Electrode Kinetics

Reaction rates

- Rate of the forward reaction is given by:

$$R_f = k_f * C_A \quad (2)$$

- Rate of the backward reaction is given by:

$$R_b = k_b * C_B \quad (3)$$

Equilibrium

Equilibrium is defined as the point at which the net reaction rate is zero

- From equation 4, we obtain an equilibrium concentration ratio

$$k_f / k_b = K = C_B / C_A \quad (5)$$

- K is a constant, and is called the equilibrium constant (K)

Activation energy

- Above relationship - called Arrhenius relationship
- **Activation energy** : Energy barrier that has to be surmounted by the reactants before they can be converted to product
- Larger the activation energy - more energy needed by reactants to surmount barrier

Any electrode kinetics theory must reduce to the Nernst equation when equilibrium conditions are placed upon it - 1st requirement of an electrode kinetic theory

At equilibrium

- It is possible to adjust the electrode potential and O and R concentrations make net reaction rate zero. At this point:

$$i_c = i_a \; ; \; R_f = R_b \; (14)$$

In other words:

$$k_f \; C_O \; (0, t) = \; k_b \; C_R \; (0, t) \; (15)$$

Standard rate constants

- Equation 19 on integration gives:

$$\ln (1/k_f) = \alpha FE/RT + c \quad (21)$$

- If $k_f = k_f^\circ$ @ $E = E^\circ$

$$k_f = k_f^\circ \, e^{\{-[\alpha F/RT](E-E^\circ)\}} \quad (22 - a)$$

Similarly:

$$k_b = k_b^\circ \, e^{\{[(1-\alpha)F/RT][(E-E^\circ)\}} \quad (22 - b)$$

End Result

$$i = nF\,k^{\circ}\,[C_O(0,t)\,e^{\{-[\alpha nF/RT](E-E^{\circ})\}} - C_R(0,t)\,e^{\{[(1-\alpha)nF/RT](E-E^{\circ})\}}] \quad (25)$$

(n – stands for no. of electrons transferred)

This formulation is called the Butler – Volmer formulation of electrode kinetics

- **Note – two components (anodic and cathodic) of current**
- **Note – exponential dependence on potential**

- Eqn. 28 reduces to:

$$e^{(nF/RT)[E_{eq}-E^\circ]} = C_O^* / C_R^* \quad (29)$$

- Restatement of the Nernst equation (8)
- Though the net current is zero, faradaic activity is still in progress at the electrode surface

An equal magnitude of anodic and cathodic current flows

Tafel plots

- A plot of log i vs. ή is called a Tafel plot
- Shown in Fig.
- Comprises an anodic branch and a cathodic branch
- Slopes of (1- α)nF/2.3 RT and – αnF/2.3 RT respectively

Sharp deviation from linearity as ή approaches zero – due to breakdown of assumptions

$$i/i_o = [C_O(0, t) / C_O^*]e^{\{-[\alpha nF/RT]\,\acute{\eta}\}} - [C_R(0, t)/ C_R^*]\, e^{\{[(1-\alpha)nF/RT]\,\acute{\eta}\}} \quad (34)$$

- Incorporating limiting currents into eqn 34:

$$i/i_o = [1 - (i/i_{l,c})]\, e^{\{-[\alpha nF/RT]\,\acute{\eta}\}} - [1 - (i/i_{l,a})]\, e^{\{[(1-\alpha)nF/RT]\,\acute{\eta}\}} \quad (41)$$

Current –overpotential equation corrected for mass transfer effects