PRECISION COMPARISON OF STABILITY AND ACCURACY OF THERMOCOUPLES OVER THE RANGE FROM 0° TO 1600°C

Thesis

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AIM OF WORK

One aim of the present work is to seek a precision in the measurement of temperature by thermocouples and to study the precautions that must be observed in order to obtain various degrees of accuracy in the calibration of thermocouples over the range 0° to 1600°C.

The following two thermocouples :

1) Platinum versus platinum - 10 percent rhodium.
2) Nickel - nickel chrome.

have been selected for investigating the melting and freezing temperaturos of pure metals (tin, zinc, antimony, silver, gold and copper). It is planned to test the e.m.f.-temperature relations using different fixed point combinations and to study the effect of these selected bombinations on the International combination (antimony - silver - gold).

It is also planned to investigate the effect of extending the thermocouple scale beyond the International range and to study the observed uncertainties and deviations.

S U M M A R Y

An investigation of freezing and melting temperatures with two thermocouples (Platinum versus platinum - 10 percent rhodium and nickel - nickel chrome) on 6 grades tin and zinc and 5 grades antimony, silver, gold and copper has been carried out. The metal of the order of 350 gms was placed in a narrow graphite crucible heated in a tubular electric furnace. The metal was covered with about 2 cms of ultra pure graphite to reduce oxidation. The melting point of gold was determined by the wire method using a limited amount of the material. The techniques and difficulties encountered in measuring temperatures to the highest precision are discussed. Extention of the scale below and above the range of the International Temperature Scale has been tried to investigate the validity of the equation :

$$E = a + bt + ct^2$$

Values of the constants a , b and c determined by different selected fixed point combinations (gold - silver - antimony, copper - silver - antimony, copper - silver - zinc, gold - antimony - zinc, silver - zinc - tin, copper - silver - antimony - zinc, gold - silver - antimony - zinc) have been compared with those obtained using the International Temperature Scale combination (gold - silver - antimony).

By using an equation of the form :

$$E = a' + b't + c't^2 + d't^3$$

the temperature range of the platinum versus platinum - 10 percent rhodium thermocouple can be extended down to 300°C without introducing an uncertainty of more than 0.1°C in the International range (630.5°C to 1063°C) and may be in error ranging from 0.2° to 2°C if applied to the chromel-alumel thermocouple in the range 400°C to 1100°C.

Values of e.m.f. at different temperatures with interval of 10°C were computed using the different mentioned combinations and formulas. These values are compared with each others and with those tabulated in the N.B.S. circular 561. The results indicate that the platinum thermocouple can be used in the range 0°-1600°C with an error not greater than 0.3 degree and the maximum error in using the chromel-alumel in the range 0° to 1100°C is 1 degree.

The only difference between the IPTS - 58 and the IPTS - 48 in the range 630°C to 1063°C is the values assigned to the defining fixed points. The values 630.74°C, 961.93°C and 1064.43°C were assigned instead of the values 630.5°C, 960.8°C and 1063°C for the freezing points of antimony silver and gold respectively.

The difference between the two scales is discussed and the computed values of temperature in the two scales show that the difference increases steadily from 0.165° at 630°C to 1.42° at 1063°C.

CHAPTER I

INTRODUCTION

The object in the calibration of any thermocouple is to dtermine an e.m.f. - temperature relationship in which the temperature is expressed on a definite and reproducible scale. The International Temperature Scale (ITS) adopted in 1927[1, 2] and revised in 1948[3, 4] is now in practically universal use. The scale is based upon a number of fixed and reproducible equilibrium temperatures to which numerical values are assigned and upon specified formulae for the relations between temperature and the indications of instruments calibrated at these fixed points. From the freezing point of antimony to the freezing point of gold the temperature (t) is defined by the formula :

$$E = a + bt + ct^2$$

where E is the electromotive force of a standard thermocouple of platinum and rhodium platinum alloy, when one junction is at 0°C and the other is at the temperature t°C. The constants a, b and c are to be calculated from measured values of E at the freezing points of antimony, silver and gold.

The antimony used in determining these constants shall be such that its freezing temperature, determined with a standard resistance thermometer is not lower than 630.3°C. Alternatively, the thermocouple may be calibrated by direct comparison with a standard resistance thermometer in a bath at any uniform temperature between 630.3° and 630.7°C.

The Platinum wire of the standard thermocouple shall be annealed and of such purity that the ratio R_{100}/R_0 is greater than 1.3910. The alloy wire shall consist nominally of 90 % Platinum and 10 % rhodium by weight, When one junction is at 0°C and the other at the freezing point of antimony (630.5°C) silver or gold, the completed thermocouple shall have electromotive forces, in microvolts, such that :

$$E_{AU} = 10.300 \pm 50 \ \mu V$$

$$E_{AU} - E_{Ag} = 1.183 \ \mu V + 0.158 \ (E_{Au} - 10.310 \ \mu V) \pm 4 \ \mu V$$

$$E_{AU} - E_{630.5} = 4.776 \ \mu V + 0.631 \ (E_{Au} - 10.310 \ \mu V) \pm 8 \ \mu V$$

In order to calibrate thermocouples to yield temperatures on the ITS, it is apparent from the definition that they must be so calibrated that their indications agree with those of standard Platinum resistance thermometer in the range - 182.97°C to 630.5°C the standard platinum versus platinum - 10 percent rhodium thermocouple in the range 630.5°C to 1063°C, and the optical pyrometer above 1063°C. The most direct procedure would therefore be to compare the thermocouples directly with these primary instruments in the appropriate temperature ranges. However, to follow such a procedure in the calibration of every thermocouple, requires more time and apparatus than is justifiable or necessary because, in most cases, other methods are available which yield results sufficiently accurate. For example, a thermocouple may be compared indirectly with any of the primary instruments by determining its e.m.f. at a number of fixed points, either those which are used in defining the scale or others, the values of which have been determined with the primary instruments. If a few laboratories maintain the apparatus necessary to calibrate thermocouples as working standards to yield temperatures on the ITS, these standards may be used subsequently to calibrate other thermocouples. This procedure is used for more than any other because the comparison of the indications of two thermocouples is usually simpler than the comparison of two different types of instruments.

The temperature - e.m.f. relationship of a homogeneous thermocouple is a definite physical property and therefore, does not depend upon the details of the apparatus or method employed in determining this relation. Consequently, there are innumerable methods of calibrating thermocouples, the choice of which depends upon the type of thermocouple, temperature range, accurancy required, size of wires, apparatus available, and personnel preference.

Thermocouple calibrations are required with various degrees of accuracy, ranging from 0.1°C to 5°C or 10°C. For an accuracy of 0.1°C, agreement with the ITS and methods of interpolating between the calibration points become problems of prime importance, but for an accuracy of about 10°C, comparatively simple methods of calibration will usually suffice. The most accurate calibrations in the range - 190° to 300°C are made by comparing the thermocouples directly with a standard platinum resistance thermometer in a stirred liquid bath. In the range 300°C to 630.5°C thermocouples are most accurately calibrated at the freezing or boiling points of pure substances. Between 630.5°C and 1063°C, the platinum versus platinum - 10 percent rhodium thermocouple calibrated at the freezing points of gold, silver, and antimony serves to define the ITS, and other types of thermocouples are most accurately calibrated in this range by direct comparison with the standard thermocouple calibrated as specified. Other platinum versus platinum - rhodium thermocouples may be calibrated just as accurately at the fixed points as the platinum versus platinum - 10 percent rhodium thermocouple, but interpolated values at intermediate points may depart slightly from the ITS. Above 1063°C, the most basic calibrations are made by observing the e.m.f. when one junction of thermocouple is in a black-body furnace, the temperature of which is measured with an optical pyrometer. However, the difficulties encountered in brining a black-body furnace to a uniform temperature make the direct comparison of these two types of instruments by no meants a simple matter.

Although the platinum versus platinum - 10 percent rhodium thermocouple serves to define the scale only in the range 630.5°C to 1063°C, this type of thermocouple calibrated at fixed points is used extensively both above and below this range as a working standard in the calibration of other thermocouples. For most industrial purposes, a calibration accurate to 2°C or 3°C in the range from room temperature to 1200°C is sufficient. Other thermocouples can be calibrated by comparison with such working standards almost as accurately as the calibration of the standard is known. However, it might be pointed out that outside the range 630.5°C to 1063°C any type of thermocouple suitable for the purpose, and calibrated to agree with the resistance thermometer or optical pyrometer in their respective ranges, has as much claim to yielding temperatures on the ITS as the platinum versus platinum - 10 percent rhodium thermocouple. In fact, at the lower temperatures, certain types of base-metal thermocouples are definitely better adopted for precise measurements.

The calibration of thermocouples then may be divided into two general classes, depending upon the method of determining the temperature of the measuring junction,

1. Calibration at fixed points.
2. Calibration by comparison with standard instruments, such thermocouples, resistance thermometers, ... etc.

Roeser and Lonberger[5] in their excellent publication describe testing methods as primary and secondary methods for calibrating the platinum versus platinum - 10 percent rhodium and platinum versus - 13 percent rhodium thermocouples.

Barber[6] describes the calibration of platinum thermocouples over the range 0° to 1760°C. He employed a resistance thermometer in various baths for calibration from 0°C to 630°C. The higher temperatures were determined by silver point (960.8°C) gold point (1063°C) and by freezing points of palladium (1552°C) and platinum (1769°C). In addition a comparison was made with an optical pyrometer.

Selinocourt[7] in his investigation with the reporducibility of the standard platinum couple at the three fixed points, gold, silver and antimony for realization of the International Temperature Scale, considered three factors, namely, electrical measurement, temperature conditions in the furnaces containing the ingot, and the homogeneity of thermocouple wires. The electrical measuring unit was found to be adequate for an accuracy of the order of ± 0.01°C, whilst in connection with the other two factors improvements were made which render such an increased accuracy just attainable as an upper limit with repreoducibility beyond the normal limit of ± 0.1°C.

W. Heyne[8] describes a prcision measuring method for testing the e.m.f. - temperature relation of platinum versus platinum - 10 percent rhodium thermocouple using three easily, realizable fixed points namely, the freezing points of copper, aluminium and zinc. By testing the e.m.f. - temperature relation, an uncertainty of less than 0.5 degree in the range from 0° to 1063°C, and of less than ± 2 degrees in the range from 1063°C to 1500°C are claimed. Using the gold - silver - antimony scale, Heyne[9] found an uncertainty less than ± 0.2 μ v in realizing the IPTS between 630.5° and 1063°C. The freezing point of copper was determined by extrapolation and the average value amounted to 1083.29 ± 0.1°C. A correction for the extrapolated gold - silver - antimony scale amounts to - 1.8 μ v on the average for temperatures near the freezing point of copper, so a correction of 0.15°C must be considered for temperature belonging to the extrapolated scale Using the scale gold silver - zinc, Heyne[10] found reproducibility ranging from ± 2 to ± 10 μ v in the range 0°C to 1500°C.

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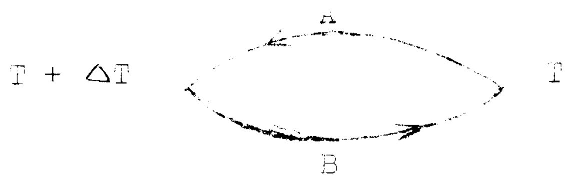
CHAPTER II

THERMOELECTRIC RELATIONSHIPS

A. Thermodynamic Considrations :

When a thermoelectric circuit is considered as a reversible engine, the laws of thermodynamics may be applied and the algebraic sum of the Peltier(11) and Thompson(12) effects gives the Seebeck effect(13). The Peltier effect (P) may be defined as the change in heat content of the circuit when current flows across its junctions. The Thompson effect ( ) is defined as the change in the heat content of a single metallic conductor (A or B) when a unit amount of electricity flows along it through a temperature gradient of one degree.



(Fig. 1)

In the following discussion of these quantities, thermodynamically ideal heat reservoirs are employed for both the measuring and reference junctions, and the I^2R losses approach zero in magnitude.

Consider a thermoelectric circuit composed of two homogeneous metallic conductors A and B (Fig. 1) such that the current is flowing from A to B at the measuring junction