

PHARMACEUTICAL ANALYSIS – BP102T

UNIT: V ELECTRO ANALYTICAL METHOD OF ANALYSIS

CLASS:41

TOPIC: ELECTROCHEMICAL CELL-HYDROGEN ELECTRODE

Indicator Electrodes

- To measure potential of a solution, an appropriate electrode is needed
- Indicator electrode measures potential when connected to a suitable reference electrode
- Electrode which is used to measure potential or pH of a solution is called as indicator electrode

Types of indicator electrode used are:

- Hydrogen electrode
- Quinhydrone electrode
- Antimony electrode
- Glass electrode

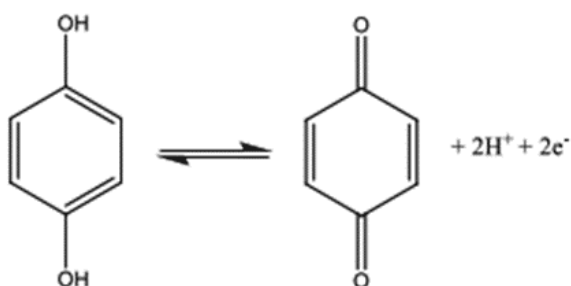
Hydrogen Electrode :

- Construction is similar to Normal Hydrogen Electrode (NHE)
- Electrode is similar to NHE
- Electrode is responsive to hydrogen ion concentration
- Can be used for pH measurement
- Can be used for pH measurement
- Platinum of electrode do not take part in electrochemical reaction
- Only acts as site for transfer of electrons

- Potential of hydrogen electrode is
- $E_{H^+, H_2} = E^0(H^+, H_2) - 0.0591/n (H^+)$
 $= 0.0591 \text{ pH}$, as $E^0(H^+, H_2) = 0$

Quinhydrone Electrode :

- Electrode is used in measuring pH of a given solution
- Consists of a bright platinum wire dipping into a solution saturated with quinhydrone
- In solution, quinhydrone dissociates into equimolecular quantities of quinone and hydroquinone



- pH of a solution can be determined by a redox system
- Because reduction to hydroquinone or oxidation to benzoquinone involves H^+ ions

Advantages:

- Attains equilibrium rapidly
- Can be used where hydrogen electrode is unsuitable
- Gives accurate results

Disadvantages:

- Cannot be used in more alkaline solution, whose pH is above 8
- Gets readily oxidized by air in alkaline medium

Antimony Electrode:

- Used in pH measurements
- Consists of rod coated or covered with antimony trioxide

- Electrode is prepared by placing a stick or a rod of antimony metal covered with thin crust of its oxide
- It is dipped into a solution whose pH is to be measured
- Electrical connection is made with reference electrode like saturated calomel electrode

Reaction involved is

- $\text{Sb} + \text{H}_2\text{O} \rightleftharpoons \text{SbO}^+ + 2\text{H}^+ + 3\text{e}^-$
- $\text{Sb}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Sb(s)} + 3\text{H}_2\text{O}$

Advantages:

- Can be used for measuring pH from 2 to 8
- Can be used in viscous or turbid solvents
- It is sturdy- very useful where continuous pH recording are made
- Do not get readily poisoned

Disadvantages:

- Cannot be used in measuring pH below 3, as oxide gets dissolved
- Cannot be used in the presence of strong oxidizing and complexing agents

Cannot be used in the presence of metals such as Cu, Ag, Au which are more noble than antimony (i.e., below in electromotive series)

- It suffers from salt error

Glass Electrode:

- Very useful electrode for determination of hydrogen ion (or pH) of a solution
- It involves no electron exchange but allows transfer of H^+ ions through its membrane
- Consists of very thin bulb made from glass membrane having high electrical conductivity
- Bulb contains hydrochloric acid solution of definite concentration and or Ag/AgCl wire to make electrical contact with it

- Thin membrane of bulb is prepared from special type of glass, sensitive and permeable to H^+ ions
- Glass membrane is made from soft soda-lime glass containing lithium silicate with lanthanum and barium ions added to it
- Sensitivity of membrane of protons and other cations depend upon the composition of glass membrane
- Corning glass contains 22% Na_2O , 6% CaO and 72% SiO_2
- Membrane of glass is specific to H^+ ions upto pH 9.0 above which it is somewhat responsive to Na^+ and other charged cations
- Potential of glass electrode is given by
- $E = k + 0.0592 (pH_1 - pH_2)$ at 25 $^{\circ}C$
- Where k = constant for the electrode

Advantages:

- Gives a rapid response
- It is chemically resistant to oxidizing and reducing agents, dissolved gases, colloids and salts, etc
- Can be used over the entire pH range when lithia-silica glasses are used

Disadvantages:

- Extremely fragile- contains a very thin bulb
- Minute abrasions on the surface of tip, damages electrode