Derivation of Nernst Equation

$\Delta G = \Delta G^\circ + RT \ln Q$

Q = reaction quotient

$Q = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$

$Ox + ne^- \rightleftharpoons Red$

① We know that:

1. $\Delta G = -nFE$ non-standard condition
2. $\Delta G^\circ = -nFE^\circ$ standard condition

② substituting into the 1st equation gives:

$-nFE = -nFE^\circ + RT \ln Q$

③ divide through by $-nF$ gives:

$E = E^\circ - \frac{RT}{nF} \ln Q$ ← subst. $Q = \frac{[RED]}{[OX]}$

$E = E^\circ - \frac{RT}{nF} \ln \frac{[RED]}{[PROD]}$

④ assume 25°C and converting lon $\ln x$ to $\log x$

$\ln x = \ln (10^{\log x}) = \log x (\ln 10)$ → 2.303

$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[RED]}{[OX]}$

$\frac{2.303RT}{F}$ at 25°C = 0.0591

$E = E^\circ - \frac{0.0591}{n} \log \frac{[RED]}{[OX]}$ OR $E = E^\circ + \frac{0.0591}{n} \log \frac{[OX]}{[RED]}$

$$f = \frac{F}{RT}$$

Collapse of BV Equation into a Thermodynamic Form

$$i_{net} = nFAk^{\circ}\left[C_O(0,t)\exp(-n\alpha f\eta) - C_R(0,t)\exp((1-\alpha)nf\eta)\right]$$

① at equilibrium, $i_{net} = \emptyset$ so. $i_f \equiv i_b$ exchange rates are equal

$$nFAk^{\circ}C_O(0,t)\exp(-\alpha nf\eta) = nFAk^{\circ}C_R(0,t)\exp((1-\alpha)nf\eta)$$

② divide both sides by $nFAk^{\circ}$, this leaves:

$$C_O(0,t)\exp(-\alpha nf\eta) = C_R(0,t)\exp((1-\alpha)nf\eta)$$

③ Expand right exponential

$$C_O(0,t)\exp(-\alpha nf\eta) = C_R(0,t)\exp(nf\eta)\exp(-\alpha nf\eta)$$

④ divide both sides by $C_R(0,t)$, this gives:

$$\frac{C_O(0,t)}{C_R(0,t)}\exp(-\alpha nf\eta) = \exp(nf\eta)\exp(-\alpha nf\eta)$$

$\eta = E - E^{\circ}$

⑤ divide both sides by $\exp(-\alpha nf\eta)$, this gives:

$$\frac{C_O(0,t)}{C_R(0,t)} = \exp(nf\eta) = \exp\left(\frac{nF}{RT}E - \frac{nF}{RT}E^{\circ}\right)$$

⑥ take log of both sides, this gives:

$$\ln\frac{C_O(0,t)}{C_R(0,t)} = \frac{nF}{RT}E - \frac{nF}{RT}E^{\circ}$$

⑦ multiply both sides of equation by $\frac{RT}{nF}$, this gives

$$\frac{RT}{nF}\ln\frac{C_O(0,t)}{C_R(0,t)} = E - E^{\circ}$$ (add $+E^{\circ}$ to both sides)

$$E^{\circ} + \frac{RT}{nF}\ln\frac{C_O(0,t)}{C_R(0,t)} = E$$

Collapses to Nernst Equation!