electrode reaction rate constants

The electrode reaction rate constants are related to the partial currents by

$$k_{\mathrm{ox}} = l_a / nFA\Pi c_i^{\nu_i}$$

$$k_{\mathrm{red}} = l_c / nFA\Pi c_i^{\nu_i}$$

where k_{ox} and k_{red} are the rate constants for the oxidizing (anodic) and reducing (cathodic) reactions respectively, n is the charge number of the cell reaction, F is the Faraday constant, A is the geometric area of the electrode, the product $\Pi c_i^{\nu_i}$ includes all the species i which take part in the partial reaction, c_i is the volume concentration of species i and ν_i is the order of the reaction with respect to species i.

The conditional rate constant of an electrode reaction is the value of the electrode reaction rate constant at the *conditional (formal) potential* of the *electrode reaction*. When α the transfer coefficient is independent of potential,

$$k_{\mathrm{c}} = k_{\mathrm{ox}} / \exp[\alpha_{\mathrm{a}}(E - E_c^{0\prime})\, nF / \nu RT]$$

$$= k_{\mathrm{red}} / \exp[-\alpha_{\mathrm{c}}(E - E_{\mathrm{c}}^{0\prime})\, nF / \nu RT]$$

where α_{a} and α_{c} are the anodic and cathodic transfer coefficients respectively, E is the electric potential difference, $E_{\mathrm{c}}^{0\prime}$ is the conditional (formal) potential, ν is the *stoichiometric number*, R is the gas constant and T is the thermodynamic temperature.

Similar rate constants can be defined using activities in place of concentrations in the first two equations, and the standard electrode potential in place of the conditional potential in the latter two equations. This type of rate constant is called the standard rate constant of the electrode reaction.

The observable electrode rate constant is the constant of proportionality expressing the dependence of the rate of the electrode reaction on the *interfacial concentration* of the chemical species involved in the reaction.

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