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Temperature control and calibration in quench furnaces and some new temperature measurements in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$

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SUMMARY. Techniques associated with temperature control and measurement in quench furnaces are described and a study made of calibration problems. Systematic temperature errors as great as 30 °C in published results from separate laboratories are explicable. A comprehensive redetermination of temperatures of invariant equilibria in systems containing CaO, MgO, Al₂O₃, SiO₂, Na₂O, Fe-O₂, has been initiated and the results to date are presented, including approximate determinations of three invariant equilibria in the system CaO-MgO-Al₂O₃-SiO₂ involving liquid, monticellite, spinel, and two of merwinite, periclase, and forsterite, which are important in the melting of magnesia refractories, and precise determinations of the three newly recognized invariant equilibria involving liquid, spinel, diopside, and two of forsterite, melilite, and anorthite.

. . . though the heat did not always exert its greatest force where I intended it to do so. HALL (1804)

SIR JAMES HALL could well have been referring to the quenching furnace as used for the determination of phase equilibrium diagrams. Many institutions have bought or constructed quench furnaces, and a very great number of phase diagrams are based on results obtained in such furnaces. There has never been a comprehensive and systematic study of the operating conditions of quenching furnaces, or a discussion of their accuracy and there have been few data published to enable meaningful comparisons to be made between results from different laboratories. In the past it has often been the case that one furnace has been used for one system by one investigator with little attempt at close cross calibration other than reference to one or two of the accepted calibration points, commonly gold and diopside.

This study shows that discrepancies of the order of 30 °C are possible and a careful perusal of the literature reveals some instances of these. Although the discrepancies are often assumed to result from compositional errors rather than systematic temperature errors, several types of systematic temperature error are described that are capable of

producing up to 30 °C difference between laboratories using the same calibration points. A long-term and comprehensive redetermination of temperatures in oxide systems (primarily CaO, MgO, Al₂O₃, SiO₂, Na₂O) has been commenced using a range of compositions obtained from common starting materials. The first results of these studies are reported here.

Equipment

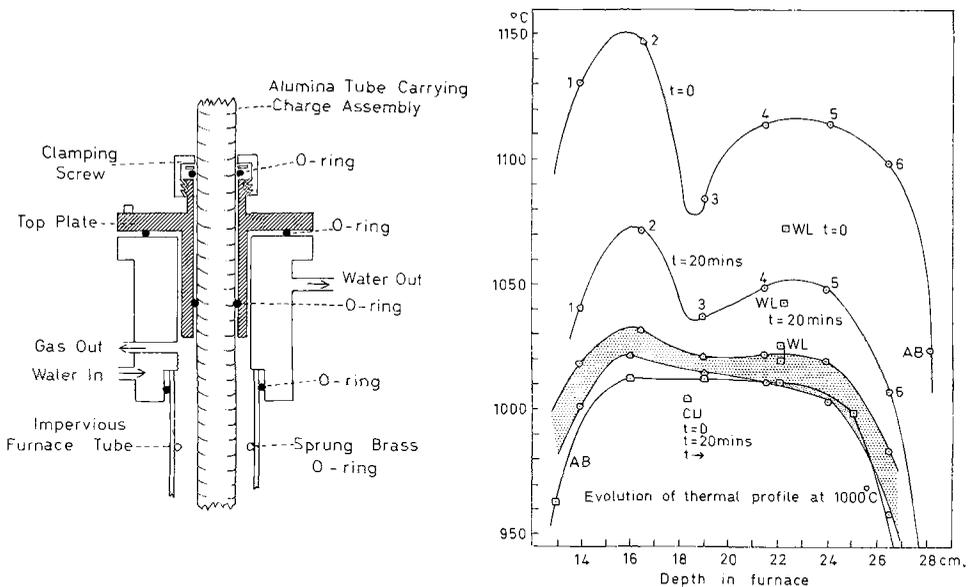
The main technical objectives were: to find equipment and conditions such that a number of charges could be run at one time (to assist in cross calibration); to ensure that temperature gradients within and between charges were insignificant; and to ensure that temperature fluctuations were minimal during an experiment long enough to attain equilibrium within charges (30 days was considered sufficient). Perhaps the greatest innovation of recent years has been the appearance of control instruments capable of maintaining a thermocouple within $\pm 2 \mu\text{V}$ ($\pm 0.15 \text{ }^\circ\text{C}$) of a set point, thus effectively removing any effect due to cyclical temperature fluctuations, which were often of the order of 2 or 3 °C with the previous generation of controllers.

The furnaces common to all the subsequently described trials were Johnson, Matthey Co., V25B, 105 V, 1 kW, furnaces wound with platinum-10 %-rhodium and rated for operation at 1500 °C. They were used briefly at 1550 °C for calibration experiments. These furnaces were used in the vertical position. An impervious alumina lining tube 40 cm \times 22.5 mm I.D. \times 28.5 mm O.D. was inserted in each furnace and projected a centimetre or two at each end of the furnace. On these projecting ends were brass clamps to hold the lining tube and also water-cooled brass jackets bearing the gas inlet and outlet tubes. A gas-tight seal was made between the water jackets and the alumina lining tube by neoprene O-rings (fig. 1). The furnace atmosphere was controlled by passing any gas or gas mixture upwards at a known and controlled flow rate. Alternatively, air was left in the furnace with the inlet blocked and the outlet restricted to avoid surging of cold air into the furnace. With gases that contained water vapour, or formed it by reaction, there was a tendency for water to condense on the upper water jacket and run down the lining tube and crack it. This was overcome by inserting a spring brass O-ring inside the lining tube (fig. 1) to evaporate the water into the exit gases.

The lower brass jacket had cemented to it with Araldite a B 34 glass cone which carried an easily removable flask. The quenching fluid was admitted to this flask by a side arm shortly before the end of an experiment. During an experiment a mirror enabled a visual inspection of the charge to be made through the base of the flask. A brass top plate was screwed down and sealed by a neoprene O-ring to the upper brass jacket. Through this top plate a variety of probe designs were passed and these are the subject of a later section. All such probes were gas tight and were held in an axial position by two O-rings and a clamping screw (fig. 1). All measurements of depths within the furnace are with reference to the top of the syndanyo board that tops the furnace.

Temperature control and measurement

Each furnace is supplied by the makers with two Pt:Pt-13 % Rh thermocouples embedded in the element close to the winding, and arranged radially. There was electrical contact between these thermocouples and the winding in many cases, hence all control and measuring equipment must be capable of operating at potentials above earth. The thermocouples are located on either side of the mid-point of the element in a sparsely wound central zone of the furnace and were at approximately



FIGS. 1 and 2: FIG. 1 (left). The upper water-cooled brass jacket used to achieve gas-tight seals between the furnace tube and charge assembly. FIG. 2 (right). Thermal profiles in a V25B furnace. The two upper curves record temperature profiles on the furnace wall at the instant of coming to temperature and 20 minutes later. The lowest curve (AB) records the thermal profile measured by an axial bare-wire thermocouple some hours later. The shaded zone encloses the temperatures recorded by six bare-wire thermocouples rotated about the inner wall of the furnace tube under the same conditions. Points CU and WL record the temperatures at the two built-in thermocouples on the furnace winding.

180 and 220 mm depth. Either thermocouple could be linked to the controllers, which were West Instruments Ltd. Viscount potentiometric controllers incorporating proportional and integral terms. The controllers operate through 1-kW saturable reactors. Thermocouples, other than those built into the furnaces, were constructed from thermopure Pt and Pt-13 % Rh and all thermocouple e.m.f.s were measured with reference to a Weston cell and ice junctions on a precision potentiometer and galvanometer. Precision switches were used to select the thermocouple to be measured and also allowed for the simultaneous reversal of all the circuits. Differences between the e.m.f. readings of a thermocouple when the circuits were reversed were equivalent to 0.25 °C.

Since the installation of the present controllers some two years ago there has been an improvement in performance and reduction in cost of later models of controller. The degree of control attained is not, therefore, the best obtainable but it is probably true that other errors in connection with temperature measurement and calibration (see later) are great enough that improved control would not materially improve accuracy.

The basic operation of the controller is to adjust power to the furnace to maintain a constant predetermined e.m.f. across the control thermocouple, normally one of those embedded in the element. In furnaces with a static air atmosphere a range of $\pm 7 \mu\text{V}$ about a set point was the maximum observed over 30 days and individual controllers have achieved $\pm 2 \mu\text{V}$ ($14 \mu\text{V}$ is approx. 1°C). For shorter runs of less than 48 hours a range of $\pm 2 \mu\text{V}$ is common. The precision of temperature control at thermocouples introduced through the brass top into the furnace hot zone was slightly worse (± 2 or $\pm 3 \mu\text{V}$ greater) in short runs. In longer runs the effect was overshadowed by long-term drift (see later).

The precision of control was tested in one furnace using thermocouples other than the upper built-in couple (designated U). A bare-wire thermocouple (H) was inserted between the alumina lining tube and the furnace element at 180 mm depth. With this as control, thermocouple variations with a period of a few minutes were observed, the range being $\pm 33 \mu\text{V}$ ($\pm 2\frac{1}{2}^\circ\text{C}$) on H, $\pm 200 \mu\text{V}$ ($\pm 15^\circ\text{C}$) on U, and $\pm 8 \mu\text{V}$ ($\pm \frac{2}{3}^\circ\text{C}$) on a thermocouple sheathed with alumina (AS) introduced axially through the top plate to a depth of 180 mm. With this last couple as control, thermocouple variations with a period of about 12 minutes and a range of $\pm 205 \mu\text{V}$ ($\pm 15^\circ\text{C}$) were observed on AS with very much greater variations on H and U. Despite the disadvantages of contamination and drift later encountered with the built-in thermocouples they are the only practicable control thermocouples.

The furnaces were subject to a variety of changes with use that vitally affected the accuracy with which furnace temperatures could be selected and maintained. There was a variable slow drift to lower values of e.m.f. output for a given temperature in each furnace thermocouple amounting to $1-3^\circ$ a month. As the controllers were designed to maintain the e.m.f. of the control couple the result was a rise in temperature of $1-3^\circ$ a month. This was an embarrassment when 30 days' run were required to achieve equilibrium and when a distinction between equilibria a few degrees apart was required.

Abrupt changes occurred in which a particular thermocouple that was previously insulated from the furnace winding became electrically connected with it and exhibited a small a.c. potential on both limbs relative to earth. This change was accompanied by a drop in the e.m.f. of that thermocouple equal to about 4°C due either to contamination or to short-circuiting of the thermocouple junction by the winding. A variant of this effect was a drift of the e.m.f. of the thermocouple at a given temperature equivalent to a change of up to 60°C at the junction over a period of a few days. This effect may also be due to contamination. Both effects gave equivalent rises in the experimental temperatures with consequent loss of some experiments.

Some of the built-in thermocouples picked up a small high-frequency a.c. potential

across the two limbs of the thermocouple, which severely affected the galvanometer and prevented the controllers from functioning. It was eliminated by including a 3 H inductance in series and a 220 μ F condenser in parallel with the thermocouple connections to each of the controllers and to the potentiometer.

Distribution of temperature within the furnaces

An initial failure to achieve uniform and satisfactory operating conditions initiated an investigation of the furnaces to ensure that the best compromise in operating conditions was selected and to determine in what respects the compromise differed from ideal conditions.

The makers claimed zones of even temperature ($\pm 2\%$) extending for 5 in. (130 mm) in the V25B furnaces when used with closed ends in a *horizontal* position. This range of $\pm 2\%$ amounts to ± 16 – 30°C in the range of the intended experiments and fell far short of the desired accuracy of charge temperatures. The distribution of temperature within the furnace was, therefore, investigated.

In the course of these tests, thermocouples made from thermopure wire were used and as a test of their reliability seven were placed one after another in the inner sheath of an axial assembly in a furnace at 1250°C . All yielded the same e.m.f. ($\pm 20\ \mu\text{V}$) equivalent to a variation of $\pm 1\frac{1}{2}^\circ\text{C}$ in indicated temperature. Deliberate attempts to influence the e.m.f. by excessive work-hardening of the exposed upper ends of such thermocouples produced only small differences in the e.m.f. recorded corresponding to a temperature error of 0.2°C . The axial temperature profile in one of the furnaces was investigated by moving a bare-wire thermocouple stretched between simple end closures to different positions along the axis of the furnace after it had settled down at one temperature (1000°C). Temperatures recorded by this thermocouple were constant $\pm 1^\circ\text{C}$ in the hot zone (fig. 2), and were $+8^\circ\text{C}$ relative to the upper built-in furnace thermocouple but -10°C relative to the lower built-in thermocouple.

The circumferential and longitudinal temperature profiles on the inner wall of the furnace lining tube were studied in the same furnace at the same time as the axial temperature profile, six bare-wire thermocouples being stretched along the length of the inner surface of the purox alumina lining tube, their junctions being arranged $\frac{1}{6}$ rotation and 2.5 cm apart. By rotation of these thermocouples the temperatures at six points around the circumference were recorded at six different depths within the furnace hot zone (fig. 2).

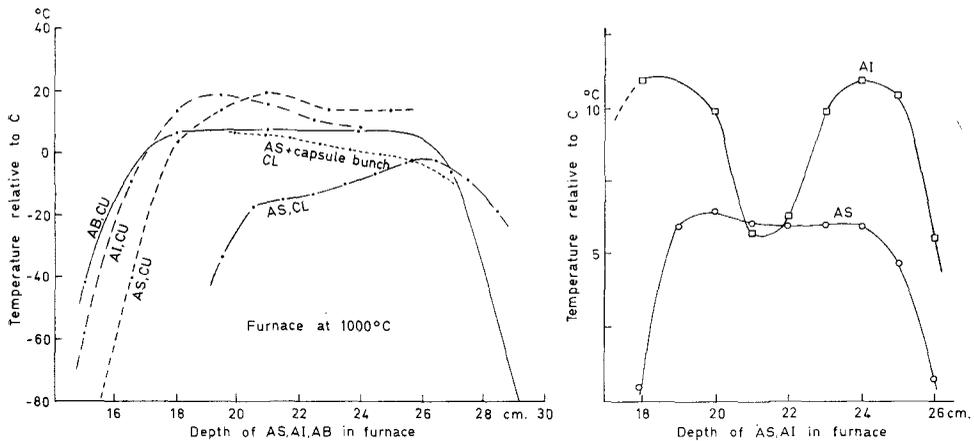
This experiment indicated the existence of a temperature range of 12°C around the inner wall of the lining tube at all levels within the hot zone, and of longitudinal gradients on the same surface of the order of 4°C per cm. The real stable existence of circumferential gradients was confirmed in a further experiment with four thermocouples situated $\frac{1}{4}$ -turn apart at the same depth. These effects reflect the irregular distribution of the element winding and are aggravated by the fact that the ceramic coating immediately overlying the winding protrudes slightly into the bore of the furnace.

These temperature differences observed in a furnace selected for the apparent regularity of its temperature distribution lie well within the limits claimed by the makers.

Nevertheless, the presence of temperature gradients of this magnitude on the inner wall of the furnace adjacent to the likely position of capsules and measuring thermocouple gave reason to expect a temperature range at least as great as 6°C within capsules 1.5 cm long and of up to 12°C between capsules. Using a bunch of twenty capsules containing bare-wire thermocouples located at base, middle, and top of the capsules and using a seventh thermocouple located 0.5 cm above the centre top of the capsule bunch, temperature differences of up to 30°C and never less than 15°C were observed between the seven thermocouples. The differences between any two thermocouples changed rapidly with depth in the furnace and often reversed their sense. These results confirmed the prediction of the previous tests and revealed the operation of other factors as well. Clearly no simple procedure of suspending bare metal capsules in these furnaces could be expected to yield results the accuracy of whose temperatures were better than $\pm 15^{\circ}\text{C}$. The temperature distribution in a V25B furnace on reaching set-point temperature was studied in a further experiment. The furnace used in the axial temperature profile test (see above) was brought to temperature at 1000°C , 1 kW power having been applied following an adjustment of set point from 800°C . Fig. 2 records the temperatures indicated at various subsequent times by the two built-in thermocouples (the upper of which was used for control), six bare-wire thermocouples arranged in a spiral 2.5 cm and $\frac{1}{6}$ -turn apart on the inner wall of the furnace lining tube, and an axial bare-wire thermocouple in the lower part of the furnace. Fig. 2 records the extrapolated temperature profile in this furnace at the moment when the control thermocouple had reached the desired temperature, when control was established after a $\frac{1}{2}^{\circ}\text{C}$ overshoot lasting for a few minutes, and again 20 minutes later. Several conclusions follow from these results; these furnaces should be given several hours to reach equilibrium following a change of set-point temperature; the set-point temperature should never be adjusted once the capsules are in the furnace otherwise serious overshoot or undershoot of the intended run conditions may occur, amounting to tens or even hundreds of degrees. The necessity for this precaution has been confirmed by direct tests with smaller adjustments of set point, noting the overshoot or undershoot recorded by the thermocouple in the axial assembly, which is in general of the same order of size as the adjustment of the set point. Great care must be exercised when bringing furnaces up to temperatures near the operating limit of the windings, ceramics, or any other part of the inserted assemblies.

A variety of probe designs were inserted into the furnace and fig. 3 records the temperature attained as a function of depth at the same set-point temperature in the same furnace for which results were presented in fig. 2. These profiles were measured by an axial bare-wire thermocouple (AB); the same thermocouple insulated in twin-bore ceramic (AI); and the same thermocouple insulated with twin-bore ceramic and enclosed in a ceramic sheath (AS). The upper built-in thermocouple was used for control (CU). Two further profiles show the results obtained with the lower built-in thermocouple used for control (CL). Four conclusions follow from examination of this figure. Two samples of different thermal capacity and reflectivity, when placed in the same position in the furnace at the same set-point temperature, will in general reach different temperatures. These differences may be at least as large as 20°C and

calibration must be carried out with axial and capsule assemblies that are identical with those used for the experiments. The techniques of measuring the temperature at the position occupied by the capsules before and after the run with a thermocouple enclosed in an axial assembly differing in any important respect from that used in the run may lead to errors of the order of size of 20 °C. In a furnace with two built-in thermocouples they are not equivalent and a change from one to the other for control purposes leads to major changes in the temperatures attained and thermal profiles recorded. The built-in thermocouples cannot be used in any simple way to indicate the temperature of the inserted samples with an accuracy better than ± 10 °C. The



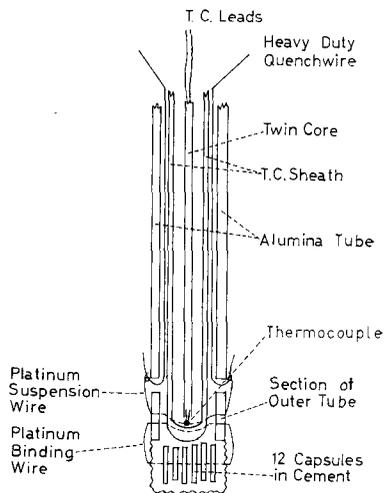
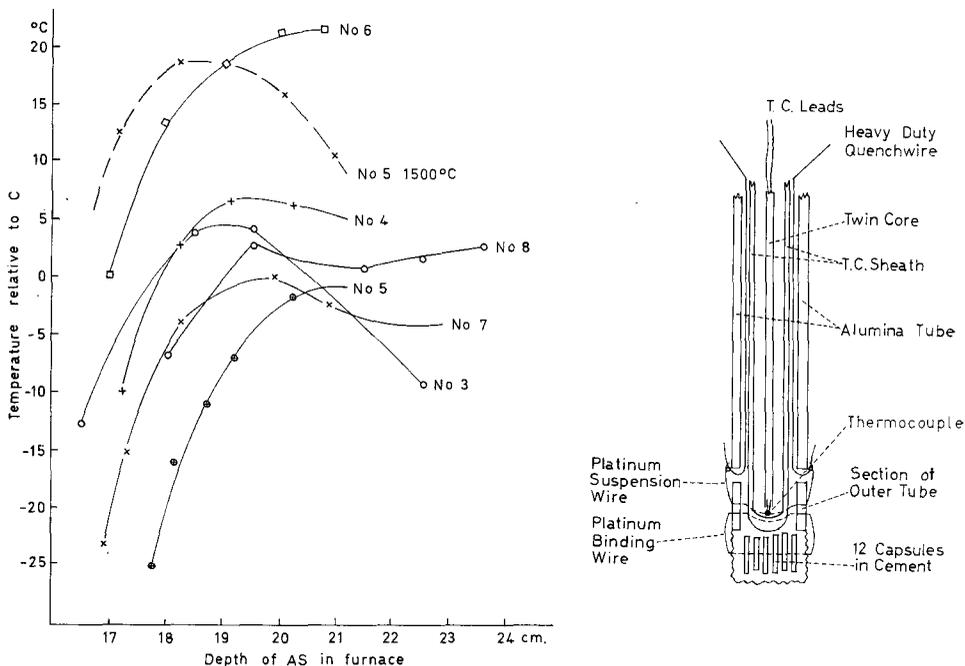
FIGS. 3 and 4: FIG. 3 (left). Temperature profiles in a furnace reported relative to the control thermocouple temperature (nominal 1000 °C). Explanation in the text. FIG. 4 (right). Simultaneous temperature profiles recorded by two differently insulated thermocouples side by side in the same furnace.

problems involved in calibration of an axial thermocouple were also investigated and fig. 4 records the temperatures attained by a sheathed thermocouple (AS) and by an insulated thermocouple (AI) attached alongside AS and extending to the same depth, as a function of depth and set-point temperature within a single furnace. The significant point was the large difference between the temperatures attained by two thermocouples of different thermal capacity and reflectivity both as a function of depth and as a function of temperature. Even if calibration were carried out with a capsule assembly identical with that to be used in the runs, the temperature difference between thermocouple and capsules, for which it was hoped to compensate by calibration, was liable to vary so rapidly within the hot zone that unless accurate repositioning of the whole assembly in successive runs could be guaranteed non-reproducibility of calibration and errors as great as ± 3 °C might be encountered.

The influence of gas flow on the relationships recorded in figs. 2-4 was not determined but it is desirable that all calibrations should be carried out in the gas atmosphere and flow rate appropriate to the intended group of experiments.

Thermal profiles for the six nominally identical furnaces at various temperatures

were determined from readings on AS thermocouples in axial probes (fig. 5). Furnace temperature was controlled through the upper built-in thermocouple (CU). Each furnace displays a region (approx. 18–23 cm depth) within which axial temperature gradients are 10–15 °C but there are distinct upper and lower hot zones with a small saddle in the thermal profile between them.



FIGS. 5 and 6: FIG. 5 (left). Thermal profiles recorded by sheathed thermocouples in six nominally identical furnaces, all at the same control temperature (1050 °C). Temperatures recorded relative to that of the control thermocouple. The dashed line shows the effect of increased temperature on one of the profiles. FIG. 6 (right). Sketch of the final charge assembly of twelve capsules used for all experiments.

Two types of profile, characterized by an upper hot zone which is either hotter (type 1) or cooler (type 2) than the lower, may be distinguished. Most furnaces have a type 1 temperature profile at high temperatures (fig. 5). As the set-point temperature is reduced the temperature of the lower hot zone tends to increase relative to that in the upper hot zone and some furnaces develop type 2 profiles at lower temperatures. In all the furnaces the depth at which the temperature peaks in the upper hot zone migrates upwards by 1–2 cm as temperature increases from 1000 to 1500 °C.

These results indicate the individuality of the furnaces, and the need to explore each one independently for the selection of suitable operating conditions. Some furnaces are more suitable for use in certain temperature ranges than others because of the presence or absence of steeper thermal gradients at the intended sample position. The results also emphasize that a thermocouple must be calibrated for a particular axial

assembly at a particular depth in a particular furnace, the difference between apparent thermocouple temperature and charge temperature being compounded of thermal gradient effects (which are a property of the axial assembly *and* the furnace) and drift or contamination effects (which are a property of the thermocouple).

Passage of cold gas up a furnace in which the upper built-in thermocouple was used for control resulted in no change of control thermocouple temperature, but the temperature of the AS thermocouple, representing that of the experimental samples, did change. In furnaces with a type 1 profile the passage of gas raised the temperature of AS, while in those with a type 2 profile it lowered the temperature of AS. This apparently paradoxical effect results from the mechanism of the control, which increases power to the furnace in the first case because the upper control thermocouple is initially cooled by the passage of the gas and reduces power in the second case because the thermocouple is initially heated. This has the effect of changing the whole thermal profile in the furnaces, tending to convert type 1 profiles into type 2 and vice versa.

The effect was found to be relatively independent of gas-flow rate in the range likely to be used (1 cm per second) but its magnitude was different for pure CO₂ and pure H₂. Intermediate gas mixtures (which react largely to H₂O and CO as they pass through the hot zone) have an effect that is not intermediate between the pure H₂ and CO₂ gases. The gas flow shifts the peak of the upper hot zone to shallower depth in any given furnace.

Selection of the final charge assembly

In order to eliminate effects due to differences in thermal capacity and reflectivity all charge assemblies were made up from twelve capsules of $\frac{1}{8}$ -in.-diameter tubing each $1\frac{1}{2}$ cm long, arranged in a cylindrical bundle. Each capsule was painted externally in the lower three-quarters of its length with a suspension of MgO powder in xylene to prevent their welding together. The bundle was then coated with alumina cement on the base and sides to form a cylinder about 2 cm long having the same external diameter and reflectivity as the outer alumina tube of the axial assembly (fig. 6). A short cylinder of that outer alumina tube, drilled to permit its attachment by wire to the top of the capsule bunch, and also independently to the quenching leads, completed the assembly which slid up on to the end of the thermocouple sheath as illustrated (fig. 6).

A fixed operating depth for the axial assembly was chosen for each furnace, such that the charge assembly was suspended at a depth close to the upper built-in control thermocouple, while both the capsules and the AS thermocouple lay near the peak of the upper hot zone, being above or astride it at low temperatures and below it at higher temperatures.

It was necessary to place the 'cold' axial assembly and attached capsule bunch into the desired position in the furnace with a minimum of disturbance of the thermal profile. This was achieved by placing the assembly in the furnace at a depth 6–8 cm less than that of the final run either overnight or for some hours prior to the start of the run. At this stage the whole assembly preheated to a temperature some 200–300 °C below that of the final run temperature. The axial assembly was then lowered to

the final position in four stages separated by 15-minute intervals. The temperature recorded by the AS thermocouple took a further 30 minutes to approach within 10°C of the final temperature and was within 1°C of the final temperature within 1 hour. Run times were reckoned from the moment of reaching the final position. This technique avoids cracking of the purox alumina ceramic by thermal shock and there is no overshoot of the AS thermocouple temperature, which was liable to occur if cool charges are brought rapidly to the final run position.

Experiments with two calibration capsules, one central, the other marginal in the capsule bunch, at the gold melting-point, showed both to be all solid or all liquid at AS thermocouple temperatures $\frac{1}{2}^{\circ}\text{C}$ apart. Thermal gradients within and between the capsules in this type of assembly therefore appear to be less than $\frac{1}{2}^{\circ}\text{C}$ at 1063°C .

Although some of the details of furnace management and charge assembly are obviously specific to the furnaces described, it is hoped that the demonstration of several types of possible systematic temperature error will serve as a warning to investigators that quoted temperatures may differ considerably with technique used although any particular technique may give internally consistent results.

The calibration problem and results

Calibration of the AS thermocouple of each furnace was carried out at the melting-points of sodium chloride, 800.5°C ; silver, 980.6°C ; gold, 1063°C ; lithium metasilicate, 1201°C ; diopside, 1391.5°C ; and palladium, 1552°C . Details of the materials used are listed in table I. It must be emphasized that the charge assembly for all calibration runs consisted of twelve capsules and was an exact replica of the assembly used for the experiments. The metal calibrants as 0.5 cm lengths of fine wire were enclosed in a purox alumina sheath and inserted into one of the twelve capsules. The crystalline salts were placed directly in a capsule. Melting of the metals produced a small bead, and melting of the salts was ascertained by microscopical examination. Using this technique it was possible to find two values of the e.m.f. of the AS couple such that at the lower the calibrant was all solid while at the upper it was all liquid. The differences between these e.m.f.s corresponded to temperature intervals of less than 2°C (details in table I) and these results are the minimum values determined to date and are acceptably close in relation to other errors.

Typical results of calibration studies are shown in fig. 7 as a plot of the correction necessary to the thermocouple temperature to obtain the true capsule temperature in a particular furnace. Each furnace has a unique plot but the form of fig. 7 indicates that there is an advantage to be gained by using a particular furnace in the temperature range over which its correction curve is nearly horizontal. Where the correction changes rapidly it may vary by as much as 1°C per 7°C temperature change. Although there is no basis for assuming that the correction factors vary linearly with temperature it was decided to interpolate between calibration points on a linear basis having selected for each furnace a horizontal portion of the correction curve as the working range of that furnace. It is important to note that had fewer calibrants been used, for example, silver and diopside only, and a linear interpolation been used, the recorded temperature would differ by as much as 10°C near 1200°C (fig. 7). Discrepancies of

TABLE I. *Details of calibrants*

Assumed m.p.		Purity	Minimum observed temperature interval °C
NaCl	800.5	AnalaR	4.5*
Ag	960	99.90 %	2.5*
Au	1063	less than 10 ppm impurities	0.5
Li ₂ SiO ₃	1201	0.03 % Na ₂ O; prepared from AnalaR Li ₂ CO ₃ and tetraethyl orthosilicate†	1.9
Diopside	1391.5	Prepared from AnalaR CaCO ₃ , spec. pure Mg, and tetraethyl orthosilicate	1.5
Pd	1552	99.99 %	1.0

* Not yet fully studied or purer materials required.

† A preparation with 0.13 % Na₂O melted approx. 2 °C lower.

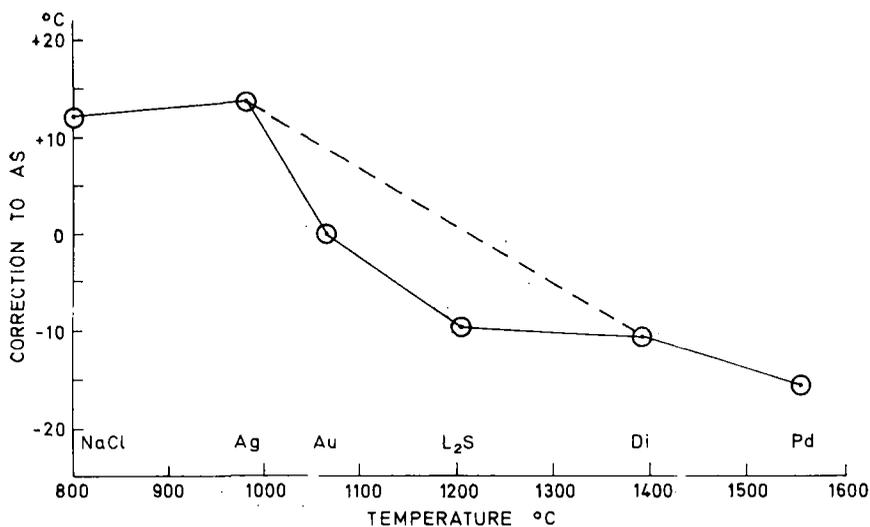


FIG. 7. A plot of the corrections necessary to the AS thermocouple reading to obtain the temperature of the melting-point of calibrants in the capsules. The dashed line illustrates the type of discrepancies introduced if a limited number of calibrants is used.

this magnitude may exist in comparisons of published work and are expected to be largest at temperatures away from the calibration points actually used.

Essentially the method adopted in this laboratory is to define a temperature scale given by the melting-points of the selected calibrants with linear interpolations and it is intended in the long term to re-establish on this scale other important temperatures in systems containing CaO–MgO–Al₂O₃–SiO₂–Na₂O–Fe–O₂ using compositions made from common starting materials by a gel technique to be described elsewhere. The majority of temperatures in these systems were originally determined by different groups of workers interested in a small part of the system and using compositions made from a variety of starting materials. Before presenting the limited data obtained

to date, a few comments on the various types of equilibria whose temperature it is intended to redetermine are necessary. The observation of the melting-points of compounds has been much favoured as a calibration technique but it is probably the least satisfactory as the composition must be accurate; any excess or deficiency may raise or lower the melting temperature. The observation of a reaction temperature is potentially more accurate as the ratio of the major components need not be precisely controlled and similarly for the observation of a binary or ternary or higher order eutectic. The massive change from all solid to nearly all liquid is shown by a range of compositions close to the eutectic composition. A possible disadvantage of reaction and eutectic observations occurs when one or more of the solid phases exhibits solid solution and it is not always possible to ensure that equilibrium solid solution exists in the charge prior to melting.

The principle factors that influence the comparability of results from different workers and different laboratories are: the temperature scale employed and the number and purity of the calibrants; the proximity of the experimental temperatures to the calibration points; the type of assembly used for the experiments and particularly if this differed from the calibration assembly; and the nature of the phase change observed.

Corrections need to be applied to earlier workers' results because of changes in the definition of the temperature scale, but are relatively small in the temperature range under investigation. Proximity to calibration point and the precise technique used in calibration introduce large potential discrepancies between laboratories. Where calibrations were carried out with one capsule present and runs are made with a greater number of capsules and ceramic spacers present, the results presented above suggest that systematic differences of up to 20 °C might arise. When the temperature of the equilibrium observed lies between calibration points (e.g. near 1460 °C, and especially near 1290 °C, 1120 °C, and 1020 °C) still larger discrepancies might be possible.

The type of container used for the sample affects the observation and where foil envelopes are used it is difficult to recover the lowermost part of the sample which becomes wedged and welded into the fold of the envelope. When $\frac{1}{8}$ -in.-diameter tubing is used, the recovery of the lowermost part of the charge is comparatively simple. This consideration is unimportant where the observation is of a major change in the physical state of the whole charge, such as at melting-points and eutectic temperatures, but where the equilibrium observed is the appearance of a small proportion of dense primary crystals the recovery of the lowermost part of the charge is important, the more so in cases where the amount of crystalline phase increases only slightly with falling temperature in the first 20–30 °C below the liquidus.

Two compositions lying in the diopside–pyrope and diopside–alumina joins (forsterite liquid determined by O'Hara and Schairer, 1963; Hytönen and Schairer, 1961, near 1400 °C; foil envelope technique) yielded forsterite and liquid at temperatures more than 30 °C higher than expected.

Less precise comparisons are available between determined liquidus temperatures for cristobalite and spinel in other parts of the system CMAS compared with those

TABLE II. *Experimental data**

Molar composition		Subsolidus assemblage	Temp.	Result	Temp.	Result	Previous determinations	Ref.
CaO	MgO Al ₂ O ₃ SiO ₂							
1	1	enstatite	1557	En, Fo, L	1549	En	confirms 1557°	1
1	1	anorthite	1557	L	1545	An	confirms 1550°	2
1	1	wollastonite	1545	L			consistent with 1544°	3
3	1	tricalcium aluminate	1545	L			consistent with 1535°	4
1	1	Mo, Merw†	1501	Merw, Per, L	1490	solid	1498°; 1485°	5, 6
2	1	åkermanite	1456	L	1451	Åk	confirms 1454°	3
3	2	rankinite	1456	C ₂ S, L	1452	Ra	discrepancy 1475°; 1464°	2, 7
3	1	Fo, Mo, Sp, Per	1452	Fo, Sp, Per, L	1420	solid	discrepancy 1417°; 1380°	8, 9
3	1	Mel 33, Merw, Sp	1446	Mel, Sp, L	1420	solid	new determination	
6	1	alleged compound†	1391	CA, Sp, L	1367	solid	consistent with 1380°	10
6	4	Mel 50, Mo, Merw, Sp	1385	Merw, Sp, L	1371	solid	new determination	
3	7	Mel 75, Mo, Fo, Sp	1352	Fo, Mo, Sp, L	1324	solid	new determination	
38 % ‡	20 %	An, Woll, Geh	1271	Woll, L	1268	solid	confirms 1265° ± 5°	2
3	1	An, Woll, Mel 75§	1245	An, Mel, L	1230	solid	discrepancy in subsolidus assemblage. Confirms 1234°	11
Numerous compositions		(An, Di, Fo, Sp) (Mel, Di, Fo, Sp) (Mel, Di, An, Sp)					new determination 1233.5° ± 1.5° new determination between 1231° ± 1.0° and 1233.5° ± 1.5° new determination 1230° ± 0.5°	
3	2	An, Trid, Di	1223	Di, L	1204	solid	An Di Trid L reported at 1218°	12

* Mel 33 signifies the approximate per cent åkermanite, Åk = åkermanite, An is anorthite, CA is calcium aluminate, C₂S is dicalcium silicate, Di is diopside, En is enstatite, Fo is forsterite, Geh is gehlenite, L is liquid, Merw is merwinite, Mo is monticellite, Per is periclase, Ra is rankinite, Sp is spinel, Trid is tridymite, Woll is wollastonite or a polymorph.
 † Subsolidus assemblages require clarification.
 ‡ Weight % composition, close to reported eutectic composition.
 § De Wys and Foster found almost pure åkermanite.
 References: 1, Bowen and Andersen, 1914; 2, Rankin and Wright, 1915; 3, Osborn and Schairer, 1941; 4, Lea, 1956; 5, Ferguson and Merwin, 1919; 6, Ricker and Osborn, 1954; 7, Osborn, 1943; 8, Berry, Allen, and Snow, 1950; 9, Solacolu, 1962; 10, Prince, 1954; 11, de Wys and Foster, 1956; 12, Clark, Schairer, and Neufville, 1961.

details to be published separately

expected on the basis of interpolation between previous workers' data. Liquidus temperatures appeared to be consistently 30 °C or more above those expected, except in the case of the melilite liquidus, where the proportion of crystals increased very rapidly with falling temperature.

Present indications, therefore, are that liquidus temperatures determined in this laboratory will compare poorly with, and may be up to 30 °C above, those reported by other laboratories. Temperatures of equilibria in which there are no observational problems will not be comparable within closer limits than ± 15 °C except close to calibration points.

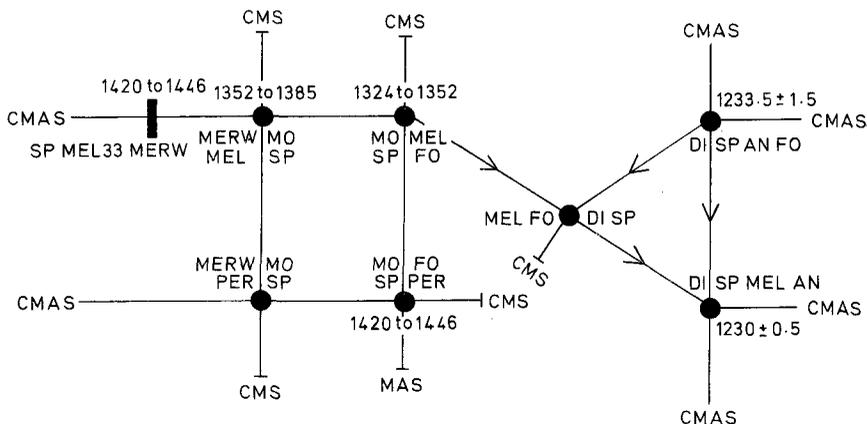


FIG. 8. Partial flow diagram for (monticellite plus spinel)-bearing and (diopside plus spinel)-bearing equilibria for the quaternary system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS). Abbreviations used are defined in table II, footnote. See also note added in press.

Experimental data are listed in table II for the equilibria that have been determined in whole or in part. Many of these temperatures will be more closely defined in subsequent work but the programme of temperature redetermination is subsidiary to a major study in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe-O}_2$. Some of the temperatures close to calibration points agree well with previous determinations but others are discrepant, for example, the reaction of rankinite to dicalcium silicate and liquid occurs in the same temperature interval as the melting of åkermanite, which is confirmed as 1454 °C. In this case the advantage of the twelve-capsule assemblage for comparative work is demonstrated.

Also listed in table II are provisional values for the beginning of melting of four-phase assemblages in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS). These fall in two groups: a group of four equilibria (only three of which are determined) with monticellite and spinel as common phases and two others from melilite, merwinite, periclase, or forsterite and a group of three equilibria with diopside and spinel as common phases and two others from anorthite, forsterite, or melilite. A partial flow diagram of these equilibria in the system CMAS is shown in fig. 8 and serves to illustrate these seven equilibria. Provisional estimates of the melilite composition involved in some of these equilibria were obtained by X-ray diffractometry and are listed in table II. Also

approximately determined was the beginning of melting of merwinite plus spinel plus melilite (åkermanite 1, gehlenite 2), which is a point on an isobaric univariant (divariant) equilibrium, and this is shown diagrammatically in fig. 8. Solacolu (1962) gives a temperature based on undisclosed data of 1380 °C for the equilibrium periclase + spinel + forsterite + monticellite + liquid, redetermined here as 1436 ± 16 °C (table II).

The equilibria involving diopside and spinel and others lie so close to each other that the relative temperature order could only be determined by comparative studies of capsules from the same batch of twelve and as this is a large topic it is reserved for a separate paper (O'Hara and Biggar, in press).

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Note added in press: Since fig. 8 was drawn the assemblage Merw, Mo, Mel₅₀, Sp has been shown to be still solid at 1371 °C.