

Temperature measurement and distribution in Tuttle hydrothermal pressure vessels

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MS received 18 November 1971, in revised form 11 February 1972

Abstract The temperature of an experiment performed in a Tuttle hydrothermal pressure vessel may be subject to error from two sources (thermocouple error and thermocouple location error) and uncertainties from five sources (uncertainties in the previous two errors, temperature fluctuations, temperature gradients and pressure effects). The evaluation of each of these effects is discussed. The narrowest limits of accuracy which may be achieved with this apparatus in routine use is $\pm 3^\circ\text{C}$. Two definitions in which the limits of accuracy of a measured temperature are taken as the sums of the uncertainties from all sources are proposed to describe the meaning of quoted temperatures in phase equilibrium work.

1 Introduction

Hydrothermal apparatus described by Tuttle (1949) is used extensively in the determination of phase equilibria by the quenching method. The use of simple furnaces tailored to suit the pressure vessels allows many such units to be economically manufactured and operated simultaneously with ease and the requisite accuracy. The pressure vessel employs either an external or internal thermocouple situated as close as practicable to the sample chamber. The sample temperature is deduced from the thermocouple EMF by a calibration procedure. As the vessel operates in a longitudinal temperature gradient of up to 800°C between the 'hot spot' and seal, this gradient being asymmetrical due to the vessel protruding from only one end of the furnace, there has always been some doubt about the accuracy of the temperature of an experiment. Published results commonly use the phrase "... believed to be within $\pm 5^\circ\text{C}$..." The purpose of this paper is to present a more accurate interpretation of this phrase.

The limits of accuracy of the measured temperature of an experimental sample have not been adequately defined. Since there are a number of sources from which temperature uncertainties might arise, quite apart from the measurement procedure (Hall 1954, p 138), the following definitions are proposed to prevent misinterpretations of quoted temperatures.

(i) The limits of uncertainty in the temperature, on the current International Practical Temperature Scale, of an experimental sample are the upper and lower values of temperature between which *all* parts of the sample are *known* to lie.

(ii) The limits of uncertainty in the temperature of a phase equilibrium boundary determined by the quenching method are the highest possible temperature value of the coolest experiment containing the high temperature assemblage and the lowest possible temperature value of the hottest experiment containing the low temperature assemblage.

The temperature may be written as plus or minus half the difference in each case. Wherever a temperature is specified without accuracy limits it should be understood to be subject to possible errors and that the author's estimate of uncertainty may not conform to the definitions given above. A consistent error in temperature measurement in apparatus in which there are no random errors would enable the uncertainty in the second definition to approach that in the first and without accurate assessment of possible uncertainties in the temperature measurement would allow apparently precise yet inaccurate phase boundary determinations. Each of the principles to be discussed may be applied to any piece of apparatus which is supposed to maintain a given sample at a constant temperature.

2 Apparatus

2.1 Pressure vessel and furnace units

Pressure vessels of Rene 41 and Nimonic 105 alloys are mounted vertically with the sample chamber uppermost unless otherwise stated and employ water as the pressure medium. The vessels are 30.5 cm long by 3.2 cm OD by 0.64 cm ID with the bore 28.6 cm long. The well for the external thermocouple located in the end of the vessel at a radius of 1.1 cm is 0.2 cm diameter and 2.2 cm long. The filler rod used in conjunction with external thermocouples is a stainless steel rod of 0.5 cm diameter while for internal thermocouples a stainless-steel tube of 0.21 cm bore by 0.5 cm OD is used. The sample chamber details are shown inset in figure 1. Sample capsules are normally of platinum, silver, gold or silver-palladium alloys of 0.3 cm OD by 1.9 cm long and either are used in groups of three or one capsule is embedded in an oxygen buffer assemblage in a gold tube of 0.5 cm OD by 0.4 cm ID by 3.2 cm long.

Furnace elements are spirally wound on ceramic tubes 30 cm long by 5 cm OD by 3.8 cm ID using 55 Ω of resistance wire which is insulated by a layer of cement and 9 cm of ceramic fibre. Approximately 700 W are required to maintain 1000°C . Furnace temperatures are controlled by Eurotherm 'three term' solid state controllers employing automatic cold junction compensation and thyristor output. The time constants are fixed at 15 s for the derivative term and 5 s for the integral term. The adjustable proportional band is set at approximately 2%. The optimum location of the control thermocouple has been found to be on the internal wall of the furnace with the tip exposed at a depth of 10 cm from the top of the furnace.

2.2 Thermocouples

External thermocouples made of fine gauge Chromel-Alumel wire and calibrated before use in the conventional manner (e.g. Tuttle and Bowen 1958, p 8) deteriorate during the course of an experiment. The rate of deterioration is dependent on temperature and time and would be of the order of 2°C after 7 days at 800°C (Dahl 1941).

With the Tuttle apparatus in this laboratory control and external measuring thermocouples are made from Johnson-Matthey 'thermopure' platinum and 87% platinum-13% rhodium wire of 0.02 cm diameter and guaranteed to be initially accurate to BS 1826-1952 (within 1°C at the gold point). The thermocouples are used many times, with the accuracy being checked at the end of every experiment by a rapid

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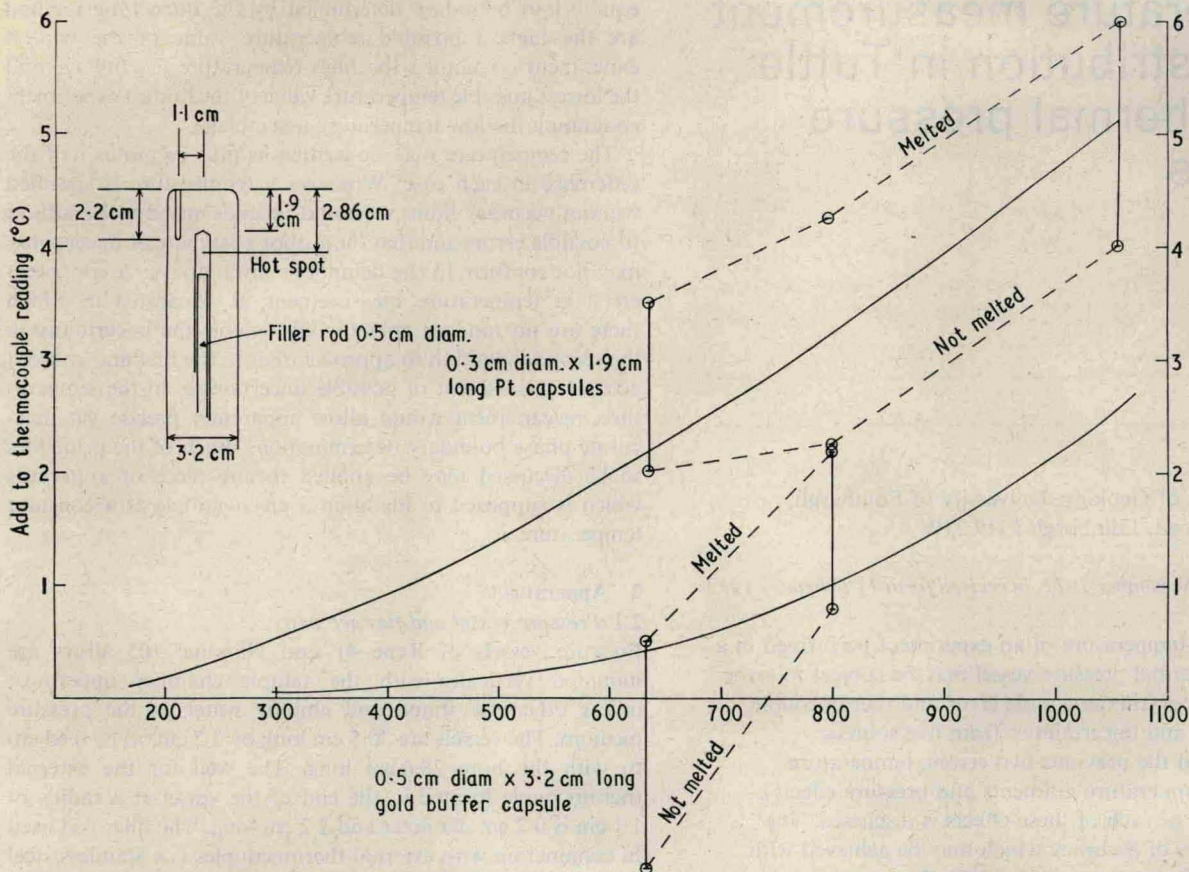


Figure 1 Corrections to be applied to the recorded thermocouple temperature to derive the sample temperature for two types of capsule and the geometrical arrangement shown inset. The data points are the results of individual experiments each subject to definitions (i) and (ii) but only

to uncertainties in temperature gradient. The assumed melting points of the calibrants are plotted against the difference between their assumed melting points and the nominal temperatures of individual experiments on the calibrants

method to be described. The wires are insulated by a double alumina tube of 0.155 cm OD by 0.04 cm bore. Internal thermocouples for use at pressure are inconel sheathed Chromel-Alumel of 0.15 cm diameter with ungrounded tip. The measuring thermocouple cold junction is inserted into a Zeref 136 ice chamber with a calculated deviation from the ice point not exceeding 0.01°C. EMF is measured on a Pye precision decade potentiometer tested at the National Physical Laboratory, Teddington.

2.3 Calibrants

Calibrants used are Johnson-Matthey grade 1 gold wire, spectroscopically standardized aluminium rods and spectroscopically standardized NaCl and also Analar standard NaCl and Na₂CO₃ the latter mixed in the ratio of 1 to 2 by weight. The thermocouple wire is initially calibrated at the melting point of gold by the wire bridge method and aluminium by heating and cooling curves. The EMFs of new thermocouples have been found to be in accordance, within 0.1°C, of both melting temperatures in the conversion tables. The 1948 International Practical Temperature Scale was used throughout the present study. Using a thermocouple which was accurate at the melting points of gold and aluminium, the melting point of the NaCl sample was found to be 800.25°C and that of the NaCl-Na₂CO₃ mixture 637.5°C both by a heating and cooling curve method. These materials, which were not specially purified, were used simply as convenient intermediate calibration points between the freezing points of aluminium and

gold. Below the melting point the NaCl-Na₂CO₃ mix contains large conspicuous grains of NaCl still with originally included air bubbles among irregular grains of sodium carbonate. Above the melting points the quenched product contains large rounded crystals of sodium carbonate (the 1:2 composition being displaced from the eutectic) embedded in a mass of irregularly intergrown Na₂CO₃ in which NaCl is inconspicuous.

Aluminium in the form of wire was found to be unsuitable as a calibrant as it retained the wire form well above the melting point. Silver is unsuitable as a calibrant with this apparatus since the melting point is strongly dependent on the partial pressure of oxygen (Hansen 1958) which cannot be conveniently excluded from the apparatus.

3 Sources of error and uncertainties

For the purposes of this paper it is necessary to distinguish between two types of inaccuracy. An error may be described as the known difference between the measured value of a physical quantity and its actual value whilst uncertainty may be described as the limits of unknown difference between the measured and real value of a quantity. From this distinction it follows that errors can be removed by calibration but uncertainties must be summed in the final statement of sample temperature. Some sources of inaccuracy contribute both error and uncertainty whilst others simply contribute uncertainties. These effects are discussed below in terms of the source of inaccuracy.