ENGINEERING CHEMISTRY

Department of Science and Humanities

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Electrochemical equilibria

Class content:

- ***Reference electrodes***
  - ***Primary reference electrode***
    - ***Standard Hydrogen electrode***
  - ***Secondary reference electrodes***
    - ***Calomel electrode***
    - ***Silver – silver chloride electrode***

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Electrochemical equilibria

Reference electrodes

- Electrodes whose potentials are accurately known, stable and with reference to which the electrode potential of any electrode can be measured
- Reference electrode is combined with indicator electrode and emf of the cell is measured
- Two types of reference electrodes:
  - **Primary reference electrodes**
    - Standard Hydrogen electrode(SHE)
  - **Secondary reference electrodes**
    - Calomel electrode
    - Silver-silver chloride electrode

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Electrochemical equilibria

Primary reference electrode: Standard hydrogen electrode

- Electrode potential is assigned a value of 0.0 V
- Gas electrode
- $Pt/H_2/H^+$
- $2H^+ + 2e^- \rightleftharpoons H_2$
- Used to measure potential of other electrodes

e.g.,

$Zn/Zn^{2+}//H^+(1M)/H_2(1atm),Pt$

$E_{cell} = E_{rhs} - E_{lhs} = E_{cathode} - E_{anode}$

$0.76 = 0.0 - E_{Zn/Zn^{2+}}$

$E_{Zn/Zn^{2+}} = -0.76\ V$

$Pt, H_2(1atm) / H^+(1M)// Cu^{2+}/ Cu$

$E_{cell} = E_{rhs} - E_{lhs} = E_{cathode} - E_{anode}$

$0.34 = E_{Cu/Cu^{2+}} - 0.0$

$E_{Cu/Cu^{2+}} = 0.34\ V$

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Disadvantages of SHE:

- Maintaining concentration of H^+ ions at 1M and pressure of H_2 gas at 1 atm is difficult.
- Platinum is highly susceptible to poisoning by different impurities in gas
- It cannot be used with oxidizing and reducing environment

Secondary reference electrodes:

- Due to the limitations of standard hydrogen electrode some other electrodes whose electrode potentials are accurately known and remain stable over a long period of time and can be easily assembled. With respect to these electrodes , electrode potentials of other electrodes can be assigned

e.g.,**Calomel electrode, silver silver chloride electrode**

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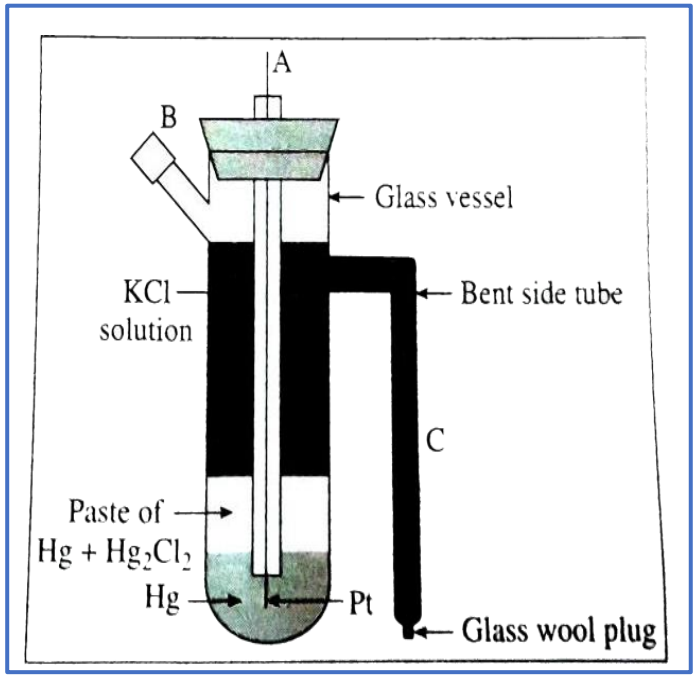
Secondary Reference electrodes:

Calomel electrode

- Most widely used reference electrode
- Metal-insoluble salt –ion electrode

Construction:

- A glass tube containing a layer of mercury over which a paste of insoluble salt Hg_2Cl_2 (calomel) + Hg and the next layer is a solution of KCl
- A Pt wire dipped in Hg provides electrical contact
- Tube is fitted with a side tube to fill KCl solution of known concentration and another side tube which connects to the salt bridge



https://doubtnut.com/question-answer-chemistry/describe-the-construction-and-working-of-the-calomel-electrode-96607395

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- $Hg/Hg_2Cl_2(s)/Cl^-$

Working :

- Can act as anode or cathode depending on the nature of the electrode with which it is coupled

As anode:

$$2Hg \rightleftharpoons Hg_2^{2+} + 2e^-$$

$$Hg_2^{2+} + 2\,Cl^- \rightleftharpoons Hg_2Cl_2$$

$$2Hg + 2\,Cl^- \rightleftharpoons Hg_2Cl_2 + 2e^-$$

As cathode:

$$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg$$

$$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$$

$$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2\,Cl^-$$

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Applying Nernst's equation

$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$

$$E = E^o - 2.303RT/2F \log [Cl^-]^2$$

at 298K

$$E = E^o - 0.0591 \log [Cl^-]$$

- Electrode is reversible to chloride ions
- Electrode potential depends on chloride ion concentration

Types of calomel electrodes:

[KCl]	Name	Electrode potential at 298K
0.1M	Decinormal electrode	0.3358 V
1M	Normal electrode	0.2824 V
Saturated solution of KCl	Saturated Calomel Electrode(SCE)	0.2422 V

THANK YOU

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