ENGINEERING CHEMISTRY

Department of Science and Humanities

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Electrochemical equilibria

Class content:

- ***Types of electrodes***
  - ***Metal-metal-ion electrode***
  - ***Metal-insoluble salt –ion electrode***
  - ***Gas electrode***
  - ***Amalgam electrode***
  - ***Redox electrode***
  - ***Ion selective electrode***

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Electrochemical equilibria

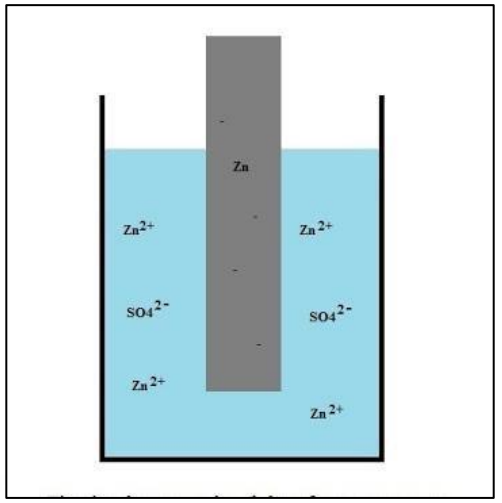
Types of electrodes

- In order to form a cell, 2 half cells or 2 electrodes are required
- Various types of electrodes are available which are constructed based on the application

1. Metal-metal ion electrode:

- Metal in contact with a solution of its own ions
  e.g., Zn/Zn^{2+}, Cu/Cu^{2+}, Ag/Ag^{+}
- $M^{n+} + ne^{-} \rightleftharpoons M$
- Nernst equation

$$E_{M/M^{n+}} = E^{o}_{M/M^{n+}} + \frac{2.303RT}{nF} \log\left[M^{n+}\right]$$



Source:http://www.valgetal.com/physics/Batteries/batteries.htm

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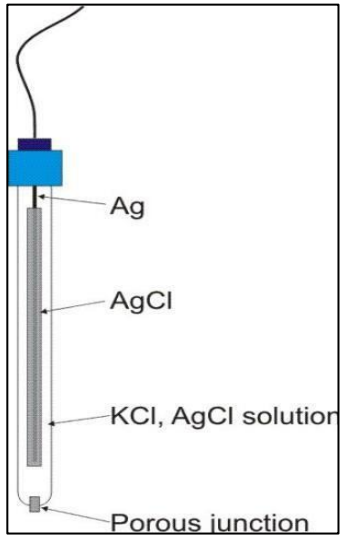
2. Metal-Metal insoluble salt- ion electrode:

- These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution of soluble salt of the same anion
  e.g.,Calomel electrode $Hg/Hg_2Cl_2/KCl$, $Ag/AgCl(s)/HCl$
- For silver –silver chloride electrode

  $AgCl + e^- \rightleftharpoons Ag + Cl^-$

- Nernst equation:

$$E_{Ag/AgCl/Cl^-} = E^o_{Ag/AgCl/Cl^-} - \frac{0.0591}{1}\log[Cl^-]$$



Source:https://www.corrosion-doctors.org/Corrosion-Thermodynamics/Reference-Half-Cells-Silver.htm

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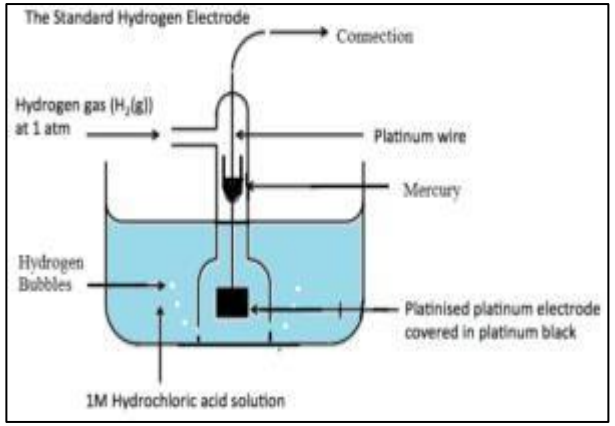
3. Gas electrode:

- It consists of gas bubbling about an inert metal foil, immersed in solution containing ions to which the gas is reversible.
- The metal provides electrical contact and facilitates the establishment of equilibrium between the gas and its ions

  e.g.,Hydrogen electrode $Pt/H_2/H^+$,Chlorine electrode $Pt/Cl_2/Cl^-$
- For a hydrogen electrode

  $2H^+ + 2e^- \rightleftharpoons H_2$
- Nernst equation:

$$E_{PtTH_2TH^+} = E^0{}_{PtTH_2TH^+} - \frac{0.0591}{2}\log\left(\frac{p_{H_2}}{[H^+]^2}\right)$$



Source:https://thefactfactor.com/facts/pure_science/chemistry/physical-chemistry/reference-electrodes/5844/

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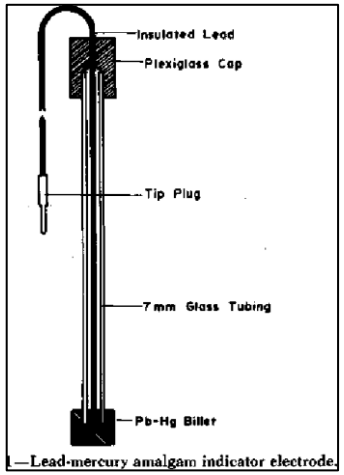
4. Amalgam electrode:

- It is similar to metal- metal ion electrode in which metal amalgam is in contact with a solution containing its own ions
  e.g., Lead amalgam electrode Pb-Hg/Pb^{2+}
- For lead amalgam electrode

  Pb^{2+} + $2e^-$ ⇌ Pb-Hg

- Nernst equation:

$$E_{Pb^{2+}/Pb-Hg} = E^{0}{}_{Pb^{2+}/Pb-Hg} - \frac{0.0591}{2}\log\left(\frac{[Pb-Hg]}{[Pb^{2+}]}\right)$$



1—Lead-mercury amalgam indicator electrode.

Source:https://www.semanticscholar.org/paper/Potentiometric-Titration-of-Sulfate-in-Water-and-a-Robbins-Carter/c823ab0578481e876975ee707a5f8adca14c512f

THANK YOU

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