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Butler-volmer equation

Let us suppose that reactant ion M^{z+} has approached quite close to an electrode. Reaction will occurs if electrons are transferred from electrode to ion,

$$M^{z+} + ze^- \rightarrow M.$$

we are oing to apply the Eyring equation for the rate constant K_2 of a chemical reaction to this process, using the following form.

$$K_2 = (KT/hC^0) \exp(-\Delta G_s^{0*}/RT) \quad \text{——— (1)}$$

where ΔG_s^{0*}, is the Gibbs free energy of activation.

If the potential difference across the double layer is changed by even a fraction of a volt, large effects on the rate of the electrode reaction can be expected.

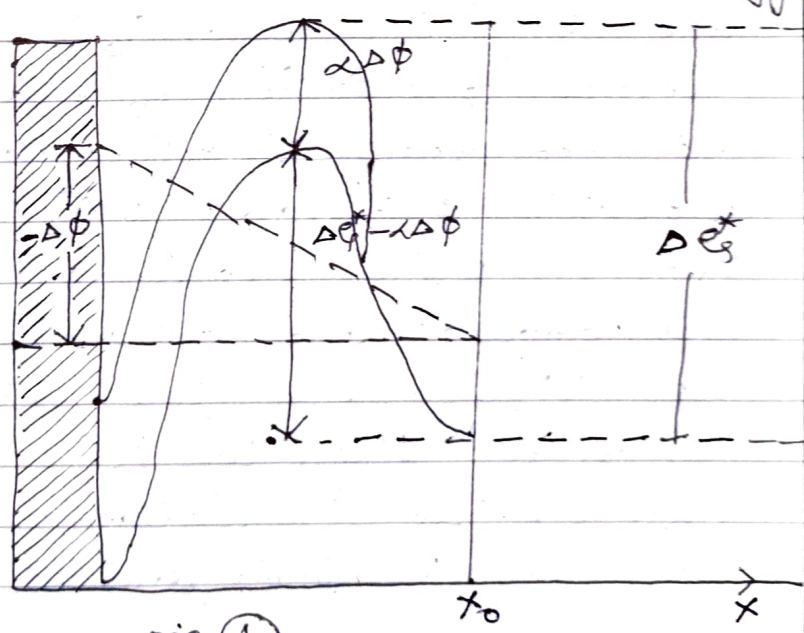

fig (1)

As fig (1) shows, a change from the equilibrium potential increases the current in one direction and decreases in the other. By convention, a net cathodic current is taken as positive.

and a net anodic current as negative.

Thus, α corresponds to the cathodic (reduction) process and $(1-\alpha)$ to the anodic (oxidation) process.

From the general equation (1) for a rate process, given by the transition state theory, we can write the anodic and cathodic current densities as follows.

$$\text{Anodic}: \; i_a = zFK_a C_O R \exp\left[\frac{-\Delta G_a^* - (1-\alpha) zF\Delta\phi}{RT}\right]$$

$$\text{cathodic}: \; i_c = zFK_c C_O O \exp\left[\frac{-\Delta G_c^* + \alpha zF\Delta\phi}{RT}\right]$$

Where K_a and K_c are the pre-exponential parts of the rate constant for the forward (anodic) and reverse (cathodic) electron transfer. $C_O R$ and $C_O O$ represents the surface concentration of reduced product and oxidized reactant of the electrochemical reaction. ΔG_a^* and ΔG_c^* are the thermal Gibbs free energy barriers for the anodic and cathodic electrode reaction respectively. When the extent of reaction is small, then the ioni concentration adjacent to the electrode can be taken as constant, independent of i and also time.

At equilibrium,

we can thus write for exchange current per unite area.

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$$i_0 = zFK_a C_0 R \exp - \left[\frac{\Delta G_a^* + (1-\alpha) zF \Delta\phi_{rev}}{RT} \right]$$

$$= zFK_c C_0 O \exp - \left[\frac{-\Delta G_c^* - \alpha zF \Delta\phi_{rev}}{RT} \right]$$

In terms of i_0 and $\eta_i = \Delta\phi - \Delta\phi_{rev}$ the activation potential

$$i = i_c - i_a$$

$$= i_0 \left[\exp\left(\frac{\alpha zF\eta_i}{RT}\right) - \exp\left(\frac{-(1-\alpha) zF\eta_i}{RT}\right) \right] \quad (2)$$

Equ. (2) is known as Bulter-volume equation.