ELECTROCHEMISTRY-II: ELECTROMOTIVE FORCE AND RELATED CONCEPTS (8 LECTURES)

ELECTROMOTIVE FORCE (EMF)

Electromotive Force (EMF) is the potential difference across the terminals of an electrochemical cell when no current is flowing. It is the driving force for the electron flow in an external circuit, originating from chemical reactions within the cell.

RULES OF OXIDATION/REDUCTION BASED ON HALF-CELL POTENTIALS

The tendency of a species to get reduced or oxidized is quantified by its **standard electrode potential (E°)**. For a reaction to be spontaneous in a cell, the overall EMF must be positive.

- Oxidation occurs at the anode (loss of electrons).
- Reduction occurs at the cathode (gain of electrons).
- The overall cell potential (E_{cell}) is calculated as: $E_{cell} = E_{cathode} - E_{anode}$ (using reduction potentials for both).

A positive E_{cell} indicates a spontaneous reaction. Conversely, a negative E_{cell} implies the reaction will proceed in the reverse direction spontaneously.

CHEMICAL CELLS, REVERSIBLE AND IRREVERSIBLE CELLS

Chemical Cells

A chemical cell (also known as a galvanic or voltaic cell) is an electrochemical device that converts chemical energy into electrical energy through spontaneous redox reactions.

Reversible and Irreversible Cells

- **Reversible Cells:** These cells operate in equilibrium. The reaction can be reversed by applying an external EMF just slightly greater than the cell's EMF.

The cell potential remains constant and is independent of the direction of current flow (theoretically). An example is the Daniell cell under specific conditions.

- **Irreversible Cells:** These cells operate with a significant potential difference between the forward and reverse reactions. The reaction is not easily reversed, and significant energy is lost as heat. Most real-world electrochemical cells, like batteries during discharge and recharge, are irreversible.

ELECTROMOTIVE FORCE (EMF) OF A CELL AND ITS MEASUREMENT

The EMF of a cell is the difference in electric potential between the two electrodes. It is measured in volts (V).

- **Measurement:** EMF is typically measured using a **potentiometer**. This instrument compares the cell's EMF with a known standard EMF, ensuring no current is drawn from the cell during measurement, thus yielding the true EMF.

THERMODYNAMIC DERIVATION OF NERNST EQUATION

The Nernst equation relates the EMF of an electrochemical cell to the concentrations of reactants and products, and temperature.

The Gibbs free energy change (ΔG) for a reaction is related to the cell potential (E) by: $\Delta G = -nFE$

For standard conditions: $\Delta G^\circ = -nFE^\circ$

Using the thermodynamic relation $\Delta G = \Delta G^\circ + RT\ln Q$, and substituting the electrochemical equivalents:

$-nFE = -nFE^\circ + RT\ln Q$

Dividing by $-nF$, we get the Nernst Equation:

E = E° - (RT/NF)LNQ

Where:

- E = Cell potential under non-standard conditions
- E° = Standard cell potential

- R = Ideal gas constant (8.314 J/mol·K)
- T = Absolute temperature (in Kelvin)
- n = Number of moles of electrons transferred in the balanced redox reaction
- F = Faraday constant (96485 C/mol)
- Q = Reaction quotient

At 25°C (298.15 K), the equation can be simplified using common logarithms ($\log_{10}$):

$$E = E° - (0.0592/N)LOGQ$$

STANDARD ELECTRODE (REDUCTION) POTENTIAL

The standard electrode potential (E°) is the potential of an electrode measured under standard conditions (1 M concentration for solutes, 1 atm pressure for gases, and 25°C). It represents the tendency of a species to be reduced.

Application to Different Kinds of Half-Cells

- **Metal/Metal Ion Half-Cells:** E.g., Zn^{2+}/Zn, Cu^{2+}/Cu.
- **Gas/Ion Half-Cells:** E.g., H^+/H_2 (Standard Hydrogen Electrode - SHE).
- **Redox Half-Cells:** E.g., Fe^{3+}/Fe^{2+}.

By convention, the standard hydrogen electrode (SHE) is assigned a potential of 0.00 V. Other electrode potentials are measured relative to SHE.

APPLICATION OF EMF MEASUREMENTS

EMF measurements are crucial for determining various thermodynamic quantities and properties.

(i) Free Energy, Enthalpy, and Entropy of a Cell Reaction

- **Free Energy (ΔG):** $\Delta G = -nFE_{cell}$. A spontaneous reaction has $\Delta G < 0$, corresponding to $E_{cell} > 0$.
- **Enthalpy (ΔH):** $\Delta H = -nF[E_{cell} - T(dE_{cell}/dT)]$. Where (dE_{cell}/dT) is the temperature coefficient of the cell EMF.

- **Entropy (ΔS):** $\Delta S = nF(dE_{cell}/dT)$. Entropy change reflects the change in disorder of the system.

(ii) Equilibrium Constants (K)

At equilibrium, $\Delta G = 0$ and $E_{cell} = 0$. The reaction quotient Q becomes the equilibrium constant K.

From $\Delta G° = -RT\ln K$ and $\Delta G° = -nFE°$:

E° = (RT/NF)LNK

Or at 25°C:

E° = (0.0592/N)LOGK

This allows the calculation of K from standard cell potentials.

(iii) pH Values

EMF measurements can be used to determine pH using specific electrodes:

- **Hydrogen Electrode:** The half-cell potential of the H^+/H_2 electrode is given by $E = E°_{H+/H2} - (0.0592/1)\log(1/[H^+])$. Since $E°_{H+/H2} = 0$, $E = -0.0592\log[H^+] = 0.0592pH$. Measuring E allows calculation of pH.
- **Quinhydrone Electrode:** This electrode involves the equilibrium between quinone (Q) and hydroquinone (H_2Q) in acidic solution. Its potential is also directly related to the $[H^+]$ concentration, hence pH.
- **Glass Electrode:** This is a widely used potentiometric sensor for pH measurement. It consists of a thin glass membrane that develops a potential difference across it, which is proportional to the pH difference between the internal solution and the external solution being measured.

CONCENTRATION CELLS

A concentration cell is an electrochemical cell where both electrodes are made of the same material, but the electrolyte solutions have different concentrations of the active ion.

- **With and Without Transference:**
    - **Without Transference:** These are cells where the electrolyte concentration difference is only in the solutions separated by a salt bridge, and ion migration across the bridge is not considered.
    - **With Transference:** These cells involve direct contact between electrolytes of different concentrations, leading to a liquid junction potential due to differential migration of ions.

Liquid Junction Potential (LJP)

LJP arises at the interface between two electrolyte solutions of different concentrations or mobilities. It is due to the difference in the rates at which ions migrate across the boundary, creating a small charge separation and hence a potential difference.

POTENTIOMETRIC TITRATION

Potentiometric titration is a method used to determine the equivalence point of a titration by monitoring the change in cell potential (EMF) as a titrant is added to a solution containing an analyte.

- **Princ:** An indicator electrode (sensitive to the analyte or titrant) and a reference electrode (with a constant potential) form an electrochemical cell. The EMF of this cell is measured as the titrant is added.
- **Plotting:** A graph of EMF versus volume of titrant added shows a sharp change in potential around the equivalence point, which can be precisely identified.

NUMERICAL PROBLEMS EXAMPLES

Type 1: Calculating Cell EMF

- Given standard electrode potentials, calculate the standard cell EMF ($E°$) and the cell EMF (E) under non-standard conditions using the Nernst equation.

- *Example: Calculate* E°_{cell} *for a Daniell cell given* $E^\circ_{Zn^{2+}/Zn}$ *and* $E^\circ_{Cu^{2+}/Cu}$*. Then, calculate* E_{cell} *if concentrations are not standard.*

Type 2: Determining Equilibrium Constants

- Calculate the equilibrium constant (K) for a reaction from its standard cell potential (E°).
- *Example: Find the equilibrium constant for the reaction* $Ag(s) + Cd^{2+}(aq) \rightarrow Ag^{+}(aq) + Cd(s)$ *at 25°C, given standard electrode potentials.*

Type 3: Calculating Thermodynamic Quantities

- Determine ΔG°, ΔH°, and ΔS° from standard cell potentials and their temperature coefficients.
- *Example: A cell has* $E^\circ = 0.45$ V *at 25°C and a temperature coefficient (dE°/dT) of -0.001 V/K. Calculate ΔG°, ΔH°, and ΔS° for the cell reaction.*

Type 4: pH Measurements

- Calculate the pH of a solution using EMF readings from a hydrogen electrode or a glass electrode.
- *Example: A hydrogen electrode in a solution at 25°C has an EMF of +0.25 V relative to the SHE. Calculate the pH of the solution.*

Type 5: Concentration Cells

- Calculate the EMF of a concentration cell based on the concentration difference of the electrolyte.
- *Example: Calculate the EMF of a cell where one electrode is in 0.1 M* $AgNO_3$ *and the other is in 0.01 M* $AgNO_3$*, with both electrodes being silver.*