Bureau International des Poids et Mesures

Guide to
the Realization of the ITS-90

Fixed Points: Influence of Impurities

APPENDIX 1: *Derivation of an approximate relation between the equilibrium distribution coefficient and thermodynamic quantities*

Consultative Committee for Thermometry
under the auspices of the
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APPENDIX 1

Derivation of an approximate relation between the equilibrium distribution coefficient and thermodynamic quantities

At an equilibrium solid-liquid phase transition, the chemical potentials of the host material A in the liquid (μ_{lA}) and solid phases (μ_{sA}) have to be equal:

$$\mu_{\mathrm{lA}} = \mu_{\mathrm{sA}} \; , \tag{A1.1}$$

where their general expressions are:

$$\mu_{\mathrm{lA}} = \mu^{0}_{\mathrm{lA}} + RT \ln\left(\frac{a_{\mathrm{lA}}}{a^{0}_{\mathrm{lA}}}\right) , \tag{A1.2}$$

$$\mu_{\mathrm{sA}} = \mu^{0}_{\mathrm{sA}} + RT \ln\left(\frac{a_{\mathrm{sA}}}{a^{0}_{\mathrm{sA}}}\right) . \tag{A1.3}$$

In these expressions, a is the symbol for the chemical activity, and the zero marks the reference values. If the pure host material A is used as the reference, one has

$$a^{0}_{\mathrm{sA}} = a^{0}_{\mathrm{lA}} = 1 \text{ , and} \tag{A1.4}$$

$$\Delta\mu^{0}_{\mathrm{A}} = \mu^{0}_{\mathrm{lA}} - \mu^{0}_{\mathrm{sA}} = \Delta G_{\mathrm{MA}} \; , \tag{A1.5}$$

with ΔG_{MA} being the free enthalpy of fusion of material A. For ideal solutions, the chemical activity a is equal to the concentration c. In a binary system, the concentrations of the components A and B are directly linked: $c_{\mathrm{sA}} = 1\text{-}c_{\mathrm{sB}}$ and $c_{\mathrm{lA}} = 1\text{-}c_{\mathrm{lB}}$. From Equations (A1.1) to (A1.5) it follows in this case:

$$\Delta G_{\mathrm{MA}} = RT \ln\left(\frac{1-c_{\mathrm{sB}}}{1-c_{\mathrm{lB}}}\right) . \tag{A1.6}$$

For small concentrations of component B, the following approximation can be used:

$$\ln\left(\frac{1-c_{\mathrm{sB}}}{1-c_{\mathrm{lB}}}\right) \approx (c_{\mathrm{lB}} - c_{\mathrm{sB}}) \; . \tag{A1.7}$$

The application of the Gibbs-Helmholtz equation ($\Delta G = \Delta H - T\Delta S$) to the melting yields

$$\Delta G_{\mathrm{MA}} = \Delta H_{\mathrm{MA}} - T\Delta S_{\mathrm{MA}} \; , \tag{A1.8}$$

where ΔH_{MA} is the enthalpy of fusion and $\Delta S_{\mathrm{MA}} = \Delta H_{\mathrm{MA}}/T_{\mathrm{MA}}$ is the entropy of fusion (T_{MA} melting temperature of the pure material A). Since the equilibrium distribution coefficient is defined by $k_0^{\mathrm{B}} = c_{\mathrm{sB}} / c_{\mathrm{lB}}$, Equations (A1.6) to (A1.8) yield

$$k_0^{\mathrm{B}} = 1 - \frac{\Delta H_{\mathrm{MA}} (T_{\mathrm{MA}} - T)}{RTc_{\mathrm{lB}}T_{\mathrm{MA}}} \; . \tag{A1.9}$$

For small concentrations of component B, it is furthermore possible to assume that $T \approx T_{\mathrm{MA}}$ and ΔH_{MA} is independent of concentration and temperature, i.e. Equation (A1.9) can be simplified further:

$$k_0^{\mathrm{B}} = 1 - \frac{\Delta H_{\mathrm{MA}} (T_{\mathrm{MA}} - T)}{RT_{\mathrm{MA}}^2 c_{\mathrm{lB}}} = 1 - A\frac{(T_{\mathrm{MA}} - T)}{c_{\mathrm{lB}}} \; . \tag{A1.10}$$

In Equation (A1.10), A is the first cryoscopic constant. Since the ratio $(T\text{-}T_{\mathrm{MA}})/c_{\mathrm{lB}}$ is practically equal to the slope of the liquidus line $m_{\mathrm{l}}^{\mathrm{B}} = \partial T_{\mathrm{l}} / \partial c_{\mathrm{lB}}$, one obtains finally the following approximate relation

$$m_{\mathrm{l}}^{\mathrm{B}} = \partial T_{\mathrm{l}} / \partial c_{\mathrm{lB}} = -(1 - k_0^{\mathrm{B}}) / A \; . \tag{A1.11}$$

In summary, the following assumptions were made for deriving Equation (A1.11) at low concentrations of component B: (i) ideal solution, (ii) Relation (A1.7), (iii) $T \approx T_{\mathrm{MA}}$, and (iv) ΔH_{MA} is independent of concentration and temperature.

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