Use of a phenomenological chemical scale for the identification of high distribution coefficient impurities within the ITS-90

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The Problem
The freezing temperatures of certain metals are used as the basis of the International Temperature Scale of 1990 (ITS-90). For European laboratories to be competitive there is a need for reduced uncertainties. Since the biggest contribution to uncertainties is usually the purity of the reference metals used, better understanding of the behaviour of impurities is desirable.

Evaluating $k$
Divide the purity analysis into:
- Elements that can be ignored
- Elements whose effects can be estimated
- Elements that can be corrected for
- Elements that have to be included as uncertainty

Many times this comes down to knowing if an impurity element has $k\approx 0$, $k\approx 1$, or $k$ is $>> 1$. Which elements are present as compounds? Heat of fusion is possibly important.

Predictability of $k$, $H$ for gold

- The distribution or partition coefficients, $k$, determines the composition of the liquid phase and so sets the shape of a freeze curve. The enthalpy of fusion, $H$, is related to whether an impurity forms a compound with the metal. Published experimentally determined values of $k$ and theoretically calculated values of $H$ both show signs of periodicity with atomic number, $Z$, but have an apparent phase and magnitude behaviour when viewed in terms of $\chi$.

chemical potential scale $\chi$
Known correlation of $k$ with the periodic table, but no obvious fitting function.

Chemical scale $\chi$
was developed by David Pettifor at Imperial College as a one dimensional representation of the two dimensional periodic table. Using $\chi$ instead of $Z$ there is a change in the pattern of ordering. The heat of fusion has the form of a resonance phase suggesting using a resonance type function as a fitting equation to published $k$ values plotted as a function of their chemical potential.

The results of applying a Lorentz oscillator based equation for $k(\chi)$ to the metals used for defining ITS-90 above the triple point of water are given.

Background
Identification of which impurities may be present and what effect they have on measured freezing behaviour can greatly overestimate the uncertainty.

Assess shape of freezing curve based on assumptions about the behaviour of impurities in a metal, one of the most important parameters being the distribution coefficient, $k$. Often has widely discrepant experimental values and agreement to thermodynamic modelling can be poor.

Fit to data using resonance function
Fitting published data for distribution coefficients using an equation based on a resonance $\chi$, specific to each of the metals used as ITS-90 reference materials. In most cases impurities with $k > 1$ are grouped in a restricted range of $0.8 < \chi < 1.2$ corresponding to transition metals from group 5 to group 11. Error bars show the spread in $k$ values where more than one measurement has been published.

Conclusion
The effect of impurities on the solidification of metals is difficult to assess as concentrations are hard to measure with sufficient accuracy and the effect of each impurity may not be well known. This can lead to overestimating uncertainties. Correction strategies based on assumptions about $k$ can improve matters, but his means knowing which impurities are likely to cause a serious error in the correction. Plotting $k$ as a function of $\chi$ reveals a pattern that might help identify problematic impurities. Results are suggestive of the Einstein model of a solid.