

Kinetics of electrode reaction

A reaction occurring at the surface involves the following step in succession:-

- ① Diffusion of reactant at the surface of electrode.
- ② Adsorption of reactant on the electrode.
- ③ Transfer of electrons to or from the adsorbed reactant species.
- ④ Desorption of product from the electrode.
- ⑤ Diffusion of product away from the surface of electrode.

In an electrode reaction, the charged species, viz. ions and electrons, are enabled to surmount the activation energy barrier by the energy of the electric field.

Since electrochemical reactions are investigated at $T > 0$, there is both thermal and electrical contribution to the activation energy.

For ionic species at equilibrium, the rate of electron transfer in the cathodic direction is exactly balanced by the rate of electron transfer in the anodic direction so that current density i.e. current per unit area is given by,

$$i_c = i_a = i_0 \quad \text{--- ①}$$

The current density i_0 at equilibrium is called exchange current density. The rate r of the chemical reaction at the surface of electrode is given by

$$r = \frac{i_0}{z} F \quad \text{--- (2)}$$

where z is the charge on the ionic species & F is the Faraday, 96458 C mol^{-1} .

hence

$$r \propto i \quad \text{--- (3)}$$

- For a given electrochemical reaction at the electrode, the electrodes are said to be non-polarizable if they have high current density and polarizable if they have low exchange current density.
- Application of potential difference across a non-polarizable electrode results in an increased flow of charge between the electrode and solution, though the potential difference across the electrical double layer does not change.
- The charge moves rapidly to and from the electrode with the result that has no charge density is built up in the surface layers.
- The best example for non-polarizable electrode is calomel electrode.

- If the applied potential difference across a polarizable electrode is increased, there is little flow of charge into the solution. The charge remains in the electric field in the electrical double layer and increase the potential difference across it.
- The dropping mercury electrode is an example of polarizable electrode.

- When an electrochemical cell operates under non-equilibrium condition,

$$i_c \neq i_a$$

and hence the net current density

$$i = i_a - i_c$$

- In such a case the potential difference between the cell terminals ~~transposed~~ departs from the equilibrium value

$$\Delta\phi = E \quad (\text{cell EMF})$$

- If the cell is converting free energy into electrical energy

$$\Delta\phi < E$$

If the cell is converting external energy to chemical reaction

$$\Delta\phi > E$$

The actual value of $\Delta\phi$ depends upon the current density i at the electrodes. The diff. is called overpotential.

$$\Delta\phi_{\text{act}} = \Delta\phi - \Delta\phi_{\text{eq}} = \eta$$