2. Types of Electrodes

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TYPES OF ELECTRODES

① Metal - metal ion electrode

$Zn \mid Zn^{2+}$ $\quad Zn^{2+} + 2e^- \longrightarrow Zn$ $\quad E = E_0 - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$

$Cu \mid Cu^{2+}$ $\quad Cu^{2+} + 2e^- \longrightarrow Cu$ $\quad E = E_0 - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$

$Ag \mid Ag^{+}$ $\quad Ag^{+} + e^- \longrightarrow Ag$ $\quad E = E_0 - \frac{0.0591}{1} \log \frac{1}{[Ag^{+}]}$

② Metal - metal salt ion electrode

[OR]

Metal - metal in soluble salt ion electrode

- Calomel electrode

$Hg \mid Hg_2Cl_2 \mid Cl^-$

Both anode and cathode

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

$E = E^\circ - \frac{0.0591}{2} \log [Cl^-]^2$

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

- $Ag \mid AgCl \mid Cl^-$

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

$E = E^\circ - \frac{0.0591}{1} \log [Cl^-]$

- $Ag \mid Ag_2CrO_4 \mid CrO_4^{2-}$

$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$

$E = E^\circ - \frac{0.0591}{2} \log [CrO_4^{2-}]$

- $Pb \mid PbSO_4 \mid SO_4^{2-}$

$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

$E = E^\circ - \frac{0.0591}{2} \log [SO_4^{2-}]$

③ Gas electrode

$Pt|H_2|H^+$ $\quad 2H^+ + 2e^- \longrightarrow H_2$ $\quad E = E^\circ - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$

$Pt|Cl_2|Cl^-$ $\quad Cl_2 + 2e^- \longrightarrow 2Cl^-$ $\quad E = E^\circ - \frac{0.0591}{2} \log \frac{[Cl^-]^2}{P_{Cl_2}}$

$Pt|Br_2|Br^-$ $\quad Br_2 + 2e^- \longrightarrow 2Br^-$

$Pt|I_2|I^-$ $\quad I_2 + 2e^- \longrightarrow 2I^-$

$Pt|O_2|O^{2-}$ $\quad \frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$ $\quad E = E^\circ - \frac{0.0591}{2} \log$

(4) Oxidation - reduction electrode

$Pt|Fe^{2+}, Fe^{3+}$ $\quad Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\quad E = E^\circ - \frac{0.0591}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$

$Pt|Cr^{6+}, Cr^{3+}$ $\quad Cr^{6+} + 3e^- \longrightarrow Cr^{3+}$ $\quad E = E^\circ - \frac{0.0591}{3} \log \frac{[Cr^{3+}]}{[Cr^{6+}]}$

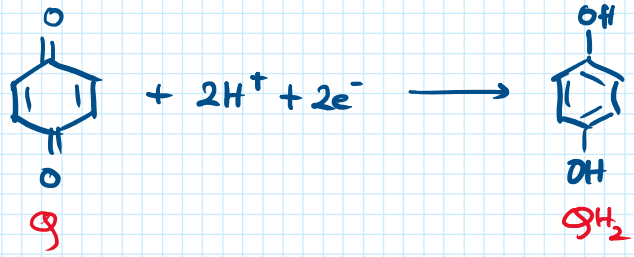
$Pt|Sn^{2+}, Sn^{4+}$ $\quad Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$ $\quad E = E^\circ - \frac{0.0591}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]}$

$Pt|Ce^{3+}, Ce^{4+}$ $\quad Ce^{4+} + e^- \longrightarrow Ce^{3+}$ $\quad E = E^\circ - \frac{0.0591}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$

$Pt|Q, QH_2|H^+$

Q - quinone

QH_2 - hydroquinone



Q $\qquad$ QH_2

$E = E^\circ - \frac{0.0591}{2} \log \frac{[QH_2]}{[Q][H^+]^2}$

(5) Amalgam electrode

$Zn-Hg|Zn^{2+}$ $\quad Zn^{2+}(Hg) + 2e^- \longrightarrow Zn-Hg$ $\quad E = E^\circ - \frac{0.0591}{2} \log \frac{[Zn-Hg]}{[Zn^{2+}]}$

$Cu-Hg|Cu^{2+}$ $\quad Cu^{2+}(Hg) + 2e^- \longrightarrow Cu-Hg$

$Pb-Hg|Pb^{2+}$ $\quad Pb^{2+}(Hg) + 2e^- \longrightarrow Pb-Hg$

(6) Ion selective electrodes

Eg: glass electrode

PROBLEMS

① Calculate E_{cell}, E°_{cell} at 25°C for the following cell

$$Pt|I_2|I^-(0.03\,M)\,||\,Fe^{3+}, Fe^{2+}\,(1M)\,|Pt$$
$$(0.1M)$$

$E^\circ_{Fe^{3+}|Fe^{2+}} = 0.77\,V$ (Cathode)

$E^\circ_{I_2|I^-} = 0.54\,V$ (Anode)

Soln: $I_2 + 2e^- \longrightarrow 2I^-$

Anode: $2I^- \longrightarrow I_2 + 2e^-$

Cathode: $(Fe^{3+} + e^- \longrightarrow Fe^{2+}) \times 2$

$$2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$$

$$Q = \frac{[Fe^{2+}]^2}{[I^-]^2 \times [Fe^{3+}]^2}$$

$$= \frac{1^2}{(0.03)^2(0.1)^2}$$

$E^\circ_{cell} = E^\circ_c - E^\circ_A$

$= 0.77 - 0.54$

$= 0.23\,V$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\left(\frac{1^2}{(0.03)^2(0.1)^2}\right)$$

$= 0.08\,V$

② Calculate E_{cell}, E°_{cell} at 25°C for:

$$Ag|Ag_2CrO_4|CrO_4^{2-}(0.2M)\,||\,Cl^-(0.025M)\,|Cl_2\,(0.5\,atm)|Pt$$

$E^\circ_{Ag_2CrO_4|Ag} = 0.446\,V$

$E^\circ_{Cl_2|Cl^-} = 1.359\,V$