

Plot of the Butler-Volmer equation for a redox reaction with an appreciable exchange (Current)].

(D6) \* TAFEL Equation From BUTLER-VOLMER Equation -

When the over potential  $\eta$  is very small so, that  $\eta F/RT \ll 1$   
 then since  $e^x = 1 + x + \frac{x^2}{2!} + \dots$

We get

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

i.e.  $i(\text{net}) = i_0 \frac{\eta F}{RT}$

i.e. Current density is proportional to the over potential.

$$\eta = \frac{RT}{F} \left( \frac{i_{\text{net}}}{i_0} \right)$$

(a) When  $\eta$  is small & positive, the current is anodic ( $i_{\text{net}} > 0$ )

(b) When  $\eta > 0$   
 &  $i_{\text{net}} < 0$  when  $\eta < 0$

(A) when the over potential is large and  $+ve$ , the second exponential in Butler-Volmer eq<sup>n</sup> is much smaller than the first and may be neglected, giving

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

$$\Rightarrow \ln i_{(net)} = \ln i_0 + (1-\alpha) \eta F/RT \quad \text{--- (I)}$$

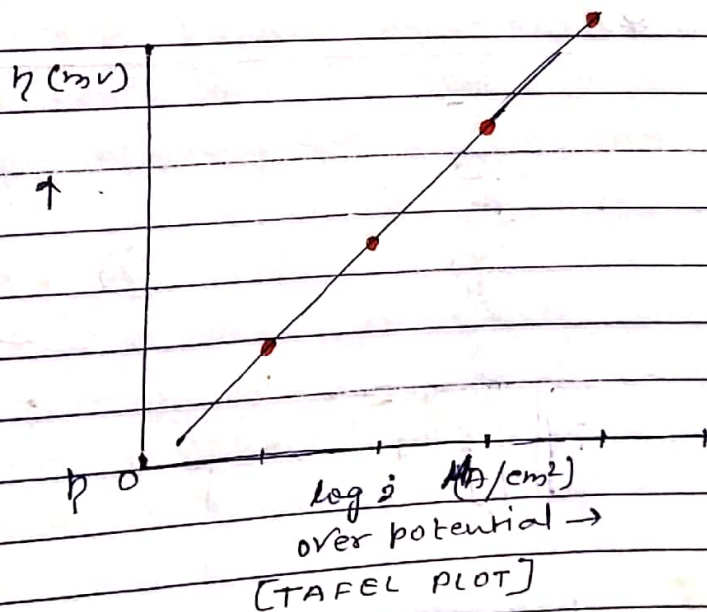
(B) when the over potential is large but  $-ve$ , the 1st exponential in Butler-Volmer eq<sup>n</sup> is much smaller than the second & may be neglected, so,

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

$$\Rightarrow -\ln i_{(net)} = \ln i_0 - \alpha \eta F/RT \quad \text{--- (II)}$$

Equation - (I) and - (II) are called TAFEL Equations.

These equations suggest that a graph of  $\ln i$  against the overpotential should give a straight line.



The intercept at  $\eta = 0$  is the exchange current &  $\alpha$  can be estimated from the slope.