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.

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