THERMODYNAMICS OF ELECTRIFIED INTERFACE

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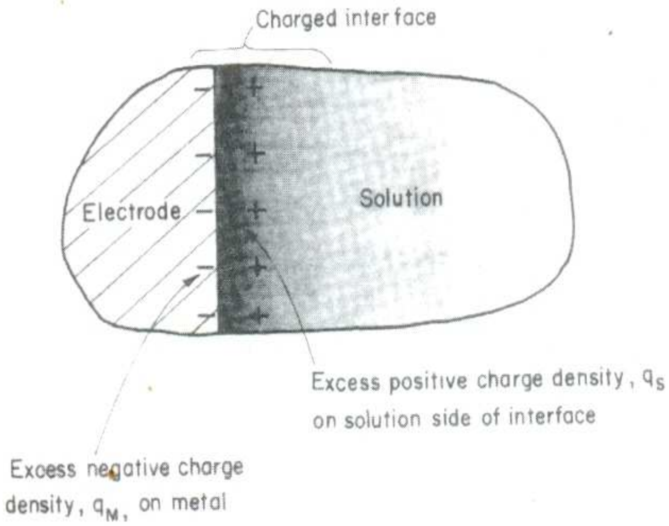
- all about the study of Electrified Interfaces and its consequences.

What is an Electrified Interface?

It is the two dimensional geometrical boundary surface separating the two phases.

What is an Electrified Interphase?

It is the three dimensional region of contact between the two phases in contact at their boundary.



Electrified interface are of two types

- **Lippmann Equation**
- **Electro capillary curve**

Lippmann Equation

- This equation relates surface tension and surface charged density of the ideally polarizable interface to the potential drop across the interface

II. ELECTRIFIED INTERFACES

A. Quantitative Thermodynamic Treatment of Electrified Interfaces

The system of interest is an electrode-electrolyte interface. If the system is a closed one (*i.e.*, no matter enters or leaves it), the combined statement of the First and the Second laws of thermodynamics is

$$dU = TdS - PdV \qquad .....1$$

For an open system, this statement becomes

$$dU = TdS - PdV - \sum_i \mu_i \, dn_i \qquad .....2$$

where the last term represents the work done by the system in expelling dn_i moles of species i and μ_i is the chemical potential of the species i. For the electrode-electrolyte interface M_1 - S (M stands for metal and S for solution), in addition to the work of volume expansion (the second term in Eq. 63), we have the work, γdA, required to increase the area A of the interface, where γ is the interfacial tension. Finally, we have to take into account the work involved in connecting the metallic phase to an external source of electricity thereby altering the charge on the metal by an amount dq'_M. The electrical work involved in transferring the charge dq'_M is given by ${}^{M_1}\Delta^S\phi\, dq'_M$. In this expression M_1 is the metal and $\Delta\phi$ is the potential difference between the metal M_1 and the electrolyte interface (S). Introducing all the work terms in Eq. 63, we get

$$dU = TdS - PdV - \gamma dA - {}^{M_1}\Delta^S\phi\, dq'_M - \sum_i \mu_i dn_i \qquad \text{......3}$$

Each term on the R.H.S. of Eq. 64 is a product of an intensive factor (one that does not depend on the amount of matter present in the system) and an extensive factor (one that does depend on the amount of matter in the system). Thus,

$$dU = \Sigma \text{ intensive factor} \times \text{extensive factor} \qquad .....4$$

Keeping the intensive factors (T, P, γ, $\Delta\phi$, μ) constant, let the extensive factors be, increased from their differential values to their absolute values for the system concerned, *viz.*, S, V, A, q_M, n_i. Thus, we have for the internal energy of the system

$$U = TS - PV - \gamma A - {}^{M_1}\Delta^{S}\phi\, q'_M - \sum_i \mu_i n_i \qquad ....5$$

Differentiation of this equation gives

$$dU = (TdS - PdV - \gamma dA - {}^{M_1}\Delta^{S}\phi\, dq'_M - \sum_i \mu_i dn_i + [SdT - VdP - Ad\gamma - q_M d\,({}^{M_1}\Delta^{S}\phi) - \sum_i n_i d\mu_i] \quad ....6$$

Since Eqs. 64 and 67 are equal to each other, we have

$$0 = SdT - VdP - Ad\gamma - q'_M d\,({}^{M_1}\Delta^{S}\phi) - \sum_i n_i d\mu_i \quad ....7$$

At constant T and P, Eq. 68 becomes

$$0 = -Ad\gamma - q'_M d\,({}^{M_1}\Delta^{S}\phi) - \sum_i n_i d\mu_i \quad ....8$$

or,

$$d\gamma = -\frac{q'_M}{A} d\,({}^{M}\Delta^{S}\phi) - \sum_i \frac{n_i}{A} d\mu_i \quad .....9$$

From Eq. 70 we see that changes in surface tension have been related to changes in the absolute potential differences across an electrode–electrolyte interface and to changes in the chemical potential of all the species, *i.e.*, to changes in solution composition. Next, we define surface excess by recalling that

$$n_i/A = \Gamma_i + n_i^0/A \qquad ...10$$

whence

$$(n_i/A)\, d\mu_i = \Gamma_i d\mu_i + (n_i^0/A)\, d\mu_i \qquad .....11$$

or

$$\sum_i (n_i / A) d\mu_i = \sum_i \Gamma_i d\mu_i + \sum_i (n_i^0 / A)\, d\mu_i \qquad ....12$$

From the Gibbs-Duhem equation, we know that

$$\sum_i n_i^0 d\mu_i = 0 \qquad ......13$$

Substituting this relation in Eq. 73, we have

$$\sum_i (n_i / A)\, d\mu_i = \sum_i \Gamma_i d\mu_i \qquad ....14$$

Substituting this expression in Eq. 70 gives

$$d\gamma = -q'_M\, d({}^{M_1}\Delta^S\phi) - \sum_i \Gamma_i d\mu_i \qquad ....15$$

Eq. 15 contains the quantity $d({}^{M_1}\Delta^{S}\phi)$ which is the change in the inner (or galvanic) potential difference across the interface under study. Though the absolute value of ${}^{M_1}\Delta^{S}\phi$ cannot be determined, a change in ${}^{M_1}\Delta^{S}\phi$, *i.e.*, $d({}^{M_1}\Delta^{S}\phi)$, can be measured provided the M_1-S interface is polarizable and is linked to a non-polarizable interface M_2-S to form an electrochemical system or cell. If such a cell is connected to an external source of electricity, we have

$$V = {}^{M_1}\Delta^{S}\phi + {}^{S}\Delta^{M_2}\phi + {}^{M_2}\Delta^{M_1}\phi \quad .....16$$

since the sum of the potential drops around a circuit must be zero. The inner potential difference ${}^{M_2}\Delta^{M_1}\phi$ does not depend upon the potential V applied from the external source or upon the solution composition. Hence, differentiation of Eq. 16 yields

$$-d({}^{M_1}\Delta^{S}\phi) = -dV + d({}^{S}\Delta^{M_2}\phi) \qquad \text{......17}$$

Substituting for this expression in Eq. 15 we find that

$$d\gamma = -q_M dV + q_M d\,({}^{S}\Delta^{M_2}\phi) - \sum_i \Gamma_i d\mu_i \qquad \text{.........18}$$

We now introduce the non-polarizable characteristics of the second interface M_2–S which is a necesseary part of the cell and the measuring set up. There is equilibrium at this interface so that

$$d({}^{S}\Delta^{M_2}\phi) = -(1/z_j F)\, d\mu_j \qquad \text{...........19}$$

where j is the particular species involved in the leakage of charge across the non-polarizable interface. Thus, for example, for the hydrogen electrode (with $z_+ = 1$), we have

$$d({}^{S}\Delta^{M_2}\phi) = -(1/F)\, d\mu_{H^+} \qquad \text{.......20}$$

If we use a calomel electrode in which Cl^- ions can be considered as leaking across the interface, then (with $z_- = 1$),

$$d({}^{S}\Delta^{M_2}\phi) = +(1/F)\, d\mu_{Cl^-} \qquad \text{..........21}$$

Substitution of Eq. 20 in Eq. 18 gives

$$d\gamma = -q_M\, dV - (q_M/z_jF)\, d\mu_j - \sum_i \Gamma_i d\mu_i \qquad \text{..........22}$$

Eq. 22 is the fundamental equation for the thermodynamic treatment of polarizable interfaces. It relates interfacial tension γ, surface excess Γ_i, applied potential difference V, charge density q_M and solution composition. It shows that interfacial tension varies with the applied potential and the solution composition.

In order to obtain experimentally an electrocapillarity curve, a solution of a fixed composition is taken, *i.e.*, $d\mu_i$ for all the species is zero. Thus, the conditions for the determination of the electrocapillary curve correspond to

$$\sum \Gamma_i d\mu_i = 0 \quad \text{and} \quad d\mu_j = 0 \qquad \text{.............23}$$

Thus, it follows from Eq. 22 that

$$(\partial\gamma/\partial V)_{\text{const. comp}} = -q_M \qquad \text{.............24}$$

This equation is known as the **Lippmann equation.** The slope of the electrocapillary curve at any cell potential V is equal to the charge density on the electrode (Fig. 8).

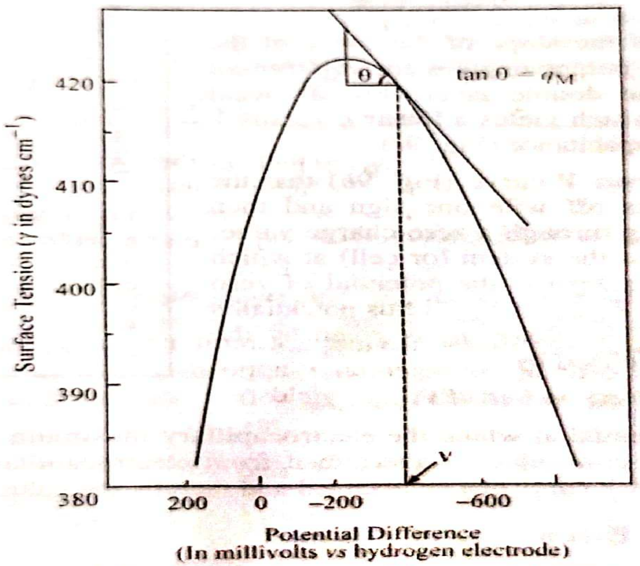


Fig. 8. The charge density on the electrode at a particular value of the potential difference V is given by the slope of the electrocapillary curve at that potential. The curve shown is for mercury in contact with 1·0 MHCl.