Comments on the underestimation of the change of fixed-point temperatures by impurities due to a non-justified application of Raoult's law

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In Document CCT/99-11 prepared by Working Group 1 of the CCT, the basic crystallographic facts concerning the behaviour of impurities during the freezing of fixed-point samples are briefly summarised. This behaviour determines essentially the shape of the freezing curves and is therefore important for an evaluation of the curves. In thermometry, the main goal of such an evaluation is to get an information on the uncertainty component caused by the impurities when realising temperature fixed points. But from the basic crystallographic facts it follows that unfortunately this uncertainty component can be only reliably estimated from the slope of the freezing curve if all impurities are not soluble in the solid phase. In this very rare case, the difference ΔT between the temperature of the ideally pure fixed-point substance T_{pure} and the observed freezing temperature of the sample T_{obs} is given by the relation

$$\Delta T(F) = T_{\mathrm{pure}} - T_{\mathrm{obs}}(F) = c_{11}/FA$$

(F fraction of sample melted, A first cryoscopic constant, c_{11} total impurity concentration), which is often called Raoult's law. At the liquidus point ($F = 1$), the freezing temperature is shifted by the impurities by $\Delta T(F = 1) = c_{11}/A$. For most of the fixed-point substances, this favourable case is not fulfilled, i.e. at least a few impurities are soluble in the solid phase. The segregation of these impurities during freezing is, in a first approximation, described by the equilibrium distribution coefficient $k_{\mathrm{o}} = c_{\mathrm{s}}/c_{\mathrm{l}}$, where c_{s} and c_{l} are mole fraction concentrations of the impurity in the solid and liquid equilibrium phases of the sample, respectively. (To simplify the discussion, it is assumed that only one impurity is soluble in the solid phase. The evaluation of the freezing curves is even more complicated if several impurities are soluble in the solid phase.) The solution in the solid phase changes the dependence ΔT versus $1/F$. In the case of complete mixing in the liquid and no diffusion in the solid phase, it is determined only by c_{11}, k_{o} and the slope m_{l} of the liquidus line in the phase diagram for the host-impurity system:

$$\Delta T(F) = c_{11}\, m_{\mathrm{l}} \,/\, F^{1-k_{\mathrm{o}}}.$$

Thus, the dependence ΔT versus $1/F$ is not a straight line and the application of Raoult's law yields an underestimation of the change of the freezing temperature by impurities. In Document CCT/99-11, an example for this underestimation is given: "For instance, the influence is underestimated by a factor of nearly 5 if equation (4) is used to approximate $\Delta T(F)/\Delta T(F{=}1)$ versus $1/F$ in the $1/F$ range from 1.1 ($F = 0.9$) to 10 ($F = 0.1$) for impurities having an equilibrium distribution coefficient k^{i}_{o} of 0.5.". (Equation (4) in Document CCT/99-11 represents Raoult's law.) Since this statement may not be obvious, it is the purpose of this short note to illustrate the errors caused by a non-justified application of Raoult's law in more detail.

At the liquidus point, the change of the freezing temperature by the impurity is given by $\Delta T_{\mathrm{liquidus}} = \Delta T(F = 1) = c_{11}\, m_{\mathrm{l}}$. (Due to the supercooling, this temperature can be determined of course only by extrapolating the freezing curve to $F = 1$, but this does not concern the discussion in this short note.) It is equal to the slope of the freezing curve, represented T versus $1/F$, if Raoult's law is valid, e.g. if k_{o} is equal to zero ($c_{\mathrm{s}} = 0$ in the solid phase). A non-justified application of Raoult's law means that a straight line is fitted to the freezing curve $T(1/F)$ in a chosen F range F_1 to F_2 although the impurity is soluble in the solid phase ($k_{\mathrm{o}} \neq 0$). The slope of this straight line is approximately given by $c_{l1}\, m_l\, (1/F_1^{\,1-k_o} - 1/F_2^{\,1-k_o}) / (1/F_1 - 1/F_2)$. This slope yields a wrong estimate $\Delta T_{\mathrm{wrong}}$ of the impurity effects if it is wrongly assumed that the freezing curve is sloped due to the influence of an impurity with $k_o = 0$, i.e. it yields an underestimation of $\Delta T_{\mathrm{liquidus}}$ by the factor

$$E_R = \Delta T_{\mathrm{liquidus}} / \Delta T_{\mathrm{wrong}} = (1/F_1 - 1/F_2) / (1/F_1^{\,1-k_o} - 1/F_2^{\,1-k_o}).$$

In the figure, the "factor of underestimation of the influence of impurities due to the application of Raoult's law", $E_R = \Delta T_{\mathrm{liquidus}} / \Delta T_{\mathrm{wrong}}$, is shown in dependence on the distribution coefficient k_o for two different F ranges ($F_1 = 0.1$, $F_2 = 0.9$ and $F_1 = 0.5$, $F_2 = 0.9$, respectively). The narrower range is often used to evaluate the freezing curves because thermal effects may influence their shape at lower F values. But even for this range, the estimate for the change of the liquidus temperature by the impurity is to small by a factor of about 2.5 for an impurity having a distribution coefficient of $k_o = 0.5$. (For the larger range, the correct factor is equal to 4.2, i.e. a rounded up value is given in CCT/99-11.) The factor E_R approaches one for $k_o \ll 1$, i.e. Raoult's law becomes applicable for these small distribution coefficients, but it is very large if k_o is close to one, e.g. $E_R \approx 15$ for $k_o = 0.9$ and $F_1 = 0.5$, $F_2 = 0.9$. This illustrates very clearly that impurities with $k_o \approx 1$ cannot be detected by evaluating the freezing curves. For $k_o > 1$, E_R is negative, i.e. the application of Raoult's law yields a wrong impression on the direction of the change of the liquidus temperature due to the impurity (it is increased compared with T_{pure}) and the difference $T_{\mathrm{pure}} - T_{\mathrm{obs}}$ has its smallest absolute value at $F = 0$. Impurities with $k_o > 1$ are especially dangerous because they can change the broadening of the freezing curve due to the influence of other impurities with $k_o < 1$ in a misleading direction, especially near to the liquidus point ($F = 1$).

Unfortunately, for $k_o > 0.2$, the E_R values shown in the figure differ significantly from one. This causes great efforts in realising temperature fixed points at the highest level of accuracy because a reliable estimation of the influence of impurities on the fixed-point temperature requires to determine the concentration of all impurities with $k_o > 0.2$ individually applying an appropriate analysis method. But it should be emphasized that these E_R values illustrate the limits for estimating the influence of impurities on the fixed-point temperature under the best conditions. Under the real conditions existing during the fixed-point realisation, the indication of the impurity effects can be even worse by two reasons. First, the maximum possible change in the overall impurity content and thus the maximum possible indication of the impurity effects occur in the case of complete mixing in the liquid phase. If the fixed-point sample freezes too fast, the mixing in the liquid phase is not complete and the segregation is described by an effective distribution coefficient k_{eff}, which is closer to one than the equilibrium distribution coefficient k_o, i.e. the effective E_R value deviates more from one than that corresponding to k_o. Second, for optimal realisation of the fixed points at and above the triple point of mercury, two liquid/solid interfaces are usually induced in the fixed-point cell. In such a situation, the outer interface (close to the cell wall) completely surrounds the inner interface (adjacent to the thermometer well) and advances slowly inwardly. The inner interface is essentially static. The outer interface thermally protects and stabilises the inner interface. The segregation of impurities influences the temperatures of the outer and inner interfaces. The effect is more pronounced for the outer interface if the mixing in the liquid is not complete and it is described by the effective distribution coefficient k_{eff} for this interface. But it is the temperature of the inner interface that is measured by the thermometer. The temperature of the inner interface is influenced by the segregation in dependence on the diffusion of the impurities from the outer to the inner interface. This may cause a further weakening of the indication of impurities effects.

Factor of Underestimation of the Influence of Impurities due to the Non-justified Application of Raoult's Law (*F* Liquid Fraction)