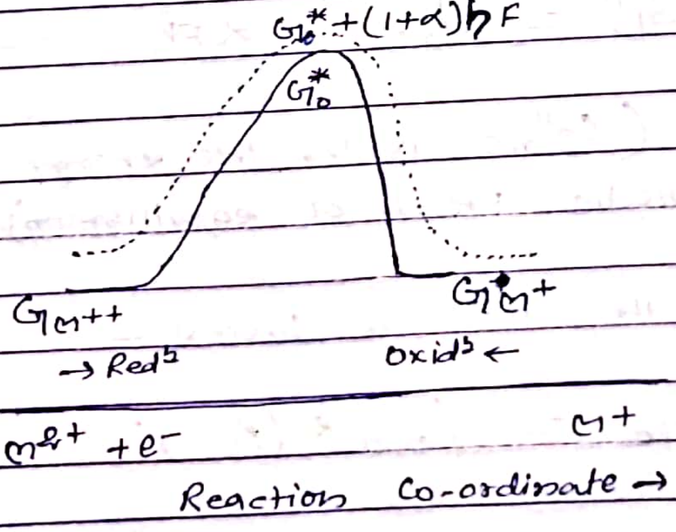
*. Butler - Volmer Equation -

The Current (i.e. the rate of an electrochemical reaction) Voltage relation is described in the Butler-Volmer equation. The transition state theory explains the change in Current density with applied voltage.

The figure shows the energy profile of the system as a function of the reaction co-ordinate. The solid ~~like~~ line shows the energy profile without the applied voltage. we have M^{+2} and a free electron on one side and M^+ on the other. The peak corresponds to the minimum energy of the activated complex which may be an ion with a different geometry of hydration than that of the product or the reactant ions. The complex is beond to the surface of the metal with weak intermolecular forces.



The dashed line shows the energy profile along the reaction Co-ordinate. when the potential difference between pt and the solution is changed The free energy of the ions in an electric field is given by

$$G = G_0 + ZF\eta \quad \text{——— ①}$$

where, z is the charge on the ion
η is the overpotential (the voltage difference between the equillibrium value and the applied voltage).

The free energy of the activated complex may be assumed to be ionising by a value intermediate between the values for the two ions. then -

$$G^{\#} = G_0^{\#} + (1+\alpha) F\eta \quad \text{——} (II)$$

where, α takes a value between 0 & 1.
If $\alpha = 0.5$,
the change in the free energy of the activated complex is the average of the free energy changes in the two ions.
So, the free energy of activation for the oxidation process is given by -

$$G_a^{\#} = G_{a,0}^{\#} + \alpha F\eta \quad \text{——} (III)$$

($G^{\#}_{a,0}$ is the free energy of activation for anodic process of equillibrium).

and

For the reduction process -

$$G_c^{\#} = G^{\#}_{c,0} + (\alpha-1) F\eta \quad \text{——} (IV)$$

A/c to transition state theory, Current is related to the Gibb's free energy of activation through the equation.

$$i = \text{Const} \times \exp \frac{-\Delta G^{\#}}{RT} \quad \text{——} (V)$$

Comparing eqⁿ (III) & (V) (anodic current)

$$i_a = Const \cdot e^{-\Delta G^{\#}_{a,0}/RT} - e^{-\alpha\eta F/RT}$$
$$= i_{a,0} \cdot e^{-\alpha\eta F/RT}$$

and the cathodic current (from eqⁿ (IV) & (V)

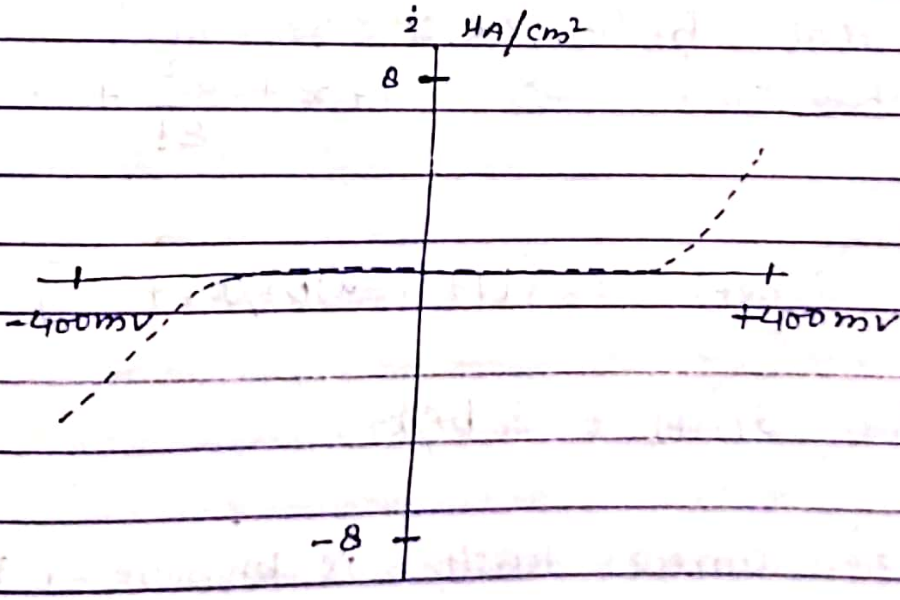
$$i_c = Const. \, e^{-\Delta G^{\#}_{c,0}/RT} \cdot e^{(1-\alpha)\eta F/RT}$$
$$= i_{c,0} \cdot e^{(1-\alpha)\eta F/RT}$$

Hence, the net current is given by

$$i(net) = i_c - i_a$$

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

This equation is known as Butler-Volmer equation.



[Plot of the Butler-Volmer equation for a redox reaction with a relatively small exchange Current)].