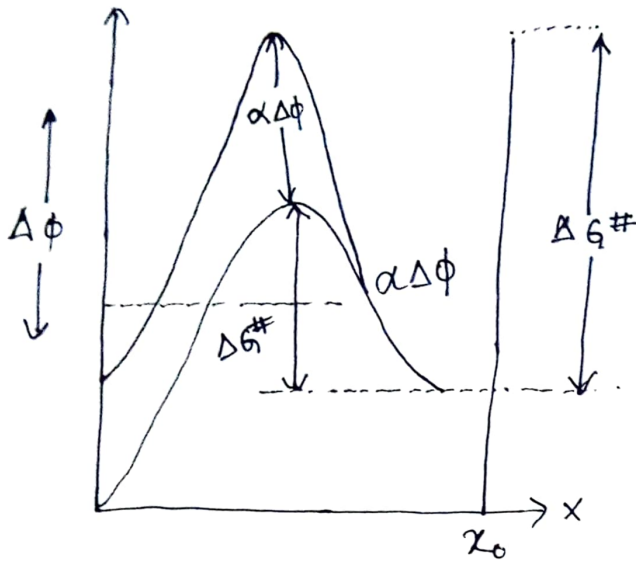
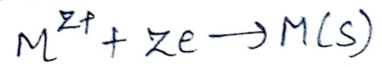


Kinetics of an electrode reaction



Gibbs free energy curves for electrode reaction



in the vicinity of the electrode surface showing the lowering of ΔG^\ddagger by the electrode potential.

Consider the electrode reaction



occurs when the reactant ion M^{Z+} is in the vicinity of an electrode surface so that the electrons are transferred from electrode to ion.

According to Eyring activated complex theory (ACT), the rate constant k_2 of the reaction is given by

$$k_2 = B \exp(-\Delta G^\ddagger / RT) \quad \text{--- (1)}$$

ΔG^\ddagger is Gibbs free energy of activation and B is constant.

The above plot shows the reaction paths along the free energy surfaces between the reactants and products.

- The reaction coordinate is normal to the electrode surface.
- The electrochemical reaction involving electron transfer occurs in a region near the electrode that coincides with the region of the electrical double layer.
- The thickness of electrical double layer is around 10^9 nm and the intensity of the electrical field is 10^9 V m^{-1} .
- The high electric field may cause tearing of ions from the metal surface and drag them into the solution.

According to Helmholtz model, the potential varies linearly with the x . The position of outer Helmholtz plane is x_0 where the reactant molecule can be located.

- Let us now discuss the single electron transfer process and its rate determining step.
Let $[Ox]$ and $[Red]$ be the concentration of oxidized and reduced form of the species, outside the double layer.

The net current at the electrode is the difference of the currents resulting from the reduction of $[Ox]$ and oxidation of $[Red]$. The rates of the processes be $k_c [Ox]$ and $k_a [Red]$ respectively.

For reduction, the magnitude of charge transferred per mole of reaction events is $F = eNa$,

$F \rightarrow$ Faraday constant.

Hence cathodic current density i_c , arising from the reduction is given by

$$i_c = F k_c [\text{Ox}] \quad \text{--- (2)}$$

An opposing anodic current density i_a , arising from the oxidation is given by

$$i_a = F k_a [\text{Red}] \quad \text{--- (3)}$$

k_c and k_a are corresponding rate constants for cathodic and anodic reactions.

\therefore Net current density at the electrode is given by

$$i = i_a - i_c$$

$$= F k_a [\text{Red}] - F k_c [\text{Ox}]$$

$$= F B_a [\text{Red}] \exp(-\Delta G_a^\ddagger / RT) - F B_c [\text{Ox}] \exp(-\Delta G_c^\ddagger / RT)$$

(Using eq. (1) from above) and assumption is made that $\Delta G_a^\ddagger \neq \Delta G_c^\ddagger$.

For $i_a > i_c$, hence $i > 0$ current is anodic
 $i_c > i_a$, hence $i < 0$ current is cathodic.

- Let us consider a reduction reaction now:-

As for the electron transfer from one electrode to another, the electrical work done is $e\Delta\phi$, where

$e \rightarrow$ electronic charge

$\phi \rightarrow$ potential difference

\Rightarrow Gibbs free energy changes from ΔG^\ddagger to $\Delta G^\ddagger + F\Delta\phi$, if the transition state corresponds to the Ox being close to the electrode.

If $\Delta\phi > 0$, more work will be done to bring Ox to its transition state, with the result that Gibbs free energy of activation is increased.

\Rightarrow for Ox being far from the electrode (that is the Ox is close to the outer plane of electrical double layer), then ΔG^\ddagger is independent of $\Delta\phi$.

* The Gibbs free energy of reduction may be written as $\Delta G^\ddagger + \alpha F\Delta\phi$, where α , called transfer coefficient or symmetry factor, lies between 0 and 1 i.e. $0 < \alpha < 1$.

- For the reduction, of oxidation of Red.

The Red ejects an electron to the electrode with the result that the extra work needed for reaching the transition state is zero if this state lies close to the electrode. If the state lies away from the electrode, close to the

to the outer plane of double layer), then ΔG^\ddagger is independent of $\Delta\phi$.

The work needed = $-F\Delta\phi$

ΔG^\ddagger changes from ΔG^\ddagger to $\Delta G^\ddagger - (1-\alpha)F\Delta\phi$.

On substituting two Gibbs free energy of activation

$$i = \left\{ F B_a [\text{Red}] \exp(-\Delta G_a^\ddagger / RT) \right\} e^{(1-\alpha)F\Delta\phi / RT} \\ \left\{ F B_c [\text{Ox}] \exp(-\Delta G_c^\ddagger / RT) \right\} e^{-\alpha F\Delta\phi / RT} \quad \text{--- (5)}$$

$$= i_a - i_c \quad \text{--- (6)}$$

At equilibrium

$\Delta\phi = \Delta\phi_{eq}$ and hence the net current is zero.

If the potential difference differs from its equilibrium value by the overall equilibrium value by the overpotential η .

Hence

$$\eta = \Delta\phi - \Delta\phi_{eq} \quad \text{--- (7)}$$

And current density is,

$$i_a = \left\{ F B_a [\text{Red}] \exp(-\Delta G_a^\ddagger / RT) \right\} e^{(1-\alpha)F\Delta\phi_{eq} / RT} \\ e^{(1-\alpha)\eta F / RT}$$

$$= i_{a,e} e^{(1-\alpha)\eta F / RT} \quad \text{--- (8)}$$

$$i_c = \left\{ F B_c [\text{Ox}] \exp(-\Delta G_c^\ddagger / RT) \right\} e^{-\alpha F\Delta\phi_{eq} / RT} e^{-\alpha\eta F / RT} \quad \text{--- (9)}$$

$$= i_{c,e} e^{-\alpha\eta F / RT} \quad \text{--- (10)}$$

Since the two equilibrium current densities, $i_{a,e}$ and $i_{c,e}$ are equal, Hence the equation can be rewritten as

$$i = i_0 \left\{ e^{(1-\alpha)\eta F/RT} - e^{-\alpha\eta F/RT} \right\} \quad \text{--- (10)}$$

This equation is termed as Butler Volmer equation.

Using exponential series eq (10) becomes:-

$$e^x = 1 + x + \frac{x^2}{2!} + \dots \quad \text{(11)}$$

$$\text{and } i = i_0 \left\{ [1 + (1-\alpha)\eta F/RT + \dots] - [1 - (\alpha\eta F/RT) + \dots] \right\}$$

$$\boxed{i = i_0 \eta F/RT} \quad \text{--- (12)}$$

As from eq. (12) it's clear that ~~$\eta \propto i$~~ $i \propto \eta$
 For η small and +ve the current is anodic
 η small and -ve current is cathodic.

Notice:. Dear M.Sc. I Sem students it is becoming tedious for one side communication. Kindly mail on the email ID provided for online classes through video meet. I wish that some of online lectures would work.