18. Base-Metal Thermocouples

18.1 General Remarks

By far the largest number of thermocouples used are composed of base metals and their alloys. They are produced in large quantities by many manufacturers to conform, within acceptable tolerances, with standard reference tables [IEC (1977) (1982), CMEA (1978), GOST (1977), ASTM (1987b)].*

Although base-metal thermocouples cannot be recommended for approximating the ITS-90 with accuracies comparable to that of, for example, IPRTs, they are nevertheless so widely used that some description of them is necessary here. These thermocouples are identified by letter designations originally assigned by the Instrument Society of America and now accepted internationally (Table 18.1) [IEC (1977)]. The use of base-metal thermocouples for temperature measurements of moderate precision requires careful consideration regarding design, specifications, and application (atmosphere, temperature range).

Table 18.1: Letter-designation for Thermocouples.

Type T:	Copper(+)/Copper-nickel alloy(-)
Type J:	Iron(+)/Copper-nickel alloy(-)
Type K:	Nickel-chromium alloy(+)/Nickel-aluminium alloy(-)
Type E:	Nickel-chromium alloy(+)/Copper-nickel alloy(-)
Type N:	Nickel-chromium-silicon alloy(+)/Nickel-silicon alloy(-)
Type R:	Platinum13%Rhodium(+)/Platinum(-)
Type S:	Platinum10%Rhodium(+)/Platinum(-)
Type B:	Platinum30%Rhodium(+)/Platinum6%Rhodium(-)
-- :	Tungsten5%Rhenium(+)/Tungsten20%Rhenium(-)

18.2 Types of Base-Metal Thermocouples

Brief descriptions of the most-commonly used thermocouples are given here. The most useful of these, having a wide temperature range coupled with good accuracy, is Type N. Considerably more detail may be found in ASTM (1981).

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* ASTM: American Society for Testing and Materials (USA)
CMEA: Council for Mutual Economic Assistance (USSR)
GOST: Gosudarstvennyj Komitet Standartov (USSR)
IEC: International Electrotechnical Commission

18.2.1 Type T Thermocouple

Within its range (-200 to 350 °C) this thermocouple is the most accurate base-metal thermocouple, due in large part to the ready availability of high-purity, strain-free copper. Above 370 °C it is limited by oxidation of the copper. The accuracy usually attainable is 0.1 K, but with special calibration it may approach 0.01 K from 0 °C up to 200 °C. Because copper is universally used for electrical conductors, one may easily obtain thermal-free connections to the measuring instruments. On the other hand the high thermal conductivity of the copper thermoelement may be disadvantageous in some applications. The type T thermocouple can be used in a vacuum and in oxidizing, reducing, or inert atmospheres.

18.2.2 Type J Thermocouple

This thermocouple is most commonly used for industrial purposes in the temperature range from 0 to 760 °C in both oxidizing and reducing atmospheres. The accuracy attainable is fair to poor (0.1 to 0.5 K below 300 °C, 1 to 3 K above 300 °C); the stability is fair below 500 °C but poor above 500 °C because of the higher oxidation rate of the iron thermoelement.

18.2.3 Type K Thermocouple

This thermocouple has a wide temperature range (-200 to 1260 °C) ; in the range : above 0 °C it is the most widely used thermocouple. It is recommended for continuous use in oxidizing or inert atmospheres. At high temperatures it and Type N are the most oxidation-resistant base-metal thermocouples. In reducing, sulfurous atmospheres or in a vacuum it is necessary to use suitable protection tubes. Atmospheres with reduced oxygen content promote the so-called "green-rot" corrosion of the positive thermoelement because of the preferential oxidation of chromium; this causes large negative errors in calibration. This is most serious in the temperature range from 800 to 1050 °C, for example when the thermocouple is exposed to carbon dioxide in this temperature range. Green-rot corrosion frequently occurs when thermocouples are used in long unventilated protecting tubes of small diameter. It can be minimized by increasing the oxygen supply with large-diameter protecting tubes or ventilated tubes. Both elements of the Type K thermocouple are subject to oxidation in air above about 850 °C, but this normally leads to only a very slow increase with time of the thermocouple emf for a given temperature. Type K can be used above 1200 °C for very short periods in air without serious decalibration. Changes of up to 10 K can occur in the positive thermoelement due to short-range ordering in the nickel-chromium solid solutions, especially if the thermoelements are annealed or used near 400 °C [Fenton (1972)].

The accuracy attainable is 0.1 K below 300 °C and 1 K up to about 1000 °C. Stability is fair. The accuracy and stability of this thermocouple are limited by its susceptibility to inhomogeneities and mechanical strain (cold work) and to previous heat treatment.

18.2.4 Type E Thermocouple

This thermocouple is recommended for use up to 870 °C in oxidizing or inert atmospheres. In reducing atmospheres, marginally oxidizing atmospheres, and in vacuum it is subject to the same limitations as Type K thermocouples.

Type E thermocouples develop the highest emf per kelvin (80 μV/K at 700 °C) of all the commonly-used types and are often used primarily because of this feature. Their accuracy is better than 1 K below 300 °C and 1 to 3 K from 300 to 1000 °C.

18.2.5 Type N Thermocouple

The Type N thermocouple shows enhanced thermoelectric stability, particularly at high temperatures, compared to the other standard base-metal thermocouples (except Type T), obtained as a result of careful choice of composition of the two elements.

By suitable adjustment of composition [Burley (1972), Burley et al. (1978), Burley et al. (1982)], it has been possible to achieve higher oxidation resistance at temperatures above 1000 °C; reduce short-term cyclic variations in thermal emf due to structural phenomena (temperature range from 300 °C to 500 °C); and reduce time-independent perturbation in thermal emf due to magnetic transformations (temperature range from 50 °C to 230 °C). Furthermore, the Type N thermocouple can now be obtained in a mineral-insulated metal-sheathed construction (Section 18.3.4) with a Nicrosil sheath [Burley (1987)]. The result is an overall better long-term stability, higher reproducibility, and higher accuracy than for all other base-metal thermocouples (except Type T). Below about 500 °C, however, these advantages are not dramatic; for example, from 0 °C to 500 °C they may be more reproducible than Type K by a factor of about 2.

18.2.6 Tungsten-Rhenium Thermocouple

There are several tungsten-rhenium alloy thermocouples in use, but the only one standardized is tungsten 5% rhenium/tungsten 20% rhenium [CMEA (1978), GOST (1977)]. All have been used at 2500 °C to 2750 °C but general use is below about 2200 °C. These thermoelements are supplied as matched pairs guaranteed to meet an emf output of producer-developed tables within ± 1 percent or of standard reference tables within ± 0.5 to 0.7 percent. Tungsten as the positive leg can pose problems because heating it to or above its recrystallization temperature (about 1200 °C) causes embrittlement, resulting in a loss of room-temperature ductility, an effect that does not occur with legs containing rhenium (3 5 percent). Use is only possible in a vacuum or in high-purity reducing (hydrogen) or inert atmospheres.

18.3 Construction

A complete thermocouple temperature-sensing assembly consists of: a sensing element assembly including, in its most basic form, two dissimilar wires supported by an electrical insulator and joined at one end to form a measuring junction; a protection tube (ceramic or metal), sometimes referred to as a thermowell, which protects the sensing element assembly from the deleterious effects of corrosive, oxidizing, or reducing atmospheres; and a connector for the wire terminations of the sensing element assembly.

It is, of course, necessary to ensure that the sheath and protection tube do not themselves contaminate the thermocouple. The reader should consult ASTM (1981) for details.

18.3.1 Thermoelements

The positive and negative thermoelements for a given type of thermocouple, as supplied by anyone manufacturer, will conform to the calibration curve for that thermocouple within specified limits of error. However, because materials used for a given thermoelement by various manufacturers may differ slightly in thermal emf, larger errors may occur if positive and negative thermoelements from different sources are combined.

Recommended maximum-temperature limits according to the wire diameter of the thermoelements are given in Table 18.2. These limits apply to protected thermocouples; that is, to thermocouples in conventional closed-end protecting tubes. In actual operation, there may be instances where the temperature limits recommended can be exceeded. Likewise, there may be applications where satisfactory life will not be obtained at the recommended temperature limit.

18.3.2 Sheaths

A wide variety of materials are available for thermocouple sheaths. Up to about 100 °C the commonest include enamels and varnishes, cloth, plastics, and rubber. Most of these organic materials begin to decompose, or at least to conduct, at higher temperatures. Some silicone varnishes may be satisfactory up to about 300 °C, fibreglass up to 400 °C and with silicone as the binder up to 500 °C. The sheath has to ensure a sufficient electrical

Table 18.2: Recommended Upper Temperature Limits for Protected Thermocouples [ASTM (1987b), ASTM (1981)].

Thermocouple	Diameter				
	3.2 mm	1.6 mm	0.8 mm	0.51 mm	0.33 mm
J (JP)	760 °C	590 °C	480 °C	370 °C	370 °C
E (IN, TN, EN)	870 °C	650 °C	540 °C	430 °C	430 °C
T (TP)	--	370 °C	260 °C	200 °C	200 °C
K (KP, EP, KN), N	1260 °C	1090 °C	980 °C	870 °C	870 °C

Table 18.3: Properties of Refractory Oxides [ASTM (1981)].

Material	Composition	Maximum use Temperature	Thermal stress Resistance	Thermocouple Commonly used with
Sapphire crystal	99.9 Al_2O_3	1950 °C	very good	any
Sintered alumina	99.8 Al_2O_3	1900 °C	good	any
Sintered beryllia	99.8 BeO	1900 °C	excellent	high temperature
Sintered magnesia	99.8 MgO	1900 °C	fair-poor	any
Sintered mullite	72 Al_2O_3, 28 SiO_2	1750 °C	good	base-metals
Sintered stabilized zirconia	92 ZrO_2, 4 HfO_2, 4 CaO	2200 °C	fair-good	high temperature
Silica Glass	99.8 SiO_2	1100 °C	excellent	base-metal
Mullite porcelain	70 Al_2O_3, 27 SiO_2	1400 °C	good	base-metal
High alumina porcelain	90-95 Al_2O_3, 4-7 SiO_2	1500 °C	very good	base-metal, noble metal below 1100 °C for a variety of constructions

insulation even though it be affected adversely by moisture, abrasion, flexing, temperature extremes, chemical attack, or nuclear radiation. Hence an insulation should be selected only after considering possible exposure temperatures, the number of temperature cycles, mechanical movement, moisture, routing of the thermocouple wire, and chemical deterioration.

Above about 500 °C the various ceramics are the only materials with high enough resistivity and stability for sheaths. Fused-silica insulators are satisfactory to about 1000 °C and have excellent thermal-shock resistance. Low-purity aluminium oxide, such as porcelain or mullite, is also frequently used in this range, but above 1000 °C there is risk of contamination of the thermoelements and so its use is not recommended. Beyond 1000 °C the sheath is usually a high-purity ceramic oxide, mainly recrystallized alumina that has fair thermal-shock resistance and excellent chemical stability except in reducing atmospheres. Some properties of various refractory oxides used are given in Table 18.3.

18.3.3 Protection Tubes

A thermocouple protection tube is in principle simply a gas-tight closed-end tube containing a suitable atmosphere; it may be in the form of a well into which the thermocouple is inserted, or it may be an integral part of the thermocouple assembly. In choosing a material for the protection tube we must consider its stability, not only with respect to the thermocouple, but also with respect to the medium in which it is immersed. The choice of the proper protection tube is therefore governed by the conditions of use, such as gas tightness, thermal-shock resistance, or chemical compatibility with the medium. Metal protection tubes are adequate for base-metal thermocouples up to 700 °C (steel) or even up to 1150 °C (Ni-Cr alloys). Ceramic protection tubes are usually used at higher temperatures and sometimes also at lower temperatures in atmospheres harmful to metal tubes.

18.3.4 Thermocouple Construction

The classic construction has two wires sheathed in two single-bore or one twin-bore tube, the wire tips joined to form the hot junction, and the whole encased in a protection tube if necessary. Any of a number of methods is available for forming the hot junction (welding, brazing, hard-soldering, soft-soldering, clamping or twisting the wires). The junction must provide good electrical contact and should be as small as possible. Fluxes should be used sparingly or not at all, as the risk of contamination is great.

The compacted ceramic-insulated (also called mineral-insulated metal-sheathed) construction affords thermocouple protection together with flexibility and thermal-shock resistance. In this construction the wires are insulated by immersion in a pure, compacted. refractory-oxide powder which is contained in a thin metal sheath. Recommended sheath diameters for long-term service in air at various temperatures are given in Table 18.4. The advantages of this configuration are:

- isolation of the thermocouple wires from environment that may cause rapid deterioration ;
- reduction of long-term calibration drift;
- the lessening of temperature versus wire-size problems; whereas in the classic construction small-diameter wires have shorter lifetimes at high temperatures than large-diameter wires for a variety of reasons, in this construction the wires are firmly held in the protective sheath so that small-diameter wires can be exposed to high temperatures for long periods of time without serious deterioration.
- excellent high-temperature insulation for the thermocouple wires;
- ease of use, in particular to form bent configurations or to weld the sheath without loss of insulation;
- availability in a wide variety of sizes and materials.

For most practical purposes the sheathed thermocouple material should have a minimum insulation resistance of 100 megohms at room temperature at 500 V dc for outside diameters larger than 1.5 mm. This is readily obtained by dry, uncontaminated, compacted ceramics. The addition of moisture by hygroscopic action and subsequent movement by capillary action through exposed ends will decrease the insulation resistance. Also, the insulation resistance of all ceramics decreases with increasing temperature (approximately a factor of ten for a 200 K temperature rise).

18.3.5 Circuit Construction

The thermal emfs that must be measured are always small, ranging from near zero to a maximum of about 100 mV. Precise absolute measurements may well require a detector sensitivity of better than 0.1 μV and an accuracy of about 1 μV for base-metal thermocouple thermometry, which are possible to realize with modern digital voltmeters or classically with dc potentiometers.

In the construction of such low-level thermocouple circuits the following points must be considered [Bedford et al. (1970)]:

Table 18.4: Recommended Sheath Diameters for Mineral-Insulated Metal-Sheathed Base Metal Thermocouples for Long Term Service in Air [ASTM (1981)].

Sheath diameter (in mm)	1.0	1.5	3.0	4.5	6.0
Nominal wall (in mm)	0.18	0.25	0.5	0.62	0.8
Type K	760 °C	870 °C	870 °C	870 °C	980 °C
Type J	540 °C	650 °C	760 °C	760 °C	870 °C
Type E	650 °C	760 °C	760 °C	870 °C	925 °C

Table 18.5: Thermoelectric Power at Room Temperature of Copper versus Various Metals in Thermocouple Measurement Circuits [Bedford et al. (1970)].

Metal	Thermoelectric power in μV/K	Remarks
group a		preferred materials
copper from a different spool of wire	± 0.02	
low thermal solder	0.1	
lead free-turning copper	0.1	
group b		materials are likely to require some thermal uniformity
silver	0.2	
gold	0.2	
coin silver	-0.4	
group c		materials need very good thermal uniformity
carbon	0.6	
platinum10%rhodium	0.8	
beryllium copper	0.9	
manganin	1.5	
coin copper	1.6	
yellow brass	1.6	
phosphor bronze	3.2	
lead50%tin solder	3.0	
group d		materials likely to be unsuitable
steels	3.2 … -5.6	
Chromel	-20	
constantan	40	

- temperature gradients and variations of temperature with time should be kept as small as possible. Only strain-free copper should be used in the regions of appreciable temperature gradients; all junctions should be in a zero-gradient region.
- all connections should be shielded from thermal radiation; this applies particularly when non-copper components are involved. A further improvement in accuracy is likely to result from the introduction of some heat capacity around the components, since this tends to reduce transient temperature fluctuations.
- conductor materials should be as thermoelectrically similar as possible; in practice this means that they should have thermoelectric powers near that of copper. The relative quality of various metals that can be used in thermocouple circuits is shown in Table 18.5.

Highest system accuracy can be obtained by running the thermocouple conductors directly to the reference junction, so avoiding the use of extension wires. If extension wires must be used, however, as in the case of metal-sheathed mineral-insulated thermocouples, the extension wires become an integral part of the temperature-sensing system. The user must be aware of the need to keep the temperature of the reference junction below 200 °C in the interest of overall accuracy. In any case, the termination should be designed in such a way as to guarantee that the temperature of the terminals is uniform.

18.4 Annealing of the Thermoelements

As with noble-metal thermocouples the base-metal thermoelements should be in a condition of thermodynamic equilibrium to ensure metallurgical stability over the temperature range of application. Accurate temperature measurements are generally impossible when this equilibrium condition does not exist. Annealing removes existing non-equilibrium states; for example, strains introduced by cold working. Inadequate annealing may result in errors varying in magnitude from a few tenths of a kelvin to several kelvins depending upon the temperature being measured and the temperature gradients along the thermoelements.

All base-metal thermocouple wires are usually delivered in an annealed state. The heat treatment given by the producer can be generally considered as sufficient, and seldom is it advisable to further anneal the thermoelements before testing. If an annealing should be necessary, however, the annealing temperature should be higher and the depth of immersion greater than will be encountered in service. A rough test for the adequacy of the annealing procedure is the reproducibility of the thermocouple emf at some fixed temperatures (such as fixed points) after consecutive annealing periods.

In the case of the Types K and E thermocouples and the negative legs of Types T and J thermocouples (all containing nickel or nickel-chromium), the thermodynamic equilibrium is limited by diffusion of constituents (temperature range from 300 °C to 500 °C) and magnetic-transformation processes (temperature range from 50 °C to 200 °C) so that a high accuracy (0.1 K) can be obtained only by special heat treatment, using specified calibration procedures, and in special application conditions [Burley et al. {1982)].

18.5 Guidelines for Proper Handling and Use -Installation and Sources of Errors

For accurate temperature measurements by means of base-metal thermocouples, in particular by metal-sheathed thermocouples, the following guidelines should be considered [ASTM (1981)]:

- be sure that the sheath or protection tube material will survive the environment.
- be sure that the thermocouple assembly is fully annealed for maximum life of sheath or protection tube and stability of the thermocouple calibration.
- remember that the life of the thermocouple will decrease with higher application temperatures and smaller thermoelement and sheath diameters and is limited by grain growth (Tables 18.2 and 18.4).
- in the case of metal-sheathed thermocouples, it must be possible to bend the sheath around a mandrel twice the sheath diameter without damage.
- in metal-sheathed thermocouples, the appearance of moisture in the assembly is indicated by a diminution in insulation resistance; this can cause an error in temperature measurement by electrical shunting. Moisture can be removed by heating and sealing the exposed ends of the thermocouple.
- metal-sheathed thermocouples should not be repeatedly bent at the same location as this work-hardens the sheath and may change the thermocouple calibration.

To evaluate the performance of a thermocouple circuit, the numerous possible sources of error should be considered: thermal shunting; electrical shunting; calibration; decalibration (from instability or drift); extension wires; reference junction.

A thermocouple, just as any other contacting temperature sensor, disturbs the temperature distribution of any object to which it is attached because it has a finite size and Iconducts heat away from (or to) the object. The thermocouple itself loses heat to (or gains heat from) its surroundings by conduction, convection, and radiation. This heat transfer can cause the thermocouple hot junction to be at a different temperature from that of the object.

These effects cause a thermal-shunting error, the magnitude of which depends largely on the method of thermocouple installation. This error is avoided when the portion of the thermocouple near the hot junction is isothermal and at the temperature of the object whose temperature is to be measured. This error can be especially large when the heat transfer from the measuring object to the thermocouple is poor and/or the heat transfer from the thermocouple to the surroundings is large (such as in surface temperature measurement).

At higher temperatures, where the electrical resistivity of the insulator will be lower, an electrical shunting will occur and can cause temperature-measurement errors, especially at temperatures above 1500 °C. This effect is greater in metal-sheathed thermocouples than it is in the classic type of construction because of the larger area of electrical contact between the insulator and the thermoelements.

Calibration errors depend upon the accuracy of the calibration standards and the calibration method applied (Sec. 18.6).

Decalibration errors or drift, i.e. a change of the emf-temperature relationship with time, can occur even if the thermocouples are heat-treated, assembled, calibrated, and installed with utmost care. In the literature (e.g. [Kinzie (1973)]) many results are reported that show the same trends of decalibration but the magnitudes differ because of undetected differences in experimental variables that control the drift rates.

Several factors cause a thermocouple to drift, such as: chemical reactions of the thermoelements with the gaseous environment, with the electrical insulator, or with the object whose temperature is to be measured (including impurities in the environment, insulator, or object); metallurgical transformations (such as order-disorder transformations or secondary recrystallization); loss of alloying elements by selective evaporation or oxidation at higher temperatures; transmutation by nuclear radiation.

Drift rates generally increase rapidly with increasing temperature and are larger for smaller-diameter thermoelements.

Extension-wire errors arise from the differences between the thermoelectric properties of the thermoelements and of the corresponding extension wires. In high-precision measurements the use of such wires should be avoided whenever possible. If extension wires must be used due to installation conditions, any error can be reduced by calibration of the complete thermocouple/extension-wire assembly and by ensuring a uniform temperature at the junctions.

In thermocouple thermometry all emf measurements are referred to the temperature of the reference junction. Any error in this temperature, therefore, is directly involved in the error of the measured temperature. Reduction of this error is possible by ensuring that both thermoelement reference junctions have the same temperature and that this temperature is measured with the desired accuracy with another thermometer (mercury-in-glass thermometer or resistance thermometer) or by realization of a fixed-point temperature (ice point or water triple point, see Sec. 9.4).

18.6 Calibration of Base-Metal Thermocouples

The calibration of a thermocouple consists of the determination of its emf at a sufficient number of known temperatures, some of which can be fixed points, so that with some accepted means of interpolation its emf will be known over the entire temperature range in which it is to be used. In comparison to the situation with noble-metal thermocouples (Sec. 9.5), the number of calibration points necessary with base-metal !thermocouples to reach their limit of accuracy will be greater because of the more complex emf-temperature relationships and because more factors can influence the deviation of the real thermocouple characteristics from the reference table or polynomial values. Because of this the methods of interpolating between the calibration points become of prime importance for interpolation accuracies approaching 0.1 K [ASTM (1981)]. For lower accuracies comparatively simple methods of calibration will usually suffice (comparison with a standard thermometer in an isothermal environment).

The errors in calibration are of two sorts: those influencing the observations at the calibration points and those arising from the interpolation between the calibration points. The influence of the first can be reduced by use of well-designed equipment and careful techniques. The recommended method to reduce the second error is to fit the differences between the observed calibration values and the values obtained from standard reference tables, i.e. the deviation of the real characteristics of the thermocouple from the nominal one. In order to determine the mean deviation curve the application of least-squares fitting is useful, but in several cases a graphical interpolation method will be sufficient (Sec. 9.5).

Typical accuracies to be expected with the various thermocouples if calibrated using fixed points are given in Table 18.6, and when calibrated by comparison techniques are given in Table 18.7. The interpolation formulae used to generate the standard reference tables are given in Appendix F. No such formulae have *yet* been internationally agreed upon for the tungsten-rhenium types.

Table 18.6: Accuracies Attainable with Thermocouples using Fixed Point Techniques [ASTM (1981)].

Type	Temperature range (°C)	Calibration points	Calibration uncertainty at observed points (K)	total uncertainty of interpolated values (K)
S or R	0... 1100	Zn,Sb,Ag,Au	0.2	0.3
S or R	0...1100	Sn,Zn,Al,Ag,Cu	0.2	0.3
B	600...1100	Al,Ag,Au	0.2	0.5
E	0... 870	Sn, Zn, Al	0.2	0.5
J	0...760	Sn,Zn,Al	0.2	1.0
K	0...1100	Sn,Zn,Al,Ag,Cu	0.2	1.0
N	0... 1100	Sn, Zn, Al, Ag, Cu	0.2	1.0
W/Re	1000 ...	Au, Ni, Pd, Pt, Rh	0.5 ...	2.7 ...
	...2000		...5.0	...7.0

Table 18.7: Accuracies Attainable with Thermocouples using Comparison Techniques in Laboratory Furnaces [ASTM (1981)].

Type	Temperature range (°C)	Calibration points	Calibration uncertainty at observed points (K)	total uncertainty of interpolated values (K)
S or R	0...1100	every 100 K	0.3	0.5
B	600... 1100	" " "	0.3	0.5
E	0... 870	" " "	0.5	0.5
J	0... 760	" " "	0.5	1.0
K	0...1100	" " "	0.5	1.0
N	0...	" " "	0.5	1.0