

Thermodynamics of Electrified interface or electrocapillary thermodynamics for polarizable interface.

We have the expression of surface tension of the electrified interface

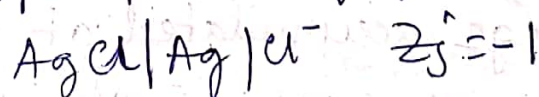
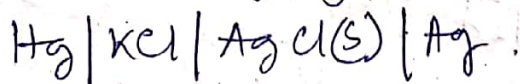
$$d\gamma = -q_m dv - \frac{q_m}{z_j F} d\mu_j - \sum \Pi_i d\mu_i$$

where j is the ion w.r.to which the nonpolarizable electrode is reversible

The condition at which $dv = 0$.

$$d\gamma = - \frac{q_m}{z_j F} d\mu_j - \sum \Pi_i d\mu_i \rightarrow \textcircled{1}$$

Now, consider a polarizable interface which consists of a metal electrode in contact with a solution of 1:1 valent electrolyte (i.e. $z_+ = 1$ & $z_- = 1$). It will be remembered that in order to apply electrocapillary thermodynamics to a polarizable interface M/S, the interface has to be assembled into a cell along with a nonpolarizable interface. Suppose that the nonpolarizable interface is one at which negative ions interchange charge with the metal surface i.e. $z_j = -1$



\therefore The equation $\textcircled{1}$ becomes

$$d\gamma = - \frac{q_m}{(-1)F} d\mu - (\Gamma_+ d\mu_+ + \Gamma_- d\mu_-)$$

$$\text{or, } d\psi = \frac{q_m}{F} d\mu_- - \Gamma_+ d\mu_+ - \Gamma_- d\mu_-$$

Now chemical potential μ of the electrolyte is the sum of the chemical potentials of the ions

$$\mu = \mu_+ + \mu_-$$

$$d\mu = d\mu_+ + d\mu_-$$

$$\begin{aligned} \therefore d\psi &= \frac{q_m}{F} d\mu_- - \Gamma_+ (d\mu - d\mu_-) - \Gamma_- d\mu_- \\ &= \frac{q_m}{F} d\mu_- - \Gamma_+ d\mu + \Gamma_+ d\mu_- - \Gamma_- d\mu_- \end{aligned}$$

$$= -\Gamma_+ d\mu + \left(\frac{q_m}{F} + \Gamma_+ - \Gamma_- \right) d\mu_-$$

$$= -\Gamma_+ d\mu + \left(\frac{q_m + F\Gamma_+ - F\Gamma_-}{F} \right) d\mu_- \quad \text{--- (2)}$$

where q_m = charge density

Γ_+ = excess number of gm moles of positive ions adsorbed per unit area at surface of the solution

$F\Gamma_+$ = positive charge accumulated per unit area at surface of the solution

$(q_m + F\Gamma_+)$ = total positive charge accumulated

$F\Gamma_-$ = charge accumulated at negative charged electrode at interface

$$\therefore (q_m + F\Gamma_+ - F\Gamma_-) = 0$$

$$\therefore d\psi = -\frac{\Gamma}{4} d\mu$$

$$\left(\frac{d\psi}{d\mu}\right)_{\text{const } V_-} = -\frac{\Gamma}{4}$$

$$\begin{aligned} \text{Now } \mu &= \mu_+ + \mu_- = \mu_+^0 + RT \ln a_+ + \mu_-^0 + RT \ln a_- \\ &= \mu_+^0 + \mu_-^0 + RT \ln (a_+ \times a_-) \\ &= \mu_+^0 + \mu_-^0 + RT \ln a_{\pm}^2 \end{aligned}$$

$$\left[\text{as } a_{\pm} = (x_+ f_{\pm}) = (x_+ f_+)^{1/2} (x_- f_-)^{1/2} = (a_+ a_-)^{1/2} \right]$$

$$\therefore a_+ a_- = a_{\pm}^2$$

$$\text{or, } \mu = \mu_+^0 + \mu_-^0 + 2RT \ln a_{\pm}$$

$$\therefore d\mu = 2RT d \ln a_{\pm}$$

$$d\psi = -\frac{\Gamma}{4} 2RT d \ln a_{\pm}$$

$$= -2\frac{\Gamma}{4} RT d \ln a_{\pm}$$

$$\therefore \frac{d\psi}{d \ln a_{\pm}} = -2RT \frac{\Gamma}{4}$$

$$\text{or } \boxed{\frac{1}{2RT} \left(\frac{d\psi}{d \ln a_{\pm}}\right)_{\text{const } V_-} = -\frac{\Gamma}{4}} \rightarrow \text{for 1:1 electrolyte } (\text{Ag}^+ \text{Cl}^-)$$

at constant potential

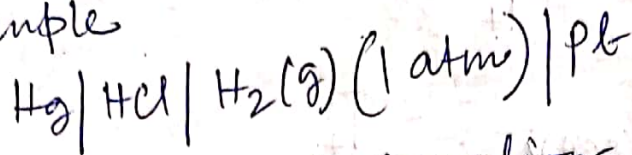
~~so~~ negative sign appears due to the fact that reference electrode is reversible with respect to a negative ion. Thus $\frac{\Gamma}{4}$ is obtained.

When reference electrode is reversible w.r. to positive ion, the $\frac{\Gamma}{4}$ is obtained

$$\text{i.e. } \boxed{\frac{1}{2RT} \left(\frac{d\psi}{d \ln a_{\pm}}\right)_{\text{const } V_+} = -\frac{\Gamma}{4}}$$

↓
for 1:1 electrolyte ($\text{H}^+ \text{Cl}^-$)

example



Thus the general equation becomes

$$-\frac{1}{2RT} \left(\frac{d\psi}{d\ln a_{\pm}} \right)_{V_{\pm}} = \frac{\sigma}{F}$$

$$\left[\text{Another proof of } (q_m + F\Gamma_+ - F\Gamma_-) = 0 \right]$$

The second step of eqⁿ ② consists in affirming that there is electroneutrality across the interface i.e. the charge on the metal is always equal and opposite to the total charge on the solution side of the interface. Before the double layer is formed, the metal is uncharged and in the solution, the charge per unit area of a lamina due to positive and negative ion is zero.

$$F \left(\frac{n_+^0}{A} \right) - F \left(\frac{n_-^0}{A} \right) = 0 \longrightarrow \text{③}$$

After double layer is formed, electroneutrality requires that

$$F \frac{n_+}{A} - F \frac{n_-}{A} + q_m = 0 \longrightarrow \text{④}$$

$$\text{Eq}^n \text{④} - \text{eq}^n \text{③}$$

$$q_m + F \left(\frac{n_+ - n_+^0}{A} \right) - F \left(\frac{n_- - n_-^0}{A} \right) = 0$$

According to the definition of surface excess

$$\Gamma_+ = \frac{n_+ - n_+^0}{A} \text{ and } \Gamma_- = \frac{n_- - n_-^0}{A}$$

Hence according to the electroneutrality condition

$$q_m + F\Gamma_+ - F\Gamma_- = 0$$

Polarizable & non-polarizable interface

To polarize an interface means to alter the potential difference across it; to be polarizable means to be susceptible to changes in potential difference.

A nonpolarizable interface is one at which the potential difference does not change easily with the passage of current. It does not polarize. The interface remains virtually at its equilibrium potential difference. This is precisely the behavior of an ideally nonpolarizable interface.