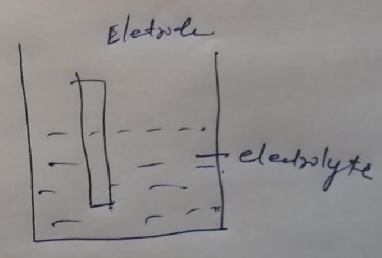


①

LIPPMAN EQUATION.

$$dE = Tds - PdV$$

$$dE = Tds - PdV - \sum \mu_i dn_i - \gamma dA - {}^M \Delta^S \phi dq_M - \gamma dA$$



${}^M \Delta^S \phi$ - Potential across Metal-solution interface.

q_M = Excess charge on the Metal Surface.

②

$$E = TS - PV - \sum \mu_i n_i - {}^M \Delta^S \phi q_M - \gamma A.$$

$$dE = (Tds - PdV - \sum \mu_i dn_i - {}^M \Delta^S \phi dq_M - \gamma dA) + (sdT - VdP - \sum n_i d\mu_i - q_M d({}^M \Delta^S \phi) - Ad\gamma)$$

$$sdT - VdP - \sum n_i d\mu_i - q_M d({}^M \Delta^S \phi) - Ad\gamma = 0$$

At Cont. T. & P.

$$-\sum n_i d\mu_i - q_M d({}^M \Delta^S \phi) - Ad\gamma = 0$$

③

$$dY = -\frac{p_M}{A} d(M\Delta^s\phi) - \sum \frac{n_i}{A} d\ell_i$$

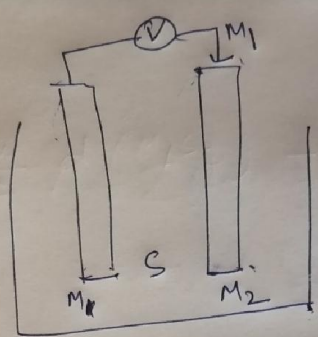
$$n_i = n_i^s + n_i^o$$

$$\frac{n_i}{A} = \frac{n_i^s}{A} + \frac{n_i^o}{A}$$

$$\frac{n_i}{A} = T_i + \frac{n_i^o}{A}$$

$$\sum \frac{n_i}{A} d\ell_i = \sum T_i d\ell_i + \sum \frac{n_i^o}{A} d\ell_i$$

$$\sum \frac{n_i}{A} d\ell_i = \sum T_i d\ell_i \quad \sum n_i^o d\ell_i = 0$$



$$V = M\Delta^s\phi + S\Delta^M\phi + M_2\Delta^M\phi$$

$$dV = d(M\Delta^s\phi) + d(S\Delta^M\phi) + d(M_2\Delta^M\phi)$$

$$dV = d(M\Delta^s\phi) + d(S\Delta^M\phi) + 0$$

$$\Rightarrow d(M\Delta^s\phi) = dV - d(S\Delta^M\phi)$$

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$$d\gamma = -z_M dV + z_M d(S_{\Delta} M_2 \Phi) - \sum T_i d\ell_i$$

$$d(S_{\Delta} M_2 \Phi) = -\frac{1}{z_i F} d\ell_j$$

For Hydrogen electrode $z=1 = -\frac{1}{F} d\ell_M$

$$d\gamma = -z_M dV + \left(\frac{z_M}{z_j F}\right) d\ell_j - \sum T_i d\ell_i$$

At constant composition $d\ell_j = 0$

$$\left(\frac{d\gamma}{dV}\right)_{\text{const. comp.}} = -z_M \quad \text{Lippman, eq.}$$