8.3.2.3 Constants and symbols

Equation for emf Response of Ion-selective Electrode Cells and Definitions of $K_{A,B}^{pot}$

The Nikolsky-Eisenman equation:

$$E = \text{constant} + \frac{2.303RT}{z_A F} \lg[a_A + K_{A,B}^{pot} a_B^{z_A/z_B} + K_{A,C}^{pot} a_C^{z_A/z_C} + \ldots]$$

E	is the experimentally determined galvanic potential difference of ISE cell (in V) when the only variables are activities in the test solution;
R	is the gas constant equal to 8.314510 J $K^{-1}mol^{-1}$;
T	is the absolute temperature, K;
F	is the Faraday constant, 9.6485309×10^4 C mol^{-1};
a_A	is the activity of ion A;
a_B&a_C	are the activities of the interfering ions, B and C, respectively;
$K_{A,B}^{pot}$	is the potentiometric selectivity coefficient for ion B with respect to the primary ion A
z_A	is the charge number- an integer with sign and magnitude corresponding to the charge of the principal ion, A;
z_B&z_C	are charge numbers corresponding to the charge of interfering ions, B and C, respectively. Signs of these charge numbers are the same as that of the primary ion.

Ionic strength of solution is defined by:

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

I	is the ionic strength of solution;
c_i	is the amount concentration of the ion i (usually in moles per liter);
z_i	is the charge of ion i.

Other Symbols

Sign conventions should be in accord with IUPAC recommendations. See 1.3.10.
t_R is response time, s

Determination methods of $K_{A,B}^{pot}$

1. Fixed Interference Method (FIM). The emf of a cell comprising an ion-selective electrode and a reference electrode (ISE cell) is measured for solutions of constant activity of interfering ion, a_B, and varying activity of the primary ion. The emf values obtained are plotted *vs*. the logarithm of the activity of the primary ion a_A. The intersection of the extrapolated linear portions of this plot indicates the value of a_A which is to be used to calculate $K_{A,B}^{pot}$ from the Nikolsky-Eisenman equation

$$K_{A,B}^{pot} = \frac{a_A}{a_B^{z_A/z_B}}$$

2. Separate Solution Method (SSM) I. The emf of a cell comprising an ion-selective electrode and a reference electrode (ISE cell) is measured for each of two separate solutions, one containing the ion A of the activity a_A (but no B), the other containing the ion B at the same activity $a_B = a_A$ (but no A). If the measured values are E_A and E_b, respectively, then the value of $K_{A,B}^{pot}$ may be calculated from the equation:

$$\log K_{A,B}^{pot} = \frac{(E_B - E_A) z_A F}{2.303RT} + (1 - \frac{z_A}{z_B}) \lg a_A$$

3. Separate Solution Method (SSM) II. The concentrations of two different solution introduced separately into the cell, a cell comprised of an ion-selective electrode and a reference electrode (ISE cell), are adjusted with each of two different solutions, one containing the ion A of the activity a_A (but no B), the other containing the ion B (but no A) of the activity a_B as much as required to achieve the same cell potential measured. From any pair of activities a_A and a_B for which the cell potential is the same, the value of $K_{A,B}^{pot}$ may be calculated from the equation:

$$K_{A,B}^{pot} = \frac{a_A}{a_B^{z_A/z_B}}$$

The FIM and SSM-s are recommended only for electrodes which exhibit a Nernstian response both to principal and interfering ions. These methods are based on the assumption that plots of E_A *vs*. lg (a_A^{1/z_A} 6) and E_B *vs*. lg (a_B^{1/z_B} 7) are parallel and separated vertical spacing is (2.303RT/F)lg $K_{A,B}^{pot}$. However, the FIM can always be used to determine a minimum primary ion concentration level at which the effect of interference can be neglected. The actual conditions of the FIM match the conditions under which the electrodes are used.