5.1. Electrochemical Kinetic parameters

(i) Overall reaction: Number of moles of product(s) formed per Faraday.

(ii) Entities in solution: Must be determined by proper physical (spectroscopic etc.,) or chemical methods.

(iii)Surface coverage: Radio tracers ; Use of a counter ; BET method etc. The value of 'θ' can also be determined by determining the number of electrons required to oxidize one gram mole of the substance adsorbed. e.g. C_6H_6 requires 30 electrons

$$C_6H_6 + 12\ H_2O \rightarrow 6\ CO_2 + 30\ H^+ + 30\ e^-$$

(iv)Reaction order:

A + e → D

$$i_c = nF\,\upsilon = nFk[A]^x = nF\ \frac{k_bT}{h}\ e^{-\Delta G\#Chem/RT}\ e^{-\beta\Delta\varphi F/RT}[A]^x$$

$$= nF\,k_c\,e^{-\beta\Delta\varphi F/RT}\,[A]^x$$

$i_a = nF\,k_a\ ^{(1-\beta)\Delta\varphi F/RT}[D]^y$; k_c & k_a are the chemical reaction rate contant for cathodic and anodic reaction , respectively.

Hence, the order, x with respect to A (cathodic order) will be given as

$$\left[\frac{\delta \log i}{\delta \log[A]}\right]_{\Delta\Phi \text{ or } \eta}$$

The order, y of the reaction with respect to D (anodic order) will be given as

$$\left[\frac{\delta \log i}{\delta \log[D]}\right]_{\Delta\Phi \text{ or } \eta}$$

The electrode reaction must be done in both directions (anodic and cathodic) to get the orders (with respect to A & D) in both directions.

DETERMINATION OF RATE OF THE REACTION

- **i = nF Rate**
- Rate is a function of applied potential. Hence, plot of **lni** vs **η** will give **i_o from intercept & symmetry factor, β** or **transfer coefficient, α from the slope.**
- Rate of an electrochemical reaction refers to the evaluation of i_o and the symmetry factors or the transfer coefficients for the electrode process.
- An electrode is perturbed from its equilibrium state by over potential and the net reaction is determined as a function of i, which is similar to change of concentration at equilibrium and studying the rate of the fast reaction.
- Thus i_o refers to rate at equilibrium and the symmetry factor or the transfer coefficients convey message regarding the symmetry of the energy profile curve with respect to the reactants and the products.