductor depends only on the end temperatures.

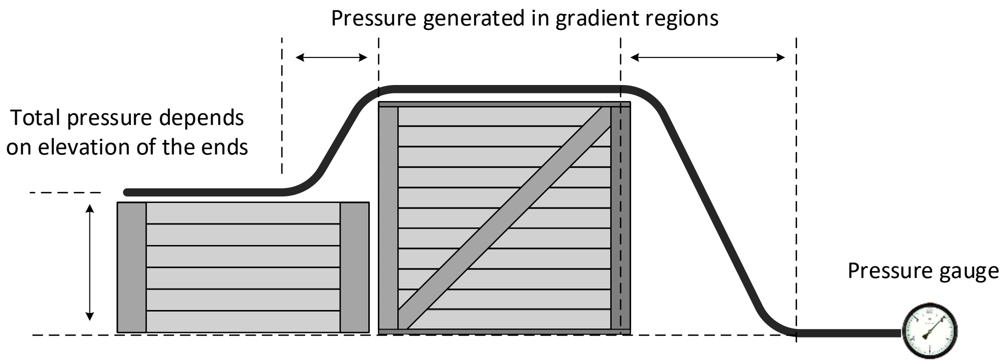

Figure 1. Hydraulic analogue of the Seebeck effect. Pressure differences in a fluid-filled tube are generated at gradients, but the total pressure generated depends only on the difference in the elevation of the ends of the tube.

Under the assumption that a wire is homogeneous, that is, the Seebeck coefficient is independent of position, $S(T,x) = S(T)$, equation (1) can be written without reference to the position within the wire, i.e.,

$$\mathrm{d}V = S(T)\mathrm{d}T\,, \tag{2}$$

where dV is the differential voltage generated by a small section of wire subject to the temperature differential dT. The Seebeck voltage generated over the length of the wire can now be found by integrating equation (2),

$$V = \int_{T_2}^{T_1} S(T)\mathrm{d}T = V(T_1) - V(T_2)\,, \tag{3}$$

where T_1 and T_2 are the temperatures at the two ends of the wire. Equation (3) shows that in a homogeneous wire, the total Seebeck voltage depends on the end temperatures of the wire and not on the temperature distribution between the ends.

The most significant problems with thermocouples arise from the failure to meet the assumption of homogeneity. Localised changes in the Seebeck coefficient, commonly called inhomogeneities, can be caused by variations in alloy composition due to manufacture, mechanical damage such as bends or strains, chemical damage such as oxidation or contamination, metallurgical changes caused by exposure to different temperatures, and damage or transmutation due to ionising radiation. In highly alloyed wires (e.g., Type K), the variations in Seebeck coefficient can be several tens of percent, while in carefully heat-treated pure-element wires such as copper, platinum, or gold, the effects can be as low as a few parts per million.

To overcome problems with inhomogeneities, there are two guiding principles for all thermocouple circuits (Reed 1992a, 1992b):

- Where thermocouple wire is exposed to temperature gradients, it must be protected and maintained in a homogenous condition so that it generates the correct voltage.
- Where the wire is inhomogeneous, it must be maintained in an isothermal environment so that it generates zero voltage.

Even with the best of care, inhomogeneity effects are unavoidable in most situations and are almost always the dominant source of measurement uncertainty. Detail on the causes and signatures of inhomogeneity effects are discussed in Section. 5.2.

In its simplest form (see Figure 2), a thermocouple consists of two electrical conductors of different composition (the thermoelements), joined at the measuring junction, and electrically insulated elsewhere. The temperature of the measuring junction is inferred from the voltage difference measured between the open ends of the wires at the reference junction, knowledge of the temperature of the reference junction, and knowledge of the Seebeck coefficient for the pair of wires. Thermocouples are used in open-circuit conditions to ensure that no electrical current flows. This is necessary to ensure there are no spurious voltages due to the Peltier and Thomson effects (the other thermoelectric effects), or due to the electrical resistance of the conductors.

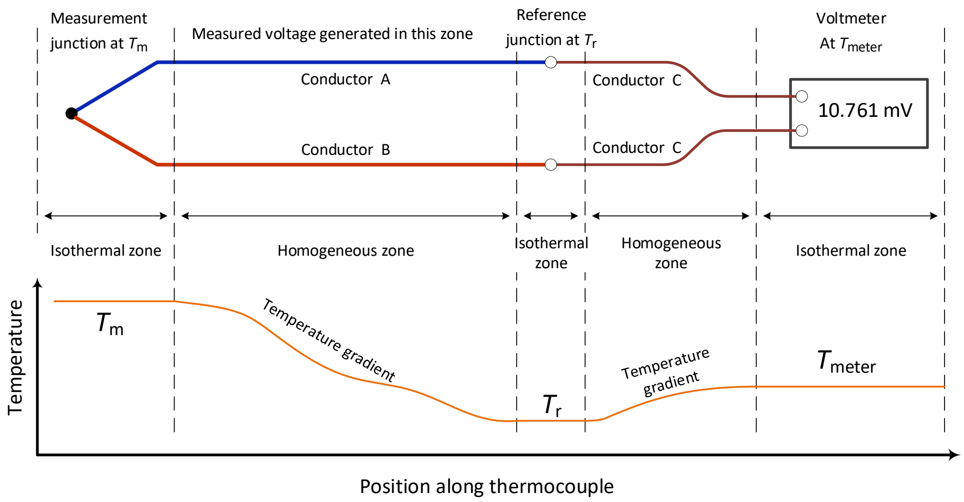

Figure 2. Simple thermocouple circuit and the temperature profile along it. Ideally, each part of the thermocouple exposed to a temperature gradient and generating the voltage is homogeneous, and every part where there may be inhomogeneities is isothermal.

Following the two principles given above, the measuring junction and the reference junction are maintained in isothermal environments. The uniform temperature ensures that any wire damaged in the manufacture of the junctions by soldering, welding, brazing, clamping, or bending does not generate a spurious Seebeck voltage. In the remaining parts of the circuit, the sections of wire that generate the Seebeck voltage must remain homogeneous. This includes the sections of the conductors A and B between the two junctions, and the two copper conductors, C, between the reference junction and the voltmeter. The Seebeck voltages generated in the two copper conductors are ideally equal so should have no effect on the measurement of the voltage difference at the reference junction.

The measured voltage difference, V_{meas}, depends on the voltages, V_A and V_B, generated in the ideally homogeneous wires A and B according to their end temperatures, as in equation (3), so that

$$V_{meas} = [V_A(T_m) - V_A(T_r)] - [V_B(T_m) - V_B(T_r)] \,, \tag{4}$$

where T_m and T_r are the temperatures of the isothermal zones enclosing the measuring and reference junctions, respectively. If the wires A and B are always used as a pair, it is convenient to combine their contributions as though from a single conductor:

$$V_{meas} = V_{AB}(T_m) - V_{AB}(T_r) \,. \tag{5}$$

The Seebeck coefficients of two wires may be combined in the same way:

$$S_{AB}(T) = S_A(T) - S_B(T) \,. \tag{6}$$

A further simplification is to define the thermocouple voltage $V_{AB}(T)$ to be zero at $T = 273.15$ K (t = 0.0 °C), the normal melting point of ice. This further simplifies equation (5) when the temperature is expressed in degrees Celsius (lower case t) and the reference junction is held at 0 °C:

$$V_{\mathrm{meas}} = V_{\mathrm{AB}}(t_{\mathrm{m}}) . \tag{7}$$

This makes the ice point a convenient means of controlling the temperature of the reference junction. See (Edler *et al.* 2016) for guidance on the preparation of ice points.

The form of equation (7) is the deceptively simple form used by documentary standards to define the reference functions for each thermocouple type (see IEC 60584:2013, IEC 62640:2008, ASTM E1751-2009, Burns *et al.* 1993). The equation is deceptive because it relates the voltage to the measuring junction temperature only. It obscures the origin of the Seebeck voltage, obscures the voltage dependence on the reference junction, and obscures the most significant sources of measurement uncertainty.

3. Standardised Thermocouple Types

Over the years, a great variety of thermocouple materials have been investigated for different environments and temperature ranges (Kinzie 1973). However, a subset has proven useful for most applications and have been adopted as standard types. These are the ten letter-designated thermocouples, Types A, B, C, E, J, K, N, R, S, and T, whose voltage–temperature characteristics (the reference functions) are defined by the International Electrotechnical Commission (IEC) in the IEC 60584: 2013 standard. IEC 62460: 2008 gives the reference functions for the pure-metal platinum-gold and platinum-palladium thermocouples, which do not have a letter designation and are amongst the most accurate thermocouples available. Table 1 summarises the main attributes of all these thermocouples, and Figure 3 plots their Seebeck coefficient as a function of temperature. The indicated temperature ranges in Table 1 and Figure 3 are the ranges over which the thermocouples are defined by the standards. The upper temperature for continuous usage is typically about 200 °C lower than the stated upper limit. When used at temperatures close to the upper limit, intermittent usage and/or large diameter wire is recommended; see Sec. 4.2 and ASTM (1993) for details. Table 2 indicates the manufacturing tolerances for the different grades for the different types. Appendix A tabulates the reference and inverse functions.

In recent years, the electrical definitions for the different thermocouple types have become harmonised world-wide, so that letter-designated thermocouples manufactured according to the IEC standards conform to those defined by other regional and national standards, including the European (DIN), British (BS), Japanese (JIS), and American standards (ANSI and ASTM). Unfortunately, the colour codes for the plastic insulation for the thermocouples, for the extension cables, and for plugs and sockets, are not harmonised, and it may be impossible to unambiguously identify a thermocouple type from the colour of any of its parts.

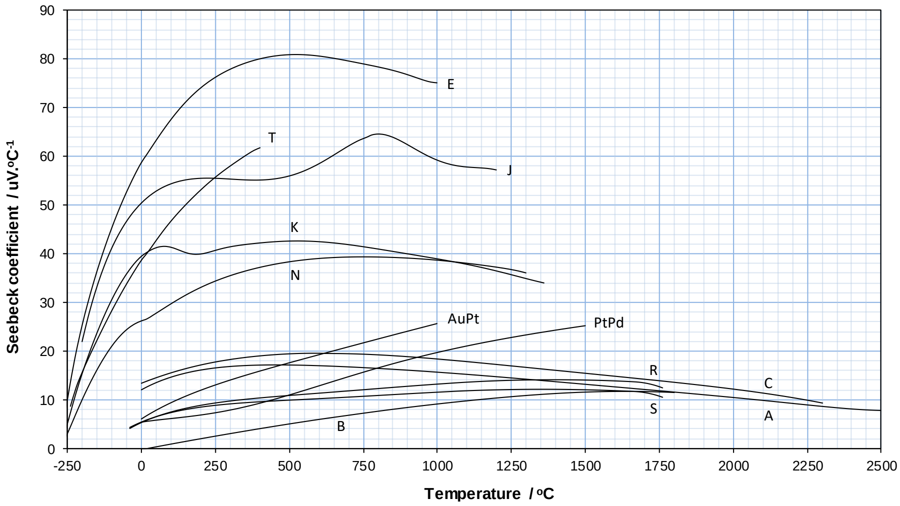

Figure 3. The Seebeck coefficient for common thermocouple types.

Table 1: Summary of the commonly used thermocouple types.

Thermocouple Type	Temperature range	Material description *	Typical usage
A	0 °C to 2500 °C	Tungsten/Rhenium	High temperatures, reducing atmospheres
B	0 °C to 1820 °C	Platinum/Rhodium	High temperatures, oxidising atmospheres
C	0 °C to 2315 °C	Tungsten/Rhenium	High temperatures, reducing atmospheres
E	–270 °C to 1000 °C	Chromel/Constantan	Medium and low temperatures, high output
J	–210 °C to 1200 °C	Iron/Constantan	Medium temperatures, reducing atmospheres
K	–270 °C 1300 °C	Chromel/Alumel	Medium and low temperatures, general purpose oxidising
N	–270 C to 1300 °C	Nicrosil/Nisil	Medium and low temperatures, general purpose oxidising
R	–50 °C to 1768 C	Platinum/Rhodium	High temperatures, oxidising atmospheres, good accuracy
S	–50 °C to 1768 C	Platinum/Rhodium	High temperatures, oxidising atmospheres, good accuracy
T	–270 °C to 400 °C	Copper/Constantan	Low temperatures, good accuracy
Au/Pt	0 °C to 1000 °C	Gold/Platinum	Medium temperatures, highest accuracy
Pt/Pd	0 °C to 1500 C	Platinum/Palladium	High temperatures, highest accuracy

***** Chromel and Alumel are registered trademarks of Concept Alloys, Inc.

Table 2: Thermocouple Manufacturing Tolerances

Thermocouple Type	Class 1	Class 2	Class 3
	0.5 °C or 0.004|*t*|	1 °C or 0.0075|*t*|	1 °C or 0.015|*t*|
T	–40 °C to 350 °C	–40 °C to 350 °C	–200 °C to 40 °C
	1.5 °C or 0.004|*t*|	2.5 °C or 0.0075|*t*|	2.5 °C or 0.015|*t*|
E	–40 °C to 800 °C	–40 °C to 900 °C	–200 °C to 40 °C
J	–40 °C to 750 °C	–40 °C to 750 °C	-
K	–40 °C to 1000 °C	–40 °C to 1200 °C	–200 °C to 40 °C
N	–40 °C to 1000 °C	–40 °C to 1200 °C	–200 °C to 40 °C
	1.0 °C for t < 1100 °C 1.0 °C +0.003|*t* – 1100|	1.5 °C or 0.0025|*t*|	4 °C or 0.005|*t*|
R	0 °C to 1600 °C	0 °C to 1600 °C	-
S	0 °C to 1600 °C	0 °C to 1600 °C	-
B	-	600 °C to 1700 °C	600 °C to 1700 °C
		0.01|*t*|	
A		1000 °C to 2500 °C	-
C		426 °C to 2315 °C	-

Note 1: Where tolerance values are expressed both as a temperature deviation and a function of temperature, the larger applies.
Note 2: Thermocouples of Type E, K, N manufactured to Class 1 and 2, will not normally meet Class 3. If Class 1 or 2 and Class 3 and required, it should be specifically requested.
Note 3: Thermocouples of Type T manufactured to Class 1 and 2 will not meet Class 3. If Class 3 is required, it should be specifically requested.

The IEC thermocouples are complemented by a set of less-frequently-used thermocouples defined by the American Society for Testing and Materials (ASTM) in the ASTM E1751-09 standard. They include Chromel vs gold/iron for cryogenic applications, Platinel II, a noble-metal thermocouple mimicking Type K at high temperatures, an iridium vs iridium/rhodium alloy thermocouple for use up to 2000 °C in inert environments, and a platinum-molybdenum alloy thermocouple that exhibits low drift under thermal neutron irradiation.

Historically, thermocouples were defined by the chemical composition of the wires. Nowadays, all the definitions use reference functions – mathematical equations of the form of equation (7) relating voltage to temperature (see Appendix A). Defining the thermocouples mathematically has the benefit of giving manufacturers the freedom to vary the wire composition to suit use in different environments and to compensate for compositional variations in the raw materials. However, these variations in composition have important consequences for practical thermometry.

In general, the thermoelements should always be bought and used as a pair, and wires from different sources or batches should not be mixed. Because manufacturers have favoured compositions, mixing thermoelements from different manufacturers or different batches may cause the thermocouple to exhibit large departures from the reference function. The no-mixing rule applies especially to the base-metal thermocouples Types E, K, and N, where both thermoelements are highly alloyed.

Secondly, the composition of some thermoelements may be varied to increase reliability in specific environments (e.g., environments with a high sulphur concentration). Mixing thermoelements from different sources or batches may compromise the thermocouple reliability in these environments.

Thirdly, the variations in composition for the same nominal thermocouple type mean that generic statements (as given in Table 1 and the sections below) about the performance characteristics of specific thermocouple types should be treated with a little scepticism. For example, Type N was developed as a replacement for Type K with reduced susceptibility to ordering effects and reduced hysteresis in the range 200 °C to 650 °C. However, not all commercial formulations of Type N achieve this aim, and some are worse than typical Type K formulations (Webster 2017a). Similarly, many Type K formulations appear to have been designed for best performance in the mineral-insulated metal-sheathed (MIMS) format, and consequently may perform poorly as bare-wire thermocouples in air at high temperatures (Webster 2017d).

The following subsections give a brief overview of the generic properties of the common thermocouple types and recommendations for usage. Further information on the suitability for general applications can be found in Bentley (1998a), ASTM (1993), Burns *et al.* (1993), Quinn (1990), and Kinzie (1973). Thermocouples for cryogenic measurements (e.g., Chromel / Au–0.07%Fe) and sources of error when using thermocouples in magnetic fields and nuclear reactors are discussed in Quinn (1990), Bentley (1998a), Guildner (1979), Rubin (1997), and Fenton (1972). For information on other thermocouples types or specific applications, see Kinzie (1973).

Detailed tables of voltage vs temperature are available in IEC 60584-1: 2013, IEC 62460: 2008, Burns *et al.* (1993), and ASTM (1993). The tables for many of the letter designated thermocouples can also be downloaded from the NIST ITS-90 Thermocouple Database at http://srdata.nist.gov/its90/main. The open-source programming language Python also includes, in its software modules, the reference functions for the letter-designated thermocouples.

3.1. Base-metal thermocouples

Base metal is the descriptor given to the low-cost thermocouple Types E, T, J, N, and K that do not use noble metals like gold and platinum in the alloys. Often one or both thermoelements include nickel as a component of the alloy to improve high-temperature durability. Base-metal thermocouples exhibit moderate performance, but the alloyed thermoelements particularly are prone to developing inhomogeneities with thermal treatment and, in general, the accuracy cannot be improved significantly with calibration. As Figure 3 indicates, the Seebeck coefficient of base-metal thermocouples is high, in the range 30 μV/°C to 80 μV/°C. With care and suitable heat treatment, some types can achieve accuracies of a few tenths of a degree over limited temperature ranges, but errors of several degrees are common. The temperature ranges, common names, nominal compositions, and properties of base-metal thermocouples are summarised in Table 3.

Table 3. Temperature ranges, common names, nominal compositions, and generic properties of the base-metal letter-designated thermocouples. The positive thermoelements for each pair are listed first.

Type	Nominal composition	Temperature range	Properties and utility
K	Chromel-Alumel 90%Ni-9.5%Cr-0.5%Si vs 95%Ni-5%(Si, Mn, Al)	–270 °C to 1300 °C	Most common industrial thermocouple. Moderately resistant to oxidation. Avoid low oxygen or reducing atmospheres, and vacuum. High susceptibility to thermal inhomogeneities.
N	Nicrosil-Nisil 84.4%Ni-14.2%Cr-1.4%Si vs 95.5%Ni-4.4%Si-0.1%Mg	–270 °C to 1300 °C	Nominal, improved replacement for Type K. Moderately resistant to oxidation. Avoid low oxygen, reducing atmospheres, and vacuum.
E	Chromel-Constantan 90%Ni-9.5%Cr-0.5%Si vs 55%Cu-45%Ni	–270 °C to 1000 °C	Highest Seebeck coefficient. Best thermocouple for low temperatures. Avoid low oxygen, reducing atmosphere, and vacuum. Moderate susceptibility to thermal inhomogeneities
J	Iron-Constantan Fe (99.5%) vs 55%Cu-45%Ni	–210 °C to 1200 °C	Highly variable composition and output. Suitable for vacuum, oxidising and reducing atmospheres. Iron thermoelement is prone to rapid corrosion. Susceptible to inhomogeneities above 500 °C. Historical standards for different countries varied.
T	Copper- Constantan Cu vs Cu-45%Ni	–270 °C to 400 °C	Good for general purpose, and low temperatures. Low susceptibility to thermal inhomogeneities. High thermal conductivity of copper can affect reference junction and measurements. Historical standards for different countries varied. Different formulations are required for above and below 0 °C.

Note 1: Colloquially, Type K is often described as the Chromel-Alumel thermocouple. The names Chromel and Alumel are trademarked by Concept Alloys Inc. and refer to specific alloy compositions.
Note 2: Constantan is a generic descriptor for copper-nickel alloys with a range of compositions. The Constantan alloys used in Types E, J, and T are not usually interchangeable.

3.1.1. Type K

The wide temperature range, low cost, and high tolerance of both oxidising and inert atmospheres make Type K the most widely used thermocouple type. However, Type K suffers most from thermally induced inhomogeneities, making it one of the least accurate of the base-metal thermocouples. The Seebeck coefficient of the positive thermoelement (Chromel) increases with exposure to temperature in the range 200 °C to 600 °C (especially around 400 °C) due to short-range ordering but returns quickly to its former value above about 650 °C (Kollie *et al.* 1975, Webster 2017e). This leads to hysteresis effects of typically between 1 °C and 4 °C, although there are reports of effects as large as 8 °C (Kinzie 1973, Burley 1972) depending on the alloy composition and the rate of change of temperature. To avoid hysteresis effects, no part of the wire of a Type K thermocouple should be used at lower temperatures once it has been used at temperatures above about 150 °C. On the other hand, complete replacement is often not necessary if the temperature along all parts of the wire can be increased, e.g., through increased immersion. Note particularly, the hysteresis effects render calibrations of Type K thermocouples ineffective unless they can be carried out *in situ* (Bentley 1998a, ASTM 1993), or the thermocouple has been preconditioned (Webster 2017b). Drift due to short-range-ordering can be difficult to distinguish from the annealing of residual cold-work, which may be deliberately or inadvertently left behind after manufacture. Cold-work in the positive thermoelement also accelerates short-range ordering (Greenen 2017).

Type K should not be used in sulphurous or reducing atmospheres without protection (ASTM 1993). In marginally oxidising atmospheres, the Chromel thermoelement suffers from ‘green rot’ due to the preferential oxidation of chromium (Bentley 1998a). In extreme cases, green rot accompanies a decrease in the Seebeck coefficient of several tens of percent (see Section 5.2.4).

The negative thermoelement (Alumel) usually exhibits a magnetic phase transition somewhere between room temperature and about 250 °C, which may cause deviations from the reference function between −3 °C and +1 °C, depending on wire composition (Burley *et al.* 1982). Alumel also oxidises rapidly in air above 700 °C (Bentley 1998a, Webster 2017d).

Type K is susceptible to the migration of alloy components, especially manganese and aluminium, either into or out of the thermoelements. Bare-wire thermocouples used in air above about 600 °C experience slow irreversible increases in Seebeck coefficient, equivalent to about 1 % for every 1000 hours at 1000 °C (Bentley 1998a, Nicholas and White 2001). In contrast, the Seebeck coefficient of a thermocouple sheathed in stainless steel or Inconel® decreases at high temperatures (−10 °C in 1000 h at 1100 °C in a steel sheath) due to net migration of manganese from the sheath (Bentley 1998a). Thermocouples used with sheath materials with the same concentration of manganese as the thermoelements (integrally-designed MIMS or ID-MIMS), including Nicrobell®, Omegaclad®, and Pyrosil®, are more stable at high temperatures (Bentley 1998a).

3.1.2. Type N

Type N was developed as a replacement for Type K. It has similar chemical properties to Type K, so is suited to the same applications. With the correct alloy composition, it outperforms Type K in most temperature ranges. In particular, hysteresis effects due to short-range ordering are two to four times less and are displaced to higher temperatures, in the range from 500 °C to 1000 °C, peaking around 700 °C (Bentley 1998a). Type N is also slightly more resistant to oxidation than Type K (Burley *et al.* 1982, Wang and Starr 1982), making Type N preferable for use as a bare-wire thermocouple in air.

Unfortunately, because mathematical functions define the thermocouple, there is no guarantee that a particular Type N formulation will improve on the performance of Type K. Some formulations exhibit greater hysteresis effects than Type K and, therefore, care in selection is required; see, for example, Bentley (1989a) and Webster (2017a).

As with Type K, integrally-designed MIMS (ID-MIMS) thermocouples, in which the sheath is chemically compatible with the thermoelements and has a similar thermal expansion coefficient as the thermoelements, outperform bare wire and conventional stainless steel and Inconel MIMS assemblies at high temperatures. Most of these sheath materials have a composition like the Nicrosil thermoelement, but may have additional elements added, e.g., 0.15 % Mg, to improve oxidation resistance. These materials are available under a wide range of different trade names, including Nicrobell®, Omegaclad®, and Pyrosil®, and are often available as a sheath material for both Type K and Type N ID-MIMS thermocouples (Bentley 1998a).

3.1.3. Type E

Constantan, the negative thermoelement of Type E, J, and T thermocouples, has the most negative Seebeck coefficient of common thermocouple materials. This contributes to Type E having the largest net Seebeck coefficient of the letter-designated thermocouples. The high sensitivity combined with low thermal conductivity and resistance to moisture makes Type E especially useful at cryogenic temperatures and gives it a slight advantage in electrically noisy environments.

Both thermoelements of Type E exhibit similar hysteresis effects, so they tend to compensate each other, leading to lower observed hysteresis than in Type K. However, manufacturing variations make the compensation highly variable. The positive thermoelement of Type E (Chromel), as in Type K, suffers from large and rapid change in Seebeck coefficient with preferential oxidation of chromium (‘green rot’) above 700 °C in low-oxygen environments. Type E may be used above 500 °C and up to 900 °C in oxidising or inert atmospheres with large diameter wire, but sulphurous and reducing atmospheres should be avoided. Type E can be used in vacuum for short periods.

3.1.4. Type J

Type J is a widely used thermocouple but is not well-suited for accurate work without calibration. The Seebeck coefficients in both thermoelements are sensitive to small changes in composition, especially above 500 °C, where large irreversible errors can occur. If accurate measurements are needed above 500 °C, a suitable MIMS sheathed Type N or K should be preferred.

The main distinguishing feature of Type J is its ability to withstand reducing atmospheres. It may be used from 0 °C to 760 °C in oxidising or reducing atmospheres. If used above 500 °C in oxidising atmospheres, large diameter wires should be used. Moist atmospheres cause the iron thermoelement to rust, and exposure to temperatures below 0 °C may lead to embrittlement. Iron undergoes a magnetic transformation around 760 °C and an α-γ crystal transformation at 910 °C, causing changes in its Seebeck coefficient at those temperatures (Bentley 1998a).

Historically, there have been significant differences between the Type J definitions in different documentary standards. The recent harmonisation of international standards should address this problem for the future, but there may still be errors of up to 8 °C at 240 °C if new Type J thermocouples are used with old instrumentation (Nicholas and White 2001).

3.1.5. Type T

Type T is one of the oldest and most popular thermocouples for use below 200 °C. The positive thermoelement of the Type T exhibits good thermoelectric homogeneity owing to the ready availability of high-purity, strain-free copper, making Type T one of the most accurate base-metal thermocouples. However, the high thermal conductivity of copper is a disadvantage in some applications. Type T may be used up to 370 °C in air (limited by the oxidation of copper) and up to 400 °C in vacuum and inert or reducing atmospheres. As in other thermocouples types, the constantan thermoelement suffers from hysteresis effects. The Seebeck coefficient increases when exposed to temperatures between about 150 °C and 350 °C, but then decreases between 350 °C and 500 °C (Webster 2015a).

The use of Type T for cryogenic applications requires care because most formulations are designed for use above 0 °C and do not meet the specified tolerances at temperatures well below 0 °C. Instead, wire formulated for cryogenic applications must be specified (see Note 2 on Table 3).

3.2. Alloyed noble-metal thermocouples

Noble-metal thermocouples are those based on platinum, rhodium, iridium, palladium, ruthenium, rhenium, osmium, and gold. The noble metals are all remarkably resistant to corrosion and function well in oxidising environments and, except for gold, they all have melting points above 1500 °C, making them attractive for high-temperature applications. The main disadvantages are that they are expensive and have relatively low Seebeck coefficients – less than 30 µV/°C and more typically about 10 µV/°C. However, most are capable of accuracies of 0.5 °C or better, so they are often preferred for reference thermocouples, i.e., thermocouples used to calibrate other thermocouples.

A wide range of different noble-metal thermocouples have been considered. Kinzie (1973) reviews the properties of the different elements and historical research. The most common of the alloyed thermocouples are platinum-rhodium alloys, which, for temperatures below 1100 °C or so, exhibit a consistent pattern of behaviour amongst the different alloy compositions. Figure 4 shows plots of the changes in Seebeck coefficient after 100 hours of use (after annealing), for six different platinum-rhodium alloys. The changes occurring between about 200 °C and 600 °C are due to ordering, with the most favoured composition being the 20% rhodium alloy with the 4:1 ratio of platinum and rhodium atoms. The ordering effect is completely reversible by annealing. Above 600 °C, the differences are due to partial oxidation and volatilisation of the platinum and rhodium oxides. The effect is almost reversible by annealing at 1100 °C, which forces the oxide to decompose and the metal elements to be redeposited on the thermoelement. Once again, the favoured alloy has about 20% rhodium (Webster 2017c, Webster 2020).

Oxidation, in combination with long exposures at temperatures above 600 °C, allows the oxide vapour to diffuse to higher or lower temperature regions and dissociate, irreversibly altering the composition of the thermoelements in several places at once (more examples later). Rhodium migration has a much larger effect if it condenses onto the pure platinum thermoelement, but this can be supressed by assembling the thermoelements in a single long twin-bore ceramic insulator.

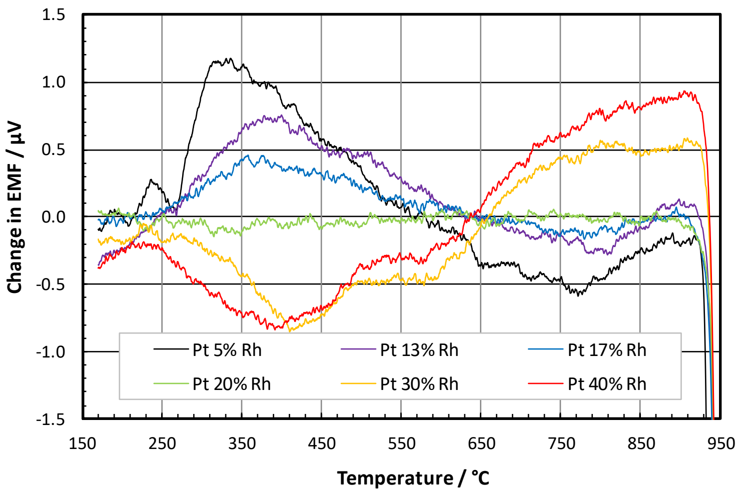

Figure 4: Changes in emf (t_m = 100 °C, t_r = 25 °C) in platinum-rhodium alloys as a function of temperature and alloy composition after 100 hours of exposure at the indicated temperature (Webster 2020).

At temperatures above 1100 °C, pure platinum thermoelements suffer from excessive grain growth (i.e., growth of the metal crystals), which substantially weakens the metal, sometimes resulting in breakage. For that reason, platinum-rhodium alloys are typically used for both thermoelements at high temperatures with a variety of different compositions (Bedford 1964, 1965, Webster *et al.* 2016, Pearce *et al.* 2014). Above 1100 °C, the migration of rhodium as a metallic vapour also occurs (Kim *et al.* 1998, Pearce *et al.* 2017, 2018) with similar effects to the diffusion of oxides at lower temperatures. Amongst the many possible platinum and rhodium alloy thermocouples, Types R, S, and B have become standardised and are the most used.

3.2.1. Types R and S

Both Type R and Type S have one pure platinum thermoelement and a platinum-rhodium alloy thermoelement (platinum-13% rhodium in Type R, and platinum-10% rhodium in Type S). The two types originate from slightly different manufacturing processes in the USA and UK when the thermocouples were developed (Quinn 1990) and are very similar in performance, with Type R being very slightly more stable, as suggested by the trends in Figure 4. In oxidising atmospheres, Types R and S may be used continuously at temperatures up to about 1300 °C and intermittently up to about 1700 °C (for 0.5 mm diameter wires). However, above 1100 °C or so, the pure platinum thermoelement suffers from grain growth making the wire fragile and susceptible to breakage in long-term installations (Burns *et al*. 1992b, 1992c).

The thermocouples are most reliable in clean oxidising atmospheres, but also work well in vacuum for short periods. Contamination is one of the main causes of drift, particularly in environments with metallic vapours or reducing agents. Contamination of the thermoelements by iron and other substances from the insulation is a significant cause of inhomogeneity in thermocouples used above 1200 °C. For example, the addition of 0.1 wt.% of Fe, Cr, Si, Ni, Rh or Cu to pure Pt changes its average Seebeck coefficient for the range 400 °C to 1100 °C by 1.7 µV/K, 0.75 µV/K, 0.64 µV/K, 0.33 µV/K, 0.21 µV/K, and 0.15 µV/K, respectively (Bentley 1998a).

Below 1100 °C, the dominant causes of drift are ordering and oxidation, as shown in Figure 4. Ordering effects cause errors of about +0.5 °C after 24 h exposure to 500 °C, whereas oxidation effects lead to errors of about −0.25 °C after 24 h exposure to 900 °C (Webster 2020). For the highest stability, the thermocouples should be annealed regularly to remove these effects, with annealing at 450 °C for thermocouples used below 800 °C, and annealing at 1100 °C and quenching for thermocouples used at higher temperatures (Jahan and Ballico 2003, 2010)

Cold work occurring when the wires are handled (e.g., while mounting them in a twin-bore insulator) causes a decrease in the Seebeck coefficient. For example, running the wires over a thumb nail to remove kinks may decrease the Seebeck coefficient by the equivalent of 1.4 °C at 1000 °C (Bentley 1998a). A one-hour anneal at 1100 °C or above (see Section. 4.8) will remove much of this cold work.

Rapid cooling (‘quenching’) from temperatures above 700 °C or so causes the equilibrium levels of lattice vacancies and other defects that are present at these high temperatures to be ‘frozen in’ (Bentley 1998a). The Seebeck coefficient is then lower until the next time the thermocouple is used above 250 °C to 500 °C, where the thermal motion of atoms is high enough for the crystal lattice to slowly relax back to its ‘low temperature’ equilibrium state and restore the Seebeck coefficient. Annealing at these temperatures may also cause a slight increase in Seebeck coefficient due to ordering (Webster 2015b).

The wires used to construct laboratory standard Type R and Type S thermocouples should be at least 0.35 mm in diameter, preferably 0.5 mm, and long enough to run in a continuous length from the measuring junction to the reference junction. Thinner wires are prone to damage during unsheathed electrical annealing at high temperatures (Section 4.8), with changes in rhodium concentration and the introduction of inhomogeneity during reassembly. Thicker wires are easier to manage and are better performing but are more expensive and can alter junction temperatures by conducting heat to or from the junction area if the isothermal zone around the junction is small.

3.2.2. Type B

Type B thermocouples share most of the properties of Types R and S thermocouples but have a greater ability to withstand long service at temperatures above 1100 °C due to improved mechanical strength, but at the expense of a poorer stability. Type B can be used continuously up to about 1500 °C and intermittently up to about 1820 °C. The use of alloys for both thermoelements also makes these thermocouples less affected by rhodium transfer (Bentley 1998a, Burns and Gallagher 1966), and slightly less sensitive to metal contamination, than Types R or S.

The effects of ordering and oxidation in the two thermoelements (see Figure 4) have opposite signs, so the overall effects are much greater and the thermocouples less repeatable than Types R and S. Note too, ordering and oxidation occur at some point along the thermoelements for all temperatures above 1100 °C, so affect all thermocouple measurements at elevated temperatures.

Type B has a very low Seebeck coefficient at low temperatures, so is rarely used below 500 °C. The very low output at low temperatures makes the thermocouple insensitive to the reference junction temperature, and in some applications, knowledge of the reference junction temperature is unnecessary, although care must be taken to ensure that the temperatures of the two thermoelements at the reference junction are the same.

3.2.3. Types A and C

Of the thermocouples suitable for use above 1750 °C, those using tungsten-rhenium alloys have been the most studied (Burns and Hurst 1972, Droege *et al.* 1972, Glawe and Szaniszlo 1972, Morice and Devin 2002). All tungsten-rhenium thermocouples are very susceptible to oxidation, and are almost exclusively used in vacuum, inert, or reducing (dry hydrogen) atmospheres. They are also susceptible to rapid drift in the presence of neutron radiation due to the transmutation of rhenium (see Section 5.2.5).

There are several tungsten-rhenium thermocouples in use, with minor variations in alloy composition: W-5%Re / W-26%Re, W-3%Re / W-25%Re, W / W-26%Re, and W-5%Re / W-20%Re are common. All have a similar performance, except that pure tungsten thermoelements are difficult to manufacture and are prone to embrittlement. The W-5%Re / W-26%Re thermocouple (Type C) and the W-5%Re / W-20%Re thermocouple (Type A) were recently adopted by the IEC 60584-2013, so are the preferred forms.

Tungsten becomes very brittle after it is heated above its recrystallisation temperature (1200 °C), so to improve the ductility of the low rhenium alloyed wires, small amounts of K, Si and Al compounds are usually added to the alloy (Burns and Hurst 1972). The negative thermoelements contain enough rhenium for embrittlement to be less of a problem. The rhenium concentrations are nominal values only – the compositions are such that matched pairs of thermoelements comply with reference tables within specified limits (Burns and Hurst 1972), so thermoelements from different sources should not be mixed.

Insulators used with W-Re thermocouples include:

- Al_2O_3 up to 1700 °C (Glawe and Szaniszlo 1972);
- MgO up to 1700 °C;
- BeO high purity and degassed (Burns and Hurst 1972, Morice and Devin 2002);
- HfO_2 (Morice and Devin 2002);
- ThO_2 and Y_2O_3 (Droege *et al.* 1972) for higher temperatures.

Elliot *et al.* (2014) give a good overview of the compatibility of different materials with tungsten-rhenium thermocouples at high temperatures. Metal sheaths of molybdenum (Droege e*t al.* 1972, Morice and Devin 2002), tantalum (Burns and Hurst 1972, Morice and Devin 2002), and W-26%Re (Asamoto and Novak 1967) have been used. Note that molybdenum is volatile (Droege *et al.* 1972). The reactivity of the sheath with graphite should also be borne in mind if the furnace contains graphite (Morice and Devin 2002).

Type A and C thermocouples operated without a sheath (bare wire) show an initial increase in Seebeck coefficient that stabilises after about 1 h at 1900 °C. The magnitude of the change is 0.1 % to 1 % (typically 0.2 %) at 1800 °C and is probably due to relief of cold work in the positive thermoelement. In vacuum, there is a continual decrease in Seebeck coefficient due to the preferential loss of Re. In high-purity degassed BeO insulators in an argon atmosphere, the thermocouple voltage at 1800 °C increases linearly at a rate equivalent to about 2.6 mK/h. The BeO must be of the highest purity and degassed, otherwise loss of tungsten from the wires is likely (Burns and Hurst 1972).

3.3. Pure noble-metal thermocouples

While noble-metal alloy thermoelements provide a high degree of flexibility and reliability in different environments, especially high temperatures, their performance is limited by the inhomogeneity problems characteristic of all alloy thermoelements, particularly ordering and oxidation effects. Pure-element thermocouples do not suffer from these effects, so are capable of higher accuracy (Kinzie 1973, Bentley 1998b). Of the many possible pairs, the gold-platinum and the platinum-palladium thermocouples are readily available and offer improved stability, repeatability, and homogeneity compared to alloyed noble-metal thermocouples.

3.3.1. Gold/Platinum

The Au/Pt thermocouple is, in principle, the most accurate thermocouple available and was one of the earliest of the pure-element thermocouples investigated (Sirota 1959). Research completed during the development of the thermocouple (McLaren and Murdock 1987, Burns *et al.* 1992a, Gotoh *et al.* 1991, 1997, 2003, 2006, Ripple and Burns 1998, 2005, Bentley 2001a) showed that carefully constructed Au/Pt thermocouples were repeatable at the level of about 10 mK to 20 mK at 1000 °C, perhaps a factor of 20 better than the best Type R or S thermocouples. However, that research used gold thermoelements at least 99.999 % pure, and it is now difficult to obtain gold and platinum wire of the same purity to attain such low uncertainties. Thermocouples with thermoelements of lower purity typically exhibit larger deviations from the reference function (more than 0.2 K at the freezing point of silver) accompanied by larger inhomogeneities and increased measurement uncertainties, perhaps as large as 100 mK (Edler 2015, Coleman 2015). On the other hand, new Au/Pt thermocouples with low deviations from the reference function (< 0.1 K at the silver point) can show low uncertainties of about 20 mK up to 961°C (Ballico and Jahan 2013, Kim *et al.* 2008).

Au/Pt thermocouples are limited by the melting point of gold to temperatures below 1000 °C, and considerable care is required to achieve low uncertainties. Firstly, a high-purity insulator is essential, especially at higher temperatures. Secondly, several measures are required to minimise strain caused by differential thermal expansion. In the temperature range from 0 °C to 1000 °C, the thermal expansion coefficients are about $(14 \text{ to } 22) \times 10^{-6}\ \text{K}^{-1}$ for gold, $(9 \text{ to } 12) \times 10^{-6}\ \text{K}^{-1}$ for platinum, and $(5 \text{ to } 10) \times 10^{-6}\ \text{K}^{-1}$ for alumina (Bentley 1998a, Gotoh and Oikawa 2006, Jahan and Ballico 2007). To eliminate strain induced by the expansion of the individual thermoelements, a fine-wire bridge or stress-relieving coil of a few turns of thin platinum wire (0.1 mm diameter) is usually inserted at the measuring junction to allow the gold wire to expand more freely relative to the platinum wire. To eliminate strain induced by differential expansion between the insulators and the wires, the insulator bore diameter should be larger than typically used for platinum-rhodium thermocouples (> 1 mm for 0.5 mm wires) to allow the wires to move freely.

Because of the low strength of gold wire at high temperatures, bare-wire electrical annealing is not practicable. Instead, the wire should be inserted into a dedicated alumina or silica insulator and annealed in a horizontal tube furnace at 1000 °C for 10 h. Longer annealing times may be required for lower purity gold, e.g., 99.99 % instead of 99.999 % (Bentley 1998a). For the Pt wire, a 10 h bare-wire electrical anneal at 1300 °C is suitable (as for Pt-Rh thermocouples). To relieve stresses induced during assembly, a 0.5 h to 1 h furnace anneal at 900 °C to 1000 °C is useful. A final vacancy-removing anneal at 450 °C may not be necessary (Bentley 2001a).

3.3.2. Platinum/Palladium

The Pt/Pd thermocouple is another elemental thermocouple that outperforms Pt-Rh alloy types above 1100 °C and up to 1500 °C, with repeatabilities of about 100 mK (Burns *et al*. 1998, Bentley 1998b, Burns and Ripple 1997, Bentley 2001b, Burns and Ripple 2002, Hill 2002, Edler *et al.* 2008, Pearce *et al.* 2009, Abdelaziz *et al.* 2004, Ongrai 2010). Palladium undergoes reversible changes in Seebeck coefficient in the range 550 °C to 800 °C, probably due to oxidation of the palladium (Hill 2002, Ohm and Hill 2010), but the Seebeck coefficient recovers within 15 minutes above 900 °C. The apparent direction of the change seems to depend on the temperature at which the wire is thermoelectrically scanned, with a more negative Seebeck coefficient observed when scanned below 700 °C (i.e., a more positive net coefficient for a Pt/Pd thermocouple), and a more positive coefficient when scanned above 800 °C (Bentley 2001b). The change in Seebeck coefficient causes the emf of a Pt/Pd thermocouple (initially quenched from 1000 °C) to increase by the equivalent of 0.15 °C at 250 °C after 115 h at 700 °C (Bentley 2001b, Hill 2002). This is comparable to the decrease in the emf of a Type S thermocouple (due to oxidation of Rh in the Pt-10%Rh leg), equivalent to 0.15 °C at 250 °C after 100 h at 800 °C (Bentley and Jones 1980). Palladium is also known to exhibit an increase in porosity and adsorption of oxygen at elevated temperatures, which may be linked to the observed changes between 550 °C to 800 °C (Ohm and Hill 2010). Irreversible changes in palladium at temperatures beyond 900 °C were found to be small compared to reversible changes (Bentley 2001b).

The palladium wire should not contact silica-based refractories, as they may form a Pd-Si eutectic with a melting temperature of 816 °C, weakening the wire and risking breakage (Edler and Lehmann 2005). The thermal expansion coefficient of palladium, (11 to 17) × 10^{-6} K^{-1} in the range from 0 to 1000 °C, is closer to that of platinum and of gold; however, a stress-relieving coil at the measurement junction is often helpful.

The palladium wire is usually annealed in the same way as the platinum wire (see Section 4.8). Prior to assembly, the wire is given an electrical anneal at 1300 °C for 10 h. Then the assembled thermocouple is annealed at 1000 °C to 1100 °C for 1 h to 50 h (Bentley 2001b, Burns and Ripple 2002). As for Au/Pt, the necessity of a vacancy anneal (near 500 °C) has not been established but, almost certainly, a vacancy anneal leaves the thermocouple in its most repeatable state.

There is some variability in the Seebeck coefficient for palladium due to the difficulty of obtaining sufficiently pure wire (99.99 % is the best commonly available), so that inhomogeneities due to impurities seem to be the major source of uncertainty. The species of impurities also appear to have a significant effect (Astrua *et al.* 2006, 2008). These factors are compounded by a lack of research on the ideal annealing time and temperature. Generally, the less pure the wire, the longer the annealing period required to establish stability. Kim *et al.* (2008) have suggested that an annealing time of 200 h may be required at 1000 °C to achieve satisfactory stability with silver-point measurements.

4. Construction and installation

The assembly of thermocouples requires knowledge and care, especially for less common applications, and usually it is best to order the thermocouples fully assembled according to specifications and application. An exception is for reference thermocouples, which can often be assembled from components of a higher quality than those supplied as a commercial item.

A complete thermocouple assembly typically consists of:

- a sensing element assembly, including two thermoelectrically dissimilar thermoelements,
- separated by an electrical insulator,
- joined at one end to form a measuring junction,
- which may be encased in a metal or ceramic protection tube,
- with lead wires or extension or compensating leads,
- and a reference junction, possibly including copper leads or a plug.

For best accuracy, all the components of the assembly, including the thermoelements, the insulation, and the sheath, must be carefully chosen after considering the compatibility with the thermal, mechanical, chemical, and nuclear environment. Heat treatment during and periodically after assembly may also be necessary.

Three broad categories of thermocouple assemblies can be distinguished, depending on the nature of the insulating materials and sheath (see Figure 5):

- Inflexible hard-fired multi-bore ceramic insulation: These tend to be necessary for use at high temperatures and are commonly used for reference thermocouples (those used to calibrate other thermometers) because of the low risk of contamination from the sheath. Each of the thermoelements is a continuous single strand of wire.
- Mineral-insulated metal-sheathed (MIMS) thermocouples: These are the most versatile assemblies as they are flexible and provide protection from oxidation and environmental contamination at high temperatures and from moisture at low temperatures. Stainless steel and Inconel sheaths are the most common, but more exotic sheaths are available for use at other temperatures. Where open leads (as in Figure 5) are used, the lead wires to the reference junction are most commonly multi-strand extension or compensating leads (see Section. 4.3). More commonly, the assembly is terminated at a plug, either at the end of the extension leads or at the end of the metal sheath.
- Flexible plastic or woven fibre insulation materials: Plastics are commonly used at low temperatures (< 250 °C), while glass and ceramic fibre are used at higher temperatures. Assemblies using woven ceramic fibre may also have a woven metal braid to protect the fragile ceramic fibre.

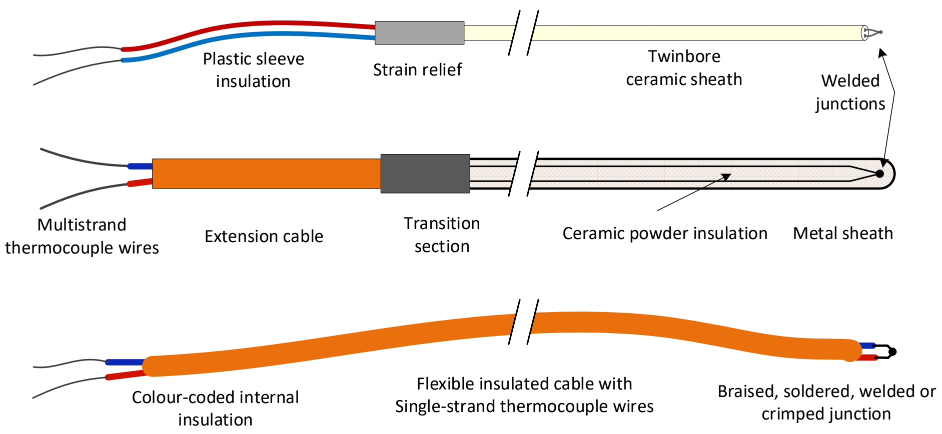

Figure 5. Examples of different thermocouple assemblies. Upper: a laboratory standard thermocouple using a hard-fired twin-bore ceramic sheath; middle: a mineral insulated metal sheathed (MIMS) assembly with extension cable; lower: a fully flexible plastic-insulated assembly.

4.1. Measuring junction

The sole purpose of the measuring junction is to ensure a reliable electrical connection between the two thermoelements. Common methods for forming the junction include electrical and gas welding, brazing, soldering, twisting, crimping, and clamping. Noble-metal thermocouple junctions are often welded using a small oxy-hydrogen torch, which produces mostly water as a combustion product, to minimise contamination of wire in the vicinity of the junction.

Always, some parts of the wire close to the junction will be damaged, either through alloying of the two thermoelements, mechanical damage, or contamination with solder or braze. However, so long as the junction and the damaged wire adjacent to the junction are isothermal in use, they do not generate a voltage and it does not matter how the junction is made. The only requirement is that the junction has the mechanical strength to maintain a reliable electrical connection at all operating temperatures.

If the measuring junction is to be situated near a temperature gradient during use, care should be taken to minimise the size of the measuring junction and to minimise contamination of the adjacent regions of the thermoelements. Such concerns may arise when measuring surface temperatures or during use at shallow immersion. MIMS thermocouples, depending on how the measuring junction is formed and encapsulated, can exhibit extensive damage, often extending many centimetres from the tip of the sheath.

4.2. Thermoelements

The properties of commonly used thermoelements are summarised in Section 3. The thermoelement materials should be chosen to be compatible with the temperature range and environment in use. The wire diameter should be determined as a compromise between thermoelectric stability over the temperature range of use (favouring thicker wires), and low thermal conduction to or from the measuring junction, cost, and flexibility (favouring thinner wires). The recommended upper-temperature limits for different wire diameters and base-metal thermoelements in closed-end protecting tubes are listed in Table 3.

The wires are usually annealed before and/or after assembly to optimise the stability of the Seebeck coefficient. Base-metal-thermocouple wire is often factory-annealed, and it may not be necessary to re-anneal before use. The annealing procedure depends on the characteristics of the thermoelements, and the proposed operating temperature (see Section 4.8).

Table 3: Recommended upper-temperature limits for thermoelements in closed-end ceramic protecting tubes (not applicable to MIMS thermocouples) (ASTM 1993).

	Diameter of thermoelement and recommended upper temperature (°C)					
Thermoelement	**0.25 mm**	**0.33 mm**	**0.51 mm**	**0.81 mm**	**1.63 mm**	**3.25 mm**
Iron	320	370	370	480	590	760
Constantan	430	430	430	540	650	870
Copper	150	200	200	260	370	na
Chromel, Alumel, Nicrosil, Nisil	760	870	870	980	1090	1260

4.3. Extension and compensating leads

High-temperature applications often require large diameter thermoelements (several millimetres in diameter) that are not appropriate for connecting to thermocouple instrumentation some distance away. For this reason, flexible, multi-strand ‘extension’ cables are available. These are usually made from materials like the thermocouple wires (perhaps of a lower grade) but suited for a limited temperature range of 0 °C to 100 °C (IEC 60584-3 2007).

For noble-metal thermocouples, the cost of long leads is an additional concern, and ‘compensating’ extension cable is available. These multi-strand cables are made from low-cost copper alloys that mimic the output of the Type R and S thermocouples over a limited temperature range. Although the compensating pair mimics the Seebeck coefficient of the noble-metal pair, the individual compensating leads are different from the individual noble-metal thermoelements. It is important that the thermocouple and the compensating leads are joined in the same isothermal zone, in the same way that copper leads are connected in an isothermal zone at the reference junction.

One of the risks of using extension leads, especially when they are at a similar temperature throughout their length, is that one or both ends of the cable are connected with the wrong polarity and the fault goes unnoticed. It is also possible that the wrong type of extension lead may be used and go unnoticed, e.g., Type T extension leads with a Type K thermocouple. A useful check is to use a hot air gun or hair dryer to sequentially warm up each join in the thermocouple cables (except the measuring junction), whether buried within a head-shell, or the end of a probe assembly, or within plugs and connectors. If the polarity of all connections is correct, then the reading on the thermocouple indicator will not change as a join is heated. If the reading is not sufficiently stable for a discerning test, put the measuring junction of the thermocouple in an ice point. It should continue to read close to 0 °C as the joins are heated.

4.4. Connectors

Because the leads transmitting the signal to the instrumentation are an integral part of the sensor and contribute to the thermoelectric voltage, care must be taken to ensure that all wires between the measuring and reference junctions are in a homogeneous state. Thermocouple plugs, sockets, and terminal blocks manufactured with matching thermoelectric materials (Figure 6) are an important aid and are available for all the letter-designated thermocouples. For base-metal thermocouples, the connectors are made using the appropriate base metals and alloys. The connectors for the Type R and S thermocouples are identical and use two copper alloys that together mimic the output of the Type R and S thermocouples, so should be kept isothermal. For Type B thermocouples, copper-copper plugs and connectors of the same dimensions as the other plugs and sockets are available. Most of the connectors use plastics rated for temperatures above 100 °C.

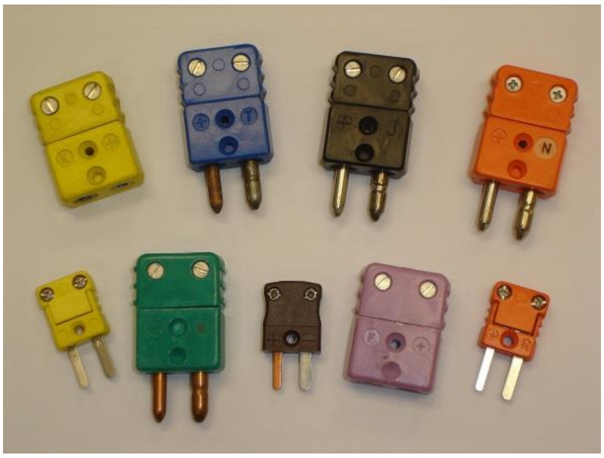

Figure 6: Thermocouple plugs and sockets, made of the appropriate thermocouple materials and colour coded, are readily available.

The connectors are colour coded according to the thermocouple type and are available in two sizes. More exotic connectors are also available for use with vacuum chambers and autoclaves. Unfortunately, the colours for the different plugs and sockets have not been harmonised amongst the different documentary standards, so care is required if the source of plugs and sockets is uncertain. If there is any doubt about the suitability or connections to the connectors, the completed circuit should be checked using a heat gun, as described in Section 4.3. As with extension leads, all connectors and plugs should be isothermal in use and maintained at temperatures below 100 °C, and ideally below 50 °C so they are touchable by hand.

4.5. Insulator and sheath

The materials that electrically insulate, separate, protect, and mechanically support the thermoelements are an important part of a thermocouple. Chemical compatibility of the insulator with the thermoelements is particularly important at high temperatures, and especially so for noble-metal thermocouples. For lower temperatures, enamels (100 °C), plastics (e.g., PTFE: 260 °C), and fibreglass (500 °C) may be used. Above about 500 °C, the insulator is usually a refractory ceramic, usable to high temperatures and providing high insulation resistance. Woven ceramic fibre insulation is also available, but it tends to be fragile and not suited to installations requiring repeated movement of the cable or exposed to high vibration.

The choice of refractory ceramic depends upon the operating conditions and the required lifespan of the thermocouple. While there is no general rule covering every installation, there are general points to consider:

- the likelihood of chemical reactions between the thermoelements and ceramic increases with increasing temperature;
- the electrical resistivity of ceramic decreases exponentially with increasing temperature (much like a thermistor); and
- some insulators can melt or undergo changes in crystal structure at elevated temperatures.

The thermoelements of mineral-insulated metal-sheathed (MIMS) thermocouples are insulated by high-purity compacted refractory oxide powder. Magnesia, the most used refractory, absorbs moisture from the atmosphere and, if the sheath is not welded satisfactorily at the tip and not well-sealed at the transition to the extension cable or plug, moisture will slowly be absorbed and reduce the insulation resistance. The moisture may also encourage corrosion of the thermoelements or the sheath. The presence of moisture can be checked using an insulation tester. For thermocouples with outside diameters larger than 1.5 mm, 500 V insulation testers may be used, and at room temperature the resistance should be greater than 100 MΩ. For finer thermocouples, low-voltage insulation testers (< 100 V) should be used to prevent dielectric breakdown and damage of the thermocouple. Typically, the maximum working temperature of MIMS thermocouples is not limited by the insulation material but by the properties of the metal sheaths (ASTM 1993).

Base-metal thermocouples are generally less susceptible to contamination than noble-metal thermocouples, and various forms of stainless steel (800 °C) or Ni-Cr alloys, such as Inconel® (1150 °C), are often used for sheaths. Most manufacturers cite temperature limits for stainless steels and Inconel® that are the limits for sheath survival; in long-term installations, the maximum temperature should be 200 °C below these specified limits (e.g., 600 °C for steel and 800 °C for Inconel®) to slow the migration of contaminants from the sheath. The stability of MIMS thermocouples at high temperatures is significantly improved if the sheath material is chemically compatible with the thermoelements and if all components have a similar thermal expansion coefficient. An example of such an integrally-designed MIMS (ID-MIMS) sheath is Type K or Type N sheathed in Nicrosil®, Omegaclad®, Pyrosil®, or one of the Nicrobel® alloys (Bentley 1998a).

Noble-metal thermocouples are usually assembled in a single high-purity twin-bore ceramic insulator, though thermocouples with platinum-rhodium alloy MIMS sheaths are also available. The ceramic insulators, which may be up to 1.2 m long, should be baked for several hours at 1200 °C in air before assembly to drive off contaminants or bind them to the surface of the ceramic. For oxidising atmospheres, the choice of refractory ceramic is wide. However, under reducing conditions or in vacuum, siliceous refractories should not be used – in contact with platinum they are reduced, releasing elemental silicon, which embrittles the wire. In the worst case, a platinum-silicon eutectic forms and melts when the temperature exceeds the eutectic point at 816 °C, and the thermocouple fails.

Pure magnesia is one of the more stable refractories and can be used under inert conditions. Under reducing conditions, it has been found occasionally to be reduced and alloyed with platinum. Beryllia (Darling and Selman 1972), thoria, and hafnia (Zysk and Robertson 1972) are good in conjunction with platinum at higher temperatures, but they are more expensive. Also, beryllia is toxic and thoria slightly radioactive, so appropriate caution should be exercised.

Impurities in the insulator can produce changes in the Seebeck coefficient of noble-metal thermocouples. For Pt-Rh thermocouples, the largest effect is caused by iron and can be minimised using high-purity alumina or beryllia. The effect is smaller in an oxidising atmosphere than in vacuum or inert atmospheres (Bentley 1998a).

Table 4. Properties of some electrical insulators (Bentley 1998a, ASTM 1993).

Refractory Oxides				
Material	**Composition**	**Maximum temperature (°C)**	**Thermal stress resistance**	**Common uses**
Sintered stabilised zirconia	92% ZrO_2, 4% HfO_2, 4% CaO	2200	fair – good	high temperature
Sapphire crystal	99.9% Al_2O_3	1950	very good	any
Sintered hafnia	99.8% HfO_2	2400	fair – good	high temperature base metal
Sintered beryllia	99.8% BeO	1900 to 2200	excellent	high temperature
Sintered magnesia	99.8% MgO	2200	fair – poor	any
Sintered alumina	99.8% Al_2O_3	1800	good	any
Sintered mullite	72% Al_2O_3, 28% SiO_2	1600	good	base metal
High alumina porcelain	90%-95% Al_2O_3, 4%-7% SiO_2	1500	very good	base and noble metal below 1100 °C
Mullite porcelain	70% Al_2O_3, 27% SiO_2	1400	good	base metal
Silica glass	99.8% SiO_2	1100	excellent	base metal
Other insulators				
Material	**Minimum temperature (°C)**	**Maximum temperature (°C)**	**Moisture resistance**	**Abrasion resistance**
Glass fibre		480	poor	fair
Teflon® PTFE	–70	260	excellent	good
Nylon®	–60	125	poor	good
Polyvinyl chloride	–35	85	excellent	good

For laboratory standard or reference thermocouples, the thermoelements are usually mounted in a single twin-bore insulator of 3 mm to 4 mm outside diameter and 500 mm to 1000 mm in length, i.e., sufficient to extend from the measuring junction to the outside of the furnace. The bores should be large enough to allow unhindered movement of the thermoelements when driven by differential thermal expansion and contraction, especially for softer wires such as gold and platinum. With platinum-rhodium thermocouples used above 500 °C, there is a risk of rhodium transfer between the wires, and the use of multiple sections of ceramic insulator is strongly discouraged (Bentley 1998a). The twin-bore insulator is usually enclosed in a close-fitting and closed-end ceramic protection tube, to further minimise contamination. Outside of the hot zone, from the end of the twin-bore insulator to the reference junction, the thermoelements are insulated with a flexible material such as plastic or fibreglass. The flexible insulators are often attached to the ceramic tube by a heat-shrinkable sleeve for strain relief or assembled in a protective head (see Figure 5).

Table 4 summarises the key properties of electrical insulators used for thermocouples.

4.6. Reference junction

The reference junction must be isothermal and kept at a stable known temperature. For laboratory standard thermocouples, this can be accomplished by immersing the reference junction in an ice-point, typically a vacuum flask containing a mixture of shaved ice and distilled water (0 °C). It is relatively easy to prepare an ice-point to an accuracy of ±0.01 °C or better (Edler *et al.* 2016). The thermoelements are typically connected to pure copper wires (~ 0.25 mm diameter) by twisting or soldering and inserted into closed-end tubes that are in turn inserted into the ice–water mixture. The thermoelement-to-copper junctions should be placed at sufficient depth in the ice (~ 200 mm) to ensure negligible immersion errors. Automatic ice-point devices using Peltier cooling elements are convenient but are often too shallow for high-accuracy applications.

Many thermocouple measuring instruments feature automatic reference junction compensation (a.k.a. cold-junction compensation), where the reference junction temperature is maintained near ambient temperature and the temperature is measured using a suitable sensor, such as a thermistor or platinum resistance thermometer. This is discussed in detail in the next section.

4.7. Instrumentation

4.7.1. Reference junction compensation

Superficially, the measurement of a thermocouple voltage appears to require only an appropriate digital voltmeter. However, the measurement is complicated by the possible need for reference junction compensation. Equation (5) shows that the measured voltage from the thermocouple is ideally

$$V_{\mathrm{meas}} = V_{\mathrm{AB}}(t_{\mathrm{m}}) - V_{\mathrm{AB}}(t_{\mathrm{r}}) , \qquad (8)$$

where $V_{\mathrm{AB}}(t)$ is the temperature–voltage relation defined by the reference function for the thermocouple pair AB, t_{m} is the temperature of the measuring junction and t_{r} is the temperature of the reference junction. To infer a value for the measuring junction temperature from the measured voltage, we must first add the voltage $V_{\mathrm{AB}}(t_{\mathrm{r}})$ to the measured voltage, and then use the reference function (or its inverse) to convert that voltage to temperature. Three different situations can be recognised.

Reference junction at 0 °C: If the reference junction for the thermocouple is maintained at 0 °C, either with the use of an ice point or a temperature-controlled zone maintained at 0 °C, then $V_{\mathrm{AB}}(t_{\mathrm{r}}) = 0$ by definition, so $V_{\mathrm{meas}} = V_{\mathrm{AB}}(t_{\mathrm{m}})$ and the measured voltage can be converted directly to temperature. The use of an ice point to control the reference junction temperature is preferred for the highest-accuracy applications.

Analogue compensation: When the reference junction is not at 0 °C, then the voltage $V_{AB}(t_r)$ must be added to the thermocouple voltage. There are many electronic circuits, including readily available integrated circuits, that measure the reference junction temperature and produce a voltage that closely approximates the $V_{AB}(t_r)$ relation for a particular thermocouple type. These circuits are connected so that the compensating voltage is added to the thermocouple voltage, and the total voltage can then be measured by the DVM and converted to temperature.

Analogue compensation is common in hand-held thermocouple indicators and low-cost instruments. Also, several manufacturers make small battery-powered cold-junction compensators, usually colour coded like the thermocouple plugs and connectors, to interface thermocouples to any DVM. To work effectively, the thermometer of the compensation circuit must be at the same temperature as the thermocouple terminals, which can be difficult to achieve when the connecting terminals are on the outside of the instrument. The best solution is to have a male plug on the thermocouple and a female plug on the indicator or compensator. Depending on the thermal behaviour of the device, analogue compensation may exhibit errors of a couple of degrees when the ambient temperature is changed quickly, for example when an instrument is handled, or withdrawn from clothing close to the body, or when taken into a cool store. The electronic circuits also tend to be less accurate when the ambient temperature is very much different from the nominal operating temperature of 20 °C to 25 °C or so.

Digital compensation: Instead of adding the compensating voltage directly to the measured voltage, it is possible to first measure and convert the thermocouple voltage to a digital number, and then add a digital number corresponding to $V_{AB}(t_r)$ according to the measured temperature of the reference junction. This approach is usually more accurate than the analogue compensation method and is typical of bench-top thermometers and high-accuracy instruments. The approach is essential for indicators that work with multiple thermocouple types because the compensating voltage $V_{AB}(t_r)$ is different for every thermocouple type, something easily accommodated in software.

4.7.2. Thermocouple calibrators

There are a wide range of thermocouple calibrators available. The calibrator is a voltage source that mimics the thermocouple, and typically can be programmed to produce a voltage corresponding to any thermocouple type, for any temperature (sometimes for both degrees Fahrenheit and degrees Celsius), and with and without cold-junction compensation. While they are very useful for calibrating the indicators and for carrying out diagnostic work, by themselves they cannot make a thermocouple measurement traceable – that requires both the thermocouple and the indicator to be calibrated (see Section 6 and Part II of this Guide (Edler *et al.* 2021).

4.7.3. Digital voltmeter

The requirements of the digital voltmeter (DVM), whether an independent meter or included in a fully integrated thermocouple indicator, are not particularly onerous. The maximum voltages from all the letter designated thermocouples are between 10 mV and 100 mV, so comfortably fall in a single voltage range on most DVMs. For low-cost instrumentation with base-metal thermocouples, an electronic resolution of 10 μV (0.01% of full scale), corresponding to a resolution of about 0.3 °C, is often satisfactory.

Greater resolution and accuracy are required for applications using noble-metal thermocouples, in part because of the lower Seebeck coefficients and in part because of the greater accuracy achievable. In these cases, the resolution of the DVM should be 1 μV or better (corresponding to 0.001% of full scale and 0.1 °C resolution), and for high-accuracy laboratory work, 0.1 μV. These DVMs should also have good linearity and an autozero feature to eliminate any offset voltages.

4.7.4. Thermocouple scanners

Thermocouple scanners are indicating instruments that include the DVM, the reference junction, and a series of relays to allow connection of many different thermocouples to the measuring circuit. Usually, the scanners operate with different thermocouple types and use digital reference-junction compensation.

To work effectively, the enclosure containing the terminations to each thermocouple, the relays, the terminations for the copper lead wires to the DVM, and the thermometer measuring the reference junction temperature must all be at the same temperature. The temperature control of such a large volume is not as simple as for an indicator with a single thermocouple, so the measurement uncertainty with scanners is usually a little larger than with a single thermocouple. Where electromechanical relays are used, they are usually latching types to minimise the heat dissipated in the relay coils. Latching relays prevent the formation of large temperature gradients across the relay connections, which have a different composition from the thermoelements, and the resulting introduction of spurious emfs. With careful selection and operation of latching relays housed in a well-designed thermal enclosure, the spurious emfs can be kept below a few nanovolts. In a badly designed system, errors of 10 μV or more are likely. Care should be taken to place the scanner away from extraneous heat sources and drafts.

4.8. Annealing

All inhomogeneity effects occurring in thermocouples can be classified into two groups:

- Reversible effects: including cold work, ordering, vacancies, and oxidation (in noble metals only).
- Irreversible effects: all forms of contamination, whether due to the environment, the migration of alloy components between the thermoelements and the sheath, transmutation, and preferential oxidation. In base-metal thermocouples, all oxidation is irreversible.

Annealing is a heat-treatment process that erases the reversible inhomogeneity effects with the aim of restoring the thermocouple to a known, reproducible, and homogeneous state. Typically, the thermocouple is uniformly heated to a specific temperature for a period, and then allowed to cool to room temperature, either by quenching in air or more slowly under control.

Annealing may be used for two main purposes. Firstly, it places the thermocouple in a well-defined, readily accessible, and ideally homogeneous state for calibration. The thermocouple can later be easily annealed and restored to the same state to make the highest-accuracy measurements. With some base-metal thermocouples (specifically Types K and N), the erasure of reversible effects can be accomplished very quickly, usually with a few minutes of exposure at a temperature exceeding the recrystallisation temperature – about 650 °C in Types K and N (Bentley 1998a, Webster 2017c). With other thermocouples, especially heavily alloyed noble metal thermocouples, several hours of annealing is usually required.

Annealing may also be used to precondition a thermocouple to reduce the extent and duration of the drift that occurs when the thermocouple is first installed (Webster 2017b).

4.8.1. Noble-metal thermocouples

There are three recognised annealing processes used for noble-metal thermocouples (Bentley 1998a, Guildner 1979, McLaren and Murdock 1979): high-temperature electric anneals in the range 1100 °C to 1450 °C; high-temperature furnace anneals between 1000 °C and 1100 °C; and low-temperature vacancy anneals between 450 °C and 700 °C.

Electrical annealing is accomplished by passing an electric current through the thermoelements to heat them to the required temperature. It is typically used for new thermocouple wire prior to assembly of the thermocouple and for heavily-used thermocouples with severe cold work (e.g., due to bending associated with a broken insulator). Direct contact between the wire and hands prior to annealing should be avoided to prevent contamination. Additionally, for used thermocouples, it is advisable to clean the thermocouples in dilute nitric acid prior to annealing to remove any surface contamination.

The main purpose of the electric anneal is to remove cold work and strain, but it may also evaporate or stabilise (oxidise) some types of impurities. For the same reason, cleaning in dilute nitric acid after the electrical anneal may also remove impurities driven to the outside surface and improve long-term stability.

For already assembled thermocouples, the junction is removed by clipping off the last few millimetres of the thermocouple. The wires are then withdrawn from the ceramic insulator and separately suspended from two electrodes in air. The electrodes for each end of the wire should be placed a short distance from each other to minimise the tension and stretching of the wire during the heating process. Note that a different current will be required for the two thermoelements so they must be treated sequentially or connected individually to separate power supplies and not connected in series or parallel. It is also important that platinum-rhodium alloy wire be annealed separately from that of platinum wire to prevent rhodium oxide contaminating the platinum thermoelement.

During annealing, the temperature of the thermoelements should be measured using a dual-wavelength radiation thermometer. When the thermocouples are fully annealed, the wires should glow uniformly with no obvious hot spots, and the wire should have a uniform temperature, within about 50 °C (Bentley 1998b).

The temperature for the electric annealing should be between 1100 °C and 1200 °C for pure platinum thermoelements and between 1400 °C and 1450 °C for platinum-rhodium alloy thermoelements. Usually, one to two hours is sufficient. Thermoelements with higher proportions of rhodium benefit from a higher annealing temperature and longer annealing periods, up to 10 hr for 40% rhodium thermoelements. However, be guided by the temperature and appearance of the wire. Excessive annealing exposes the wires to unnecessary oxidation and evaporation processes, which change the alloy composition.

Pure thermoelements should not be annealed for long periods or much above 1200 °C because they will be weakened mechanically due to grain growth. If the wire diameter is smaller than 0.35 mm, pure wires may not support their own weight under heating and may stretch or even break. Electrical annealing should not be applied to gold thermoelements, which melt at 1064 °C.

High-temperature furnace annealing at 1000 °C to 1100 °C is performed after the thermoelements have been reassembled into their insulators, for an hour or two, to remove cold work introduced during the reassembly. The furnace should be long enough to immerse almost the whole of the useful length of the thermocouple into the uniform temperature zone within the furnace (i.e., excluding the lead wires and the cold end of the insulator). Special care must be taken when annealing gold thermoelements (1000 °C max.).

A low-temperature furnace anneal at 450 °C to 700 °C for two hours eliminates vacancies frozen in during the cooling from 1100 °C and places the thermocouple in its most reproducible state, ready for calibration. For thermocouples used predominately below 800 °C, the thermocouples often exhibit greater stability if the vacancy anneal is extended to 16 to 24 hours. This preconditions the thermocouple by inducing ordering in the platinum-rhodium thermoelement, which then reduces subsequent drift in use (Jahan and Ballico 2007, Webster 2015b).

4.8.2. Base-metal thermocouples

Because of the greater magnitude of both irreversible effects and thermally induced inhomogeneity effects in base-metal thermocouples, it is not usual for them to be annealed. However, there are two types of annealing that may prove useful.

With base-metal thermocouples used below the temperatures where they oxidise significantly, annealing may be used to erase ordering and cold-work effects and to put the thermocouple in to its most reproducible state. In many cases, this will be close to its as-received state. For example, heating Type K thermocouples to 650 °C for as little as a few minutes erases any ordering effects, and the temperature is high enough to remove most cold work and low enough to avoid significant vacancy effects (Webster 2017d, 2017e).

Heat treatment may also be used to precondition base-metal thermocouples, by placing them in an ordered state to minimise the drift occurring immediately after the thermocouples are first installed. For example, annealing Type K thermocouples at 500 °C places the wire in a pre-ordered state and minimises further drift caused by ordering effects when they are operated at temperature below 500 °C (Wang and Star 1997, Kollie *et al.* 1975, Burley 1972). However, this ordered state differs from the usual ‘as received’ state of thermocouples, so may depart further than expected from the reference function. Calibration is necessary if improved accuracy is required, as well as improved stability.

4.9. Installation

To get the best performance from a thermocouple, it must be installed in accordance with the two guiding principles given in Section 1: all parts of the thermocouple must be either isothermal or homogeneous. Figure 7 gives an example of an industrial installation complying with these principles.

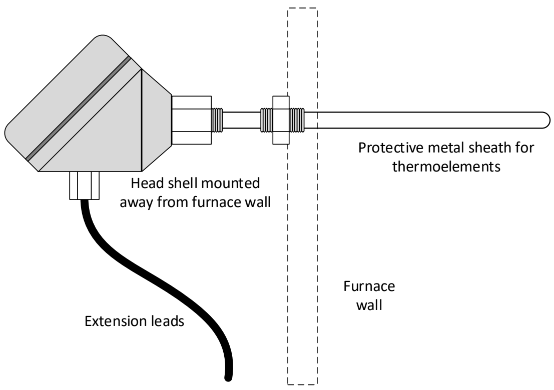

Figure 7: Typical industrial thermocouple installation.

Where thermoelements are exposed to temperature gradients, most often through a furnace or oven wall, they must be protected and maintained in a homogenous condition to ensure they generate the correct voltage. In Figure 7, the thermoelements are protected from the contaminating furnace environment and from mechanical damage by the inflexible stainless-steel sheath. Note especially that thermoelements are not bent, and the damaged parts at the measuring junction and the connections to the extension leads are located away from the furnace wall where the temperature gradient is located. Secondly, where the wire is inhomogeneous, it must be maintained in an isothermal environment. In Figure 7, the measuring junction is inserted deep into the furnace, and the connections between the thermoelements and the extension leads are maintained in the thermally conductive metal head shell mounted away from the furnace wall and sheltered from air drafts. The extension leads, including the connections in the head shell should be below 100 °C throughout their length to ensure they operate within their tolerance band. A useful practical guide is that the head shell and the extension leads (and all other nominally cool parts of the thermocouple circuit) should be touchable by hand, which, for metal parts, means the temperature is no higher than about 50 °C.

To emphasise the key aspects of thermocouple installation, Figures 8 and 9 show two further installation examples, one good and one bad. Figure 8 shows an example of a bad installation for the measurement of pipe temperature (e.g., steam pipe). The errors with this type of installation can be 10% or higher (e.g., the thermocouple indicates 90 °C when the pipe is at 100 °C). Unfortunately, this type of installation is recommended in some books and manufacturers' guides. It suffers from two problems. Firstly, heat conducted down the sheath of the thermocouple causes localised cooling of the pipe and even greater cooling of the measuring junction. Secondly, because of the heat flow, there is a temperature gradient over the junction of the thermocouple causing damaged wire there to generate a spurious voltage. Both effects cause errors.

Figure 9 shows a good installation for a pipe-temperature measurement. In this case, the area of pipe cooled by the heat loss down the thermocouple is away from the measuring junction. That is, the measuring junction is in an isothermal zone at the same temperature as the pipe. This ensures that the damaged wire at the junction does not generate any spurious voltages. If the thermocouple operates at temperatures below about 500 °C, the bend in the thermocouple where it exits the insulation should have a large radius to minimise the effects of cold work. At higher temperatures, any cold-worked regions due to bending will be rapidly annealed and are unlikely to affect the measurement (see Section 4.8).

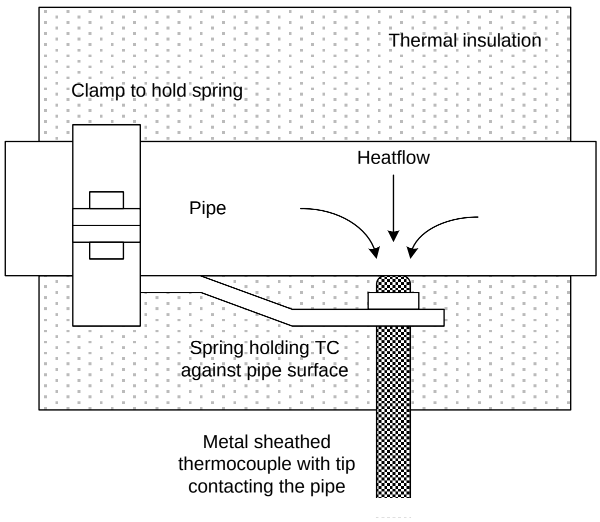

Figure 8: A poor thermocouple installation susceptible to poor thermal connection with the pipe and gradients across the measuring junction.

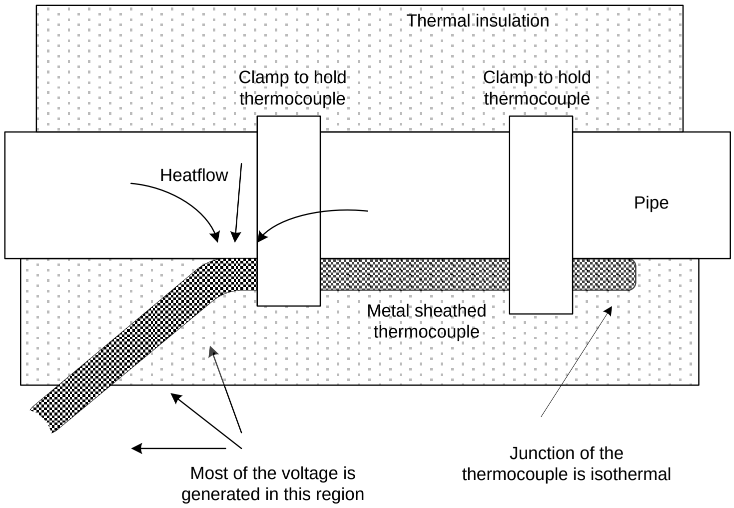

Figure 9: A good thermocouple installation that ensures good thermal connection between thermocouples and the pipe with no gradient over the junction.

5. Sources of Error

This section discusses the various sources of error that occur in thermocouple circuits with the aim of enabling users to recognise and fix problems that occur in practice.

5.1. Departures from reference function

Because the thermocouple type definitions are based on mathematical functions, the only requirement for a thermocouple to be recognised as a letter-designated type is that the voltage–temperature relation for the thermocouples lies within the specified tolerance band (Table 2). Typically, the voltage–temperature characteristic of a thermocouple meanders within the tolerance band and varies from batch to batch. In some cases, small changes in composition can lead to quite large differences over quite narrow temperature ranges. For example, magnetic phase changes in the Alumel thermoelement of Type K may cause variations as large as a few degrees in the range from room temperature to 250 °C.

In thermocouples where this error makes a large contribution to the measurement uncertainty, calibration of the thermocouple and the application of corrections to temperature readings will enable a useful reduction in the measurement uncertainty.

5.2. Thermoelectric inhomogeneity

Thermoelectric inhomogeneities are unwanted contributions to the thermocouple voltage caused by regions within the thermocouple wire where the Seebeck coefficient differs from the nominal or typical behaviour of the rest of the wire. The most common causes of inhomogeneity can be grouped as cold work and strain, vacancy effects, ordering effects, oxidation, and contamination, with most thermocouple types suffering from all effects to some degree. This section describes the origin of the effects, with examples, and gives advice on mitigation of the effects.

5.2.1. *Cold work and strain*

Cold work is any flexing, bending, or other form of mechanical damage that introduces major defects into the crystalline structure of the metal. Strain or elastic deformation of the crystal lattice through stretching or compression also causes smaller temporary changes. The magnitude of the effects of cold work and strain vary amongst different thermocouple materials. One of the most sensitive materials is the Chromel thermoelement of Types K and E, while the Alumel and copper thermoelements used in Types K and T are two of the least sensitive. Figure 10 shows the effect of cold work on a sample of Chromel wire. The left-hand side of the plot shows the Seebeck coefficient for the wire in its ‘as received’ state, which in this case is about 0.6% higher than the value defined by the reference function. After the wire is wound around a mandrel and straightened (right-hand side of the plot), the Seebeck coefficient has changed more than −1.2% (Greenen and Webster 2017). This example shows the importance of protecting thermocouple wires from mechanical damage where they are exposed to temperature gradients. Unfortunately, it is common to find wires bent where they exit furnace walls, exactly where the cold work will cause the greatest errors. A single sharp bend in a Type K thermocouple placed at the peak of the temperature gradient, e.g., at a furnace wall or the surface of a calibration bath, can induce a shift in the temperature reading of 2 °C or more.

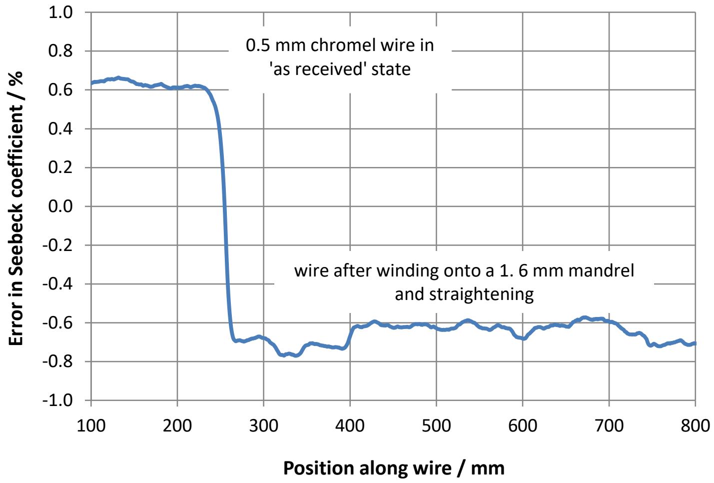

Figure 10: The effect of cold work on a Chromel thermoelement of Type K.

If thermocouples must be bent, the bend should be located away from any temperature gradients, preferably in an isothermal zone, and with the largest practicable bending radius. Thermocouple installations should also be designed to minimise strain on the wire while in service; for example, use in a horizontal orientation may be preferable to use in a vertical orientation. Most damage due to cold work and strain can be repaired by annealing (see Section 4.8).

5.2.2. *Vacancy effects*

Vacancies are empty sites in a crystal lattice where atoms should be located. They are created by the thermal motion of the atoms causing some to jump out of place, and occasionally, to jump back into place. Vacancy formation is a natural phenomenon that occurs in all solids and increases exponentially with rising temperature. Although vacancies are normal and contribute to the Seebeck coefficient of all thermocouples, if a thermocouple is exposed to high temperatures and cooled rapidly to low temperatures, a fraction of the vacancies generated at the high temperature may be frozen into the crystal lattice, causing an anomalous Seebeck coefficient at lower temperatures. Figure 11 shows the Seebeck coefficient of a length of Type S thermocouple in two different thermoelectric states. The lower (blue) curve shows the effect of annealing at 1100 °C followed by withdrawal from the furnace and natural cooling to room temperature. The upper (red) plot is the same thermocouple after it was annealed at 450 °C for 24 hours to achieve a low vacancy concentration. The difference between the Seebeck coefficients is about 0.1 %. Vacancies in most thermocouples can be removed by annealing at temperature around 450 °C to 550 °C (see Section 4.8). Higher annealing temperatures are required for more highly alloyed materials, especially those used at high temperatures.

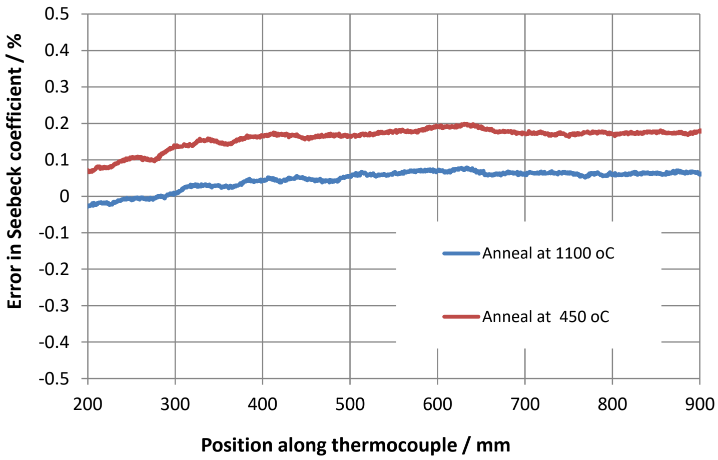

Figure 11: Effect of vacancies on the Seebeck coefficient of a Type S thermocouple.

5.2.3. Ordering effects

Ordering effects, which occur when the atoms in the crystalline structures move about and reorganise themselves in response to temperature changes, are found in most alloys. Although the details for some alloys are not clear or proven, it seems that at some temperatures, the atoms move so they are distributed uniformly at regular positions in the crystal lattice rather than distributed at random. Ordered lattices are in a slightly lower-energy state and have a higher Seebeck coefficient.

Figure 12 shows ordering effects in a Type K thermocouple. The graph plots the changes in Seebeck coefficient caused by exposure to different temperatures for periods ranging from 5 min to 4 h. The plot for the initial state is the Seebeck coefficient for the thermocouple in its as-received state without any additional heat treatment beyond that provided by the manufacturer and gives an indication of the initial homogeneity of the wire. The uppermost line in the plot shows that the Seebeck coefficient for this sample changes by more than 1% when it is exposed to temperatures near 400 °C for 4 h or more. If such heat-treated wire was moved to a different installation and the gradient placed over this heat-treated region, the temperature indication may be in error by as much as 1% (e.g., 4 °C at 400 °C).

Ordering effects occur slowly at low temperatures, and with increasing rates as the temperature increases. The effects in some thermocouples continue after 200 h at temperatures as low as 100 °C (Webster 2014). At higher temperatures, the ordering occurs rapidly so that an equilibrium state is reached very quickly. This is shown in Figure 12, where the right-hand edges of the peaks in the four curves lie on top of each other, indicating no further change with time. As the temperature is increased further, the ordered state becomes less stable and the atoms redistribute randomly. Wire heated above this temperature (about 650 °C for this sample) and then cooled rapidly to room temperature will be restored to its initial un-ordered state.

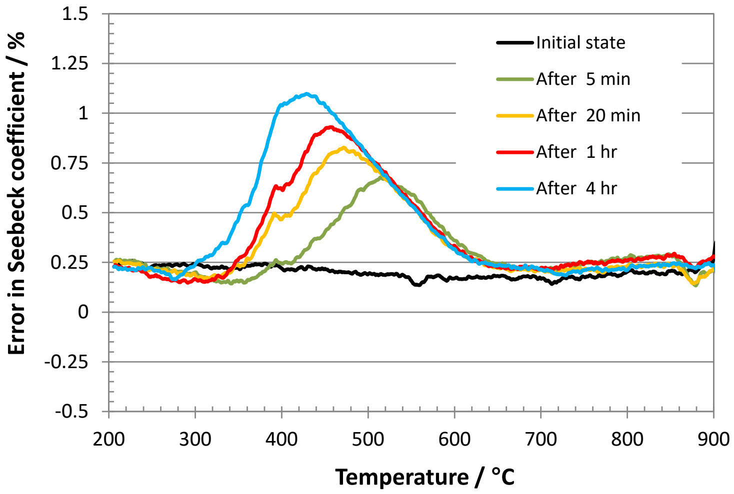

Figure 12: Measured change in Seebeck coefficient in a Type K sample due to ordering, for different operating temperatures and exposure times.

Vacancies and crystal defects, such as those caused by cold work, increase atomic diffusion within metals with the consequence that vacancies and defects usually accelerate ordering effects (Greenen and Webster 2017). Annealing will reduce the concentration of vacancies and defects and will slow drift due to ordering.

5.2.4. Contamination

Contamination is by far the most significant cause of error in thermocouples and, in some cases, can result in mechanical failure of the wires. Contamination is minimised by: (i) careful cleaning and handling of the materials during assembly; (ii) using insulator and sheath materials that do not contaminate the thermoelements; and (iii) ensuring the sheath is impermeable to contaminants in the environment. For some environments, particularly those at high temperatures, high pressures, or with high concentrations of carbon monoxide and hydrogen, such as within flames, multiple layers of specialised sheath materials may be required to prevent migration of the contaminants through the sheath to the thermoelements. The atmosphere in the sheath should also be compatible with the thermocouple; for example, oxidising or inert for platinum-rhodium thermocouples, or vacuum, reducing, or inert for tungsten-rhenium thermocouples.

The sheath in MIMS thermocouples can be a major source of contamination. This is particularly true of stainless steel and Inconel sheaths used at elevated temperatures, because some of the components of the steel alloys are very mobile, especially manganese. For this reason, in long-term installations, stainless steel and Inconel sheaths should be limited to temperatures about 200 °C below their specified upper operating temperature to limit the migration of the contaminants. Care is also required with thermocouples that are sensitive to contaminants, such as the platinum-rhodium thermocouples. Where MIMS assemblies are required for long-term elevated temperature applications, the sheath composition should be a close match to the thermocouple materials. Platinum-rhodium MIMS sheaths, although expensive, are available.

While contamination is an obvious cause of inhomogeneity in thermocouples, management of the oxygen atmosphere around thermocouples is often important too. Some base-metal thermocouples, Types K, N, and E especially, rely on a moderately high concentration of oxygen, such as in air. to perform well at high temperatures. A passive oxide layer forms on the surface of the thermoelements, helping to prevent further oxidation and inhibiting the migration of contaminants into the bulk of the wire. While the thermocouples perform satisfactorily in zero oxygen, such as inside a metal sheath or in a vacuum, they generally perform badly when there is a low level of oxygen.

With Type K, N, and Type E thermocouples in a low oxygen environment, the chromium in the positive thermoelement (Chromel and Nicrosil) oxidises preferentially, almost completely depleting the metal immediately below the chromium oxide layer and forming a layer of relatively pure nickel that dominates the thermoelectric behaviour of the wire. The chromium oxide is easily identified because of the characteristic green colour and is often described as green rot. Figure 13 plots the Seebeck coefficient of a Type K thermocouple exposed to a low oxygen environment for 100 h over a range of temperatures. The plot shows the onset of the preferential chromium oxidation just above 700 °C, and a very large change in Seebeck coefficient of about 90%. With bare-wire thermocouples used at temperatures above 700 °C, it is important to ensure that the thermocouples have good air circulation. Alternatively, mineral-insulated metal-sheathed (MIMS) thermocouples should be used so that practically no oxidation occurs.

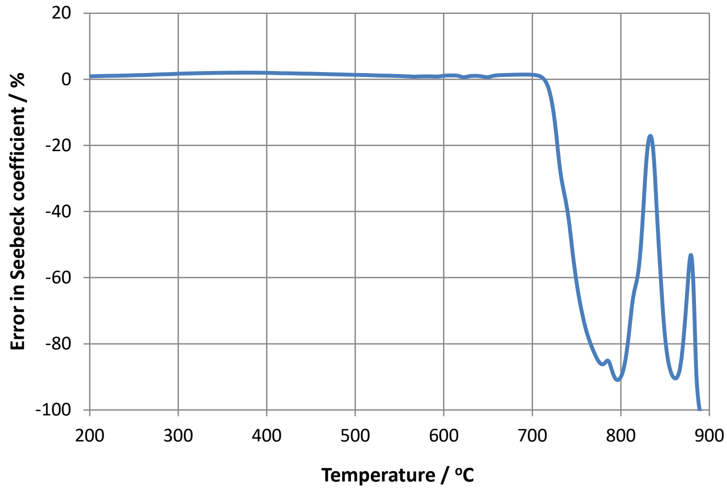

Figure 13: The changes in Seebeck coefficient due to green rot in a Type K thermocouple exposed to a low oxygen environment for 100 h over a range of temperatures.

Green rot can also occur in MIMS thermocouples if there is a sheath failure, usually at the point where the end of the sheath has been welded. In such cases, the low-oxygen environment develops quickly, leading to embrittlement of the positive thermoelement and, possibly, failure of the junction. The problem occurs in a worryingly high ~ 10 % of MIMS thermocouples when exposed to high temperatures (Bentley 1998a).

The migration of alloy components in the sheath or the accompanying thermoelement is another major cause of contamination. Figure 14 shows the effects of rhodium-oxide migration on a Type S thermocouple that was immersed into a furnace beyond the length of the ceramic insulator so that rhodium oxide vapour migrated from the alloy thermoelement and condensed on the pure platinum thermoelement at the cooler end of the insulator. The slope on the plot beyond 250 mm shows the effect of rhodium depletion in the alloy thermoelement, while the large spike at 200 mm is largely due to contamination of the platinum thermoelement. The ‘spike’ signature of the contamination of the platinum thermoelement is a common feature of Type R and Type S thermocouples assembled into multi-section twin-bore ceramic insulators.

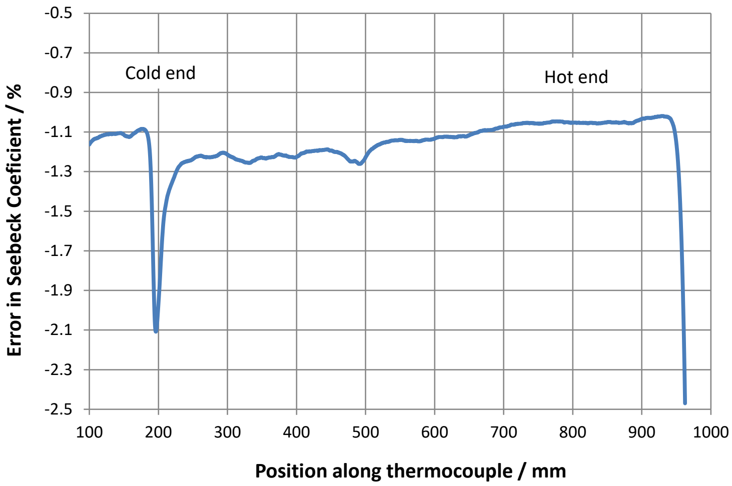

Figure 14: The Seebeck coefficient of a Type S thermocouple adversely affected by rhodium migration. Note the large downward spike at 200 mm where rhodium has contaminated the platinum thermoelement.

5.2.5. Ionising radiation

There are three classes of ionising radiation commonly encountered in nuclear environments: fast neutrons, slow (thermal) neutrons, and gamma radiation. The most damaging effects occur with fast neutrons, which collide with the atomic lattice of the thermocouple material, causing a cascade of collisions leading to the dislocation of hundreds or thousands of atoms. Fast neutrons have a similar effect to cold work, except that when the neutron flux is large, the damage can be so severe that it causes significant swelling, weakening, and increased porosity of the material.

Slow neutrons tend to be absorbed by the nuclei of the atoms in the lattice, causing transmutation. Elements such as rhodium (Types R, S, and B) and rhenium (Types A and C), which have a large neutron-capture cross section, are particularly susceptible. Shepard *et al.* (1974) describe a reactor core in which 90% of rhenium atoms are transmuted to osmium within a year. A Type C thermocouple used in the same reactor core drifted at the initial rate of about 1.5 °C/hr due to the transmutation. Similarly, rhodium suffers ready transmutation into palladium, causing rapid drift in all platinum-rhodium thermocouples. For temperatures below 1000 °C, Type N and Type K thermocouples usually exhibit an acceptable slow drift due to transmutation, but at temperatures above 1000 °C, more exotic thermocouples are required. In some applications, the platinum-molybdenum alloy thermocouple (max. temperature 1600 °C) defined by the ASTM E1751 standard may be satisfactory (Pollock 1971). Another possibility is the recently developed molybdenum-niobium thermocouple, (Kim *et al.* 2011, Rempe *et al.* 2012), which may be usable up to 1800 °C.

Gamma radiation is much less damaging than either of the neutron radiations, typically increasing the rates of chemical reactions and phase changes (including ordering) that would otherwise require higher temperatures to occur. The absorption of gamma radiation also causes heating at high flux levels.

5.3. Measuring junction

During the manufacture of the measuring junction, it is inevitable that parts of the wire near the junction become alloyed, contaminated, or mechanically damaged in some way. So long as the damaged wire is isothermal during use, it will not generate a thermoelectric voltage, and therefore there will be no error (see also Section 5.7).

With MIMS thermocouples, there are two options for the formation of the junction. In grounded-junction thermocouples, the two thermoelements are welded to the tip of the sheath. This has the advantage of giving the thermocouple a faster thermal response to temperature changes, but with some combinations of alloys, it can be difficult to make a reliable weld. The alternative is the ungrounded junction, where the junction is formed between the thermoelements and then enclosed and insulated from a metal cap welded onto the end of the sheath.

In general, exposed junctions yield thermocouples with a faster thermal response, but with an increased risk of perforation and contamination.

5.4. Insulation Breakdown

The main function of the insulation material is to prevent the flow of electrical current between the thermoelements. In general, so long as the manufacturer's guidelines are followed, errors due to insulation breakdown are negligible, but there are a few applications where some care is required.

When measuring low temperatures, there may be a risk of condensation or frost forming on parts of the thermocouple. Care should be taken to ensure that these parts are covered by waterproof insulation, such as plastic, to prevent corrosion and electrochemical activity.

MIMS thermocouples are amongst the most versatile and useful thermocouples, but they do suffer frequent failures caused by flaws in welds near the tips of the thermocouples. The holes in the sheath allow moisture to be taken up by the magnesia insulation, which is hydrophilic (attracted to water), so that the insulation gradually gets wetter and more conductive over time. The accumulation of moisture may also lead to corrosion and eventual failure of the thermocouple. Typically, the insulation resistance for ungrounded MIMS thermocouples is required to be greater than 100 MΩ at room temperature, and periodic checks of the electrical resistance between the sheath and the thermoelements, using a low-voltage (100 V) insulation tester, can often identify faulty thermocouples. A more thorough test is to immerse the MIMS tip into boiling water. Any perforations in the sheath will lead to a rapid ingress of moisture, which can then be confirmed with the electrical resistance check. Grounded-junction thermocouples are more problematic because they are more difficult to weld and cannot be tested in this way. They also fail more frequently because of differences in thermal expansion between the thermoelements and the sheath, which leads to fatiguing, and due to accelerated oxidation at the weld interface between sheath and junction.

At high temperatures, there is no such thing as a good electrical insulator. All metal-oxide insulators have electronic behaviour like a very high resistance thermistor so that the resistance falls exponentially with increasing temperatures, with the useful temperature range of the insulation determined by the electronic properties of the metal oxide and the dimensions of the thermocouple assembly, especially its length (Roberts and Kollie 1977, Hastings *et al.* 2012). It is difficult to recommend general rules, but Table 4 gives a guide for the maximum temperatures for insulation materials.

5.5. Reference junction

The enclosure containing the reference junction performs two functions. Firstly, it must keep the wires contained within its volume isothermal, so that any damage to the wires incurred during manufacture or assembly has no effect on the measured voltage. Secondly, it must keep the two junctions between the thermocouple wires and the lead wires to the meter at a known temperature, so that cold-junction compensation can be applied if necessary.

Where the reference junction is immersed in an ice point, the only practical concern is to ensure that there is sufficient immersion to prevent heat conducted down the wires from warming the junctions (Caldwell 1965).

When the junction is not in an ice point, it is usually necessary to contain the junction within a thermally conductive metal container surrounded by thermal insulation. Thermal anchoring of the leads to the metal box may be necessary to avoid heat conduction along heavy-gauge wires, and the metal container must also contain the thermometer used to measure the reference junction temperature. In good-quality thermocouple instrumentation, this will be an integral part of the construction.

Cold-junction compensation systems can produce significant errors if the reference junction is not stable. This is a common problem with hand-held thermocouple meters, especially if they are carried in pockets before use, or carried into zones that are very much warmer or colder, especially cool stores.

5.6. Extension and compensating leads

The Seebeck coefficient of extension or compensating wire is unlikely to match that of the thermoelements exactly, in part because the composition of the wires may be slightly different, and in part because the manufacturing tolerances on extension and compensating leads are greater than for the thermocouple wires themselves. The larger the temperature gradient across the extension wires, the larger the error caused by this mismatch. Although extension leads are specified to operate over the 0 °C to 100 °C range, ideally, all the extension wires should be at the same temperature so that they make no contribution to the measured voltage. The junctions between the thermoelements and the extension cables should also be treated much like the reference junction and kept isothermal. This is especially true for compensating extension leads. The use of compensating leads should be avoided in high-accuracy measurements.

5.7. Voltage measurement

Generally, the performance of modern digital voltmeters (DVM) greatly exceeds the requirements of thermocouple thermometry. The best DVMs have uncertainties below 0.1 μV for the entire range of voltages produced by thermocouples, up to 100 mV. Generally, a resolution of 0.1 μV and accuracy of 0.5 μV is sufficient for almost all laboratory measurements. Most modern digital voltmeters also have autozero features, ensuring that the effects of offset voltages in the electronics are negligible.

For traceable measurements, the DVM must be calibrated at enough points over the range to ensure that the DVM is linear and to measure any error in the voltage scale. The uncertainty reported on a DVM calibration certificate is often expressed as a fraction of the full-scale range plus a fraction of the reading. For example, the reported uncertainty might be 1 ppm (part per million) of scale + 0.15 ppm of the reading. When used with the 200 mV range to measure a 40 mV voltage produced by a thermocouple, the uncertainty, $u(V_{meas})$, would be 0.2 μV.

5.8. Immersion and heat leaks

All contact thermometers, including thermocouples, suffer from the effects of heat leaking up or down the thermometer body into the zone where the temperature is measured, and altering the temperature there. The effects of the heat leaks can be modelled most simply by relating the relative temperature error in the measurement to the immersion length (White and Jongenelen 2010)

$$\frac{T_{\mathrm{sys}} - T_{\mathrm{meas}}}{T_{\mathrm{sys}} - T_{\mathrm{amb}}} = K \exp(-L / L_0), \tag{8}$$

where T_{sys} is the temperature of the system of interest, T_{meas} is the measured temperature, T_{amb} is the ambient temperature, K is a constant less than 1, L is the length of the thermocouple immersed in the system, and L_0 is the effective diameter, a constant usually of similar magnitude to the diameter of the thermocouple.

Equation (8) shows that the temperature error scales approximately in proportion to the system temperature and decreases exponentially as the immersion of the thermocouple is increased. The effect has been investigated for some noble-metal thermocouples (Kim 1994, 2008), motivated by the higher thermal conductivity of the pure thermoelements, and another model is discussed by Kerlin and Johnson (2012). Otherwise, there has been little research carried out on the immersion effect in thermocouples. The effect is reasonably well understood in stainless steel sheathed industrial platinum resistance thermometers (White and Jongenelen 2010), which are constructed very much like MIMS thermocouples. The following conservative guidelines are recommended:

- For 1% accuracy (e.g., ±1 °C at 100 °C), the length of immersion should be greater than 10 times the diameter of the thermocouple, thermowell, or drywell, whichever is greater.
- For 0.01% accuracy, the length of immersion should be greater than 30 times the diameter of the thermocouple, thermowell, or drywell, whichever is greater.
- In oil baths, the effective diameter should be increased by about 20 mm to account for the insulating effect of the boundary layer of oil attached to the thermocouple.
- For temperatures below 200 °C, immersion can be improved by adding a couple of centimetres of oil, water, or alcohol in the thermowell.
- At temperatures above 400 °C or so, heat transfer is dominated by infrared radiation, which is more effective than direct metallic contact (White and Nicholas 2001).
- At temperatures below −150 °C, immersion problems worsen due to the increasing thermal conductivity of metals in the thermocouple assembly, especially copper.

One of the usual techniques for estimating the magnitude of immersion effects is to change the immersion and observe any change in reading. Unfortunately, this is not good practice for thermocouples, for two reasons. Firstly, the test is not reliable because the change in reading may be due to a change in the location of an inhomogeneity rather than an immersion error. Also, the act of changing the immersion conditions for thermocouples used at 200 °C or higher may induce a change in the state of the thermocouple in the gradient region where the voltage is generated, which results in a different temperature reading when the thermocouple is returned to normal immersion.

5.9. Electromagnetic interference

Electromagnetic interference (EMI) can be classified into two main forms (Ott 2011). The first is caused by direct connections to the thermocouple circuit causing unwanted currents to flow in the measurement circuit. This is commonly associated with insulation breakdown combined with contact with other large metal objects that may be at a different electric potential. The problem can also occur with MIMS thermocouples, especially if they have grounded junctions (the junction is welded to the metal sheath to improve the response time). Care should be taken to ensure the integrity of the insulation and, at high temperatures, avoid contact with metal objects.

The second form of EMI arises from unwanted electromagnetic fields, and may be classified as electrostatic, electromagnetic, or plane-wave depending on the proximity and nature of the source. With thermocouples, electromagnetic coupling between a nearby circuit carrying currents can induce an unwanted ac noise voltage into the thermocouple loop. Examples of troublesome noise sources include mains cables carrying currents from switch-mode power supplies, electric motors, temperature controllers, and digital electronics. The effects of magnetic coupling can be reduced by twisting the cables causing the interference to reduce effective area of the source, and by maximising the distance between the two circuits. Whereas metallic shielding of thermocouples (e.g., MIMS) is effective for electrostatic and plane-wave fields, it is generally ineffective for low-frequency magnetic fields. Advice on assembly of interference-free electrical measurements can be found in Ott (2011).

With some thermocouples, there is also a risk that the Seebeck coefficient changes in the presence of very strong magnetic fields (Kollie *et al.* 1977).

6. Calibration

The calibration of a thermocouple consists of the determination of its output voltage at a sufficient number of known temperatures over the range of interest, to enable accurate determination of unknown temperatures from other measured voltages. Perhaps the most important aspect of thermocouple calibration is that the measurement procedures, operating conditions, and the thermoelectric state of the thermocouples should ideally be the same as employed during use. This ensures that the correction equations and measurement uncertainties determined during calibration correspond to the thermocouple use. For the same reasons, it is essential that critical parts of the calibration procedure, the conditions, and the thermoelectric state of the thermocouples are reported on the calibration certificate, so that they can be reproduced by the user. For most calibrations, especially where the thermocouples are not in a well-defined thermoelectric state as received by the laboratory, the homogeneity of the thermocouple should be measured beforehand (see Part II of this Guide, Edler *et al.* 2021). For this reason, thermocouple calibrations generally cannot be used retrospectively.

Noble-metal thermocouples are well suited to calibration due to the relatively small magnitude of thermally-induced inhomogeneities and the relative ease of annealing the thermocouples to erase most forms of inhomogeneity. Nevertheless, some care is required. For noble-metal thermocouples, both calibration and use should be preceded by appropriate annealing. Thereafter, the thermocouples may be used with varying degrees of constraint on their usage. For example, to achieve the lowest practical measurement uncertainties, the thermocouples should be annealed and restored to the thermoelectric state specified on the calibration report prior to every measurement. Additionally, the duration of measurements should be restricted to a few hours to prevent the evolution of thermally-induced inhomogeneities. For simpler procedures, and a slightly poorer uncertainty, it may be sufficient to restrict the usage to 100 hours.

In contrast to noble-metal thermocouples, inhomogeneity effects in base-metal thermocouples are large, difficult to avoid or erase by annealing, and the cost-benefit ratio for calibration is poor – the thermocouples are cheap, but the calibration is expensive. Calibration of base-metal thermocouples is also often a futile exercise unless great care is taken to ensure the calibration procedures match the procedures in use. There are a few situations where base-metal thermocouples can usefully be calibrated:

- When the temperatures of use are below the temperatures where thermally-induced inhomogeneity effects occur (e.g., below 150 °C).
- A few samples from a group of thermocouples made with the same batch of wire may be calibrated to confirm compliance of the batch with a documentary standard or technical specification.
- A few samples from a group of thermocouples made with the same batch of wire may be calibrated as representative samples of the batch. After calibration, each of the remaining unused thermocouples in the group will be used once to measure a temperature and discarded after use.
- The thermocouples may be calibrated *in situ* so that the thermoelectric signature imprinted on the thermocouple and the temperature gradient are identical in use and in calibration.
- When thermocouples are used at temperatures where ordering effects occur, which is usually below the temperature where contamination occurs, it may be practical to precondition the thermocouples so that drift during calibration and use is minimised.

If high-accuracy (< 1% of reading in degrees Celsius) traceable temperature measurements are required at temperatures much above 150 °C, noble-metal thermocouples are nearly always a better investment than base-metal thermocouples. They suffer from the same problems as base-metal thermocouples, but the magnitude of inhomogeneity effects is perhaps a factor of ten smaller, and the usable temperature range is greater.

Appendix A: Thermocouple reference functions

This appendix lists the tolerance classes for each of the letter designated thermocouples, the coefficients for the reference and inverse functions for all the letter designated thermocouples according to IEC 50684, and the reference and inverse functions for the Pt/Au and Pt/Pd thermocouples according to ASTM E1751. The reference and inverse function coefficients are given in an exponential notation suited for import directly into spreadsheets and tables of software constants.

Except for the Type K thermocouple in the range 0 °C to 1372 °C, the reference functions for all the thermocouples have the form

$$E = \sum_{i=0}^{n} a_i t^i \ ,$$

where t is the temperature in degrees Celsius and E is the thermocouple voltage in microvolts. This equation can be rearranged in the form

$$E = a_0\left(1+\frac{a_1}{a_0}t\left(1+\frac{a_2}{a_1}t\left(1+\frac{a_3}{a_2}t\left(1+\frac{a_4}{a_3}t\left(1+\frac{a_5}{a_4}t(....)\right)\right)\right)\right)\right) .$$

This form requires fewer multiplications so tends to be executed faster by computers, and the round-off errors in the calculation are smaller.

For Type K in the range 0 °C to 1372 °C, the reference function has the form

$$E = \sum_{i=0}^{9} a_i t^i + c_0 \exp\left[c_1\left(t-126.9686\right)^2\right] .$$

Except for the gold-platinum thermocouple, the inverse functions all have the form

$$t = \sum_{i=0}^{n} b_i E^i \ ,$$

where t is in degrees Celsius and E is the thermocouple voltage in microvolts. For the gold platinum thermocouple, the inverse function is

$$t = \sum_{i=0}^{11} b_i \left(\frac{E-9645}{7620}\right)^i .$$

The inverse functions are all approximate. Each of the tables of inverse function coefficients indicates the maximum and minimum error, *err*, in temperatures calculated using the inverse functions, relative to the reference functions. In all cases the magnitude of the error is less than 0.06 °C. Neither the reference functions nor the inverse functions should be extrapolated beyond the specified ranges.

Type A

Tungsten 5% Rhenium(+) vs Tungsten 20% Rhenium(-)

IEC 60584 Tolerance classes
Class 2: 0.01|*t*| for 1000 °C to 2500 °C

Reference function coefficients

0 °C to 2500 °C	
a_0	0.0000000E+00
a_1	1.1951905E+01
a_2	1.6672625E-02
a_3	-2.8287807E-05
a_4	2.8397839E-08
a_5	-1.8505007E-11
a_6	7.3632123E-15
a_7	-1.6148878E-18
a_8	1.4901679E-22

Inverse function coefficients

100 °C to 2480 °C (1337 µV to 33485 µV)	
b_0	9.643027E-01
b_1	7.9495086E-02
b_2	-4.9990310E-06
b_3	0.6341776E-09
b_4	-4.7440967E-14
b_5	2.1811337E-18
b_6	-5.8324228E-23
b_7	8.2433725E-28
b_8	-4.5928480E-33
-0.3 °C < *err* < 0.3 °C	

Type B

Platinum 30%Rhodium (+) vs Platinum (-)

IEC 60584 Tolerance classes
Class 2: 1.5 °C or 0.0025|*t*| for 600 °C to 1700 °C
Class 3: 4.0 °C or 0.005|*t*| for 600 °C to 1700 °C

Reference function coefficients

	0 °C to 630.615 °C	630.615 °C to 1820 °C
a_0	0.0000000000E+00	-3.8938168621E+03
a_1	-2.4650818346E-01	2.8571747470E+01
a_2	5.9040421171E-03	-8.4885104785E-02
a_3	-1.3257931636E-06	1.5785280164E-04
a_4	1.5668291901E-09	-1.6835344864E-07
a_5	-1.6944529240E-12	1.1109794013E-10
a_6	6.2990347094E-16	-4.4515431033E-14
a_7	-	9.8975640821E-18
a_8	-	-9.3791330289E-22

Inverse function coefficients

	250 °C to 700 °C (291 µV to 2431 µV)	630.615 °C to 1820 °C (2431 µV to 13820 µV)
b_0	9.8423321E+01	2.1315071E+02
b_1	6.9971500E-01	2.8510504E-01
b_2	-8.4765304E-04	-5.2742887E-05
b_3	1.0052644E-06	9.9160804E-09
b_4	-8.3345952E-10	-1.2965303E-12
b_5	4.5508542E-13	1.1195870E-16
b_6	-1.5523037E-16	-6.0625199E-21
b_7	2.9886750E-20	1.8661696E-25
b_8	-2.4742860E-24	-2.4878585E-06
	-0.02 °C< *err* <0.26 °C	-0.007 °C< *err* <0.012 °C

Type C

Tungsten 5%Rhenium (+) vs Tungsten 26% Rhenium (-)

IEC 60584 Tolerance classes
Class 2: 0.01|*t*| for 426 °C to 2315 °C

Reference function coefficients

	0 °C to 630.615 °C	630.615 °C to 2315 °C
a_0	0.0000000E+00	4.0528823E+02
a_1	1.3406032E+01	1.1509355E+01
a_2	1.1924992E-02	1.5696453E-02
a_3	-7.9806354E-06	-1.3704412E-05
a_4	-5.0787515E-09	5.2290873E-09
a_5	1.3164197E-11	-9.2082758E-13
a_6	-7.9197332E-15	4.5245112E-17

Inverse function coefficients

	0 °C to 2315 °C (0 µV to 37070 µV)
b_0	0.00000000E+00
b_1	7.41247326E-02
b_2	-4.28082813E-06
b_3	5.21138920E-10
b_4	-4.57487201E-14
b_5	2.80578284E-18
b_6	-1.13145137E-22
b_7	2.85489684E-27
b_8	-4.07643828E-32
b_9	2.51358071E-37
	-0.5 °C < *err* < 0.5 °C

Type E

Nickel-Chromium (+) vs Copper-Nickel (-)

IEC60584 Tolerance classes
Class 1: 1.5 °C or 0.004|*t*| for -40 °C to 800 °C
Class 2: 2.5 °C or 0.0075|*t*| for -40 °C to 900 °C
Class 3: 2.5 °C or 0.015|*t*| for -200 °C to 40 °C

Reference function coefficients

	-270 °C to 0 °C	0 °C to 1000 °C
a_0	0.0000000000E+00	0.0000000000E+00
a_1	5.8665508708E+01	5.8665508710E+01
a_2	4.5410977124E-02	4.5032275582E-02
a_3	-7.7998048686E-04	2.8908407212E-05
a_4	-2.5800160843E-05	-3.3056896652E-07
a_5	-5.9452583057E-07	6.5024403270E-10
a_6	-9.3214058667E-09	-1.9197495504E-13
a_7	-1.0287605534E-10	-1.2536600497E-15
a_8	-8.0370123621E-13	2.1489217569E-18
a_9	-4.3979497391E-15	-1.4388041782E-21
a_{10}	-1.6414776355E-17	3.5960899481E-25
a_{11}	-3.9673619516E-20	-
a_{12}	-5.5827328721E-23	-
a_{13}	-3.4657842013E-26	-

Inverse function coefficients

	-8825 µV to 0 µV (-200 °C to 0 °C)	0 µV to 76373 µV (0 °C to 1000 °C)
b_0	0.0000000E+00	0.0000000E+00
b_1	1.6977288E-02	1.7057035E-02
b_2	-4.3514970E-07	-2.3301759E-07
b_3	-1.5859697E-10	6.5435585E-12
b_4	-9.2502871E-14	-7.3562749E-17
b_5	-2.6084314E-17	-1.7896001E-21
b_6	-4.1360199E-21	8.4036165E-26
b_7	-3.4034030E-25	-1.3735879E-30
b_8	-1.1564890E-29	1.0629823E-35
b_9	-	-3.2447087E-41
	-0.010 °C< *err* <0.022 °C	-0.012 °C< *err* <0.016 °C

Type J

Iron (+) vs Copper-Nickel (-)

IEC60584 Tolerance classes
Class 1: 1.5 °C or 0.004|*t*| for -40 °C to 750 °C
Class 2: 2.5 °C or 0.0075|*t*| for -40 °C to 750 °C
Class 3: 2.5 °C or 0.015|*t*| for -200 °C to 40 °C

Reference function coefficients

	-210 °C to 760 °C	760 °C to 1200 °C
a_0	0.0000000000E+00	2.9645625681E+05
a_1	5.0381187815E-01	-1.4976127786E+03
a_2	3.0475836930E-02	3.1787103924E+00
a_3	-8.5681065720E-05	-3.1847686701E-03
a_4	1.3228195295E-07	1.5720819004E-06
a_5	-1.7052958337E-10	-3.0691369056E-10
a_6	2.0948090697E-13	
a_7	-1.2538395336E-16	
a_8	1.5631725697E-20	

Inverse function coefficients

	-8095 mV to 0 mV (-210 °C to 0 °C)	0 mV to 42919 mV (0 °C to 760 °C)	42919 mV to 69553 mV (760 °C to 1200 °C)
b_0	0.0000000E+00	0.0000000E+00	-3.11358187E+03
b_1	1.9528268E-02	1.978425E-02	3.00543684E-01
b_2	-1.2286185E-06	-2.001204E-07	-9.94773230E-06
b_3	-1.0752178E-09	1.036969E-11	1.70276630E-10
b_4	-5.9086933E-13	-2.549687E-16	-1.43033468E-15
b_5	-1.7256713E-16	3.585153E-21	4.73886084E-21
b_6	-2.8131513E-20	-5.344285E-26	-
b_7	-2.3963370E-24	5.099890E-31	-
b_8	-8.3823321E-29	-	-
-0.020 °C< *err* <0.026 °C		-0.003 °C< *err* <0.005 °C	-0.011 °C < *err* < 0.01 °C

Type K

Nickel-Chromium (+) vs Nickel (-)

IEC60584 Tolerance classes
Class 1: 1.5 °C or 0.004|*t*| for -40 °C to 1000 °C
Class 2: 2.5 °C or 0.0075|*t*| for -40 °C to 1200 °C
Class 3: 2.5 °C or 0.015|*t*| for -200 °C to 40 °C

Reference function coefficients

	-270 °C to 0 °C	0 °C to 1300 °C
a_0	0.0000000000E+00	-1.7600413686E+01
a_1	3.9450128025E+01	3.8921204975E+01
a_2	2.3622373598E-02	1.8558770032E-02
a_3	-3.2858906784E-04	-9.9457592874E-05
a_4	-4.9904828777E-06	3.1840945719E-07
a_5	-6.7509059173E-08	-5.6072844889E-10
a_6	-5.7410327428E-10	5.6075059059E-13
a_7	-3.1088872894E-12	-3.2020720003E-16
a_8	-1.0451609365E-14	9.7151147152E-20
a_9	-1.9889266878E-17	-1.2104721275E-23
a_{10}	-1.6322697486E-20	-
c_0	-	1.185976E+02
c_1	-	-1.183432E-04

Inverse function coefficients

	-5891 µV to 0 µV (-200 °C to 0 °C)	0 µV to 20644 µV (0 °C to 500 °C)	20644 µV to 52410 µV (500 °C to 1300 °C)
b_0	0.0000000E+00	0.0000000E+00	-1.318058E+02
b_1	2.5173462E-02	2.508355E-02	4.830222E-02
b_2	-1.1662878E-06	7.860106E-08	-1.646031E-06
b_3	-1.0833638E-06	-2.503131E-10	5.464731E-11
b_4	-8.9773540E-13	8.315270E-14	-9.650715E-16
b_5	-3.7342377E-16	-1.228034E-17	8.802193E-21
b_6	-8.6632643E-20	9.804036E-22	-3.110810E-26
b_7	-1.0450598E-23	-4.413030E-26	-
b_8	-5.1920577E-28	1.057734E-30	-
b_9	-	-1.052755E-35	-
-0.018 °C< *err* <0.041 °C		-0.047 °C< *err* <0.033 °C	-0.046 °C< *err* <0.054 °C

Type N

Nickel-Chromium-silicon (+) vs Nickel-silicon (-)

IEC60584 Tolerance classes
Class 1: 1.5 °C or 0.004|*t*| for -40 °C to 1000 °C
Class 2: 2.5 °C or 0.0075|*t*| for -40 °C to 1200 °C
Class 3: 2.5 °C or 0.015|*t*| for -200 °C to 40 °C

Reference function coefficients

	-270 °C to 760 °C	0 °C to 1300 °C
a_0	0.0000000000E+00	0.0000000000E+00
a_1	2.6159105962E+01	2.5929394601E+01
a_2	1.0957484228E-02	1.5710141880E-02
a_3	-9.3841111554E-05	4.3825627237E-05
a_4	-4.6412039759E-08	-2.5261169794E-07
a_5	-2.6303357716E-09	6.4311819339E-10
a_6	-2.2653438003E-11	-1.0063471519E-12
a_7	-7.6089300791E-14	9.9745338992E-16
a_8	-9.3419667835E-17	-6.0863245607E-19
a_9	-	2.0849229339E-22
a_{10}	-	-3.0682196151E-26

Inverse function coefficients

	-3990 µV to 0 µV (-200 °C to 0 °C)	0 µV to 20613 µV (0 °C to 500 °C)	20613 µV to 47513 µV (500 °C to 1300 °C)
b_0	0.0000000E+00	0.0000000E+00	1.972485E+01
b_1	3.8436847E-02	3.86896E-02	3.300943E-02
b_2	1.1010485E-06	-1.08267E-06	-3.915159E-07
b_3	5.2229312E-09	4.70205E-11	9.855391E-12
b_4	7.2060525E-12	-2.12169E-18	-1.274371E-16
b_5	5.8488586E-15	-1.17272E-19	7.767022E-22
b_6	2.7754916E-18	5.39280E-24	-
b_7	7.7075166E-22	-7.98156E-29	-
b_8	1.1582665E-25	-	-
b_9	7.3138868E-30	-	-
-0.013 °C< *err* <0.027 °C		-0.016 °C < *err* <0.027 °C	-0.039 °C< *err* <0.021 °C

Type R

Platinum 13% Rhodium (+) vs Platinum (-)

IEC60584 Tolerance classes
Class 1: 1.0 °C or [1+0.003(*t*-1100)] °C for 0 °C to 1600 °C
Class 2: 1.5 °C or 0.0025|*t*| for 0 °C to 1600 °C

Reference function coefficients

	-50 °C to 1064.18 °C	1064.18 °C to 1664.5 °C	1664.5 °C to 1768.1 °C
a_0	0.00000000000E+00	2.95157925316E+03	1.52232118209E+05
a_1	5.28961729765E+00	-2.52061251332E+00	-2.68819888545E+02
a_2	1.39166589782E-02	1.59564501865E-06	1.71280280471E-01
a_3	-2.38855693017E-05	-7.640859475 76E-06	-3.45895706453E-05
a_4	3.56916001063E-08	2.05305291024E-09	-9.34633971046E-12
a_5	-4.62347666298E-11	-2.93359668173E-13	-
a_6	5.00777441034E-14	-	-
a_7	-3.73105886191E-17	-	-
a_8	1.57716482367E-20	-	-
a_9	-2.81038625251E-24	-	-

Inverse function coefficients

	-226 µV to 1923 µV (-50 °C to 250 °C)	1923 µV to 11361 µV (250 °C to 1064 °C)	11361 µV to 19739 µV (1064 °C to 1664.5 °C)	19739 µV to 21103 µV (1664.5 °C to 1768.1 °C)
b_0	0.0000000E+00	1.334584505E+01	-8.199599416E+01	3.406177836E+04
b_1	1.8891380E-01	1.472644573E-01	1.553962042E-01	-7.023729171E+00
b_2	-9.3835290E-05	-1.844024844E-05	-8.342197663E-6	5.582903813E-04
b_3	1.3068619E-07	4.031129726E-09	4.279433549E-10	-1.952394635E-08
b_4	-2.2703580E-10	-6.249428360E-13	-1.191577910E-14	2.560740231E-13
b_5	3.5145659E-13	6.468412046E-17	1.492290091E-19	-
b_6	-3.8953900E-16	-4.458750426E-21	-	-
b_7	-2.8239471E-19	1.994710149E-25	-	-
b_8	-1.2607281E-22	-5.313401790E-30	-	-
b_9	3.1353611E-26	6.481976217E-35	-	-
b_{10}	-3.3187769E-30	-	-	-
	-0.011 °C < *err* <0.01 °C	-0.003 °C < *err* <0.005 °C	-0.011 °C < *err* <0.01 °C	-0.001 °C < *err* <0.001 °C

Type S

Platinum 10%Rhodium (+) vs Platinum (-)

IEC60584 Tolerance classes
Class 1: 1.0 °C or [1+0.003(t-1100)] °C for 0 °C to 1600 °C
Class 2: 1.5 °C or 0.0025|t| for 0 °C to 1600 °C

Reference function coefficients

	-50 °C to 1064.18 °C	1064.18 °C to 1664.5 °C	1664.5 °C to 1768.1 °C
a_0	0.00000000000E+00	1.32900444085E+03	1.46628232636E+05
a_1	5.40313308631E+00	3.34509311344E+00	-2.58430516752E+02
a_2	1.25934289740E-02	6.54805192818E-03	1.63693574641E-01
a_3	-2.32477968689E-05	-1.64856259209E-06	-3.30439046987E-05
a_4	3.22028823036E-08	1.29989605174E-11	-9.43223690612E-12
a_5	-3.31465196389E-11	-	-
a_6	2.55744251786E-14	-	-
a_7	-1.25068871393E-17	-	-
a_8	2.71443176145E-21	-	-

Inverse function coefficients

	-235 µV to 1874 µV (-50 °C to 250 °C)	1874 µV to 10332 µV (250 °C to 1064 °C)	10332 µV to 17536 µV (1064 °C to 1664.5 °C)	17536 µV to 18694 µV (1664.5 °C to 1768.1 °C)
b_0	0.00000000E+00	1.291507177E+01	-8.087801117E+01	5.333875126E+04
b_1	1.84949460E-01	1.466298863E-01	1.621573104E-01	-1.235892298E+01
b_2	-8.00504062E-05	-1.534713402E-05	-8.536869453E-06	1.092657613E-03
b_3	1.02237430E-07	3.145945973E-09	4.719686976E-10	-4.265693686E-08
b_4	-1.52248592E-10	-4.163257839E-13	-1.441693666E-14	6.247205420E-13
b_5	1.88821343E-13	3.187963771E-17	2.081618890E-19	-
b_6	-1.59085941E-16	-1.291637500E-21	-	-
b_7	8.23027880E-20	2.183475087E-28	-	-
b_8	-2.34181944E-23	-1.447379511E-31	-	-
b_9	2.79786260E-27	8.211272125E-36	-	-
	-0.011 °C < *err* <0.02 °C	-0.009 °C < *err* <0.006 °C	-0.000 °C < *err* <0.000 °C	-0.002 °C < *err* <0.001 °C

Type T

Copper (+) vs Copper-nickel (-)

IEC60584 Tolerance classes
Class 1: 0.5 °C or 0.004|*t*| for -40 °C to 350 °C
Class 2: 1.0 °C or 0.0075|*t*| for -40 °C to 350 °C
Class 3: 1.0 °C or 0.015|*t*| for -200 °C to 40 °C

Reference function coefficients

	-270 °C to 0 °C	0 °C to 400 °C
a_0	0.0000000000E+00	0.0000000000E+00
a_1	3.8748106364E+01	3.8748106364E-01
a_2	4.4194434347E-02	3.3292227880E-02
a_3	1.1844323105E-04	2.0618243404E-04
a_4	2.0032973554E-05	-2.1882256846E-06
a_5	9.0138019559E-07	1.0996880928E-08
a_6	2.2651156593E-08	-3.0815758772E-11
a_7	3.6071154205E-10	4.5479135290E-14
a_8	3.8493939883E-12	-2.7512901673E-17
a_9	2.8213521925E-14	-
a_{10}	1.4251594779E-16	-
a_{11}	4.8768662286E-19	-
a_{12}	1.0795539270E-21	-
a_{13}	1.3945027062E-24	-
a_{14}	7.9795153927E-28	-

Inverse function coefficients

	-5603 mV to 0 mV (-200 °C to 0 °C)	0 mV to 20872 mV (0 °C to 400 °C)
b_0	0.0000000E+00	0.0000000E+00
b_1	2.5949192E-02	2.592800E-02
b_2	-2.1316967E-07	-7.602961E-07
b_3	7.9018692E-10	4.637791E-11
b_4	4.2527777E-13	-2.165394E-15
b_5	1.3304473E-16	6.048144E-20
b_6	2.0241446E-20	-7.293422E-25
b_7	1.2668171E-24	-
-0.011 °C < *err* <0.01 °C		-0.003 °C < *err* <0.005 °C

Au-Pt

Gold (+) vs Platinum (-)

Reference function coefficients

	0 °C to 1000 °C
a_0	0.0000000E+00
a_1	6.03619861E+00
a_2	1.93672974E-02
a_3	-2.22998614E-05
a_4	3.28711859E-08
a_5	-424206193E-11
a_6	4.56927038E-14
a_7	-3.39430259E-17
a_8	1.42981590E-20
a_9	-2.51672787E-24

Inverse function coefficients

	0 μV to 1953 μV (0 °C to 209 °C)	1953 μV to 17085 μV (209 °C to 1000 °C)
b_0	0.0000000E+00	6.763360E+02
b_1	1.6543903E-01	3.735504E+02
b_2	-8.4098835E-05	-5.537363E+01
b_3	8.4166132E-08	1.701900E+01
b_4	-7.5174691E-11	-6.098761E+00
b_5	4.8495536E-14	2.457162E+00
b_6	-2.0138760E-17	-3.385575E+00
b_7	4.7475626E-21	3.853735E+00
b_8	-4.7973082E-25	1.178891E+00
	-	-2.702558E+00
	-	-1.686158E+00
	-	1.876968E+00
	-0.005 °C < *err* <0.003 °C	-0.002 °C < *err* <0.002 °C

Pt-Pd

Platinum (+) vs Palladium (-)

Reference function coefficients

	0 °C to 660.323 °C	660.323 °C to 1500 °C
a_0	0.000000E+00	-4.9771370E+02
a_1	5.296958E+00	1.0182545E+01
a_2	4.610494E-03	-1.5793515E-02
a_3	-9.602271E-06	3.6361700E-05
a_4	2.992243E-08	-2.6901509E-08
a_5	-2.012523E-11	9.5627366E-12
a_6	-1.268514E-14	-1.3570737E-15
a_7	2.257823E-17	-
a_8	-8.510068E-21	-

Inverse function coefficients

	0 µV to 5782.4 µV (0 °C to 660.323 °C)	5782.4 µV to 22932 µV (660.323 °C to 1500 °C)
b_0	1.1286481E-03	1.314565E+00
b_1	1.8867850E-01	1.944512E-01
b_2	-3.0012521E-05	-2.439432E-05
b_3	1.8468737E-08	2.735961E-09
b_4	-1.2498608E-11	-2.131711E-13
b_5	5.2416509E-15	1.114340E-17
b_6	-1.3915286E-18	-3.715739E-22
b_7	2.3872908E-22	7.121084E-27
b_8	-2.5802436E-26	-5.954960E-32
b_9	1.6018819E-30	-
b_{10}	-4.3608166E-35	-
	-0.003 °C < *err* <0.002 °C	-0.035 °C < *err* <0.025 °C

References

Abdelaziz Y A, Megahed F M, Halawa M M (2004) Stability and calibration of platinum/palladium thermocouples following heat treatment *Measurement* **35** 413-420.

Asamoto R R and Novak P E (1967) Tungsten-rhenium thermocouples for use at high temperatures *Rev. Sci. Instrum.* **38** 1047-1052.

ASTM (1993) *MNL 12: Manual on the Use of Thermocouples in Temperature Measurement*, 4th ed. Philadelphia, American Society for Testing and Materials.

ASTM E1751:2009 *Standard Guide for Temperature Electromotive Force (emf) Tables for Non-Letter Designated Thermocouple Combinations.* Philadelphia, American Society for Testing and Materials.

Astrua M, Battuello M, Girard F (2006) Facility for the calibration of Pt/Pd thermocouples in the temperature range from 960 C to 1500 C *Meas. Sci. Technol.* **17** 2186.
Ballico M J, Jahan F (2013) Analysis of inhomogeneity in Au/Pt thermocouples to allow intercomparisons at better than 10 millikelvins. In AIP Conference Proceedings (Vol. 1552, No. 1, pp. 544-548). American Institute of Physics.

Bedford R E (1964) Reference tables for platinum - 20% rhodium / platinum - 5% rhodium thermocouples *Rev. Sci. Instrum.* **35** 1177-1190.

Bedford R E (1965) Reference tables for platinum - 40% rhodium / platinum - 20% rhodium thermocouples, *Rev. Sci. Instrum.* **36** 1571-1580.

Bentley R E and Jones T P (1980) Inhomogeneities in type S thermocouples when used to 1064 °C *High Temp. – High Press.* **12** 33-45.

Bentley R E (1998a) *Handbook of Temperature Measurement Vol 3: Theory and Practice of Thermoelectric Thermometry* Singapore, Springer-Verlag.

Bentley R E (1998b) The use of elemental thermocouples in high-temperature precision thermometry *Measurement* **23** 35-46.

Bentley R E (2001a) Thermoelectric changes in Au and Pt: metals used in elemental thermocouples *Meas. Sci. Technol.* **12** 627-634.

Bentley R E (2001b) Thermoelectric instability in Pd within the elemental thermocouple Pt/Pd *Meas. Sci. Technol.* **12** 1250-1260.

Burley N A (1972) Nicrosil and Nisil: highly stable nickel-base alloys for thermocouples, In *Temperature: Its Measurement and Control in Science and Industry,* Vol. 4 (Edited by H. H. Plumb), Pittsburgh, Instrument Society of America, 1677-1695.

Burley N A, Cocking J L, Burns G W, and Scroger M G (1982) The nicrosil versus nisil thermocouple: the influence of magnesium on the thermoelectric stability and oxidation resistance of the alloys, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 5 (Edited by J. F. Schooley), New York, American Institute of Physics, 1129-1145.

Burns G W and Gallagher J S (1966) Reference tables for the Pt-30 percent Rh versus Pt-6 percent Rh thermocouple, *J. Res. NBS* **70C** 89-125.

Burns G W and Hurst W S (1972) Studies of the performance of W-Re type thermocouples, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 4 (Edited by H. H. Plumb), Pittsburgh, Instrument Society of America, 1751-1766.

Burns G W, Strouse G F, Liu B M, and Mangum B W (1992a) Gold versus platinum thermocouples: performance data and an ITS-90 based reference function, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 531-536.

Burns G W, Strouse G F, Mangun B W, Croarkin M C, Guthrie W F, Marcarino P, Battuello M, Lee H K, Kim J C, Gam K S, Rhee C, Chattle M, Arai M, Sakurai H, Pokhodun A I, Moiseeva N P, Perevalova S A, de Groot M J, Zhang J, Fan K, and Shuyuan W, (1992b) New reference function for platinum-10% rhodium versus platinum (type S) thermocouples based on the ITS-90. Part II: Experimental procedures, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 541-546.

Burns G W, Strouse G F, Mangun B W, Croarkin M C, Guthrie W F, and Chattle M, (1992c) New reference functions for platinum-13% rhodium versus platinum (type R) and platinum-30% rhodium versus platinum-6% rhodium (type B) thermocouples based on the ITS-90, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 559-564.

Burns G W, Scroger M G, Strouse G F, Croarkin M C, and Guthrie W F (1993) Temperature-Electromotive Force Reference Functions and Tables for the Letter-Designated Thermocouple Types Based on the ITS-90, *Natl. Inst. Stand. Technol. Monograph 175*, 630 pp.

Burns G W and Ripple D C (1997) Techniques for fabricating and annealing Pt/Pd thermocouples for accurate measurements in the range 0 °C to 1300 °C, In *TEMPMEKO 96: Proc. 6th International Symposium on Temperature and Thermal Measurements in Industry and Science*, Torino, Levrotto & Bella, 171-176.

Burns G W, Ripple D C, and Battuello M (1998) Platinum versus palladium thermocouples: an emf-temperature reference function for the range 0 °C to 1500 °C, *Metrologia* **35** 761-780.

Burns G W and Ripple D C (2002) Variations in the thermoelectric behavior of palladium following heat treatment, In *TEMPMEKO 2001: Proc. 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, Berlin, VDE Verlag, 61-66.

Caldwell F R (1965) Temperatures of Thermocouple Reference junctions in an Ice Bath, In NBS Special Publication 300, Vol 2, *Precision Measurement and Calibration: Selected papers on Temperature*. National Bureau of Standards.

Coleman M J, Wiandt T J, Harper T (2015) A Comparison of Contemporary Gold Versus Platinum Thermocouples with NIST SRM 1749-Based Thermocouples and Reference Function *Int. J. Thermophys*. **36** 3384-3392.

Darling A S and Selman G L (1972) Some Effects of Environment on the Performance of Noble Metal Thermocouples, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 4 (Edited by H. H. Plumb), Pittsburgh, Instrument Society of America, 1633-1644.

Droege J W, Schimek M M, and Ward J J (1972) Chemical compatibility in the use of refractory metal thermocouples, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 4 (Edited by H. H. Plumb), Pittsburgh, Instrument Society of America, 1767-1779.

Edler F and Lehmann H (2005) Mechanical stability of Pt/Pd thermocouples, In *TEMPMEKO 2004: Proc. 9th International Symposium on Temperature and Thermal Measurements in Industry and Science*, Zagreb, University of Zagreb, 625-630.

Edler F, Morice R, and Pearce J (2008) Construction and investigation of Pt/Pd thermocouples in the framework of the Euromet Project 857. *Int. J. Thermophys*. **29** 199-209.

Edler F, Arifovic N, Atance G, Dinu C, Elliott C J, Izquierdo C G, Hodzic N, Kalisz S, Pearce J V, Simic S, Strnad R (2015) Thermoelectric properties of currently available Au/Pt thermocouples related to the valid reference function. *Int. J. Metrol. Qual. Eng*. **6** 303.

Edler F, Kim Y G, Machin G, Pearce J V, White D R (2016) *BIPM Guide on Secondary Thermometry, Specialised Fixed Points above 0 °C*, BIPM.

Edler F, Kim Y G, Pearce J V, Webster E S, White D R (2021) BIPM Guide on Secondary Thermometry Thermocouples Part 2: Reference thermocouples and Calibration, BIPM (in preparation).

Elliott C J, Large M J, Pearce J V, and Machin G (2014) Compatibility of materials for use at high temperatures with W–Re thermocouples *Int. J. Thermophys*. **35** 1202-1214.

EURAMET (2020) *Guidelines on the calibration of Thermocouples*, Calibration Guide Number 8 Ver. 3.1, EURAMET.

Fenton A W (1972) The travelling gradient approach to thermocouple research, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 4 (Edited by H. H. Plumb), Pittsburgh, Instrument Society of America, 1973-1990.

Glawe G E and Szaniszlo A J (1972) Long-term drift of some noble- and refractory-metal thermocouples at 1600 K in air, argon and vacuum, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 4 (Edited by H. H. Plumb), Pittsburgh, Instrument Society of America, 1645-1662.

Greenen A D, and Webster E S (2017) Thermal recovery from cold-working in type K bare-wire thermocouples *International Journal of Thermophysics* **38** 179.

Gotoh M, Hill K D, and Murdock E G (1991) A gold/platinum thermocouple reference table, *Rev. Sci. Instrum.***62** 2778-2791.

Gotoh M, Iwata N and Funayama K (1997) Long term stability test for gold/platinum thermocouples, In *TEMPMEKO 96: Proc. 6th International Symposium on Temperature and Thermal Measurements in Industry and Science*, Torino, Levrotto & Bella, 207-211.

Gotoh M (2003) Thermoelectric Scanning Study of Pt/Pd and Au/Pt Thermocouples up to 960° C with a Pressure Controlled Sodium Heat-Pipe. *Proc. AIP Conf. Vol. 684*, pp. 481-484 American Institute of Physics.

Gotoh M, Oikawa H (2006) Development of durable gold versus platinum thermocouples. *Proc. XVIII IMEKO World Congress*. IMEKO.

Goupil C, Seifert W, Zabrocki K, Müller E, Snyder G J (2011) Thermodynamics of thermoelectric phenomena and applications *Entropy* **13** 1481-1517.

Guildner L A and Burns G W (1979) "Accurate thermocouple thermometry *High Temp. – High Press.***11** 173-192.

Hastings M W, Pearce J V, and Machin G (2012) Electrical resistance breakdown of type N mineral-insulated metal-sheathed thermocouples above 800° C. *Meas. Tech.* **55** 941-948.

Hill K D (2002) An investigation of palladium oxidation in the platinum/palladium thermocouple system *Metrologia* **39** 51-58.

IEC 60584-1 (2013) *Thermocouples - Part 1: EMF specifications and tolerances*, Technical Committee 65B.

IEC 60584-3 (2007) *Thermocouples - Part 3: Extension and compensating cables - Tolerances and identification system*, Technical Committee 65B.

IEC 62460 (2008) *Temperature - Electromotive force (EMF) tables for pure-element thermocouple combinations*, Technical Committee 65B.

Jahan F and Ballico M (2003) A study of the temperature dependence of inhomogeneity in platinum-based thermocouples, In Temperature: Its Measurement and Control in Science and Industry, Vol. 7 (Edited by D. C. Ripple), New York, American Institute of Physics, 469-474.

Jahan F, Ballico M (2007) Stability studies of a new design Au/Pt thermocouple without a strain relieving coil *Int. J. Thermophys*. **28** 1822-1831.

Jahan F, Ballico M J (2010) Annealing State Dependence of the Calibration of Type R and Type S Thermocouples *Int. J. Thermophys*. **31** 1544-1553.

Jahan F, Ballico M, Kim Y G, Liedberg H, Li W, Ogura H, Tsui C M (2013) Final report of APMP. T-S5: APMP regional comparison of Au/Pt thermocouples from 0 °C to 960 °C *Metrologia* **50** 03003.

Kim Y G, Gam K S, Kang K H (1994) Immersion characteristics and reproducibility of the gold/palladium thermocouple *Metrologia* **31** 145.

Kim Y G, Lee Y H, and Kim J C (1998) Composition change of type S thermocouples after high-temperature annealing at 1400 °C, *High Temp. – High Press.***30** 465-470.

Kim Y G, Yang I, Gam K S (2008) Measurement of the Inhomogeneity of Pt/Pd Thermocouples using an Immersion-into-Liquid Method. *Instrument. Sci. Technol*., **36** 257-266.

Kim B G, Rempe J L, Villard J F, Solstad S (2011) Review of instrumentation for irradiation testing of nuclear fuels and materials *Nucl. Technol*. **176** 155-187.

Kinzie P A (1973) *Thermocouple Temperature Measurement*, New York, John Wiley & Sons, 278 pp.

Kollie T G, Horton J L, Carr K R, Herskovitz M B, Mossman C A (1975) Temperature measurement errors with type K (Chromel vs Alumel) thermocouples due to short-ranged ordering in Chromel, *Rev. Sci. Instrum.* **46** 1447-1461.

Kollie T G, Anderson R L, Horton J L, and Roberts M J (1977) Large thermocouple thermometry errors caused by magnetic fields. Rev. Sci. Inst. **48** 501-511.

Kerlin T W, and Johnson M (2012) *Practical thermocouple thermometry*. Instrument Society of America.

McLaren E H and Murdock E G (1979) *The Properties of Pt PtRh Thermocouples for Thermometry in the Range 0-1100 °C: 1. Basic Measurements with Standard Thermocouples*, NRCC 17407, Ottawa, National Research Council of Canada, 126 pp.

McLaren E H and Murdock E G (1987) *The Pt/Au Thermocouple*, NRCC 27703, Ottawa, National Research Council of Canada, 111 pp.

Morice R and Devin E (2002) Calibration and conditions of use of refractory thermocouples up to 2300 K, In *TEMPMEKO 2001: Proc. 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, Berlin, VDE Verlag, 73-78.

Nicholas J V and White D R (2001) *Traceable Temperatures*, 2nd ed., Chichester, John Wiley & Sons, 295-342.

Ohm W S, and Hill K D (2010) A mechanism for the oxidation-related influence on the thermoelectric behavior of palladium *Int. J Thermophys*. **31** 1402-1416.

Ongrai O, Pearce J V, Machin G, and Sweeney S J (2010) Comparative Study of Pt/Pd and Pt–Rh/Pt Thermocouples *Int. J. Thermophys*. **31** 1506-1516.

Ott H W (2011) *Electromagnetic compatibility engineering* John Wiley & Sons.

Pearce J V, Ogura H, Izuchi M, Machin G (2009) Evaluation of the Pd–C eutectic fixed point and the Pt/Pd thermocouple Metrologia 46 473.

Pearce J V, Elliott C J, Greenen A, del Campo D, Martin M J, Izquierdo C G, Pavlasek P, Nemecek P, Failleau G, Deuze T, Sadli M (2014) A pan-European investigation of the Pt-40% Rh/Pt-20% Rh (Land–Jewell) thermocouple reference function *Meas. Sci. Technol*. **26** 015101.

Pearce J V, Greenen A D, Smith A, and Elliott C J (2017) Relating composition and thermoelectric stability of Pt–Rh alloy thermocouples *Int. J. Thermophys*. **38** 26.

Pearce J V, Edler F, Elliott C J, Greenen A, Harris P M, Izquierdo C G, Kim Y G, Martin M J, Smith I M, Tucker D, Veltcheva R I (2018) A systematic investigation of the thermoelectric stability of Pt–Rh thermocouples between 1300° C and 1500° C *Metrologia* **55** 558.

Pollock D D (1991) *Thermocouples: theory and properties* CRC Press.

Pollock D D (1995) "Sec A2: Thermoelectric Phenomena" in *CRC Handbook of Thermoelectrics*, pp7-17, CRC Press.

Quinn T J (1990) *Temperature*, 2nd ed., London, Academic Press, 286-331.

Reed R P (1992a) Thermoelectric inhomogeneity testing: Part I - Principles, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 519-524.

Reed R P (1992b) Thermoelectric inhomogeneity testing: Part II - Advanced methods, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 525-530.

Rempe J L, Knudson D L, Daw J E, Unruh T, Chase B M, Palmer J, Condie K G, Davis K L (2012) Enhanced in-pile instrumentation at the advanced test reactor. *IEEE Trans. Nucl. Sci*. **59** 1214-1223.

Ripple D C, Burns G W (1998) *Standard reference material 1749: Au/Pt thermocouple thermometer*. NIST Special Publication, 260-134.

Ripple D C and Burns G W (2005) Thermoelectric properties of a selected lot of gold versus platinum thermocouples, In *TEMPMEKO 2004: Proc. 9th International Symposium on Temperature and Thermal Measurements in Industry and Science*, Zagreb, University of Zagreb, 447-452.

Roberts M J, and Kollie T G (1977) Derivation and testing of a model to calculate electrical shunting and leakage errors in sheathed thermocouples. *Rev. Sci. Inst*. **48** 1179-1191.

Rubin L G (1997) Cryogenic thermometry: a review of progress since 1982 *Cryogenics* **37** 341-356.

Sirota A M, and Mal'tsev B K (1959) A Gold-Platinum Thermocouple, *Meas. Tech*. **2.8** 611-3.

Shepard R L, Borkowski C J, East J K, Fox R J, Horton J L, and Blalock T V (1974) Ultrasonic and Johnson noise fuel centerline thermometry (No. CONF-741226-1). Oak Ridge National Lab., Tenn.(USA); Tennessee Univ., Knoxville (USA). Dept. of Electrical Engineering.

Wang T P and Starr C D (1982) Oxidation resistance and stability of nicrosil-nisil in air and in reducing atmospheres, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 5 (Edited by J. F. Schooley), New York, American Institute of Physics, 1147-1157.

Webster E S (2014) Low-temperature drift in MIMS base-metal thermocouples. *Int. J. Thermophys*. **35** 574-595.

Webster E S, White D R, and Edgar H (2015a) Measurement of inhomogeneities in MIMS thermocouples using a linear-gradient furnace and dual heat-pipe scanner. *Int. J. Thermophys.* **36** 444-466.

Webster E S (2015b) Effect of Annealing on Drift in Type S Thermocouples Below 900 °C *Int. J. Thermophys.***36**, 1909-1924.

Webster E S, Greenen A, and Pearce J (2016) Measurement of the inhomogeneity in Type B and Land–Jewell noble-metal thermocouples *Int. J. Thermophys.* **37** 70.

Webster E S (2017a) The Type N Thermocouple: The Good, the Bad and the Ugly. *Proc. 2017 MSA Conf*. Metrological Society of Australasia.

Webster E S (2017b) Thermal preconditioning of MIMS Type K thermocouples to reduce drift *Int. J. Thermophys.***38** 5.

Webster E S, and Edler F (2017c) Drift as a Function of Temperature in Platinum–Rhodium-Alloyed Thermoelements *Int. J. Thermophys.***38** 29.

Webster E S (2017d) Drift in Type K bare-wire thermocouples from different manufacturers *Int. J. Thermophys.***38** 70.

Webster E S (2017e) Seebeck changes due to residual cold-work and reversible effects in type K bare-wire thermocouples *Int. J. Thermophys.***38** 135.

Webster E S (2020) Trials of Pt-20% Rh versus Pt thermocouples between 157° C and 962° C *Metrologia* **57** 014005.

White D R, Jongenelen C L (2010) The immersion characteristics of industrial PRTs. *Int. J. Thermophys*. **31** 1685-1695.

Zysk E D and Robertson A R (1972) Newer thermocouple materials, In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 4 (Edited by H. H. Plumb), Pittsburgh, Instrument Society of America, 1697-1734.