

## 9. Platinum Thermocouples

### 9.1 General Remarks

Thermocouples employing platinum in combination with platinum-rhodium alloys, gold, or palladium have been found to be the most reproducible of all the various types. They are resistant to oxidation in air and, because of their high melting points, can be used up to very high temperatures. The best-known member of this group is Pt10Rh/Pt\* (or type S, or 10/0). It was long considered more accurate and has probably been studied more than any other thermocouple; moreover, and presumably for these reasons, it served as a defining instrument in the ITS-27, the IPTS-48 and the IPTS-68. It is not one of the defining instruments of the ITS-90, its role having been taken over by the SPRT. Any Pt10Rh/Pt thermocouple, in order to qualify as a defining instrument for interpolation in the range from 630.74 °C to the gold point (1064.43 °C), had to meet strict requirements for purity and thermocouple emf [CCT (1976)].

The Pt13Rh/Pt (or type R, or 13/0) thermocouple is very similar in its properties to the type S; containing 13% Rh by weight, it has a little higher sensitivity and probably also a little higher reproducibility.

In many situations the precision of types S and R thermocouples, especially above 500 °C, is limited to about  $\pm 0.2$  °C. For more precise measurements McLaren and Murdock (1987) have shown that the gold/platinum thermocouple is clearly superior in stability, homogeneity, and sensitivity (about twice that of type S). It even challenges the SPRT on the basis of simplicity and economic practicality. With care, temperatures can be measured to within  $\pm 10$  mK in the range 0 °C to 1000 °C. For higher temperatures the palladium/platinum thermocouple has likewise shown considerable promise as being more accurate than type S or R. Precision within  $\pm 20$  mK at 1100 °C and  $\pm 50$  mK at 1300 °C has been achieved. Studies of both of these types are in progress.

The upper temperature limit of use for types R and S thermocouples in an oxidizing atmosphere is quoted as high as 1600 °C (for 0.5 mm diameter wires). Better platinum-rhodium alloy combinations for thermometry under oxidizing conditions above 1100 °C, however, are Pt30Rh/Pt6Rh (or type B, or 30/6) or the non-standardized combinations Pt20Rh/Pt5Rh (20/5) and Pt40Rh/Pt20Rh (40/20). These have proven to be exceptionally stable and may be used continuously in air to 1700 °C. In one test, for example, after 200 h heating at 1700 °C in air, the emf of the 20/5 thermocouples had decreased the equivalent of about 5 K at the palladium point (1555 °C) [Bedford (1964)];

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\* See footnote on page 6.

after 500 h at 1700 °C in air, the 40/20 thermocouples exhibited changes equivalent to 4 K at the palladium point [Bedford (1965)]. Compared with 20/5, type B (30/6) has some superior thermoelectric properties, better tensile properties at higher temperatures, and the additional characteristic that its emf varies only between -2.5 and 2.5  $\mu\text{V}$  in the range from 0 to 50 °C, meaning that the temperature of the reference junction can often be neglected or simply corrected for [Burns and Gallagher (1966)].

As the melting point of platinum-rhodium thermoelements increases with increasing rhodium content, thermocouples comprising platinum-rhodium elements of higher rhodium content are relatively more stable to higher limits of temperature. The 40/20 thermocouple is useful for accurate measurements up to 1850 °C and is superior to type B in stability at 1700 °C, although its thermoelectric power in the range 1700 to 1850 °C is only about 4.5  $\mu\text{V}/\text{K}$  or less than half of that of type B. Which one is chosen for measurements from 1500 to 1700 °C would have to be based on the total temperature range, the duration of the measurements, the availability of the thermoelements, and the importance of the magnitude of the thermoelectric power for the user's measuring equipment.

For all of the above thermocouple types (except Pd/Pt and Au/Pt) the emf-versus-temperature characteristics based upon the IPTS-68 were determined by national metrological institutions, resulting in the establishing of reference tables [Bedford (1964), Bedford (1965), Burns and Gallagher (1966), Bedford (1970), Bedford et al. (1972), Powell et al. (1974)]. Those for types R, S, and B have been internationally accepted [IEC (1977)]. The equations with which to generate these tables are given in Appendix F. These reference tables ensure, for users throughout the world, that manufacturers supply wires with a guaranteed accuracy of the emf-versus-temperature characteristics within known tolerances. The requirements of the user dictate whether calibration is required or not. If the desired accuracy is higher than the allowed tolerances of the standard reference tables, or when it is expected that the emf has drifted outside of these tolerances, the thermocouple should be calibrated (see Sec. 9.4).

## 9.2 Construction

The pure platinum and the alloy wires used for constructing a 10/0 thermocouple to be used as a standard interpolating instrument should be at least 0.35 mm in diameter (preferably 0.5 mm) and at least 1 m long. Smaller-diameter wires are prone to damage during unsheathed annealing at high temperatures (see Sec. 9.3) and homogeneity during fabrication is more difficult to achieve; larger-diameter wires are more expensive and can be the cause of significantly altering the junction temperature by heat conducted to or from

the junction. The wires of a standard thermocouple should run in continuous lengths from the hot junction to the reference junction. In most calibration equipment 1 m is about the minimum length that will allow this.

After the wires have been electrically annealed (see Sec. 9.3), they are mounted in an appropriate insulator. For accurate thermocouple thermometry it is better to assemble the thermocouple than to purchase it as a complete sheathed unit. This allows for the best choice for each part of the system.

The insulators which separate and protect the thermocouple wires are an extremely important part of the installation. The choice of refractory will depend upon the particular operating conditions so it is difficult to lay down rules that cover every installation. Insulators should be of highest quality. For an oxidizing atmosphere the choice of refractory is very wide. Fused silica will withstand thermal shock and can be used satisfactorily to 1000 °C. Pure alumina can be used to 1900 °C. The alumina-silica refractories such as sillimanite and mullite can be used up to 1700 °C but are not recommended for highly accurate work. These alumina-based refractories are less resistant to thermal shock than is fused silica; if they must be immersed suddenly they should be preheated to avoid fracture. Under reducing conditions, or in vacuum, silicious refractories must be avoided because, in contact with platinum, they are reduced, releasing elemental silicon which embrittles the wire. In the worst case a platinum/platinum-silicide eutectic will be formed and since this has a melting point of 820 °C, failure of the thermocouple will result. In this context pure magnesia is one of the more stable refractories and will usually provide satisfactory service. Pure alumina can be used under inert conditions, but under reducing conditions it has been found occasionally to be reduced and alloyed with platinum. Beryllia and thoria are particularly good refractories to use in conjunction with platinum but they are far more expensive than those mentioned before. Also, beryllia is slightly toxic and thoria slightly radioactive, so extreme caution should be exercised [Zysk (1964)].

These ceramic insulators are fired with organic binders so that some carbon impurities remain. In order to reduce the carbon concentration and to remove surface contamination, all insulators should be fired for an hour at 1200 °C in air before assembly. It has been demonstrated that impurities in the insulator produce substantial changes in the thermoelectric power of type S thermocouples. The largest effect is caused by iron and can be minimized by the use of ultra-high-purity alumina or beryllia. The effect is smaller in an oxidizing atmosphere than in vacuum or inert atmospheres.

Each wire can be mounted into a separate single-bore insulator or, more commonly, both are mounted in a single twin-bore insulator of outside diameter 3 to 4 mm which

normally extends about 50 cm back from the junction. This length should be sufficient to reach from the centre to the outside of the furnace. The wires at the hot junction are joined by welding. The weld should be mechanically sound and as small as possible. The wires from the reference junction to the ceramic are insulated with a flexible material such as plastic or fibreglass. Care should be taken to avoid kinking when threading the wires into the insulators. For insertion into a fixed-point or other furnace, the hot junction and ceramic insulator are enclosed in a close-fitting, closed-end, fused-silica or alumina tube to minimize thermocouple contamination.

For the reference junction, good practice is to solder or mechanically connect a small-gauge ( $\approx 0.25$  mm diameter) copper wire to each thermocouple wire.

Types S and R thermocouples of the mineral-insulated metal-sheathed construction are also in wide use. In general, they are not as stable as those of the standard construction but they have many compensating advantages (see the discussion of base metal thermocouples of this construction in Section 18.3.4).

### **9. 3 Annealing of the Thermoelements**

All thermocouples should be in a condition which is metallurgically stable over the envisaged temperature range. Generally this involves annealing the wires along their entire length. A thermocouple wire which is not uniformly annealed, particularly over that portion which is subjected to a temperature gradient, will not give a repeatable output. The purpose of annealing the wires of a standard thermocouple is to remove strain due to cold work, remove contaminants, and equilibrate point defects, without at the same time allowing excessive grain growth or significant evaporation of platinum or rhodium from the alloy wire. The annealing is usually done by passing an electric current through each wire as it hangs between two electrodes in air. If the wire diameter is smaller than 0.35 mm the annealed wires may not support their own weight, as a result of grain growth or intermittent local superheating, and may stretch substantially or even break.

It is recommended [CCT (1976)] that the bare platinum thermoelement be annealed at 1100 °C and that the bare platinum-rhodium thermoelement be annealed at 1450 °C for up to 1 h to remove strain due to cold work, to oxidize residual impurities, and to dissociate rhodium oxide. The wires should be cooled slowly (10 to 30 minutes) in order to avoid quenching-in of non-equilibrium concentrations of point defects. After the wires are mounted in insulators, the portion of the thermocouple that will be above ambient temperature in use should be briefly reheated to 1100 °C and slowly cooled to remove cold work introduced during assembly. Following this, a measurement uncertainty of a single

determination is about  $\pm 0.2$  K at the 99% confidence level in the IPTS-68 defining range (630.74 °C to 1064.53 °C) for a constant immersion depth and constant temperature gradient of the furnace used [Jones (1968)]. It has been shown, however, that such thermocouples as ordinarily prepared are inhomogeneous, and variations of the immersion depth or the temperature gradient of the furnace can result in emf variations approaching 1 K at the copper point (1084.88 °C) [McLaren and Murdock (1972)].

Another annealing procedure that appears to give a stable thermoelectric power at higher temperatures ( $\geq 1100$  °C) is to heat the thermocouple wires electrically to about 1450 °C for 45 min and then to cool them quickly in air to 750 °C. They are held at that temperature for 30 min, then cooled to room temperature in a few minutes in air. After assembly into insulators, all of the thermocouple that will be at high temperature or in a temperature gradient is annealed at 1100 °C in a furnace and then cooled slowly, taking about 2 h to fall to 300 °C [Guildner and Burns (1979)].

A more sophisticated annealing procedure which leads to better reproducibility involves the following steps [McLaren and Murdock (1972), Murdock and McLaren (1972)]: New platinum and platinum-rhodium thermoelements are first given full-length, electric, bare-wire anneals at 1300 °C for from 1 to 10 h and are then quenched (abrupt switch-off of current) to room temperature to minimize permanent oxidation of the alloy elements. This is followed by a separate 1 h bare-wire anneal of each element at 450 °C. After assembly into a sheath, the sheathed portion of the thermocouple receives a further anneal at 450 °C (16 to 24 h). This preparatory anneal places the thermoelements in a reference state. That is, they are homogeneous in thermoelectric power, are as oxide-free as possible along their full length, and are equilibrated for vacancy concentrations at 450 °C. The subsequent sequence of restoring and maintenance anneals differs from the preparatory anneal only by shortening the 1300 °C wire anneal to 10 min, a time normally sufficient to remove the surface and internally-diffused oxide from the alloy elements that have been immersed for short times in air in the oxidizing region 500 to 900 °C. Longer, oxide-cleaning anneals at 1300 °C are required to restore the thermoelectric power and homogeneity in alloy elements that have been more heavily oxidized during long periods.

#### **9.4 Guidelines for Proper Handling and Use - Installation and Sources of Errors**

Because the thermocouple emf is generated in the region of temperature gradient along the wires and not at the isothermal junctions, the principal errors arise from inhomogeneities in the portions of the wires that lie in the temperature gradient. These

inhomogeneities result from the unavoidable production of rhodium oxide on the alloy wires and from changes in vacancy concentrations in both wires in those portions that experience temperatures between 500 °C and 850 °C. Other mechanisms probably contribute also, such as order-disorder transitions in the structural lattices and differential thermal expansion between wires and the ceramics in which they are imbedded.

McLaren and Murdock (1979a, 1979b, 1983) have shown in detail that the emf of a Type S thermocouple annealed according to the procedures given in Sec. 9.3 is not constant for different depths of immersion of the hot junction in a freezing metal ingot. In freezing copper, for example, the emfs vary somewhat irregularly but generally increase with a 10 cm increase in immersion, followed by a significantly higher decrease on withdrawal. The maximum variations in emf are typically a few microvolts. These variations are caused by inhomogeneities along the wires resulting from the processes mentioned above. A different type of anneal will produce homogeneous wires, but unfortunately they cannot be maintained in the homogeneous state in service. As a result, an initial insertion of a thermocouple with this type of anneal into a fixed-point ingot produces a constant emf if the temperature is not higher than 1000 °C, but subsequent withdrawals and insertions produce emfs that increase almost linearly (but moderately reproducibly) with immersion depth. A reanneal returns the wires to their original homogeneous state. Errors from the other sources can be reduced, with a little care, below  $\pm 0.2$  K.

Apart from this, contamination is by far the most common cause of thermocouple error and often results in ultimate mechanical failure of the wires. Elements such as Si, Al, P, In, and Sn combine with platinum to form low-melting-point eutectics and cause rapid embrittlement, leading to failure of the thermocouple wires. Elements such as Ni, Fe, Co, Cr, and Mn all affect the emf output of the thermocouple to a greater or smaller degree, but contamination by these elements may not result in wire breakage and can only be detected by regular checking of the accuracy of the thermocouple.

Contamination can be minimized by careful handling of the thermocouple materials during assembly and by using appropriate refractory sheathing. Care should be taken to prevent dirt, grease, oil, or soft solder from coming into contact with the thermocouple wires. If the atmosphere surrounding the thermocouple sheath contains any metal vapor, the sheath must be impervious to such vapors. Contamination of the pure-platinum arm by transfer of rhodium (probably through the oxide phase) from the alloy arm can be suppressed by using a continuous twin-bore alumina insulator to support and protect the wire over its whole length in the temperature gradient. For the higher temperatures where this is likely to occur, it is preferable to use Pt30Rh/Pt6Rh or other double-alloy thermocouples because these are much less affected by contamination or rhodium transfer.

Contamination by reduction of the alumina can be avoided by ensuring that the furnace within which the thermocouple is used allows free access of air to the thermocouple. If the furnace itself operates under an inert or reducing atmosphere the thermocouple must be protected by a closed-end alumina or silica sheath, one end of which is open to the air.

Errors can also result from loss of homogeneity due to strain in one or both wires. The effect of strain is to reduce the emf and so give a temperature reading that is too low. The strain can be removed by reannealing the whole thermocouple. Thermocouple installations should be designed in such a way that there is no strain on the wire while in service; for example, use in a horizontal position is preferable to use in a vertical position.

Thermocouples must be installed in such a way that they have adequate immersion and the reference junction is at a uniform and known temperature (preferably 0 °C, see below). Immersion is adequate when the heat transfer to the thermocouple is such that the difference between the measuring-junction temperature and the temperature to be measured is smaller than a given tolerance. On the other hand, the means of ensuring adequate immersion must not invalidate the measurement sought. It is common that the design of the experiment is substantially affected by balancing these requirements.

Thus the installing of the thermocouple requires considerations regarding annealing, calibration, tempering, insulation of the thermoelements from each other and from the surroundings, and protection from chemical or physical deterioration. The installation should also provide for means of occasional recalibration.

Very important to the correct use of a thermocouple is the realizing of a stable reference junction. It is easy to make a reference junction at 0 °C reliable to  $\pm 0.01$  °C by using a vacuum flask into which is placed a mixture of shaved ice and distilled water. This will enable the user to refer this thermocouple cold junction directly to 0 °C, which is advantageous because most reference tables are so referred. The thermocouple wires are connected to pure copper wires, by suitably twisting them together or by soldering without flux, and inserted into separate closed-end glass tubes that are in turn inserted into the ice mixture. The thermocouple-to-copper junction is placed at a sufficient depth (> 20 cm) in the reference unit that a stable and accurate reference temperature is ensured [Sutton (1975)]. Oil should not be placed in the glass tubes (in an attempt to improve thermal contact) as this can do more harm than good; the oil tends to migrate up the insulation towards the hot zone and, in any case, thermal contact is adequate without it.

Automatically-operating ice-point devices with sufficient reproducibility are also available.

It is not recommended to use extension wires for accurate temperature measurements as they cause additional errors.

## 9.5 Approximations to the ITS-90

Platinum rhodium thermocouples can be calibrated by comparison with a laboratory standard thermocouple in an electric furnace by the techniques described in Chapter 2. Typical accuracies achievable in this way are listed in Table 18.7.

A thermocouple can also be calibrated at fixed points according to the methods described in "Supplementary Information for the ITS-90" [CCT (1990)]. However, for most thermocouple measurements, the requirements described there are unnecessarily extreme. Because of the much lower accuracy expected in secondary measurements, the quality of the furnace can be lower, melts as well as freezes are adequate, the metal need not be as pure, the mass of metal may be smaller, etc. Especially at high temperatures, where it becomes difficult to provide proper furnaces and crucibles for freezing-point determinations, fixed-point calibrations can be made by the wire, or wire-bridge, method as described in Sec. 3.3.2. Similarly, the thermocouple can be calibrated using miniature fixed points as described in Sec. 3.3.3 [Tischler and Korembliit (1982)].

Whatever method is used, to complete the calibration the differences of the thermocouple emfs from the standard-reference-table emfs at the appropriate assigned temperatures on the ITS-90 for the particular fixed points are plotted and a smooth curve is drawn through all points including the origin. These differences are generally small and the curve is only slightly non-linear. It is recommended that a second- to fourth-degree polynomial be fitted to these differences [Jones and Hall (1978); Bedford and Ma (1980)]. This deviation curve in conjunction with the reference table [Powell et al. (1974); IEC (1977)] gives the emf-versus-temperature characteristics of the individual thermocouple. The accuracy of the calibration depends upon the methods used, the temperature range of the calibrations, and the thermocouple materials. The calibration accuracy, however, is seldom the limiting factor in thermocouple measurements, being outweighed by errors associated with the type of installation and with instability and drift of the thermocouple emf. As a rough guide, overall accuracies may be better than  $\pm 0.5$  K to the gold point (1064 °C),  $\pm 1.0$  K to the palladium point (1555 °C) and  $\pm 2.0$  K to the platinum point (1769 °C). The precision attainable with thermocouples under well-defined and constant conditions (immersion depth and temperature gradient) is somewhat better than these accuracies. If only the wire-bridge method of calibration is used, accuracies can be worse. For example, in a comparison of wire-bridge Au and Pd calibrations with optical pyrometer calibrations, agreement was within 0.7 K at Au and 1.5 K at Pd amongst three laboratories [Crovini et al. (1987)]. Comparison of quadratic interpolation of these differences of Au and Pd emfs from the standard table with the pyrometer calibrations showed disagreement of from  $\pm 0.2$  K to  $\pm 0.9$  K for different



thermocouples between the two fixed points. Use of this quadratic interpolation below 1064 °C or above 1554 °C was not recommended.