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Drift of Pt/Pt10Rh and W3Re/W25Re Thermocouples in Single Stage Piston-Cylinder Apparatus[1]

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Abstract

Drift rates using 99.7 percent Al_2O_3 insulators have been determined by three methods: (1) The melting points of $MgSiO_3$ and $CaMgSi_2O_6$ have been determined by quenching runs of varying durations up to 48 hours. (2) A Pt/Pt10Rh and W3Re/W25Re thermocouple were joined at a common point and changes in *emf* of the Pt/Pt10Rh thermocouple with time were measured relative to a constant W3Re/W25Re *emf*. (3) Method (2) was repeated with the W3Re/W25Re thermocouple not touching the Pt/Pt10Rh thermocouple and in a slightly cooler part of the furnace cell. Data from (1) are considered the most reliable and show that W3Re/W25Re thermocouples can be used for very long runs at least up to 1800°C (drift $\leq$ 0.9°C/hr at 1787°C, 25 kbar). For Pt/Pt10Rh thermocouples, (1) gives a drift rate at 1620°C, 18 kbar, of -0.8 ± 0.6°C/hr and a maximum rate at 1812°C, 25 kbar, of 5.7°C/hr toward lower apparent temperatures. Using (2), drift of Pt/Pt10Rh thermocouples varies from -0.1 ± 0.1°C/hr at 1487°C (9 kbar) to -5.8 ± 0.8°C/hour at 1793°C (25 kbar). Method (3) yields erratic drift rates for Pt/Pt10Rh thermocouples 2-10 times larger than (2), and maximum drift rates established by (1) show that (3) is unreliable. Method (2) gives results compatible with (1) but may yield drift rates that are too high because of the possibility of contamination of the Pt/Pt10Rh thermocouple by the W3Re/W25Re thermocouple.

Introduction

In studies at high temperatures in the single stage piston-cylinder apparatus (Boyd and England, 1960) it is important to know the rate at which thermocouples drift so as to determine the length of an experiment that can be carried out without serious temperature errors.

Williams and Kennedy (1969) used W3Re/W25Re thermocouples insulated with McDanel 997 alumina to determine the melting curve for diopside. By using a differential thermal analysis technique, they were able to determine the melting point repeatedly during a single experiment. They stated (p. 4362) that ". . . there was no drift of the couple during a long run." However, because their runs extended over a wide range of temperature and they did not indicate which runs extended for long periods, further documentation of the stability of W3Re/W25Re thermocouples is necessary.

Mao, Bell, and England (1971, pp. 284–287) noted the drift rate of the single wire thermocouples W3Re in McDanel 997 versus W3Re in Pyrex and W25Re in McDanel 997 versus W25Re in Pyrex. These drift rates were lower than those observed in similar experiments using Pt and Pt10Rh single wires, indicating that W3Re/W25Re thermocouples are more resistant to contamination than Pt/Pt10Rh thermocouples. They also presented data indicating that W3Re/W25Re thermocouples show some contamination effects at 1900°C (see their Figure 87F), but they did not calculate a drift rate based on these data.

Using Pt/Pt10Rh thermocouples at about 1700° C, Boyd and England (1963) observed a change in the apparent melting temperature of diopside depending on the length of run. Subsequently, Boyd, England, and Davis (1964) observed the drift rate of Pt/Pt10Rh thermocouples by placing two such thermocouples in the furnace cell, one at the hot spot and one in a cooler part of the furnace. The temperature of the cooler thermocouple was held constant at 1400°C while monitoring the change in *emf* of the hotter thermocouple at about 1700°C. The high-temperature thermocouple drifted at a rate

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of about −60°C/hr, a rate similar to that previously observed in the experiments on diopside. As insulating material for the thermocouple, they used "high temperature ceramic" (a mixture of mullite and glass, referred to hereafter simply as mullite) (Boyd and England, 1963, p. 312 and Figure 1).

Mao and Bell (1971) and Mao, Bell, and England (1971) studied drift of Pt/Pt10Rh thermocouples by joining a Pt/Pt10Rh and W3Re/W25Re thermocouple together at one point. They assumed no drift of the W3Re/W25Re thermocouple and held its *emf* constant while monitoring drift of the Pt/Pt10Rh thermocouple. Drift was measured at 1600°C and 1700°C using both McDanel 997 alumina and "McDanel H. T." (mullite) as thermocouple insulators. Using mullite at 1700°C, they observed a drift in the Pt/Pt10Rh thermocouple of about −20°C/hr, about one third the drift rate observed by Boyd, England, and Davis (1964) at the same temperature. Mao and Bell found a much lower drift rate of only 2.5°C/hr at 1700°C when McDanel 997 alumina was used, indicating that the use of mullite results in contamination of the thermocouple. At 1600°C they found a drift rate of −1°C/hr when using McDanel 997 alumina and −1.8°C/hr when using mullite. When the thermocouple wires were exposed to a combination of McDanel 997 alumina and Pyrex glass, Mao, Bell, and England (1971) found a drift rate of −10°C/hr at 1600°C, indicating that Pyrex glass is much less desirable than either mullite or 997 alumina as a shield from contamination.

In some unpublished experiments, Mao and Bell (oral communication, 1972) examined the possibility that the *emf* of their W3Re/W25Re reference drifted due to contamination by the Pt/Pt10Rh thermocouple with which it was in contact. They stated that if such contamination occurs, it affects the *emf* of the W3Re/W25Re thermocouple by less than 100 microvolts (about 6°C) in 20 hours at 1700°C. They did not test for contamination at higher temperatures. Also, they did not test for the possibility that their drift rates for Pt/Pt10Rh thermocouples are due in part to diffusion of wolfram and rhenium from the reference thermocouple into the Pt/Pt10Rh thermocouple. Platinum can take up extensive amounts of wolfram and rhenium in solid solution (Hansen, 1958).

In summary, the work of previous investigators indicates that W3Re/W25Re thermocouples are more stable than Pt/Pt10Rh thermocouples and that drift is minimized by using high purity alumina as an insulating material. However, absolute drift rates using this insulator under conditions that duplicate routine run procedures are still not available. The drift rates for Pt/Pt10Rh thermocouples determined by Mao and co-workers may be correct, but it is also possible that their drift rates are due in part to effects that do not occur in routine piston-cylinder experiments.

Method

We have measured thermocouple drift at temperatures from about 1500° to 1800°C by three of the methods just discussed. In two of these methods, a Pt/Pt10Rh and W3Re/W25Re thermocouple were placed together in the furnace cell, and drift in the *emf* of the Pt/Pt10Rh thermocouple was measured relative to a constant W3Re/W25Re *emf*. In one set of experiments, the Pt/Pt10Rh and W3Re/W25Re thermocouples touched at a single point (configuration *A*, Fig. 1), as in the experiment of Mao and co-workers. In another set of experiments, the W3Re/W25Re thermocouple was placed at a slightly cooler part of the furnace cell and nowhere touched the Pt/Pt10Rh thermocouple (configuration *B*, Fig. 1), as in the experiment of Boyd, England, and Davis (1964). In the third method, apparent changes in the melting points of enstatite and diopside were measured for runs of varying lengths, as done by Boyd and England (1963). Runs quenched from above the melting points frequently showed quench crystals, but these could be distinguished easily from equilibrium crystals by microscopic examination of polished thin sections of the charges. All of the quenching experiments were of the decompression (piston out) type and no correction was applied to the observed load pressures. No pressure correction was applied to the *emf* of the thermocouples. The W3Re/W25Re thermocouples were made from calibrated, matched spools of wire obtained from the Baker Platinum division of Engelhard Industries. The Pt/Pt10Rh thermocouples were made from "premium grade" wire obtained from the Matthey-Bishop Company.

Figure 1 shows the configuration of the furnace cell. The arrangement of parts is similar to that used in several other laboratories except that the sample capsule is completely encased by McDanel 997 alumina. For the quenching experiments, the run capsule and all furnace parts within the talc sleeve were dried for one hour at 1050°C. The furnace assembly

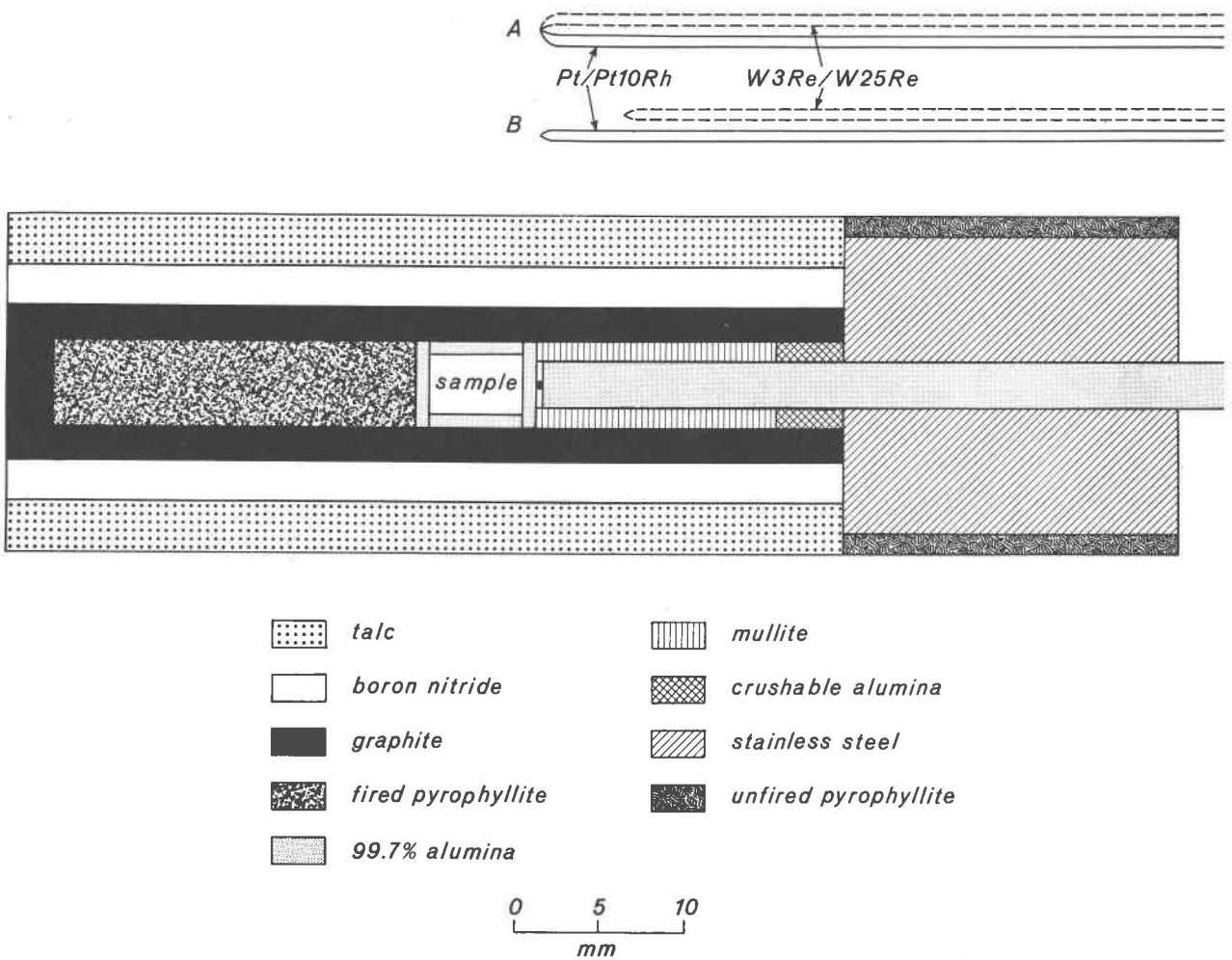

FIG. 1. Furnace cell used in single stage, piston-cylinder apparatus.

is wrapped in lead foil and Molykote G is used as a lubricant between the lead foil and carbide core. The center of the sample capsule is placed at the hot spot and the thermocouple lies just above the capsule in a slight thermal gradient.

Following Mao and Bell (1971), we have not used welded thermocouple junctions, but have simply folded the wires across each other. When using a single thermocouple with a four-hole alumina insulator, the extra two holes are used to tuck in the ends of the folded wires.

Data

In order to determine drift rates by measuring the melting points of diopside and enstatite versus time, we have assumed that the thermocouple *emf* changes linearly with time. The data of Mao and Bell (1971), Mao, Bell, and England (1971), and this paper (see Fig. 3) show that this assumption is approximately correct.

In experiments on enstatite, a mixture of quench and equilibrium crystals was comonly observed just below the melting point (Fig. 2). This effect occurs with platinum as well as graphite capsules and therefore cannot be the result of water leaking from the talc sleeve into the graphite capsules that were necessary for the longer runs. Also, quench crystals were observed only for runs immediately below the melting temperature. Introduction of water into the capsule would result in a melting interval for enstatite of more than 500°C at 25 kbar (Kushiro, Yoder, and Nishikawa, 1968). We have found that quench crystals of enstatite maintain their feathery appearance for at least one hour without recrystallization, even when the run is held just below the melting temperature. For this reason, we believe the mixture of

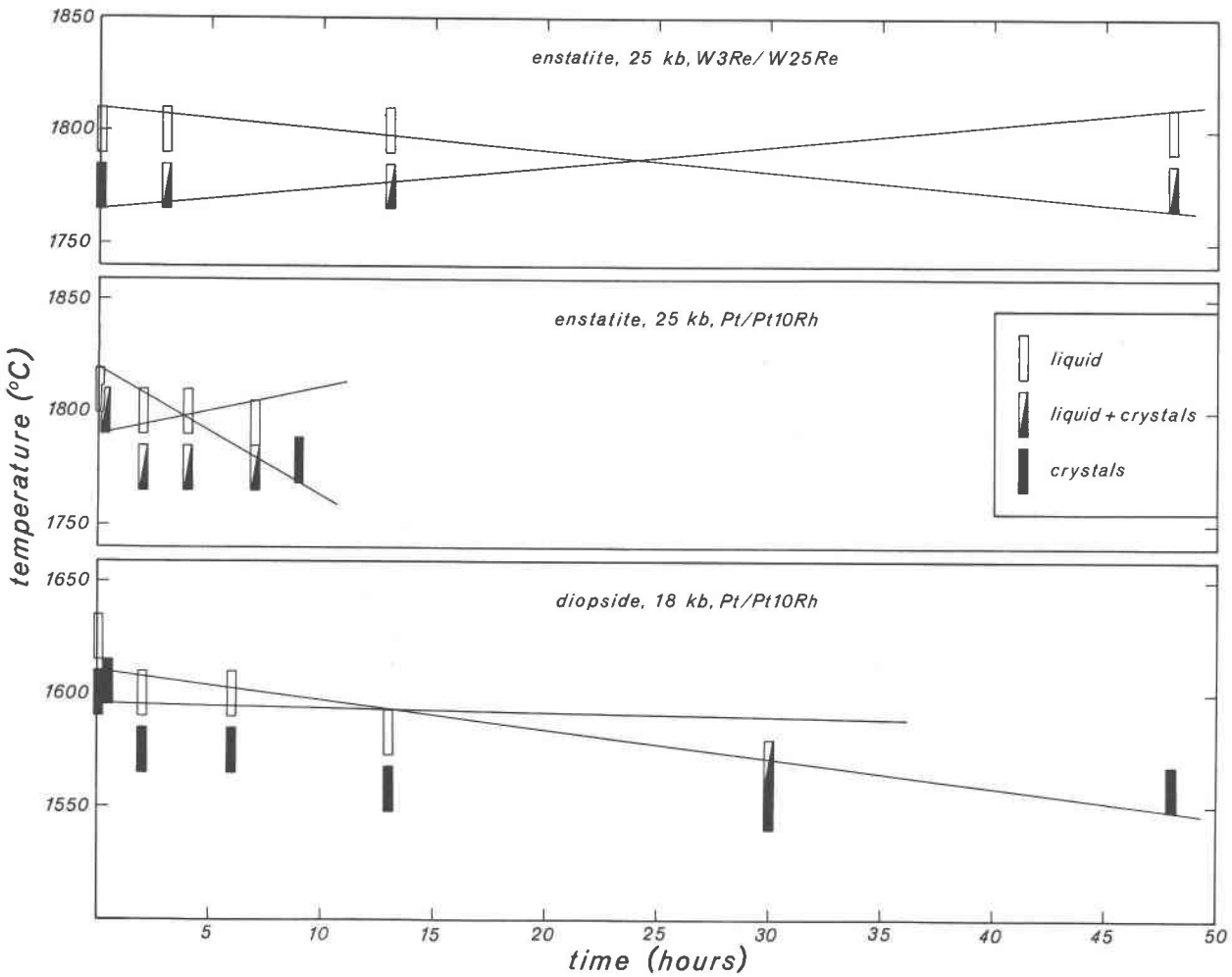

FIG. 2. Variations in apparent melting temperatures of enstatite and diopside with time. Maximum and minimum slopes are shown for each graph assuming a linear change with time. Liquid refers to glass, quench crystals, or a mixture of these two. Crystals refers to equilibrium crystals.

quench and equilibrium crystals for runs just below the melting point is due not to the existence of a melting interval, but rather to occasional cycling of the temperature above the melting point during the course of a run. In the case of diopside, a mixture of quench and equilibrium crystals was rarely found below the melting point, a result consistent with the fact that quench crystals of diopside rapidly recrystallize in a few minutes when held just below the melting point.

For W3Re/W25Re thermocouples, the melting point of enstatite was measured at 25 kbar, 1787°C for runs lasting up to 48 hours. No thermocouple drift was observed (Fig. 2) but temperature uncertainty in the experiments permits only the conclusion that drift is less than 0.9°C/hr.

For Pt/Pt10Rh thermocouples, the melting point of enstatite was measured at 25 kbar, 1812°C. The two melting temperatures, 1787°C and 1812°C, are identical within the experimental uncertainty to the value of 1802°C obtained by Boyd, England, and Davis (1964) at 25 kbar. At these temperatures, experiments lasting longer than 9 hours resulted in melting of the thermocouple, so close brackets on the drift rate could not be established. A maximum drift rate was determined at −5.7°C/hr, but no minimum could be established (Fig. 2). For the melting point of diopside at 18 kbar, 1620°C, long runs were possible and the drift rate was bracketed between −0.2 and −1.3°C/hr.

For purposes of comparison, we have also measured Pt/Pt10Rh thermocouple drift using a W3Re/

W25Re thermocouple as a reference. Figure 3 illustrates typical data on the change in *emf* of a Pt/Pt10Rh thermocouple with time when configuration *A* (Fig. 1) is used. The data are very similar to those reported by Mao and Bell (1971, Fig. 49) and Mao, Bell, and England (1971, Fig. 87). The change of apparent temperature with time is approximately linear but shows some irregularity, particularly during the first hour. The two extreme slopes for this graph (about −4.2°C/hr and −1.9°C/hr) are the basis for the uncertainty brackets at 1718°C in Figure 4. Other brackets in Figure 4, except for the two resulting from quenching experiments, are based on similar data at other temperatures. The two data points of Mao and Bell (1971) were obtained using the same thermocouple arrangement as our configuration *A* (Fig. 1) except that their thermocouple junction was placed exactly at the hot spot whereas ours lies just off the hot spot in a slight thermal gradient.

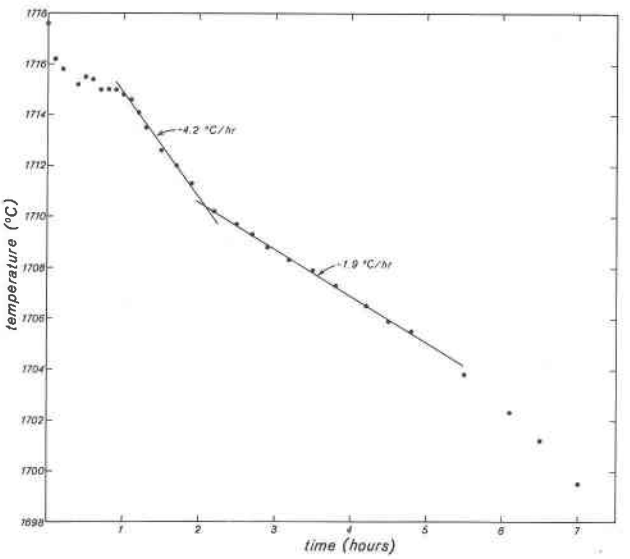

FIG. 3. Typical plot of change in *emf* of Pt/Pt10Rh thermocouple with time using configuration *A* of Figure 1.

The uncertainty brackets using configuration *B* are wider and the drift rates are much larger than with configuration *A* (Figs. 1 and 4). This difference agrees with previously published data at 1700°C in which Boyd, England, and Davis (1964) obtained a drift rate of about −60°C/hr using mullite insulators and a configuration similar to *B*, whereas Mao, Bell, and England (1971) obtained a drift rate of about −20°C/hr using mullite insulators and configuration *A*. The maximum drift rates established by the quenching experiments on diopside and enstatite show that configuration *B* gives unreliable results. The greater uncertainty using configuration *B* is possibly caused by irregular changes in the distance between the two thermocouple junctions during the course of the experiment, and the systematically higher drift rates might be caused by a small and gradual decrease in the distance between the two thermocouple junctions with time. Because the two thermocouples do not touch and there is no possibility of contaminating one thermocouple with the other, we originally thought that configuration *B* would give a more accurate measure of drift than configuration *A*. However, this appears not to be the case.

The results using configuration *A* are compatible with the upper limits of drift rates based on melting point determinations. However, it is possible that drift rates obtained from configuration *A* are too high because of contamination of the Pt/Pt10Rh thermocouple by the W3Re/W25Re reference thermocouple, as mentioned earlier in regard to the similar experiments of Mao and co-workers. Although the melting point determinations are inherently not very precise, we believe that they give the

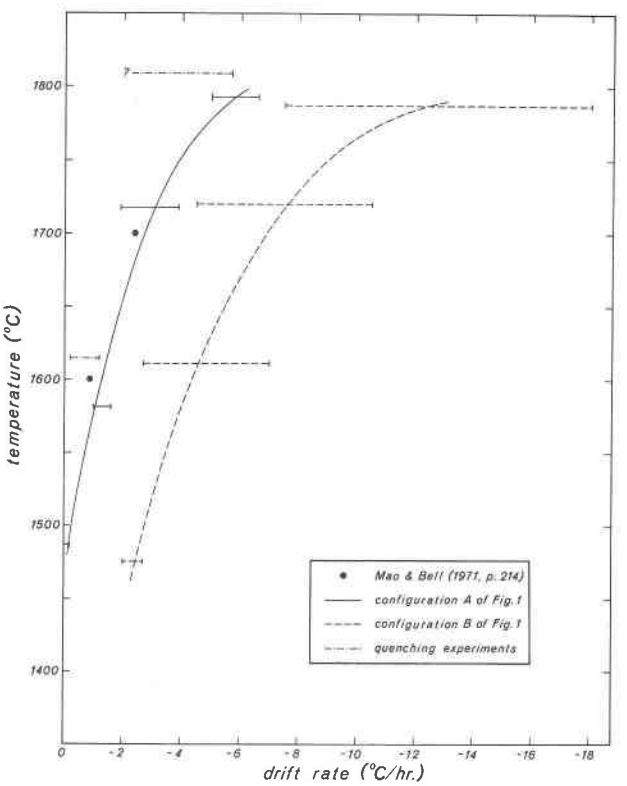

FIG. 4. Summary of drift rates of Pt/Pt10Rh thermocouples determined by different methods.

most reliable drift rate limits because they exactly duplicate conditions that exist during a routine experiment. Figure 5 shows drift rate limits for both types of thermocouples, based on quenching experiments. These limits apply to unwelded thermocouple junctions. We have not measured drift rates for welded thermocouple junctions and it is possible that they are slightly higher due to melting and mixing of the metals at the junction.

For experiments above 1600°C, our data show that W3Re/W25Re thermocouples are preferable to Pt/Pt10Rh thermocouples, for although the existence of large drift rates for Pt/Pt10Rh thermocouples has not been definitely established at these temperatures, we have established that W3Re/W25Re thermocouples are stable. According to Mao and Bell (1971), W3Re/W25Re thermocouples are also less affected by errors produced by differential tension of the wires. However, the calibration uncertainty of W3Re/W25Re thermocouples is large (±10°C), so for experiments below about 1400°C and at low pressures where tensional errors are small, Pt/Pt10Rh thermocouples would give results of comparable or slightly superior accuracy. The large cost advantage of W3Re/W25Re thermocouples and the marginal superiority of Pt/Pt10Rh thermocouples only at low pressures and temperatures dictate that W3Re/W25Re thermocouples are preferable for all routine experiments in piston-cylinder apparatus.

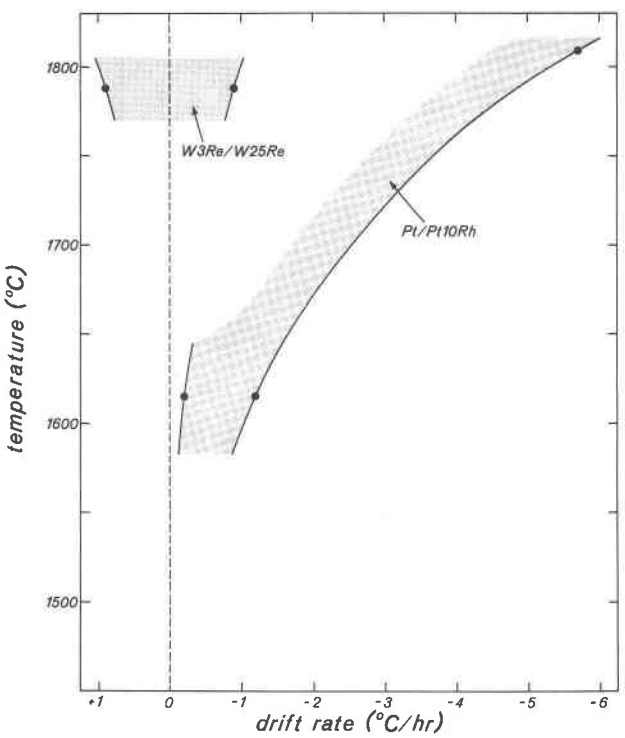

FIG. 5. Drift rate limits for Pt/Pt10Rh and W3Re/W25Re thermocouples, based on quenching experiments.

Appendix

Use of platinum and graphite sample capsules at high temperatures

During the course of this study, we have found that Pt capsules can be used at much higher temperatures than indicated in the literature. Boyd and England (1963, p. 314) stated that Pt capsules cannot be used above about 1600°C for runs longer than one hour because they become contaminated and melt. Williams and Kennedy (1969, p. 4362) gave 1500°C as the upper limit of usability for long runs unless "extreme precautions" are taken to prevent contamination. We have made successful runs using Pt capsules at temperatures up to 1825°C for a few minutes and 1800°C for 2 hours, and this extended range of usability is probably due to the fact that our capsules are completely encased by 99.7 percent Al_2O_3 ceramic (Fig. 1). Other ceramic materials apparently afford less protection from contamination. Figure 6 shows the length of runs that we have been able to make at various temperatures and pressures. The range of usability could be increased further by using Pt capsules alloyed with Rh.

In this study we have used Pt capsules whenever possible but some very long runs required the use of graphite capsules. We have found that graphite cap-

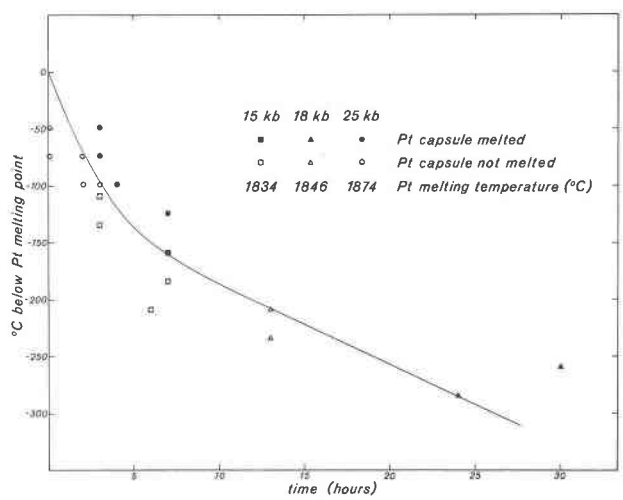

FIG. 6. Length of runs that can be made with Pt Capsules at various temperatures without melting the capsule. Melting temperatures for Pt are from Strong and Bundy (1959).

sules sometimes leak and allow contamination of the charge, as shown by the occasional presence of up to 3 percent Al_2O_3 in electron microprobe analyses of charges that should have contained only $MgSiO_3$. All of the critical graphite capsule runs in this study have been checked for Al_2O_3 contamination by electron microprobe analysis.

Acknowledgments

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