Validating the impurity component of high-temperature fixed-point uncertainty budgets with the Scheil solidification model

D Lowe¹³ and C P Morris-Crowthers¹²
¹ National Physical Laboratory, Teddington, Middlesex, UK
² Dept of Physics, Queen Mary University, London

A high temperature fixed-point cell based on a melting or freezing transition can only be as good as the purity of the metal used to make it, and that purity can be hard to quantify. Least squares fitting of the Scheil solidification model has been applied to four cobalt-carbon and four platinum-carbon fixed point cells, as measured variously at eight different laboratories, to determine the pure material liquidus temperature for each cell. If this value does not agree with the liquidus temperatures of the same melting transitions, within the assigned uncertainties, as determined directly from the melting curve then the implication is that the allowed uncertainty component for impurities may not be large enough. We find the method can be accurate enough to be useful in validating a high-temperature fixed-point cell.

1. Introduction
Impurities can be the main reason why fixed-point cells used as temperature standards do not agree with each other. It is difficult to measure what impurities are present to the necessary accuracy and it may not be clear what effect any given impurity has on the measured temperature. Therefore, a method that can help confirm if measurements are consistent with the applied uncertainty would be useful.

The Scheil model of solidification is valid where freezing is slow enough that there is complete mixing in the liquid but fast enough that there is no diffusion in the solid state. This equates to a solid-liquid interface velocity of 0.3 μm.s⁻¹ for typical impurity diffusion rates [1], and the Scheil equation has been applied with some success in this regime [2]. In contrast, the interface velocity routinely used for high-temperature fixed-points (HTFP) can be 10 – 100 times faster. Such HTFP cells have recently been assessed and liquidus temperatures and uncertainties determined [3]. Part of that uncertainty evaluation was an assessment of the possible effect of impurities. If the Scheil equation could meaningfully be applied at the faster freezing rates, this would help to validate that uncertainty analysis.

2. Numerical model
The Scheil fit method is sensitive to the choice of how much of the plateau at the phase transition is used [1]. One way around this is simply to use all combinations and accept there will be a spread of values. It is, though, helpful to exclude data from the start and end that are substantially part of the thermal environment rather than the phase transition. To help identify what range of data might be appropriate and to see if the correct value was found, a numerical model was used to generate a HTFP freeze-melt cycle, to which the Scheil equation was fitted. Parameter maps were made by iterating over wide ranges of start and end points for liquidus temperature (T₀), distribution coefficient (k), for mC₀ (the product of liquidus slope and initial composition) and for the fit residuals.

The model described in [4] was used to calculate a freeze and melt curve for cobalt-carbon with an added impurity of distribution coefficient k = 0.2. Literature values were used for the thermal properties and eutectic spacing. The use of HTFPs is based on the melting rather than the freezing curve and so it was the reversed melting curve to which the Scheil equation was fitted. This equation was formulated according to [1] as:

³ To whom any correspondence should be addressed
\[ T(t) = T_0 + mC_0(1 - a(t - t_s))^{k-1} \]  

where \( T(t) \) is the measured temperature at time \( t \), \( a \) is a scaling factor that relates time to liquid fraction and \( t_s \) is the time at completion of solidification.

Figure 1. Behaviour of the solutions of equation (1) for different combinations of start and end of the melting curve data: (a) pure material liquidus temperature \( (T_0) \), (b) distribution coefficient \( (k) \), (c) \( mC_0 \) and (d) fit residuals

The results of varying the start and end of the fitted data range are shown in Figure 1. There seems no obvious feature to choose in either \( T_0 \) or \( k \), and no rationale for choosing one solution over another. The residuals increase for earlier start point and later end point, and removing poorer fits would seem justifiable. In addition, \( mC_0 \) appears to be largely unaffected by choice of start point, and plateaux as the end point is reduced. On the basis that a solution that is very sensitive to the inclusion or removal of small amounts of data might be problematic, the approach taken was to first remove the high residual results by trimming the start and end, and then further remove data from the end if there was still a clear roll off in \( mC_0 \). Doing this for the model data, then averaging the remaining results and taking the standard deviation as the uncertainty gave \( T_0 = (1325.01 \pm 0.02) \degree C \) and \( k = (0.26 \pm 0.10) \), in agreement with the input values of 1325 and 0.2.

3. Application to Real Data

This process was then applied to some of the data from [3]: a melting curve from each of eight HTFP cells (four of cobalt-carbon and four of platinum-carbon), with measurements spread between eight National Measurement Institutes (NMIs). Where the behaviour above was seen, that data was removed, otherwise no judgement was made: we simply averaged all the data ranges that could be fitted. The fitting gives a value together with an uncertainty for the pure material liquidus temperature of each cell as measured at each relevant NMI. We can also determine the actual liquidus temperature from the same melting curves using the specified limits (SL) method [5]. Note that the Scheil method is predicting the pure material liquidus temperature, while the SL method is giving the liquidus temperature of the actual measured fixed-point cell. If impurities have been adequately accounted for, the two methods should
agree. The two methods are compared in Figure 2, where the uncertainty contribution for the SL method is based on that used in [3] for these cells.

Figure 2. Comparing Scheil to SL. “Normalised SL” is based on setting the mid-point of a rectangular probability distribution at zero. The error bars are the limits combined with an additional component for impurities. “Scheil Fit” is the difference of the averaged $T_0$ value to that “Normalised SL” value, and the error bars are the standard deviation of the $T_0$ determination. Note that NMI(4) measured all cells,
the others two at most. NMI(6) reported no result for Platinum-carbon D. Uncertainties are given at approximately 95 % confidence level.

4. Discussion
To be self-consistent the error bars of the results for the Scheil fit for all the melts of each cell should overlap. For platinum-carbon, there are some differences between NMI(4) and NMI(8) for cell C and cell D, but the differences are small. Similarly, for cobalt-carbon, there is no overlap between NMI(2) and NMI(4) for cell A, although here it is clear three of the fittings are poor. In the main, though, results are largely self-consistent.

Further, if a large enough uncertainty has been allowed for impurities the results for “Normalised SL” should overlap with the results for “Scheil Fit”. The findings here are that platinum-carbon cell C and cell D have a bigger temperature change from impurities than was allowed for in [3].

Finally, we note that some of the NMIs, such as NMI(8), and some of the cells, such as platinum-carbon cell B, seem to consistently have a smaller spread in solution values than others. It is known that making a freeze more “Scheil-like” (albeit at much slower interface velocities) is a good way to optimise furnace thermal conditions [6] and so it may that for those laboratories and cells results are actually better quality – producing melt curves with reduced effects from temperature gradients or poor solid-liquid interface growth around the blackbody cavity.

5. Conclusion
While it is not clear that the Scheil equation is valid for HTFP measured with rapid solid-liquid interface velocity, fitting to a numerical model gave the correct value within the standard deviation of the analysis. It is straightforward to fit the Scheil model to HTFP melting curves and this could be routinely done. A small spread in values of solutions that agree with the liquidus assignment would be evidence that impurities have been adequately accounted for. Continued use might show if the method could be used as a “quality indicator” for different HTFP cells and furnaces.

6. References
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