Temperature measurement and distribution in Tuttle hydrothermal pressure vessels

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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 ± 3°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 ± 5°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

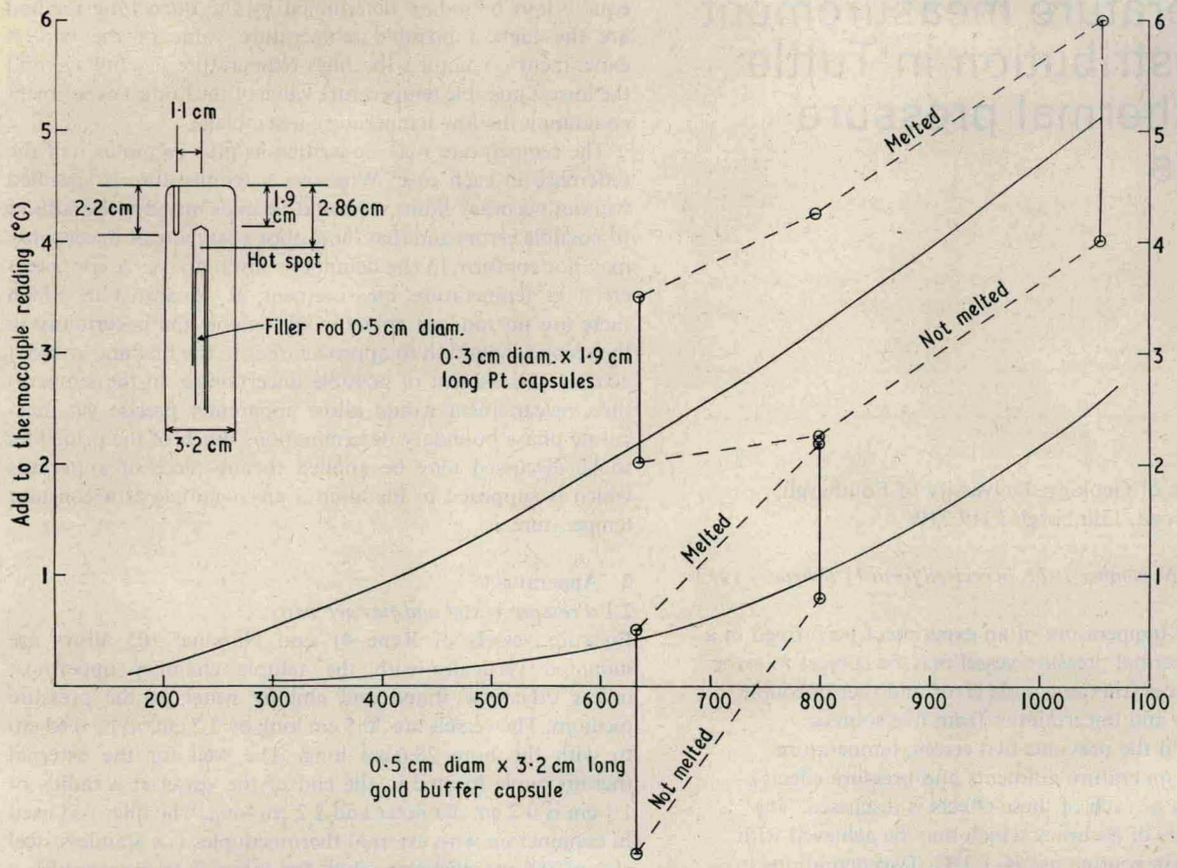

Figure 1 Corrections to be applied to the recorded thermocouple temperature to derive the sample temperature for two types of capsule and the geometrical arrangement shown inset. The data points are the results of individual experiments each subject to definitions (i) and (ii) but only to uncertainties 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 Na_2CO_3 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–Na_2CO_3 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–Na_2CO_3 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 Na_2CO_3 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 descr bed 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.

3.1 *Control precision*

The accuracy of the temperature assigned to an experiment cannot be better than the temperature 'bandwidth' through which the controller permits the furnace temperature to fluctuate. This is a complex function of factors which are specific to each individual piece of apparatus and will not be discussed further here. In this laboratory variations in the recorded temperature of experiments over periods of a month or more may be classified as good for less than $\pm\frac{1}{2}$°C, normal for $\pm\frac{1}{2}$ to ± 1°C, abnormal for ± 1 to ± 2°C but acceptable for some experiments, and bad for more than ± 2°C, which is usually traceable to a rectifiable cause.

3.2 *Temperature gradients*

Temperature gradients within the samples depend on the capsule size and location relative to the crest of the axial thermal profile which should coincide with the centre of the sample chamber. The latter should be as short as practicable. The axial thermal profile was explored at atmospheric pressure with an internal thermocouple similar to those used in the external thermocouple well. The tubular support rod and either three 1·9 cm long platinum capsules or an empty 3·2 cm long gold tube with the bottom end open were used to simulate the conditions of experiments. The crest of the axial thermal profile was found to occur 1 cm from the upper end of the 2 cm long sample chamber at 800°C when this point was 10·5 cm from the top of the furnace, i.e. approximately one third of the furnace length from the top. A similar result had been obtained previously with 20 cm long vessels and furnaces. This configuration was retained for the 3·2 cm long capsules since the displacement of the centre of the thermal profile from the centre of the 3·2 cm long sample chamber is only 0·6 cm. Longitudina temperature gradients were found to be within $\pm\frac{1}{2}$°C for 1·25 cm long capsules, ± 1°C for 1·9 cm long capsules and ± 2°C for 3·8 cm long capsules at temperatures up to 950°C. The longitudinal temperature gradient could be different in the normal arrangement with a solid support rod and at pressure. With the centre of the hot spot displaced to one end of the sample chamber due to such an effect the longitudinal temperature gradient within the sample would be approximately double the values given here.

The location of the crest of the longitudinal thermal profile within the vessel for a fixed geometrical relationship between vessel and furnace and a fixed temperature is dependent on radius within the vessel. The thermal surface formed by the connection of the crests of the longitudinal thermal profiles at all radii is conical with the apex pointing away from the seal end of the pressure vessel. This allows the thermocouple well to be either hotter or cooler than the axis of the pressure vessel at the same distance from the end depending on this distance. It is not sufficient to find the crest of the thermal profile only in the thermocouple well. With the location of the thermocouple shown in figure 1 the thermocouple well is consistently cooler than the centre of the sample chamber when the crest of the axial thermal profile is determined internally. With a similar arrangement but a 3·5 cm long thermocouple well the thermocouple well is consistently hotter than the centre of the sample chamber.

3.3 *Thermocouple accuracy and calibration*

Temperatures measured by the external thermocouple must be corrected for any error in the thermocouple itself and for any difference in temperature between the thermocouple and the sample. A pressure vessel and furnace assembly identical with those used for experiments but with two thermocouple wells close together is used to check thermocouple accuracy. The temperature difference between the two thermocouple wells measured by two thermocouples and confirmed by changing the thermocouples around is consistent, known and not more than 0·5°C at 950°C, the highest normal operational temperature. By inserting a thermocouple of known accuracy in one well any error in any other thermocouple in the other well may be read off directly at any temperature with a possible error not exceeding $\pm\frac{1}{4}$°C. It is essential to use the apparatus for which the thermocouple is intended in this comparison since the error in a thermocouple in which the thermo-elements have changed composition at the tip due to diffusion is dependent on the temperature gradient behind the tip. From a batch of new thermocouples one thermocouple is calibrated at the melting points of gold and aluminium as described previously and then compared with the rest of the batch over a range of temperature in the two thermocouple wells. A batch of new thermocouples has been found to give the same EMF reading within 2 μV at 950°C.

The calibrated thermocouple is set aside as the primary standard thermocouple and is rarely used. Two other thermocouples from the batch are taken as the secondary standards and used periodically to check the accuracy of the rest of the batch (tertiary) which are used to compare with the thermocouples used for experiments. Each comparison is performed at the temperature of the experiment and takes approximately five minutes provided that the furnace is at the required temperature. The standard thermocouples are thus exposed to high temperatures and contamination for only short periods of time. Deterioration of thermocouples used for experiments when measured at the gold point has been found to be of the order of 10–15°C per year. Deterioration of tertiary standard thermocouples amounts to less than 1°C per year at the gold point. When deterioration reaches this level the standard thermocouples are transferred to service in experiments. The total uncertainty in the temperature measured by the thermocouple is not more than $\pm\frac{1}{2}$°C.

One of a new batch of thermocouples was used to determine the charge temperature at atmospheric pressure by the quenching method using gold, sodium chloride and a sodium carbonate–sodium chloride mixture as calibrants.

The results of the calibration experiments using the three 1·9 cm long capsules and one 3·2 cm long double capsule are given in figure 1. It should be emphasized that the two curves shown apply only to the geometrical arrangement shown inset in figure 1 and that any other location of the thermocouple well would produce another set of curves. Each calibration experiment has been repeated at least twice, the result confirming the measurable difference in temperature between the two capsule assemblies.

3.4 *Pressure effects*

For a given recorded thermocouple temperature, the pressure fluid may alter the sample temperature, the temperature gradient along the length of the capsule, or the control precision by promoting convection currents. With an internal thermocouple situated at the hot spot indicated in figure 1 and surrounded by three platinum capsules at pressures up to 5000 bar and temperatures up to 950°C, variable temperature oscillations of up to $\pm\frac{1}{2}$°C were found to occur with a variable time period of a few seconds. An adjustment of pressure between 100 and 5000 bar at any temperature produced an initial temperature change in the same sense as the adjustment, but the temperature returned exactly to the previous value within a few minutes. The pressure effect on the thermocouple is less than 1°C under these conditions (Getting and Kennedy 1970) and was not detected. The temperature difference between the external thermocouple and internal thermocouple was found to be in accordance with the curve for the

three 1·9 cm long capsule assembly given in figure 1 at all pressures up to 5000 bar and from 800 to 950°C. Below this temperature the temperature indicated by the internal thermocouple became lower than the upper curve in figure 1 by up to 1°C at 700°C. This could be due to the thermocouple itself cooling the sample chamber. Possible changes in the longitudinal gradient were not measured.

With the pressure vessel arranged vertically with the sample chamber lowermost there was no appreciable change in the short term temperature oscillations. A pressure adjustment produced no change in temperature and the temperature difference between internal and external thermocouples remained as described. There appears to be nothing to choose between the two arrangements from the point of view of temperature stability.

4 Conclusions

The final temperature assigned to an experiment is made up of eight components:

Recorded temperature	e.g. 800	$\pm\frac{1}{2}$
Thermocouple correction	+2	$\pm\frac{1}{2}$
Lateral gradient correction	+3	$\pm\frac{1}{2}$
Longitudinal gradient		$\pm\frac{1}{2}$
Pressure effects		$\pm\frac{1}{2}$
Final temperature	805	± 3.

An accuracy of ± 3°C in the sample temperature is about the best which may be achieved with this apparatus in routine use with both external and internal thermocouples since the latter are also subject to the uncertainties listed in the right hand column above.

References

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