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# **POTENTIOMETRY CONCEPT, PRINCIPLE, ELECTROCHEMICAL CELL**

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**In potentiometry, the potential of an electrochemical cell is measured under static conditions because no current flows while measuring a solution's potential, its composition remains unchanged.**

- Information on a composition of the sample is obtained through the potential appearing between two electrodes.**
- The first quantitative potentiometric applications appeared soon after the formulation of Nernst equation.**
- In 1889, the Nernst equation relating an electrochemical cell's potential to the concentration of electroactive species in the cell.**



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- **PRINCIPLE:** The principle involved in the Potentiometry is when the pair of electrodes is placed in the sample solution it shows the potential difference by the addition of the titrant or by the change in the concentration of the ions.
- Potentiometric methods of analysis are based upon measurements of the potential of electrochemical cells under conditions of zero current, where the Nernst equation governs the operation of potentiometry



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## **Nernst equation:**

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF) \ln Q$$

- **$E_{\text{cell}}$  = cell potential under nonstandard conditions (V)**
- **$E^{\circ}_{\text{cell}}$  = cell potential under standard conditions**
- **$R$  = gas constant, which is 8.31 (volt-coulomb)/(mol-K)**
- **$T$  = temperature (K)**
- **$n$  = number of moles of electrons exchanged in the electro chemical reaction (mol)**
- **$F$  = Faradays constant, 96500 coulombs/mol**
- **$Q$  = reaction quotient**



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- **The reference electrode is the electrode which contains of its own potential value and it is stable when dipped into sample solution.**
- **The salt bridge is used to prevent the interference of the analyte solution with that of reference solution.**
- **Here analyte solution is the solution whose potential is to be measured. The indicator electrode is the electrode which responds to change in the potential of analyte solution The electromotive force of the complete cell is given by the following equation**



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$$E_{\text{cell}} = E_{\text{reference}} + E_{\text{indicator}} + E_{\text{junction}}$$

where  $E_{\text{reference}}$  is the electromotive force of the reference electrode

$E_{\text{indicator}}$  is electromotive force of indicator electrode,

$E_{\text{junction}}$  is the electromotive force at the junction of the liquid

### WORKING OF ELECTROCHEMICAL CELL

At its most basic, a potentiometer consists of two electrodes, whose reduction potentials differ, inserted in a test solution. The voltmeter is attached to the electrodes to measure the potential difference between them. One of the electrodes is a reference electrode, whose electrode potential is known.



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The other electrode is the test electrode. The test electrode is usually either a metal immersed in a solution of its own ions, whose concentration you wish to discover, or a carbon rod electrode sitting a solution which contains the ions of interest in two different oxidation states.

- Oxidation take place at anode. For example on zinc electrode  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
- Reduction take place at cathode. For example on copper electrode  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  When redox reaction take place than potential is develop which is measured by galvanometer.
- Electrode Potential is the potential of electrochemical cell and can be represented as :  $E_{\text{cell}} = E_{\text{indicator}} - E_{\text{reference}} + E_j$   $E_j$  = potential develops across the liquid junction at each end of salt bridge it is negligible .



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