Butler volmer Equation.

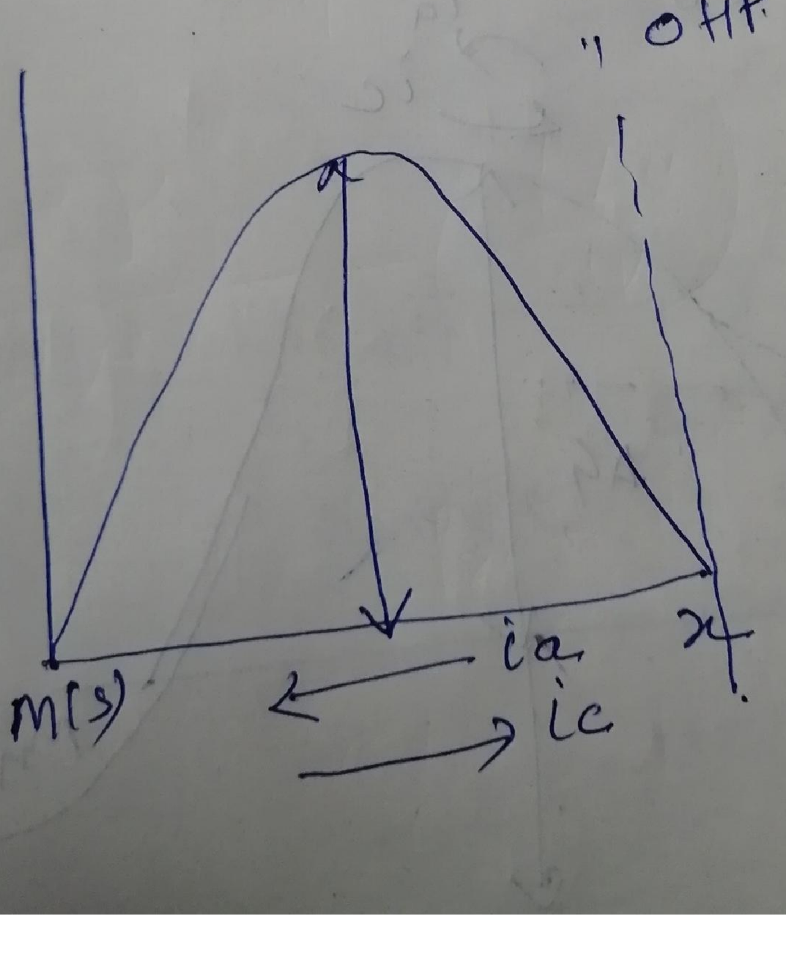
(1)

$$M_1^{n+} + M_2 \rightarrow M_1 + M_2^{n+}$$

$$M_{1(aq)}^{n+} + ne^- \rightarrow M_{1(s)}.$$

ACT theory

$$K = B e^{(\Delta G^{\neq}/RT)}$$



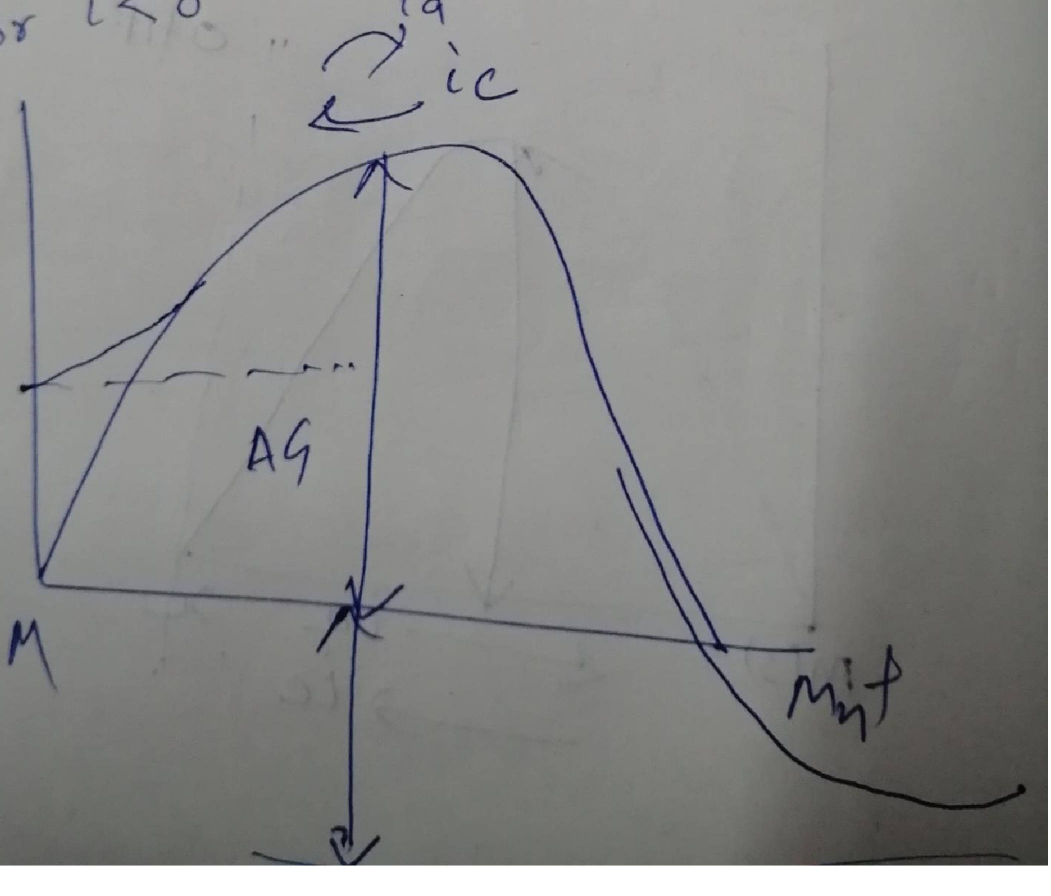
$i = i_a - i_c$

$i = F K_a C_R - F K_b C_o$

$i = F B_a C_R e^{-\Delta G_a^*/RT} - F B_c C_o e^{-\Delta G_c^*/RT}$

For $i > 0$ $\quad i_a > i_c$

For $i < 0$ $\quad i_c > i_a$



(3)

$$\Delta G_c^{*} = \Delta G^{*} + \alpha F \Delta \phi$$

$$\Delta G_a^{*} = \Delta G_a^{*} - (1-\alpha) F.$$

$$0 < \alpha < 1$$

$$i = F B_a C_R e^{(-\Delta G^{*}/RT)} e^{(1-\alpha) F \Delta \phi / RT}$$

$$- F B_c C_o e^{-\Delta G^{*}/RT} e^{-\alpha F D \phi}$$

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

$$i_a = F B_a C_R e^{\alpha \Delta G^{*}/RT} e^{(1-\alpha) \frac{F \Delta \phi_{eq}}{RT}}$$

$$e^{(1-\alpha) F \eta / RT},$$

$$i_a = i_{aeq} e^{(1-\alpha) \eta F / RT}$$

(4)

$$i_c = i_{c\,eq} \cdot e^{-\alpha \eta F/RT}$$

$$i = i_a - i_c$$

$$i_{a\,eq} = i_{c\,eq} = i_0$$

$$= i_0 \left[e^{(1-\alpha)\eta F/RT} - e^{-\alpha \eta F/RT} \right]$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!}$$

$$\text{If } \frac{\eta F}{RT} << 1$$

when η is very small.

$$i = i_0 \left\{ \left(1 + \frac{(1-\alpha)\eta F}{RT}\right) - \left(1 - \frac{\alpha \eta F}{RT}\right) \right\}$$

$$i = i_0 \left\{ 1 + \frac{\eta F}{RT} - \frac{\alpha \eta F}{RT} - 1 + \frac{\alpha \eta F}{RT} \right)$$

$$i = i_0 \frac{\eta F}{RT}$$

when η is very large & positive

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

$$\ln i = \ln i_0 + (1-\alpha)\frac{\eta F}{RT}$$ Tafel. Eq.

η is large & negative

$$i = -i_0 e^{-\alpha \eta F/RT}$$

$$-i = i_0 e^{-\alpha \eta F/RT}$$

$$\ln(-i) = \ln i_0 - \frac{\alpha \eta F}{RT}$$ Tafel Eqn