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Some predictions of a validated physical model of Pt–Rh thermocouple drift above 1200 °C

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Abstract

A simple model was recently presented which relates the electromotive force (emf) drift rate of Pt–Rh thermoelements to the vapour pressure of Pt and Rh oxides. The model assumes that the evaporation of these oxides gives rise to a continuously changing concentration of Pt and Rh, at different rates along the length of the wires, which causes a change in the Seebeck coefficient. The model was tested by comparison with high precision measurements under comparable circumstances. By considering various thermocouples of different compositions, it was demonstrated that the calculated drift rate is proportional to the measured drift rate, which represented a validation of the model. In the current study, the model is used to make some predictions concerning the set of optimum ‘zero-drift’ thermocouple wire compositions above 1200 °C. It is shown that for a wire of Pt–Rh with more than a few %Rh, there is a corresponding wire to make a thermocouple which has nearly zero thermoelectric drift, and that this is almost independent of temperature. Remarkably, this optimum relation is found to agree very well with a previous optimisation that was based on an empirical technique. An intriguing finding is that when the measurement junction is at around 1285 °C, the drift rate is very low, regardless of wire composition; the reason for this is explained by the model. This has implications for thermocouple drift testing at temperatures close to 1285 °C, which may be unreliable if the drift is inherently low regardless of the composition of the two thermoelements, as suggested by the model. The melting point of Co–C, 1324 °C, commonly used for thermocouple drift assessment, is far enough away from 1285 °C for this effect not to be a problem.

Keywords: thermocouple, thermoelectric stability, ITS-90, temperature metrology, drift testing

(Some figures may appear in colour only in the online journal)

1. Introduction

Noble metal thermocouples based on alloys of Pt and Rh are in widespread use for process monitoring applications where the demands of the process justify the high cost relative to base

metal thermocouples. A key advantage of noble metal thermocouples is the high thermoelectric stability. In the absence of significant amounts of impurities, the most important effects governing thermoelectric stability and homogeneity of Pt–Rh wires above about 1100 °C are associated with oxidation and oxide vapour transport [1], but this has never been conclusively demonstrated [2]. The vapour pressures of pure Pt and Rh [3] are several orders of magnitude lower and can be ignored when oxygen is present. The evaporation of Pt and Rh oxides causes local changes in the bulk wire composition, generally

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expressed in terms of the Rh mass fraction as a percentage, mainly due to the evaporation of PtO₂ and RhO₂ [1, 4–8]. Below about 1200 °C, PtO₂ has a higher vapour pressure than RhO₂, causing depletion of the fraction of Pt in the wire. Above 1200 °C, RhO₂ evaporates preferentially, causing depletion of the fraction of Rh in the wire [9, 10]. In general, above about 1100 °C the high temperature thermoelectric stability of Pt–Rh alloy wires is strongly dependent on the mass fraction of Rh, increasing with increasing Rh concentration. This is because the rate of change of Seebeck coefficient with changing Rh mass fraction decreases as the Rh mass fraction increases, so the thermoelements become less sensitive to local composition changes as the temperature increases [8]. Importantly, the thermocouple output is sensitive to the local composition of the Pt–Rh alloy in any region where there is a temperature gradient, so the integrated result of these competing effects along the whole wire length is important for the stability of the thermocouple, and this effect is considered in detail in the present study.

In [11] a model was described which relates the thermoelectric drift rate of Pt–Rh thermoelements to the vapour pressure of Pt and Rh oxides. The model assumes that the evaporation of these oxides gives rise to a continuously changing concentration of Pt and Rh, at different rates (which depend on the local temperature) along the length of the wires, which causes a local change in the Seebeck coefficient. The calculated drift rate was found to be linearly related to the experimental drift rate under comparable conditions.

In this paper the model is used to make some predictions concerning the set of thermocouple wire compositions which give rise to minimal thermoelectric drift, and assess the temperature dependence of this. In section 2 the model is summarised (further details can be found in [11]). In section 3 the model is used to make some predictions, which are compared with experimental findings. In section 4 a discussion is presented, and a conclusion is given in section 5. Throughout the paper, wire composition is expressed in terms of percentage by weight of Rh, e.g. Pt-30%Rh is expressed as ‘30 %’.

2. The model

The crux of the model is the calculation of the vapour pressure P (in units of Pa) of the Pt and Rh oxides in oxygen at a given temperature T (in units of K) given by Alcock and Hooper [9]:

$$\log P_{\text{Pt}} = -\frac{(8585 \pm 74)}{T} + (0.204 \pm 0.047) + 5, \quad (1)$$

$$\log P_{\text{Rh}} = -\frac{(9866 \pm 126)}{T} + (1.079 \pm 0.079) + 5, \quad (2)$$

where the uncertainties on the gradient and intercept when $\log P_{\text{Pt}}$ is plotted as a function of $1/T$ are taken to be the standard uncertainties. The vapour pressure is plotted in figure 1. Note that according to (1) and (2) the cross-over temperature

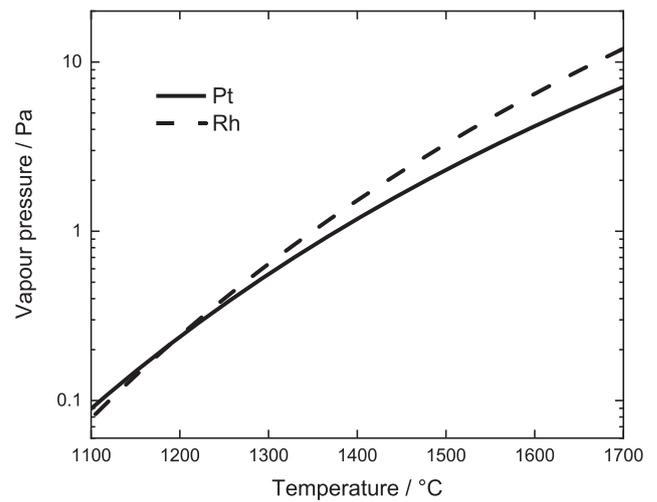


Figure 1. Vapour pressure of Pt and Rh oxides in isolation, as a function of temperature.

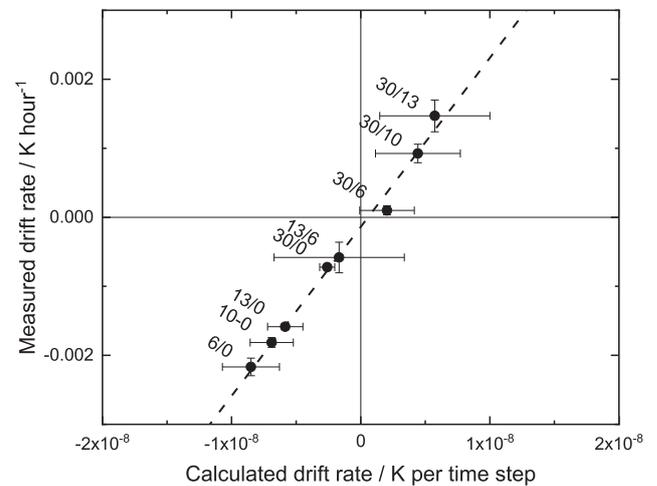


Figure 2. Measured drift rate versus calculated drift rate [11] for the thermocouples where data is available [12], showing a consistent linear relationship. Each point represents a different thermocouple composition, denoted by the composition of the two wires (e.g. the type B thermocouple is 30/6). The line shows the unweighted best fit. Uncertainty bars correspond to a coverage factor $k = 1$ (67% coverage probability). Note the uncertainties on the calculated drift rate are reliable estimates for individual points, but appear large when the points are presented as an ensemble due to the common effect of any error in the vapour pressure, as described in the text.

at which Rh oxide becomes more volatile than Pt oxide is about 1192 °C. The model divides the thermoelements into small segments and for each segment it assumes that the space between the thermoelements and the surrounding space in the insulation tube is completely empty. It then calculates how many moles of Pt and Rh are needed to fill up that space until the partial pressures of Pt and Rh given by (1) and (2) are reached. Finally, it calculates the corresponding change in the composition of the wire due to the loss of these atoms,

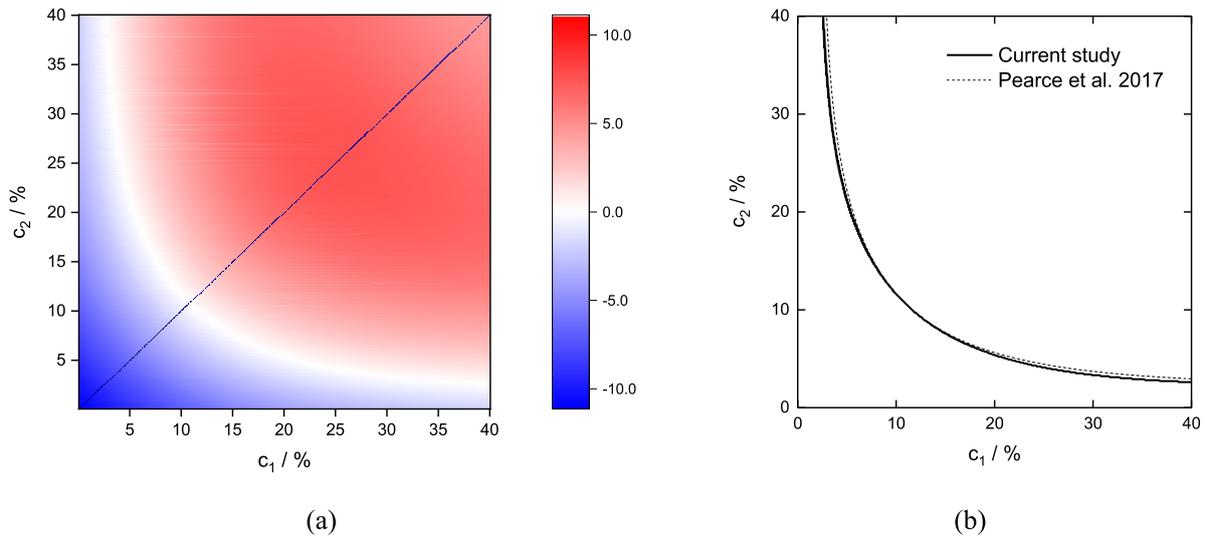


Figure 3. (a) Predicted drift rate at 1324 °C as a function of the composition (expressed in terms of Rh weight %) of the two thermocouple wires for the current model. Colour: deepening red/blue is increasingly positive/negative drift. White band shows region of minimal drift. Colour scale shows drift rate in units of nK per time step. (b) Predicted optimum composition line at 1324 °C (solid line). Thin dashed line is the optimum composition line obtained in a previous study with a completely different empirical model [12].

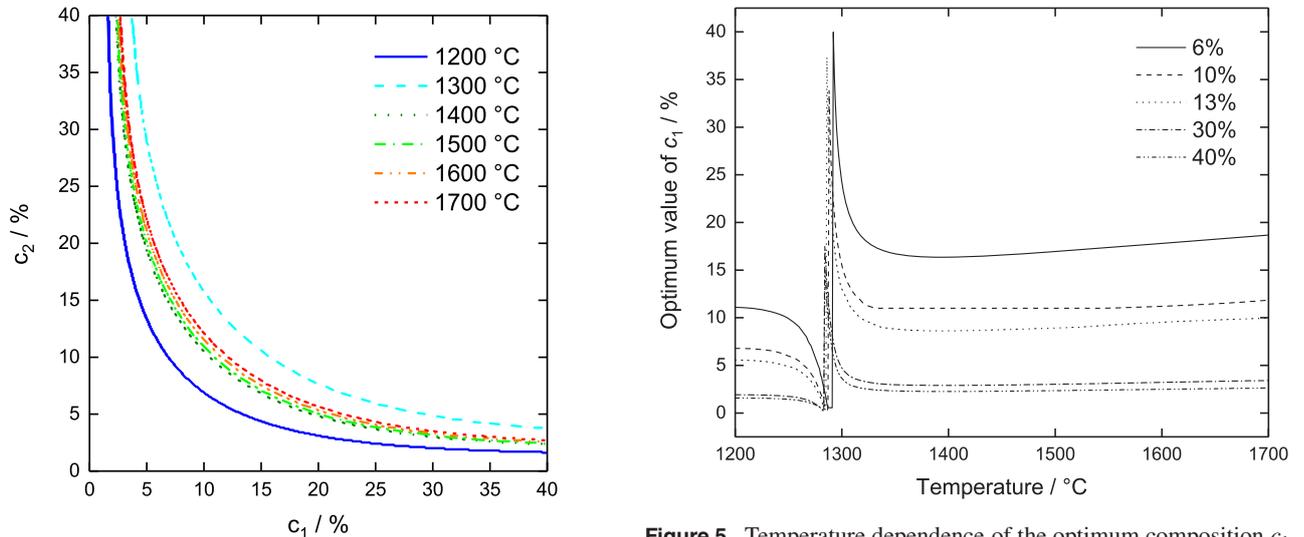


Figure 4. Temperature dependence of the line of optimum composition, i.e. the line giving the optimum value of c_2 for a given value of c_1 , or vice versa (where the composition is expressed in terms of Rh weight %).

Figure 5. Temperature dependence of the optimum composition c_1 , in the case where c_2 is fixed at the value indicated by the legend. There is a singularity at a temperature of about 1285 °C, though in this temperature region the thermocouple exhibits low drift regardless of the wire compositions (see figure 6).

and hence the new Seebeck coefficient. This permits calculation of the thermoelectric drift corresponding to the changed composition.

The model treats one wire at a time. There is a constant temperature gradient along the wire axis, i.e. the temperature is at 0 °C at the cold end (i.e. the reference junction), rising linearly to 1324 °C at the hot end (i.e. the measurement junction). Although the findings are independent of the temperature profile provided the profile remains the same throughout the calculation (this is analogous to the reason that the emf developed is independent of the temperature profile—the only parameter that matters is the temperature at either end), here a linear profile is chosen to simplify the visualisation. The wire is

divided into discrete segments. For each segment on the wire, the following steps are performed:

- Calculate the Seebeck coefficient at this position, determined from the temperature and alloy composition at this position
- Calculate the Pt and Rh oxide vapour pressure in the volume between the wire and the bore walls for this segment using equations (1) and (2) for the known temperature at this segment, scaled by the molar fraction of Pt and Rh in the wire
- Calculate the resulting number of moles of Pt and Rh in the vapour for this segment

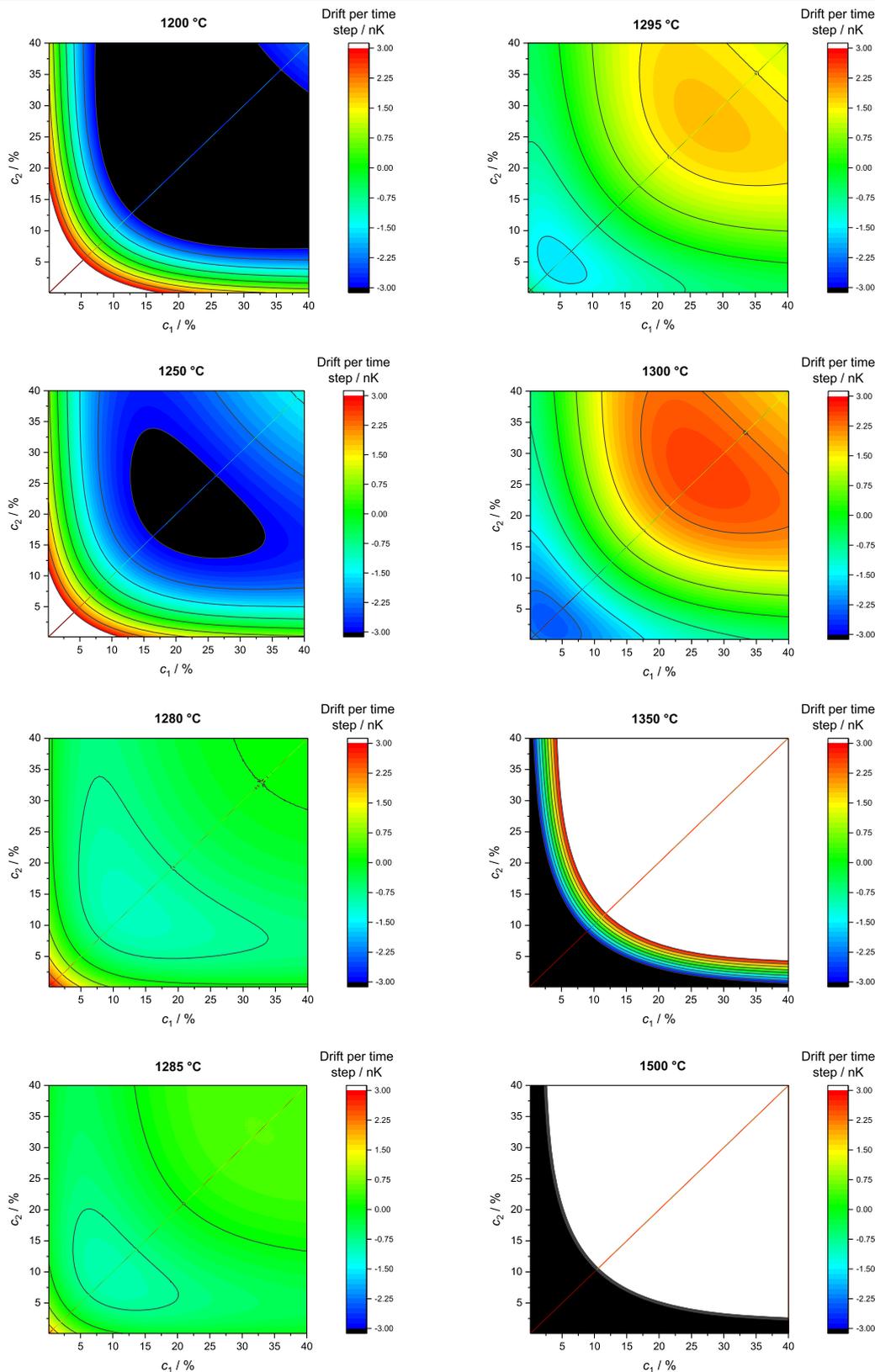


Figure 6. Colour plots showing the predicted drift rate (colour) as a function of thermocouple wire compositions c_1 and c_2 at different temperatures. Note the low drift, independent of wire compositions, at temperatures between about 1280 °C and 1290 °C. The colour scale is the same in all plots. The stability is universally good for all thermocouple compositions at around 1285 °C; above and below that temperature the optimum stability is strongly dependent on the composition.

- Remove the corresponding number of moles of Pt and Rh from the wire for this segment
- Calculate the new Seebeck coefficient at this position for the slightly changed alloy, determined from the temperature and composition at this position

Once this is performed for both wires, the emf developed by the thermocouple before and after the Pt and Rh oxide evaporation can be calculated, which yields the thermoelectric drift for this ‘time step’.

To validate the model, the calculated drift rate was compared with the measured drift rate from the very high precision drift measurements obtained by long-term exposure to a temperature of around 1324 °C with periodic *in situ* calibrations using a Co–C high temperature fixed point (melting temperature 1324 °C) [12] for eight different thermocouples, as shown in figure 2. The experimental drift rates of [12] (where the thermoelements were surrounded by air) between 200 h and 500 h duration were used to avoid initial transient short-range ordering effects and Rh oxidation effects. A well-defined linear relationship between the calculated and measured drift rates indicates excellent agreement. It is not feasible to include the time dependence in the current model because the rate of evaporation of the Pt and Rh oxides is incalculable, and published experimental values vary by several orders of magnitude [13], although the model can still be used to draw conclusions about the relative stability of different wire compositions. Although the measurements of Alcock and Hooper [9] were performed in pure oxygen, they also showed that the ratio of vapour pressures of Pt and Rh oxides is independent of oxygen partial pressure, so the findings of this model are applicable to any oxygen partial pressure (e.g. air). Of course, if there is no oxygen at all, e.g. an argon atmosphere is present, the model is not applicable because no oxides can form.

3. Predictions

The left panel (a) of figure 3 shows the drift rate for a wide range of thermocouples comprising wires of composition c_1 and c_2 for a measurement junction temperature of 1324 °C, which shows a clear band where the drift rate is close to zero. This ‘zero drift’ line is plotted as a function of the two wire compositions in the right panel (b) of figure 3, which also shows the results from a completely different empirical model [12]. The agreement between the two methods is shown to be extremely good.

The model was employed to investigate the temperature dependence of the optimum composition line of figure 3(b). The ‘zero drift line’ is shown for several different measurement junction temperatures in figure 4, which shows that below about 1300 °C the line shows some temperature dependence, but at higher temperatures this temperature dependence largely disappears.

The temperature dependence seen in figure 4 is exemplified in figure 5: here one wire composition is fixed, and the plot shows how the optimum composition of the other wire, c_1 , varies with temperature, for several different values of the fixed

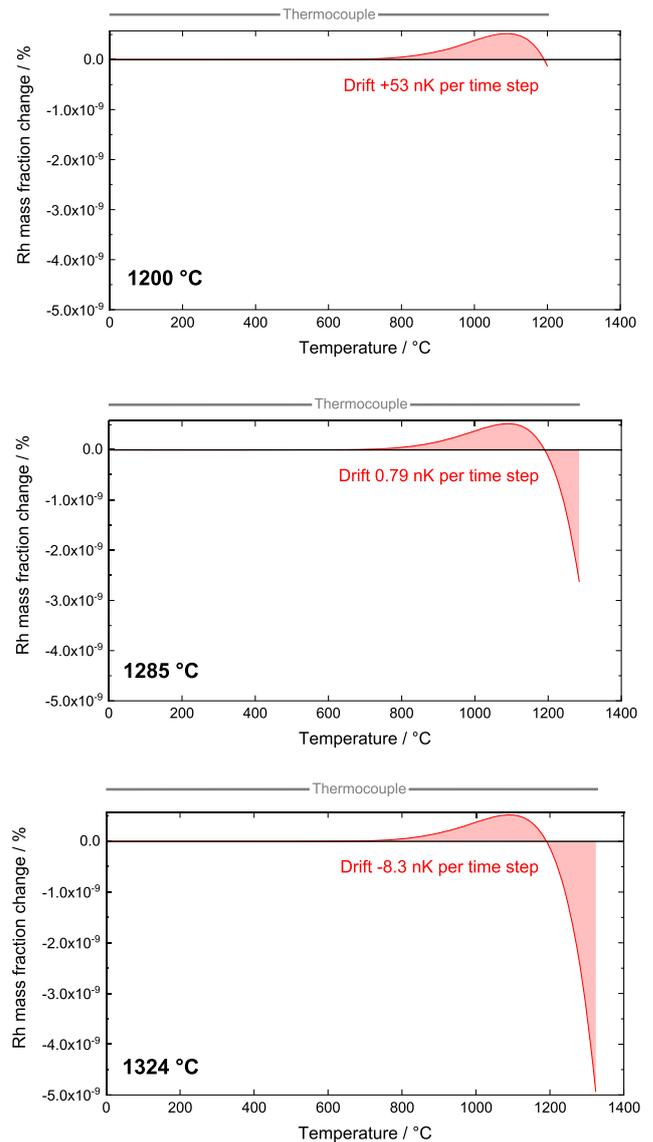


Figure 7. Change in composition of a Pt-13%Rh wire along its length due to evaporation, during one time step, as a function of temperature (i.e. as a function of distance along the wire from the reference junction, since the temperature varies linearly along the wire; the tip, or measurement junction, here is at the temperature shown). Each panel shows a different measurement junction temperature. Shaded areas illustrate the changed composition which causes the thermoelectric drift (note that the Seebeck coefficient increases with temperature, so the visual guide is only approximate); areas above and below the horizontal axis cause drift of opposing signs. The values of drift stated in the plots correspond to the Pt-13%Rh vs Pt thermocouple.

c_2 . Figure 5 shows some non-monotonic behaviour, and in particular a singularity at about 1285 °C. On closer inspection, however, it is seen that at this temperature (around 1285 °C) the drift rates are lowest for *all* thermocouple compositions. This is demonstrated in a series of colour plots is shown in figure 6, which shows that below and above about 1285 °C the drift rate is very sensitive to the two wire compositions, and at around 1285 °C the drift rates are very low, *independent* of the two wire compositions.

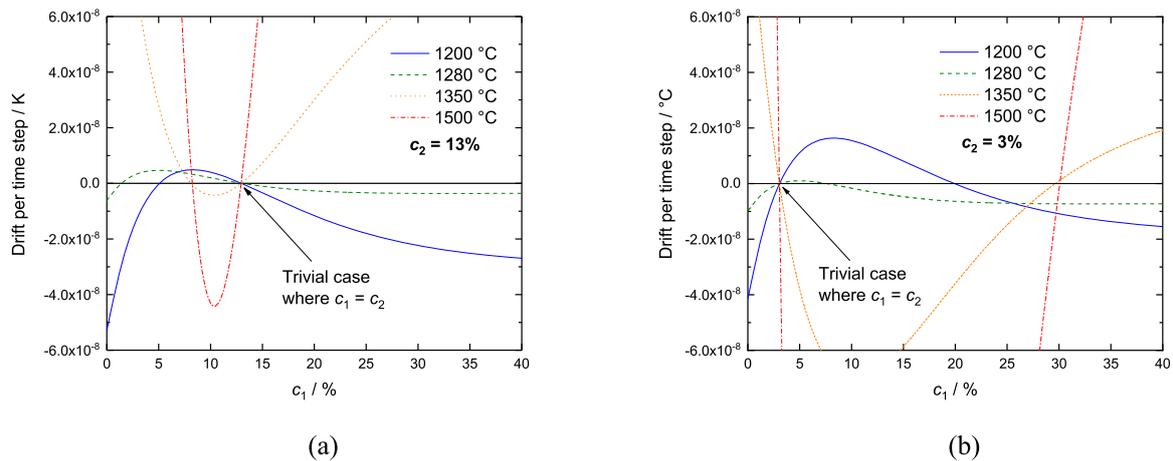


Figure 8. (a) Optimum value of c_1 corresponding to the point where the drift is zero in figure 5 (i.e. crosses the horizontal axis in that figure), at different temperatures, for the case where $c_2 = 13\%$. Note that at 1280 $^{\circ}\text{C}$ the drift is very low, regardless of wire composition. b) As for (a) except that $c_2 = 3\%$.

The reason for this temperature region of minimum drift around 1285 $^{\circ}\text{C}$ can be seen in figure 7, which shows the change in composition of the Pt-13%Rh wire as a function of temperature (i.e. position for this case where the temperature varies in a linear manner along the wire), when the thermocouple measurement junction is at three different temperatures below, at, and above 1285 $^{\circ}\text{C}$. Note that, in reality, oxidation of Pt and Rh below about 900 $^{\circ}\text{C}$ is somewhat unlikely due to the formation of a protective layer of Rh oxide, but for simplicity the model assumes continuity of the functions giving Pt and Rh oxide vapour pressures determined by Alcock and Hooper.

- Case 1. When the measurement junction is at 1200 $^{\circ}\text{C}$, almost all the wire is at a temperature below the crossover point of 1193 $^{\circ}\text{C}$ (the crossover where the vapour pressures of Pt and Rh oxides are equal), so the Pt is preferentially evaporated and the wire becomes enriched with Rh, with corresponding thermoelectric drift.
- Case 2. When the measurement junction is at 1285 $^{\circ}\text{C}$, part of the wire is at a temperature below 1193 $^{\circ}\text{C}$ and part is above; the former is subjected to preferential Pt evaporation, and the latter is subjected to preferential Rh evaporation. Hence below 1285 $^{\circ}\text{C}$ the wire becomes depleted of Rh, and above 1285 $^{\circ}\text{C}$ it is depleted of Pt, resulting in drifts of opposite sign for the two cases. Very close to a temperature of about 1285 $^{\circ}\text{C}$ the area under the curves above and below 1193 $^{\circ}\text{C}$ sums to almost zero, which would yield a net drift rate close to zero. This explains why the drift rate is so low around this temperature. This finding is universally applicable; it is not unique to the Pt-13%Rh wire, which is used here merely to demonstrate the principle.
- Case 3. Finally, when the measurement junction is at 1324 $^{\circ}\text{C}$, there is more wire exposed to temperatures above 1193 $^{\circ}\text{C}$ where the wire becomes enriched with Pt, which explains why the drift is in the opposite direction to that of the wire at 1200 $^{\circ}\text{C}$.

The preceding argument explains why the observed temperature of maximum overall stability seen in figure 6, namely about 1285 $^{\circ}\text{C}$, is approximately 100 $^{\circ}\text{C}$ higher than the crossover point (where Pt and Rh oxide vapour pressures match) of 1193 $^{\circ}\text{C}$ seen in figure 1: up to this crossover point where the Pt and Rh oxide vapour pressures match there is only Pt depletion, so for the maximum stability to occur this must be balanced by Rh depletion further along the thermocouple, which can only occur at temperatures above this crossover point. The preceding argument also means that the ‘singularity’ seen in figure 5 is unimportant, since although this singularity means that the optimum composition is undefined at about 1285 $^{\circ}\text{C}$ (and steeply changes at temperatures either side), the drift rate is also independent of composition, and is very low for all wire compositions.

Figure 8(a) shows the drift as a function of the composition of one wire, c_1 , while the other wire composition, c_2 , is fixed (here at 13%). Below and above about 1285 $^{\circ}\text{C}$ the drift rate is very sensitive to composition. However, most interesting is that around 1285 $^{\circ}\text{C}$ the drift is low regardless of the composition. As the temperature moves away from about 1285 $^{\circ}\text{C}$, the ‘basin’ of optimum stability has increasingly steep sides, and it becomes increasingly important to get the composition right to optimise the stability.

An interesting finding shown in figure 5 is that the optimal combination Pt-30%Rh/Pt-3%Rh or Pt-40%Rh/Pt-3%Rh exhibits almost no temperature dependence in the temperature range between 1350 $^{\circ}\text{C}$ and 1700 $^{\circ}\text{C}$ (i.e. they appear to be optimal over that whole temperature range), which indicates that they are promising thermocouple combinations in this temperature range. On the other hand, figure 8(a) shows that the drifts which occur at higher temperatures than 1300 $^{\circ}\text{C}$ increase rapidly when the optimal composition is departed from. This is explored further in figure 8(b) which shows the drift as a function of composition of c_1 when $c_2 = 3\%$. In this case, the Pt-30%Rh/Pt-3%Rh thermocouple appears to be stable between 1200 $^{\circ}\text{C}$ and 1500 $^{\circ}\text{C}$, although it becomes rather sensitive to the exact composition as it approaches 1500 $^{\circ}\text{C}$,

and small departures from the optimal composition result in a rapidly increasing drift rate. On the other hand, Pt-40%/Pt-3%Rh shows the highest stability only to about 1350 °C. This is evident also in figure 6, which is instructive for considering the optimal configuration at a given temperature, as well as for exploring the optimal configuration likely to provide the best compromise over a range of temperatures.

4. Discussion

At 1324 °C the agreement of the ‘zero drift line’ with that of a previous empirical model (figure 3(b)) is remarkable and builds confidence in the use of the model for predictions. The zero drift line exhibits some temperature dependence below about 1300 °C (figure 4), which would suggest that in practice the expected temperature of use would have a bearing on the wires to be selected, although figure 4 shows that above about 1300 °C there is no significant temperature dependence.

The finding that in the temperature region close to 1285 °C the thermocouple is stable regardless of which pair of thermoelements is chosen is remarkable, and may explain anecdotal evidence that drift testing at around that temperature is unreliable. This does not invalidate drift testing at the melting point of Co–C, 1324 °C, because this temperature is far enough away from 1285 °C for this not to be a problem; at the Co–C temperature the stability is once again very much dependent on the composition of the two thermoelements.

5. Conclusion

A simple model of Pt and Rh oxide vapour transport was recently presented [11], which predicts the influence of oxide transport to different regions of the thermocouple wire on the resulting thermoelectric stability. In this paper the model has been employed to make some predictions about the relative thermoelectric stability of different Pt–Rh alloys. The conclusions can be summarised as follows.

- The model predictions agree extremely well with the measured stability at 1324 °C (which were obtained through long-term heat treatment with periodic *in situ* measurements of the Co–C melting temperature), which is taken as a validation of the model, and permits the analysis presented in this paper.
- The predicted ‘zero drift line’, i.e. the pairs of wire compositions that yield zero drift, agrees extremely well with a previous empirical model, building confidence in the model as a means of making predictions.
- An intriguing finding is that there is a temperature region around 1285 °C where the drift rate is very low regardless of the composition of the two thermocouple wires, and an explanation for this has been provided.
- Great care must be taken when performing thermoelectric drift testing at temperatures close to 1285 °C, because the thermocouple may appear to be stable, regardless of the composition of the two thermoelements. Drift tests at the

melting point of Co–C, 1324 °C, are not affected by this phenomenon, and can be considered to be reliable.

- Overall, a good choice for an optimum composition above about 1200 °C appears to be one thermoelement with high Rh content, and one with low Rh content, although the envisaged temperature range will have a bearing on exactly which composition is chosen.

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