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AN AUTONOMOUS INSTITUTION



Approved by AICTE, New Delhi and Affiliated to Anna University,
Chennai

23CHT101 – APPLIED CHEMISTRY

1 – ELECTRO CHEMISTRY

1.3 – NERNST EQUATION

The Nernst equation is an equation in electrochemistry that relates the reduction potential of a half-cell (or full-cell) at any point in time to its standard electrode potential, temperature, and the concentrations (or activities) of the chemical species involved.

1. Basic Concept and Purpose of the Nernst Equation

The Nernst equation allows us to calculate the electrode potential of a half-cell in non-standard conditions, where the concentrations or pressures of the reactants and products are different from their standard states. The general form of the Nernst equation is:

$$E = E^\circ - \frac{nRT}{F} \ln Q$$

where:

- E = electrode potential of the half-cell or full cell at non-standard conditions
- E° = standard electrode potential of the half-cell or cell (measured at 1 M concentration for solutions, 1 atm for gases, and pure substances for solids or liquids)
- R = universal gas constant (8.314 J/mol·K)
- T = temperature in Kelvin
- n = number of moles of electrons transferred in the reaction
- F = Faraday's constant (96485 C/mol)
- Q = reaction quotient, which is the ratio of the concentrations (or partial pressures) of the products to the reactants, each raised to the power of their stoichiometric coefficients.

2. Derivation of the Nernst Equation

The Nernst equation can be derived from the relationship between the Gibbs free energy and the cell potential.

Step 1: Relate Gibbs Free Energy to Cell Potential

The change in Gibbs free energy (ΔG) for an electrochemical reaction is given by:

$$\Delta G = -nFE$$

At standard conditions, this equation becomes:

$$\Delta G^\circ = -nFE^\circ$$

where:

- ΔG° is the standard Gibbs free energy change,
- E° is the standard cell potential.

Step 2: Gibbs Free Energy and the Reaction Quotient

The Gibbs free energy change at any point in a reaction (non-standard conditions) can also be expressed as:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient.

Step 3: Combine the Equations

Substitute the expressions for ΔG and ΔG° in terms of cell potentials into the equation:

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

Step 4: Solve for E

Divide both sides by $-nF$ to solve for E:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

This is the **Nernst equation**.

3. Simplified Form of the Nernst Equation at 25°C

At standard temperature (25°C or 298 K), we can substitute the values of R, T and F into the equation for simplification:

- $R = 8.314 \text{ J/mol/K}$
- $T = 298 \text{ K}$
- $F = 96485 \text{ C/mol}$

Substituting these values, we get:

$$E = E^\circ - \frac{(8.314)(298)}{n(96485)} \ln Q$$

$$E = E^\circ - 0.0257 \ln Q$$

or, converting the natural logarithm

$$E = E^\circ - 0.0591 \log Q$$

This form is commonly used at 25°C for practical calculations in electrochemistry.

4. Applications of the Nernst Equation

- **Electrode Potential Calculations:** It is used to calculate the potential of a cell or half-cell under non-standard conditions.
- **Determining Equilibrium:** At equilibrium, the Nernst equation helps determine the equilibrium constant K by setting $Q=K$ and solving for E .
- **Concentration Cells:** In concentration cells, where both electrodes are the same but with different concentrations, the Nernst equation helps in calculating the EMF generated due to the concentration gradient.
- **pH Measurement:** The Nernst equation is fundamental in determining pH, as it relates the electrode potential of the hydrogen ion concentration in solution to pH values.