

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

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**Abstract.** The International Temperature Scale of 1990 standardises practical temperature measurement based on the reproducibility of the solidification phase transition temperature of highly pure metals. The effect of impurities can be the biggest block to establishing international equivalence of temperature metrology and so it is important to have knowledge of the distribution coefficients for all potential impurities. In particular impurities with a high distribution coefficient cause problems with applying corrections, and so it is helpful to identify which impurities are likely to be an issue. By plotting the published measured distribution coefficients of impurities in the metals used as references in the International Temperature Scale of 1990, as a function of a quantum mechanical based scale intended to provide separation of binary alloy crystal structure, an apparent resonance peak is found. This could allow a simple fit equation to be applied to determine whether a given impurity is likely to cause an error to any correction strategy.

## 1. Introduction

The effect of impurities on the measured freezing temperature of temperature fixed-points is often the single largest component in the uncertainty of realisation of the International Temperature Scale of 1990 (ITS-90) [1] and can cause problems when it comes to confirming international equivalence of scales [2]. The solidification behaviour of Ga, In, Sn, Zn, Al, Ag, Au and Cu is of interest. The recommended method [1] to assess the effect of impurities on the measured solid-liquid phase transition of these metals requires a full chemical analysis and knowledge of the liquidus slope,  $m$ , and distribution coefficient,  $k$ , for each element. The liquidus slope and distribution coefficient are related to each other by [3]

$$m = (k - 1)/A \quad (1)$$

where  $A = L/(RT^2)$  is the first cryoscopic constant, with  $L$  the latent heat of fusion of the solvent ( $\text{kJmol}^{-1}$ ),  $T$  its freezing temperature in kelvin and  $R$  is the gas constant ( $\text{kJmol}$ ). Since  $A$  is known for the metals listed, knowledge of  $k$  is sufficient to assess the effect of an impurity. At the uncertainty levels required the detection limits of the analysis of the impurities have to be considered and so all elements need to be characterised, not just those detected as being present. Ideally then, until there is reliable knowledge of the distribution coefficients for all the binary systems involving ITS-90 fixed points some predictor of  $k$  is desirable [4].



In fact, if it can be established that impurities with  $k$  greater than some threshold are not present in significant quantities then corrections based on analysis of the freezing curve shape may be possible. If the threshold is  $k \approx 0.1$  a single parameter (the unknown concentration,  $c$ ) fit to the freezing curve (temperature against fraction melted) gives the reduction in temperature from the pure system [1] as

$$\Delta T = \frac{c}{FA} \quad (2)$$

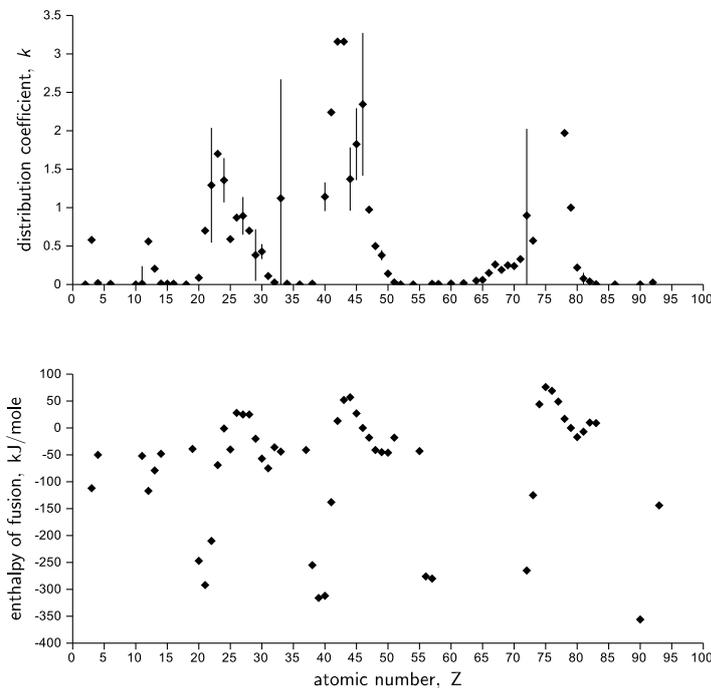
where  $F$  is the solid fraction. If the threshold is at  $k \approx 1.3$  then it is possible to correct with an uncertainty of about 30% of the correction by fitting the Scheil-Gulliver model to the freezing curve [5].

It can therefore be useful just to have an indication that a metal fixed-point cell is likely to show an erroneous freezing temperature if a particular impurity could be present in substantial amounts (and by substantial, meaning at the level of 1 ppm). When trying to predict  $k$  it has been known for some time that there is a periodicity with atomic number [6]. Recently a review of all available published  $k$  values looked for patterns in  $k$  based on the Hume-Rothery rules [4]. However, there was no clear correlation between either electronegativity, atomic size or valency with  $k$ . To see if improvement could be made to predicting which impurities would have high  $k$  the experimental data given in that publication were analysed with respect to an arbitrary chemical scale rather than atomic number or any other single atomic property.

## 2. Chemical Scale, $\chi$

Structure maps were introduced to classify and aid the identification of new binary compounds with specific crystal structure type and perhaps with particular desired property [7]. Their use involves defining a suitable co-ordinate system on two perpendicular axes. Often these are based on some aspect of the Hume-Rothery rules for solid solutions. Recognising that the choice of axes could be arbitrary, in [8][9] the periodic table was reduced to a continuous one dimensional array with the Mendeleev number  $M$  giving the position in the array and a value  $\chi$  assigned to each  $M$ . The reasoning behind the concept was fully explained in [10]. As it is not a well known concept (at least within temperature metrology), some of the reasoning of that publication is paraphrased here:

In order to construct a structure map one or more monotonic scales are needed. The Hume-Rothery rules often used for this purpose are classical in nature. Classical concepts are inadequate to describe the behaviour of valence electrons and the bonding between atoms. The periodic table, though, does reflect the fundamental quantum properties of the valence electrons. However its two dimensional nature means it is not suitable to be used in structure maps. To this end the two dimensional arrangement is reduced to one dimension, in effect by running a string through each element and then "pulling" the table into a chain. The elements are then numbered by their position on this chain, the "Mendeleev number",  $M$ . Since the way different atoms chemically combine into different structure types depends on the strength and direction of the bonds, which depend on a fundamentally quantum property – the shape of the electron orbitals – a "correct" string (more useful string) will have patterns and trends in a structure map of crystal structure, just as the periodic table has patterns and trends in chemical properties. It is then a matter of arranging the stringing of the periodic table such that it groups binary compounds according to their structure type [10]. Subsequently this scale was refined by assigning a monotonically increasing value to each  $M$  such that the separation was further improved, while requiring that there was no overlap between groups. It is this scale,  $\chi$  that is used here.



**Figure 1.** Distribution coefficient  $k$  and calculated heat of fusion  $\Delta H_{sol}$  plotted as a function of solute atomic number for gold as a solvent

### 3. Results

#### 3.1. Comparison of chemical scale to atomic number

How an impurity behaves in a solidifying melt is closely tied up with compound formation. This in turn is related to the heat of formation of the two atomic species, with bare patches in structure maps of stable compounds corresponding to regions of positive heat of formation [9]. If  $\Delta H$  is negative a compound can form, if positive it is preferable for the impurity to be dissolved as an alloy with no particular crystal structure. The heat of formation of an impurity in a metal can be estimated using the heat of solution ( $\Delta H_{sol}$ ) of alloys in the liquid phase, which can in turn be approximately calculated using known quantities (electronic work function, bulk modulus and molar volume) [11]. In figure 1 the measured values for  $k$  in gold taken from [4] and calculated  $\Delta H_{sol}$  taken from [11] are plotted against atomic number  $Z$ . The error bars (both here and elsewhere) are the standard deviation of reported measured  $k$  values, not the actual measurement uncertainties. The first thing to note is that where more than one measurement is reported there is often a big difference in the value for  $k$ . From this figure it appears there is some correlation between the two properties, and that there is a periodicity related to the atomic number.

In figure 2 the same quantities are plotted against chemical scale  $\chi$ . The measured  $k$  and calculated  $\Delta H_{sol}$  values are now more ordered. Also shown are the magnitude (3) and phase (4) of a resonance based on the Lorentz equations for classical bound electrons [12] using a least squares fit of (3) to  $k$ . This was then used to calculate a phase using (4), visually normalised to  $H$ . There is a discrepancy between the central value when comparing  $k$  to  $H$ , but it should be noted that the former is measured while the latter is a calculated approximation. It was found that the other ITS-90 fixed point materials had similar behaviour for heat of solution, and so

(3) was fitted to the measured  $k$  of the other ITS-90 metals

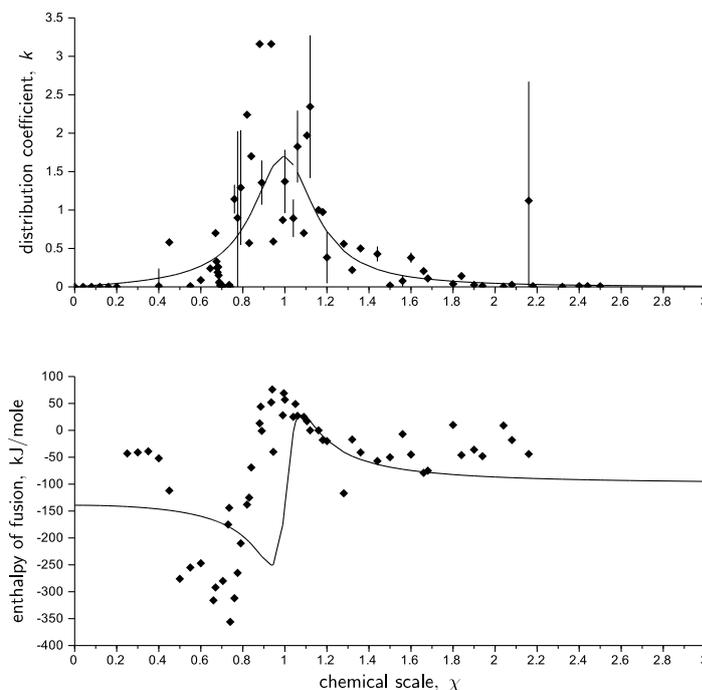
$$k(\chi) = \frac{\chi}{C_1(\chi_0^2 - \chi^2)^2 + C_2\chi^2} \quad (3)$$

$$\Delta H(\chi) = 1 + \frac{C_3(\chi_0^2 - \chi^2)}{C_1(\chi_0^2 - \chi^2)^2 + C_2\chi^2} \quad (4)$$

No sensible results were had for In 3(f) or Sn 3(g). In the other cases there are more or less well defined peaks at around  $\chi = 1$ .

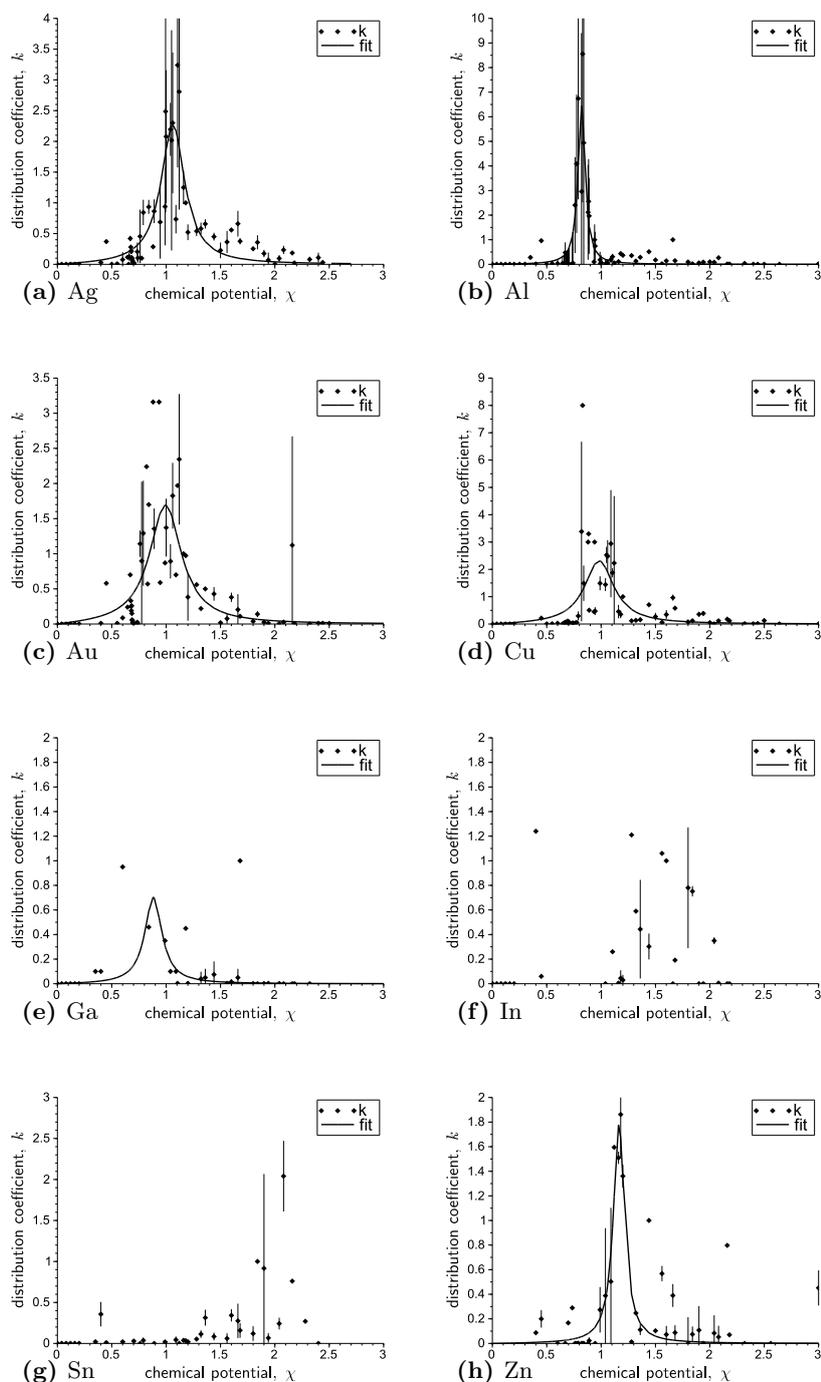
#### 4. Discussion

Like the periodic table, the chemical scale is phenomenological in its construction. It turns the two dimensional periodic table into a one dimensional scale that groups together binary compounds depending on their particular crystallographic type when used as the basis of a structure map. However this mapping of different crystal structures into different domains is reflecting the underlying quantum nature of inter-atomic bonds. The  $\chi$ -scale is in this sense more fundamental than the widely used Hume-Rothery rules which use classical concepts such as the size of an atom [13]. Many of the ITS-90 relevant metals show a peak in  $k$  when plotted as a function of  $\chi$ . It appears that as  $\chi$  increases the likelihood of compounds forming switches from high to low (with  $H_{sol}$  behaving as the phase), and at this switchover  $k$  increases rapidly - the likelihood of an impurity being preferentially taken up into the solid phase increases. This increase in  $k$  only occurs over a fairly narrow range of  $\chi$ . In the application of a resonance function to fit the peak in  $k$  there is the suggestion that the solid is behaving as the Einstein model with a collective single value oscillation into which suitable  $\chi$  valued impurities are readily absorbed. Outside this value the impurity is likely to be insoluble ( $k \approx 0$ ) or to form inclusions of



**Figure 2.** Slice through the structure map for  $k$  and  $H$  at gold,  $\chi = 1.16$  together with fits based on a central value  $\chi_0$  derived from equation 3

compounds as clusters of atoms with a definite crystal structure and not affecting the solid-liquid interface temperature.



**Figure 3.** Least squares fit to the  $k$  value of impurities in metals used as ITS-90 fixed points. No fit could be obtained for In and Sn. Error bars are the standard deviation of different measurements where more than one published value is available.

## 5. Conclusion

It is apparent that there is a periodicity in  $k$  relating to atomic number (figure 1). It is known that this periodicity can be related to the periodic table [6]. Applying the classical Hume-Rothery rules fails to improve the predictive possibilities of the periodicity [4]. Use of the quantum mechanical chemical scale,  $\chi$ , which is connected to the variation in bonding due to the arrangement of an elements valence electron orbitals leads to a single peak for high  $k$  at  $\chi \approx 0$ . An assumed association between compound formation and solid solubility suggested considering heat of fusion of elements in the liquid state as something that may be related but is readily calculable. The results look like a resonance in  $\chi$  with  $k$  as the amplitude and  $\Delta H_{sol}$  as the phase. The impurities where  $\Delta H_{sol} < 0$  should be considered as likely to form compounds and have no effect on the measured freezing temperature. There is a potential benefit to being able to predict the magnitude of  $k$ , first to assess unknown binary systems and secondly to give some element of corroboration to data that might have widely varying published values (consider the error bars in figures 2 and 3, which are often as large as the determined values). Using the chemical scale  $\chi$  to order  $k$  in place of  $Z$  gives clearer separation of high and low  $k$  impurities. The patterns suggest only elements with a  $\chi$  between 0.8 and 1.2 need to be considered when deciding if  $k \approx 0$  can reasonably be assumed so as to allow a correction based on freezing curve shape. This corresponds to transition metals from about group 5 to group 11. The application of the chemical scale  $\chi$  might therefore aid in getting better values for  $k$  and the effect of impurities and so help demonstrate international equivalence between temperature scales.

## Acknowledgements

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