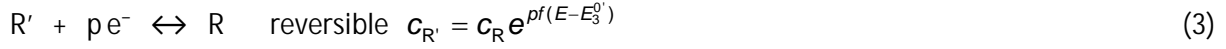
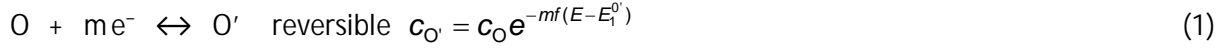


Three-step mechanism



Total number of electrons $n = m + p + 1$. The total current:

$$i = nFAk_2^0 \left[c_{O'} e^{-\alpha f(E-E_2^0)} - c_{R'} e^{(1-\alpha)f(E-E_2^0)} \right] \quad (4)$$

Inserting eqs. (1) and (3) into (4), the following equations can be derived:

$$i = nFAk_{\text{app}}^0 \left[c_O e^{-n\beta f(E-E^0)} - c_R e^{n(1-\beta)f(E-E^0)} \right] \quad (5)$$

$$i_0 = nFAk_{\text{app}}^0 (c_O^*)^{1-\beta} (c_R^*)^\beta \quad (6)$$

$$\frac{i}{i_0} = \left(\frac{c_O}{c_O^*} \right) e^{-n\beta f\eta} - \left(\frac{c_R}{c_R^*} \right) e^{n(1-\beta)f\eta} \quad (7)$$

$$k_{\text{app}}^0 = k_2^0 e^{-mf(E^0-E_1^0)} e^{-\alpha f(E^0-E_2^0)} = k_2^0 e^{pf(E^0-E_3^0)} e^{(1-\alpha)f(E^0-E_2^0)} \quad (8)$$

$$\beta = \frac{m + \alpha}{n} \quad (9)$$

If we define $\alpha' = n\beta$, eq. (5), for example, can be written as

$$i = nFAk_{\text{app}}^0 \left[c_O e^{-\alpha' f(E-E^0)} - c_R e^{(n-\alpha')f(E-E^0)} \right], \quad (10)$$

which is the form used in Comsol or suggested by IUPAC. The essential thing is that both forms (5) and (10) reduce to the Nernst equation at equilibrium and the total driving force of the reaction, $nf(E - E^0)$ is seen in the exponent, although the rate determining step has only one electron.