Lecture 3

Potential Measurements - Galvanic Cells, Concentration Cells

**Keywords:** Potentials, Reference Electrodes, Concentration Cells.

Electrode potentials can be measured using a reference electrode in any desired electrolyte at room temperature. Potential of a corroding metal or alloy ($E_{corr}$) can be measured in the corrosive media (Fig. 3.1).

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Fig. 3.1 Measurement of electrode potential with reference to standard electrode.
Brief description of a few generally used reference electrodes given below:

Often measured electrode potentials are referred to standard or Normal Hydrogen Electrode (SHE or NHE) whose standard potential is 0.0V at partial pressure of hydrogen and hydrogen ion activity both at unity

\[ 2H^+ + 2e = H_2 \]

NHE consists of a platinum electrode immersed in a solution of hydrogen ion of activity = 1. Hydrogen gas at 1 atmos. pressure is bubbled around the platinum electrode. This is a universal reference standard (Fig 3.2).

![Figure 3.2 Hydrogen reference electrode](image)
Due to efforts and expenses involved in its construction and also due to difficulties in handling H₂ gas, NHE is not generally preferred. Instead more convenient and less cumbersome standard reference electrodes such as Saturated Calomel Electrode, silver/silver chloride or Cu/CuSO₄ electrodes can be used.

**Saturated Calomel Electrode (SCE).**

\[
\text{Hg|Hg}_2\text{Cl}_2 \text{ (Sat'd), KCl (x M)|| } \ldots \ldots \ldots \ldots \ldots \text{ (see Fig. 3.3)}
\]

\[
\text{Hg}_2\text{Cl}_2 + 2e = 2\text{Hg} + 2\text{Cl}^-
\]

Standard potential = + 0.244V
Silver / Silver chloride Electrode

Silver wire coated with AgCl
Solution of KCl saturated with AgCl

Similar electrode construction as that of SCE

\[
\text{Ag} \mid \text{AgCl (Sat’d), KCl (a = xM)} \mid \ldots
\]

\[
\text{AgCl} + e = \text{Ag} + \text{Cl}^-
\]

Standard potential = + 0.222 V

![Fig. 3.4 Ag/AgCl reference electrode](attachment:fig34.png)

Copper / Copper sulfate electrode

\[
\text{Cu}^{++} + 2e = \text{Cu} \ (\text{sat’d} \text{CuSO}_4)
\]

Standard potential = + 0.316 V
Types of galvanic cells

a. Dissimilar electrode cells
b. Concentration cells

Important concentration cells

- Salt concentration
- Differential aeration (Oxygen Concentration)
- Differential temperature
- Metallographic / mechanical heterogeneities
- Differences in residual stress levels

Dissolved oxygen concentration in water, soil etc frequently varies from region to region due to various reasons. Such a difference in aeration produces a different equilibrium potential.

\[
\frac{1}{2} O_2 + 2H^+ + 2e = H_2O
\]

\[
Eh = E^0 + \frac{0.059}{2} \log \frac{[O_2]^\frac{1}{2}}{[H_2O]}
\]

Higher oxygen concentration provides a more nobler potential. Oxygen-enriched areas in a corroding metal serve as cathodes, while oxygen depleted regions act as anodes (undergoing corrosion).

Eg: Rusting of iron in atmosphere (O_2, moisture)

\[
Fe = Fe^{++} + 2e \text{ (anodic reaction at } O_2 \text{ – starved regions)}
\]

Net reaction: \( Fe^{++} + 2H_2O = Fe(OH)_2 + 2H^+ \)
See the model for rusting of iron given in Fig. 1.1.

A diagrammatic arrangement of an oxygen concentration cell is illustrated in Fig. 3.5.

Similarly, metal ion concentration gradients at metal-solution interfaces can create a potential difference and generation of anodic – cathodic sites (Fig 3.6).
Differential concentration cells

\[
(-)M \ | \ M^+ \left(a_1\right) \ || \ M^+ \left(a_2\right) \ | \ M(+) \\
E_1 = E_M^0 + \frac{RT}{nF} \ln a_1 \\
E_2 = E_M^0 + \frac{RT}{nF} \ln a_2 \\
E_{\text{cell}} = E_2 - E_1 = \frac{RT}{F} \ln \left(\frac{a_2}{a_1}\right)
\]

Water – line corrosion and corrosion of electric poles at the base are typical examples. Electrical poles fixed to soil can buckle due to failure at the junction (pole – soil interface) due to prevalence of oxygen concentration cells. In water – line
corrosion, a steel specimen submerged in a beaker of saline water can experience corrosion at the water line due to similar reasons.

Dissimilar electrode cells or bimetallic couples are separately discussed in Lecture 4.