28/10.

Q. Find the concentration of Cd^{2+} ions in the given electrochemical cell.

$$Zn/Zn^{2+}_{(0.1M)} \,||\, Cd^{2+}_{(M)}/Cd.$$

Given $E^{o}_{Zn^{2+}/Zn} = -0.76V$; $E^{o}_{Cd^{2+}/Cd} = -0.40V$ and. $E_{cell} = -0.3305V$ at 298K

Ans Net cell reaction $Zn + Cd^{2+} \longrightarrow Zn^{2+} + Cd$.

$$E_{cell} = E^{o}_{cell} - \left(\frac{0.0591}{n}\right) \log \frac{[Zn^{2+}]}{[Cd^{2+}]}$$

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$= -0.40 - (-0.76) = 0.36V$$

Substituting.

$$0.3305 = 0.36 - \left(\frac{0.0591}{2}\right) \log \frac{[0.1]}{[M]}$$

$$-0.0295 = 0.0295 \log \frac{[0.1]}{[M]}.$$

$$\frac{0.1}{M} = 1 \text{ antilog}.$$

$$= 10$$

$$M = \underline{\underline{0.01}}$$

Q. Calculate EMF of the zinc-silver cell at 25°c when $[Zn^{2+}] = 1.0M$ and $[Ag^{+}] = 10M$

Write the cell representation and cell reaction.

[Given $E^{o}_{(Zn^{2+}/Zn)} = -0.76V$ and $E^{o}_{Ag^{+}/Ag} = 0.80V$ at 25°C)

Ans. Cell representation.

$$Zn/Zn^{2+}_{(1M)} \,//\, Ag^{+}_{(10M)} / Ag$$

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Cell reaction:

$$Zn + 2Ag^{+} \rightarrow Zn^{2+} + 2Ag.$$

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$
$$= 0.80 - (-0.76) = 1.56\ V$$

$$E_{cell} = E^{o}_{cell} - \left(\frac{0.0592}{2}\right) \log \frac{[1]}{[10]^2}$$

$$= 1.6192\ V$$

ENERGETICS OF CELL REACTION

Q. For a cell, EMF is 1.018 V at 293 K. Calculate ΔG for the cell reaction at 293 K

Ans. $\Delta G = -nFE$
$= -2 \times 96500 \times 1.018$
$= -1.964 \times 10^{5}\ J$

$$\left(\begin{array}{l} Cd \rightarrow Cd^{2+} + 2e^{-} \\ Hg_2^{2+} + 2e^{-} \rightarrow 2Hg \end{array}\right)$$
$n = 2$

Q. Calculate the thermodynamic parameter (ΔG) for the reaction $Zn + FeSO_4 \rightarrow ZnSO_4 + Fe$. The reduction potentials for Zn and Fe are $-0.76\ V$ and $-0.44\ V$ respectively.

Ans $E_{cell} = E_{cathode} - E_{anode}$
$= -0.44 - (-0.76)$
$= 0.32\ V$

$\Delta G = -nFE = -(2 \times 96500 \times 0.32) = 61760\ J$

Q. EMF of Weston-Cadmium cell is 1.0183 V ~~on~~ at 293 K and 1.0181 V at 298 K. Calculate ΔG, ΔH and ΔS of the cell at 298 K.

Ans. $\Delta G = -nFE$

$n=2$ $F = 96500\ C$ $E = 1.0181\ V$

$\Delta G = -2 \times 96500 \times 1.0181 = \underline{-196.5\ kJ}$

$\Delta H = nF\left[T(\delta E/\delta T)_p - E\right]$

$(\delta E/\delta T)_p = 1.0181 - 1.0183 / 298 - 293 = -0.0002/5$
$= -0.00004\ VK^{-1}$

$T = 298\ K$

$\Delta H = \cancel{2\times}\ 2 \times 96500 \{[298 \times (-0.00004)] - \cancel{108}\ 1.0181\}$.

$= \cancel{4S} = \underline{-198.8\ kJ}$

$\Delta S = nF(\delta E/\delta T)_p$
$= 2 \times 96500 \times -0.00004$
$= \underline{-7.72\ JK^{-1}}$

Q. (H.W) The emf of the cell $Cd|CdCl_2 \cdot 2.5H_2O$ (saturated) || $AgCl_{(s)}/Ag$. is 0.6753 V and 0.6915 V at 298 K and 273 K respectively. Calculate ΔG, ΔH, and ΔS of the cell reaction at 298 K.

Ans. Here $n = 2$, $E = 0.6753\ V$ at 298 K and 0.6915 V at 273 K

$(\delta E/\delta T)_p = (0.6753 - 0.6915)V/(298-273)K$
$= -0.00065\ VK^{-1}$

Now at 298K, $\Delta H = nF[T(\delta E/\delta T)_p - E]$

$= 2 \times 96500 \{[298 \times (-0.00065)] - 0.6753 V\}$

$= -167.7 \text{ KJ}$

$\Delta G = -nFE = -2 \times 96500 \times 0.6753 = -130.33 \text{ KJ}$

$\Delta S = nF(\delta E/\delta T)_p$

$= 2 \times 96500 (-0.00065)$

$= -125.45 \text{ JK}^{-1}$

Q The EMF of the cell having Ni and Cu as the electrodes in contact with their respective electrolytes $NiCl_2$ and $CuCl_2$ is 0.5735 V at 298 K and 0.5951 V at 273 K. Calculate ΔG, ΔH and ΔS for the reaction at 298 K.

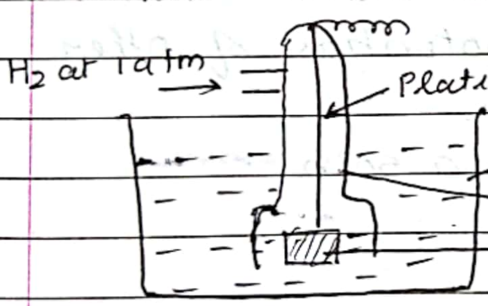
H.W

CLASSIFICATION OF ELECTRODES

- Gas Electrode (Hydrogen electrode)
- Metal-Metal Insoluble salt (Calomel electrode)
- Ion selective electrode (Glass electrode)

GAS ELECTRODE

- It consists of gas bubbling over an inert metal wire or foil immersed in a solution containing ions of the gas.
- Reference electrodes are those with reference to those, the electrode potential of any electrode can be measured.
- SHE is the primary reference electrode, whose electrode potential at all temps is 0.



Representation : Pt, $H_{2(g)}$ / H^+

Electrode reaction : $H^+ + e^- \rightleftharpoons \frac{1}{2} H_{2(g)}$

The reaction is reversible as it can be oxidation or reduction depending on half cell.

At standard conditions (1M, 298K, 1atm) it is called as standard hydrogen electrode (SHE)

- The Pt electrode is made of a small square of Pt foil (0.5 x 0.5 cm) which is platinized.
- H_2 gas at 1atm is bubbled around the Pt electrode through an inlet.
- The Pt black serves a large surface area for the reaction to take place. It adsorps H_2 gas and it speeds up the equilibrium between H_2 gas and H^+ ions.
- The redox reaction occurs at Pt electrode.
- The greater the electrode area, faster electrode kinetics.
- Use electrode material that can adsorp H_2 at its interface.

APPLICATIONS.

- To determine electrode potential of other unknown electrodes.
- To determine the pH of a soln.

$$pH = E_{cell}/0.0592$$

~~$E = E^{\circ}$~~ 0.

$$E = 0 - 0.0592 \log 1/[H^+] = -0.0592\,pH.$$

$$E_{cell} = E_C - E_A$$

$$= 0 - (-0.0592\,pH)$$

$$= 0.0592\,pH.$$

$$pH = E_{cell}/0.0592$$

LIMITATIONS.

- Construction and working is difficult.
- Pt is susceptible to poisoning
- Cannot be used in presence of oxidising agents.

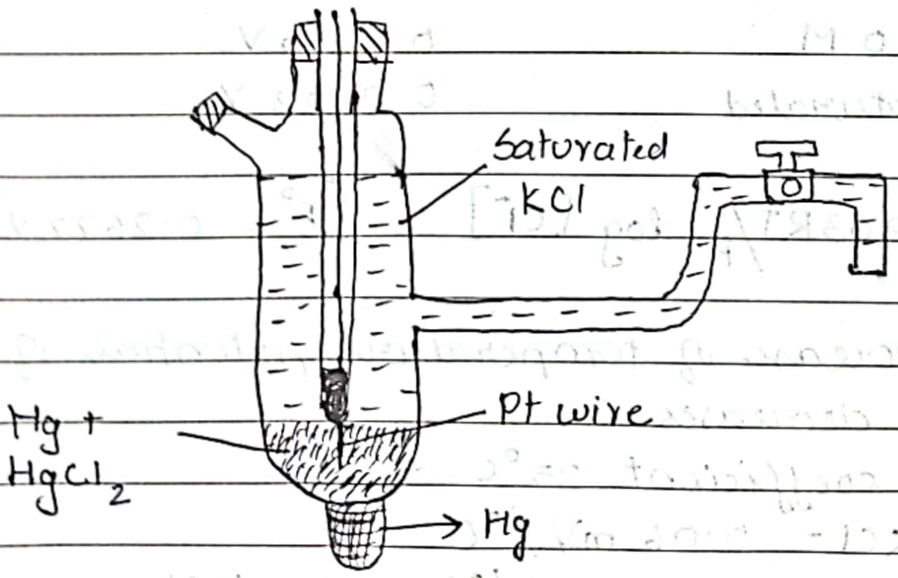
METAL-METAL SALT ION ELECTRODE

- These electrodes consist of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion

  Eg: Calomel Electrode. ($Hg / Hg_2Cl_2 \mid KCl$)

  Ag/AgCl electrode.

CONSTRUCTION :



Representation : $Hg; Hg_2Cl_2 / KCl$

It can act as an anode or cathode depending on the nature of the other electrode

As anode: $2Hg \longrightarrow Hg_2^{2+} + 2e^-$

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

Net reaction: $2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-$

As cathode: $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[Cl^-]^2}{1} \qquad n=2$$

$$= E^\circ - \frac{2.303RT}{F} \log [Cl^-]$$

Its electrode potential depends on the concentration of KCl

Conc of Cl^-	Electrode Potential
0.1 M	0.3335 V
1.0 M	0.2810 V
Saturated	0.2422 V

$E = E^\circ - 2.303RT/F \log [Cl^-]$ $[E^\circ = 0.2677\,V]$

With increase of temperature potential of calomel electrode decreases.

Temp coefficient 25°C are

0.1 N KCl - 0.06 mV/°C

1 N KCl - 0.24 mV/°C sat KCl - 0.65mV/°C