















Ex.
$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

 $Cu^{2+} + 2e^- \rightarrow Cu$
Full reaction:
 $2(Fe^{3+} + e^- \rightarrow Fe^{2+})$
 $Cu \rightarrow Cu^{2+} + 2e^-$
 $E^0 = 0.77 \vee$
 $E^0 = -0.34 \vee$
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 $E^0_{cell} = 0.77 - 0.34 = 0.43 \vee$

✓ E: concentration dependent







$$w_{max} = -qE_{max}$$

$$w_{max} = -nFE_{max}$$

$$\therefore \Delta G = w_{max}$$

$$\therefore \Delta G = -nFE_{max}$$

$$\Delta G^{\circ} = -nFE^{\circ} \qquad \text{at standard condition}$$

$$E^{\circ}(+) \Rightarrow \Delta G^{\circ}(-) \qquad \text{spontaneous}$$

Ex. $Cu^{2+}(aq) + Fe(s) \Rightarrow Fe^{2+}(aq) + Cu(s) \qquad E^{\circ} = 0.78 \text{ V}$

$$\Delta G^{\circ} = -nFE^{\circ}$$

$$= -(2)(96500)(0.78)$$

$$= -1.5 \times 10^{5} \text{ J}$$





$$\begin{split} & AG = AG^{\circ} + RT\ln Q\\ -nFE = -nFE^{\circ} + RT\ln Q\\ \text{Nernst equation:}\\ & E = E^{\circ} - \frac{RT}{nF} \ln Q\\ \text{In volt } (F: 96500 \text{ C/mol})\\ & Q = 1 \qquad E = E^{\circ}\\ Q < 1 \qquad E > E^{\circ}\\ Q > 1 \qquad E < E^{\circ}\\ \text{At } 25 \text{ }^{\circ}\text{C}\\ & E = E^{\circ} - \frac{0.0592}{n} \log Q\\ & T \qquad E = E^{\circ} - \frac{0.0592}{n} \log Q \end{split}$$

Ex. $2AI(s) + 3Mn^{2+}(aq) \rightarrow 2AI^{3+}(aq) + 3Mn(s)$ $E^{o} = 0.48 \vee A^{o}$ at $[Mn^{2+}] = 0.50 M$; $[AI^{3+}] = 1.50 M$ $E = E^{o} - \frac{0.0592}{n} \log \frac{[AI^{3+}]^{2}}{[Mn^{2+}]^{3}}$ $E = 0.48 - \frac{0.0592}{6} \log \frac{[1.50]^{2}}{[0.50]^{3}}$ $= 0.47 \vee$ As current flows, concentration change $\Rightarrow E drops$ \Rightarrow at equilibrium, E = 0, Q = K

As current flows, concentration change $\Rightarrow E \text{ drops}$ $\Rightarrow \text{ at equilibrium, } E = 0, Q = K$ $\Delta G^{\circ} = -RT \ln K$ $-nFE^{\circ} = -RT \ln K$ $E^{\circ} = \frac{RT}{nF} \ln K$ When Q = K $E = E^{\circ} - \frac{RT}{nF} \ln K$ $= \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln K = 0$











* More about the intensive property of Ex. $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^{\circ} = 0.77 \text{ V}$ $\Delta G^{\circ} = -(1)FE^{\circ}_{Fe^{3+}\rightarrow Fe^{2+}}$ $Cu^{2+} + 2e^- \rightarrow Cu$ $E^{\circ} = 0.34 \text{ V}$ $\Delta G^{\circ} = -(2)FE^{\circ}_{Cu^{2+}\rightarrow Cu}$ $2(Fe^{3+} + e^- \rightarrow Fe^{2+})$ $\Delta G^{\circ} = -(2)FE^{\circ}_{Fe^{3+}\rightarrow Fe^{2+}}$ $Cu \rightarrow Cu^{2+} + 2e^ \Delta G^{\circ} = +(2)FE^{\circ}_{Cu^{2+}\rightarrow Cu}$ $Cu(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Cu^{2+}(aq)$ $\Delta G^{\circ}_{cell} = -(2)F(E^{\circ}_{Fe^{3+}\rightarrow Fe^{2+}} - E^{\circ}_{Cu^{2+}\rightarrow Cu})$ $= -(2)FE^{\circ}_{cell}$ $\therefore E^{\circ}_{cell} = E^{\circ}_{Fe^{3+}\rightarrow Fe^{2+}} - E^{\circ}_{Cu^{2+}\rightarrow Cu}$ \Rightarrow Has no relationship with n

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 O Lead storage battery Pb^o, Pb²⁺, Pb⁴⁺
 Anode: Pb(s) + HSO₄⁻(aq) → PbSO₄(s) + H⁺(aq) + 2e⁻ Cathode: PbO₂(s) + HSO₄⁻(aq) + 3H⁺(aq) + 2e⁻ → PbSO₄(s) + 2H₂O(l)
 Cell reaction Pb(s) + PbO₂(s) + 2H⁺(aq) + 2HSO₄⁻(aq) → 2PbSO₄(s) + 2H₂O(l)
 Contains 38% H₂SO₄ (~5 M) 6 cells in series, 2 V each
 Problem: During recharging, electrolysis of H₂O may occur – refill is needed
 Solution: When Cd/Pb alloy is used as electrode – no electrolysis of H₂O
 © Dry cell batteries ✓ Zn/MnO₂ (1.5 V) Anode Zn → Zn²⁺ + 2e⁻ Cathode 2NH₄⁺ + 2MnO₂ + 2e⁻ → Mn₂O₃ + 2NH₃ + H₂O Problem: acidic electrolyte \Rightarrow Zn corrodes Alkaline cell Anode Zn + 2OH⁻ → ZnO + H₂O + 2e⁻ Cathode 2MnO₂ + H₂O + 2e⁻ → Mn₂O₃ + 2OH⁻ Under basic condition: lasts longer ✓ Nickel-cadmium (rechargeable) Anode Cd + 2OH⁻ → Cd(OH)₂ + 2e⁻ Cathode NiO₂ + 2H₂O + 2e⁻ → Ni(OH)₂ + 2OH⁻ Cd(OH)₂ and Ni(OH)₂ adhere to the electrodes















In pure water, $[H^+] = [OH^-] = 10^{-7} M$ -2.06 V is based on standard condition: $[H^+] = [OH^-] = 1 M$

In fact, E = -1.23 V

However, due to over-voltage, usually needs to be higher than 1.23 V

Over-voltage: due to interface problem of the electrode

⊚ Ele Ex.	ctrolysis of ion mixtures Cu ²⁺ , Ag ⁺ , Zn ²⁺	
	$Ag^+ + e^- \rightarrow Ag$ $E^\circ = 0.80 V$ $Cu^{2+} + 2e^- \rightarrow Cu$ $E^\circ = 0.34 V$ $Zn^{2+} + 2e^- \rightarrow Zn$ $E^\circ = -0.76 V$	
	Ag came out first, Zn came out last	
Ex.	NaCl(aq) $2Cl^{-} \rightarrow Cl_{2} + 2e^{-} \qquad E^{\circ} = -1.36 \text{ V}$ $2H_{2}O \rightarrow O_{2} + 4H^{+} + 4e^{-} \qquad E^{\circ} = -1.23 \text{ V}$	
	In fact Cl [−] oxidized first Oxidation of H ₂ O has higher over-voltage	

* Commercial electrolytic processes ③ Al Source: Al₂O₃ in bauxite (鐵礬土) Electrolysis in water - NO Al³⁺ + 3e⁻ \rightarrow Al $E^{\circ} = -1.66 \lor$ $2H_2O + 2e^- <math>\rightarrow$ H_2 + 2OH⁻ $E^{\circ} = -0.83 \lor$ Hall-Heroult process mix Al₂O₃ and Na₃AIF₆ (cryolite 冰晶石) \uparrow - melts at 1000 °C mp 2050 °C Al₂O₃ + 4AIF₆³⁻ \rightarrow 3Al₂OF₆²⁻ + 6F⁻ Cathode: AIF₆³⁻ + 3e⁻ \rightarrow Al + 6F⁻ Anode: 2Al₂OF₆²⁻ + 12F⁻ + C \rightarrow 4AIF₆³⁻ + CO₂ + 4e⁻











