Measurements (calibration functions)

Overview of the supported calibration functions follows. Notice the defined order of parameters ($\boldsymbol{\vartheta}$) and specifiers¶ of the functions (n is the number of reactants, m is the number of species, $\mathbf{q} \sim (m, n)$ is the matrix of stoichiometric coefficients, c_i is the free concentration of the i-th component†).

$\boxed{\textbf{Type } 1}$

$$y = E_0 + S \log c_1 + j_1 c_1 + j_2 \frac{\beta_1}{c_1}$$

$\boldsymbol{\vartheta} \equiv E_0,\ S,\ j_1,\ j_2$

Note: Function of type 1 describes the dependence of the difference y of potentials of a "hydrogen" (glass) electrode and a reference electrode in a cell with non-negligible liquid-junction potential on the free concentration c_1 ($\beta_1 \equiv K$ is the ionic product of water). Thus, H^+ must be the 1st reactant (1st column of the matrix $\mathbf{q}$), OH^- must be the 1st complex (1st row of the matrix $\mathbf{q}$).

$\boxed{\textbf{Type } 2}$

$$y = E_0 + S \log c_1$$

$\boldsymbol{\vartheta} \equiv E_0,\ S$

$\boxed{\textbf{Type } 3}$

$$y = E_0 + S \log c_k + j_1 c_1 + j_2 \frac{\beta_1}{c_1}$$

$\boldsymbol{\vartheta} \equiv E_0,\ S,\ j_1,\ j_2$
$k \in \langle 1, n \rangle$

$\boxed{\textbf{Type } 4}$

$$y = E_0 + S \log c_k$$

$\boldsymbol{\vartheta} \equiv E_0,\ S$
$k \in \langle 1, n \rangle$

$\boxed{\textbf{Type } 5}$

$$y = E_0 + S \log \frac{c_k}{c_l} + j_1 c_1 + j_2 \frac{\beta_1}{c_1}$$

$\boldsymbol{\vartheta} \equiv E_0,\ S,\ j_1,\ j_2$
$k \neq l \in \langle 1, n \rangle$

$\boxed{\textbf{Type } 6}$

$$y = E_0 + S \log \frac{c_k}{c_l}$$

$\boldsymbol{\vartheta} \equiv E_0,\ S$
$k \neq l \in \langle 1, n \rangle$

Note: Functions of types 5 and 6 describe the dependence of the difference y of potentials of a redox (platinum) electrode and a reference electrode on the ratio of free concentrations c_k, c_l of two reactants (i.e. the simplest case of a redox system, e.g. Fe^{3+}/Fe^{2+}, Sn^{4+}/Sn^{2+}, Ce^{4+}/Ce^{3+} etc.).

$\boxed{\textbf{Type } 7}$

$$y = \sum_{i=1}^{n+m} a_i c_i = \mathbf{a}^{\mathrm{T}} \boldsymbol{c}$$

$\boldsymbol{\vartheta} \equiv a_i,\ i = 1, \ldots, n+m$

¶ usually k (and l or d), but the problem is more complicated with calibration functions of types 9, -3, -4, -5 and -6, where $k = -i$ for $i \leq n$ and $k = i - n$ for $i > n$ ($l = -j$ for $j \leq n$ and $l = j - n$ for $j > n$)

† $n + m$ components are ordered such that the first n of them are reactants and the next (last) m are species

$\boxed{\textbf{Type } 8}$

$$y = d\sum_{i=1}^{n+m} a_i c_i = d\,\mathbf{a}^{\mathrm{T}}\boldsymbol{c}$$

$\boldsymbol{\vartheta} \equiv a_i,\ i = 1, \ldots, n+m$
$d \in \mathsf{R}$

Note: Functions of types 7 and 8 describe the dependence of an extensive *linearly additive* quantity y (absorbance in some "slow exchange" spectrometry (in the case of inseparable peaks), usually UV/VIS spectrophotometry, reaction heat in enthalpimetry, conductivity in conductimetry etc.) on the free concentrations $\boldsymbol{c}$ of all components.

$\boxed{\textbf{Type } 9}$

$$y = \frac{c_i}{c_j}$$

$i \neq j \in \langle 1, n+m \rangle$

"Subtype" 9*ln*

$$y = -\ln\frac{c_i}{c_j}$$

$i \neq j \in \langle 1, n+m \rangle$

$\boxed{\textbf{Type } -1}$

$$y = -\log c_1$$

$\boxed{\textbf{Type } -2}$

$$y = -\log c_k$$

$k \in \langle 1, n \rangle$

$\boxed{\textbf{Type } -3}$

$$y = \alpha c_i$$

$\vartheta \equiv \alpha$
$i \in \langle 1, n+m \rangle$

$\boxed{\textbf{Type } -4}$

$$y = d\alpha c_i$$

$\vartheta \equiv \alpha$
$d \in \mathsf{R},\ i \in \langle 1, n+m \rangle$

$\boxed{\textbf{Type } -5}$

$$y = \sum_{i=1}^{n+m} a_i p_i c_i/\mathcal{C} = \mathbf{a}^{\mathrm{T}}\mathbf{P}\boldsymbol{c}/\mathcal{C}\ \P\dagger$$

$$\mathbf{P} = \mathrm{diag}(p_1, \ldots, p_{n+m})$$

$\boldsymbol{\vartheta} \equiv a_i,\ i = 1, \ldots, n+m$

¶

$$p_i \in \mathsf{N} + \{0\}\ ,\quad i = 1, \ldots, n\ ,\quad p_{n+i} = \sum_{j=1}^{n} p_j q_{ij}\ ,\quad i = 1, \ldots, m\ ,\quad \mathcal{C} = \sum_{i=1}^{n+m} p_i c_i$$

† A little more complicated definition (using almost general diagonal matrix **P**) enables correct description of the dependent variable no matter what linear transformation of the matrix **q** is actually in use. Moreover, dynamic definition of the analytical concentration $\mathcal{C}$ of the "active" component (**not** exclusively reactant or complex) is necessary for the calculation of unknown chemical parameters **c**, **n**, V, **c**', **q** (the value of $\mathcal{C}$ changes).

Note: Function of type -5 describes the dependence of an intensive *linearly additive* quantity y (chemical shift or relaxation rate, i.e. reciprocal relaxation time, in "fast exchange" NMR spectroscopy, effective mobility in capillary zone electrophoresis of a labile system etc.) on the free concentrations $\boldsymbol{c}$ of all components.

"Subtype" $-5ln$

$$y = -\ln a_i - \ln p_i - \ln c_i + \ln \mathcal{C} \text{ ¶}$$

Type -6

$$y = p_i c_i / \mathcal{C} \dagger$$

$i \in \langle 1, n+m \rangle$

Note: Function of type -6 describes the dependence of an intensive quantity y (intensity of an isolated (separated) peak in some "slow exchange" spectrometry, usually NMR spectroscopy, intensity of an isolated peak in capillary zone electrophoresis of an inert system etc., normalized to the sum of intensities of all the peaks embracing all components containing the active component) on the free concentrations $\boldsymbol{c}$ of all components (but mainly on c_i).

"Subtype" $-6ln$

$$y = -\ln p_i - \ln c_i + \ln \mathcal{C}$$

Type -7

$$y = \alpha \sum_{i=1}^{n+m} c_i$$

$\vartheta \equiv \alpha$

Note: Function of type -7 describes the dependence of an extensive *linearly additive* quantity y, usually a change of some colligative property (difference of resistances in VPO, osmotic pressure in membrane osmometry etc.) on the free concentrations $\boldsymbol{c}$ of all components.

¶ $p_i \neq 0, \forall\, j \neq i : a_j = 0$

† $p_i \neq 0$