

Thermodynamics of electrified surface

If the system is a closed one (no matter enters or leaves it), the statement of the combined 1st and 2nd law is

$$dU = Q - W$$

$$\text{or, } dU = Tds - W \quad (1)$$

where, $Tds = Q$ is the heat reversibly supplied to the system in an infinitesimal change and W is the work reversibly carried out by the system.

For an open system, not only heat but also matter may be exchanged between the system and its surroundings. To introduce a mole of the species i , the chemical work done on the system is μ_i . Hence to alter the number of moles of i in the system by dn_i , the work done by the system is $-\mu_i dn_i$. Hence, for an open system, this chemical work must be written as —

$$dU = Tds - W - \sum \mu_i dn_i \quad (2)$$

where, $\sum \mu_i dn_i$ is the work done by the system in expelling dn_i moles of species i , μ_i being the work of transfer per mole.

Now, in the case of an electrode-electrolyte interface M/S, what are the various possible types of work?

There is firstly the work of volume expansion, $p dv$; Secondly, one might in some way increase the area of the

interface by an amount dA , in which case the work of increasing the area of the interface is γdA , where γ is the interfacial tension, and finally one might, e.g. connect up the metallic phase to an external source of electricity and alter the charge on the metal by an amount dq'_M in which case the electrical work of transferring the charge dq'_M is $M_\Delta S_\Phi dq'_M$.

Introducing those work terms in place of w in eqⁿ (2) the statement of the combined first and second laws of thermodynamics applied to the above system reads

$$dU = Tds - pdv - \gamma dA - M_\Delta S_\Phi dq'_M - \sum_i \mu_i dn_i$$

Now, each term on the R.H.S. is a product of an intensive factor (one which does not depend on the amount of matter in this system) and an extensive factor (one which does depend on the amount of matter in the system).

Thus

$$dU = \sum \text{Intensive factor} \times \text{Extensive factor}$$

On integration of eqⁿ (3)

$$U = TS - \gamma A - pV - M_\Delta S_\Phi q'_M - \sum_i \mu_i n_i \rightarrow (4)$$

$$dU = SdT + Tds - \gamma dA - A d\gamma - p dV - V dp - M_\Delta S_\Phi dq'_M - d(M_\Delta S_\Phi) q'_M - \sum_i \mu_i dn_i - \sum_i n_i d\mu_i \rightarrow (5)$$

Comparing eqⁿ (3) & (5)

$$dU = dU + SdT - vdp - Ad\delta - d(M_{\Delta} S_{\Phi}) q'_M - \sum_i n_i d\mu_i$$

$$\text{or, } SdT - vdp - Ad\delta - d(M_{\Delta} S_{\Phi}) q'_M - \sum_i n_i d\mu_i = 0 \quad \text{--- (6)}$$

At constant T & p

$$-Ad\delta - d(M_{\Delta} S_{\Phi}) q'_M - \sum_i n_i d\mu_i = 0$$

$$\text{or, } d\delta = -\frac{q'_M}{A} d(M_{\Delta} S_{\Phi}) - \sum_i \frac{n_i}{A} d\mu_i$$

$$= -q_M d(M_{\Delta} S_{\Phi}) - \sum_i \frac{n_i}{A} d\mu_i$$

$$q_M = \frac{q'_M}{A} = \text{charge density on metal}$$

$$\frac{n_i}{A} = \text{increase in charge per unit area}$$

From the relation of surface excess with increase in charge per unit area, we have

$$\Gamma_i = \frac{n_i}{A} - \frac{n_i^0}{A} \quad \text{or, } \frac{n_i}{A} = \Gamma_i + \frac{n_i^0}{A}$$

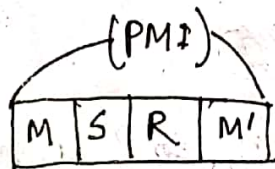
$$\therefore d\delta = -q_M d(M_{\Delta} S_{\Phi}) - \sum_i \left(\Gamma_i + \frac{n_i^0}{A} \right) d\mu_i$$

$$= -q_M d(M_{\Delta} S_{\Phi}) - \sum_i \Gamma_i d\mu_i$$

$$\left(\text{as } \sum_i \frac{n_i d\mu_i}{A} = 0 \text{ by Gibbs's solution eqn} \right)$$

$$\text{or, } d\delta = -q_M d(M_{\Delta} S_{\Phi}) - \sum_i \Gamma_i d\mu_i \quad \text{--- (7)}$$

Now



Perfectly non-polarizable electrodes

Potential difference across M-S interface $M_{\Delta} S_{\Phi}$.

Now from Kirchoff's equation,

$$M_A S_\phi + S_A R_\phi + R_A M'_\phi + M'_A M_\phi = 0$$

$$\text{or, } M_A S_\phi + S_A R_\phi + R_A M'_\phi = -M'_A M_\phi = M_A M'_\phi$$

(measured potential)

$$\text{or, } \delta V = \delta M_A S_\phi + \delta S_A R_\phi + \delta R_A M'_\phi$$

↓
(junction potential between two electronic conductors is very small)

$$\text{or, } \delta V = \delta(M_A S_\phi) + \delta(S_A R_\phi)$$

$$\text{or, } \delta V = \delta M_A S_\phi \quad \left[\text{as } S \text{ and } R \text{ are both in solution phase, so } \delta(S_A R_\phi) = 0 \right]$$

$$\delta V = \delta(M_A S_\phi) + \delta(S_A R_\phi)$$

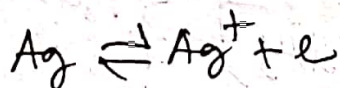
$$\text{or, } \delta(M_A S_\phi) = \delta V - \delta(S_A R_\phi)$$

$$\text{or, } d(M_A S_\phi) = dV - d(S_A R_\phi)$$

Therefore from eqⁿ (7)

$$d\mu = -q_M dV + q_M d(S_A R_\phi) - \sum \mu_i d\mu_i$$

In case of free flow of ions, reversibility occurs,



$d(\bar{\mu}_j) = 0$ Perfect eqm exist at the interface

$$\text{or, } d(\mu_j + z_j F \phi) = 0$$

$$\text{or, } d(\mu_j + z_j F (S_A R_\phi)) = 0$$

$z F \phi =$ electrical work done

$\mu =$ chemical work done

$\phi =$ inner potential or electrical potential

$z F =$ charge

$$\sigma, d\gamma_j + z_j F d(S_\alpha R_\phi) = 0$$

$$\sigma, \boxed{d(S_\alpha R_\phi) = -\frac{1}{z_j F} d\gamma_j}$$

This is the eq expression of non-polarizable electrode.

$$\therefore d\sigma = -q_M dv - \frac{q_M}{z_j F} d\gamma_j - \sum_i \Pi_i d\mu_i$$

This is the ~~the~~ equation of thermodynamics of electrified surface or known as electrocapillary thermodynamics. This surface is studied by Hg-capillary tube. (free drop, no attachment with glass wall)