

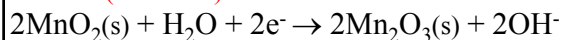
21.5 Galvanic Cells as Batteries

• Primary cells – can't be recharged

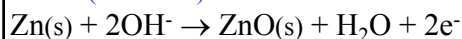
- The battery dies when the reactants are exhausted

Example: The alkaline battery – a dry cell

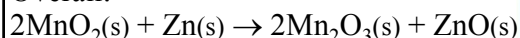
Cathode (reduction):



Anode (oxidation):

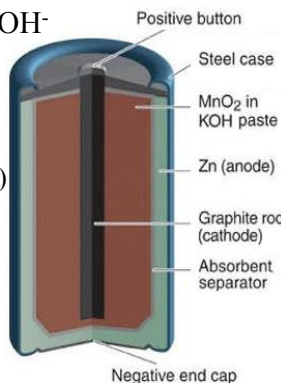


Overall:



Since all reactants and products are solids (dry cell) $\rightarrow Q = 1$

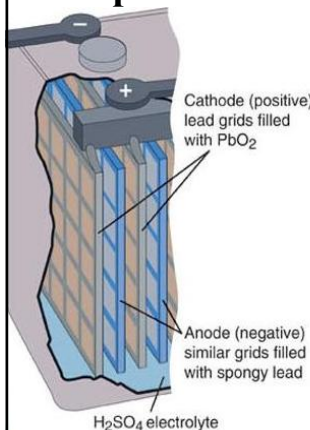
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln 1 = E_{\text{cell}}^{\circ} \approx 1.5 \text{ V}$$



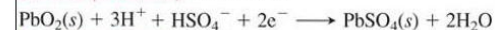
• Secondary cells – can be recharged

- The cell is periodically converted to an electrolytic cell in order to convert some of the products back to reactants

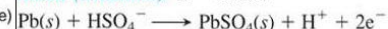
Example: The lead-acid battery



Cathode (reduction): $E^{\circ} = +1.685 \text{ V}$



Anode (oxidation): $E^{\circ} = -0.356 \text{ V}$



Overall (cell) reaction:



$$E_{\text{cell}}^{\circ} = 1.685 - (-0.356) = 2.041 \approx 2 \text{ V}$$

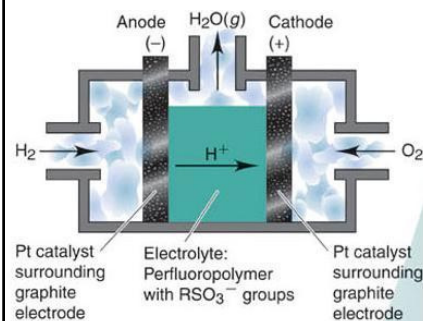
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257}{2} \ln \left(\frac{1}{[\text{H}_2\text{SO}_4]^2} \right)$$

$\rightarrow$ As H_2SO_4 is consumed, E_{cell} drops
 $\Rightarrow$ The cell needs to be recharged

• Fuel cells – use combustion reactions

- The cell must be continuously provided with fuel and oxygen (**flow cells**)

Example: The hydrogen fuel cell



$$E_{\text{cell}}^{\circ} = E_{\text{cath}}^{\circ} - E_{\text{anod}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = 1.23 - (0.00) \approx 1.2 \text{ V}$$

$$Q = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257}{2} \ln Q$$

Anode (oxidation): $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+ + 2\text{e}^-$

Cathode (reduction): $\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}(\text{g})$

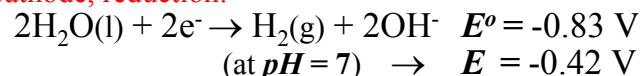
Overall (cell) reaction: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$

$\Rightarrow \uparrow P_{\text{H}_2}$ and $\uparrow P_{\text{O}_2}$
 leads to $\uparrow E_{\text{cell}}$

21.6 Corrosion

- Unwanted oxidation of metals in the environment
- If the metal (M) is in contact with water

Cathode, reduction:

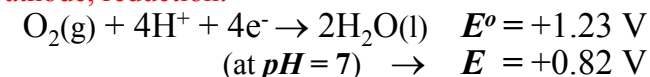


Anode, oxidation:



$\Rightarrow$ Any metal with $E^{\circ} < -0.42 \text{ V}$ can be oxidized by H_2O

Cathode, reduction:



Anode, oxidation:



$\Rightarrow$ Any metal with $E^{\circ} < +0.82 \text{ V}$ can be oxidized by H_2O in the presence of O_2

– At $pH < 7$ (acid rain, etc.), the reduction potentials of H_2O and O_2 are even higher

⇒ Easier oxidation of the metal

Example: Rusting of iron ($Fe \rightarrow E^\circ = -0.44\text{ V}$)

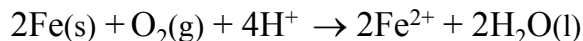
Cathode, reduction:



Anode, oxidation:



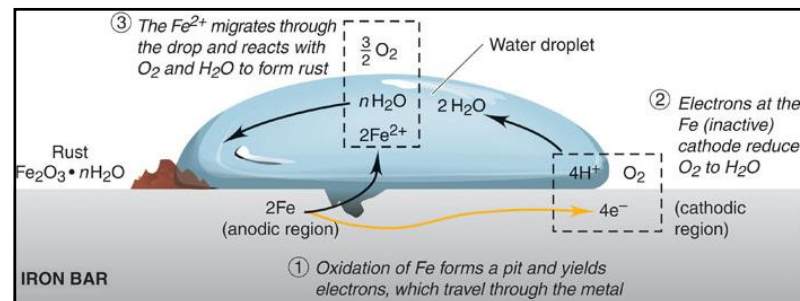
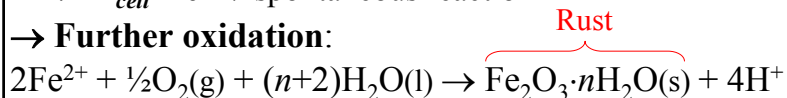
Overall:



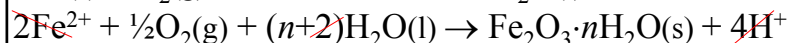
$$E^\circ_{cell} = E^\circ_{cath} - E^\circ_{anod} = +0.82 - (-0.44) = +1.26\text{ V}$$

⇒ $E^\circ_{cell} > 0 \rightarrow$ spontaneous reaction

→ **Further oxidation:**



→ **Overall rusting process:**



→ Corrosion is enhanced by acidic conditions ($\uparrow[H^+]$) and by salty solutions (improved conductivity)

• Corrosion protection

- **Anodic protection** – preoxidation of the metal by formation of a thin layer of protective metal oxide
- **Cathodic protection** – connecting the metal to a more strongly reducing metal with lower E° value called **sacrificial anode**

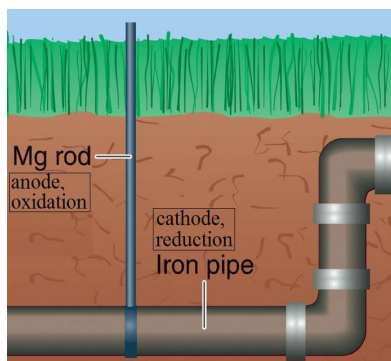
Example: Protecting Fe construction elements by connecting them to blocks of **Mg** or **Al** (sacrificial anodes)

$$E^\circ_{Mg} = -2.36\text{ V}$$

$$E^\circ_{Fe} = -0.44\text{ V}$$

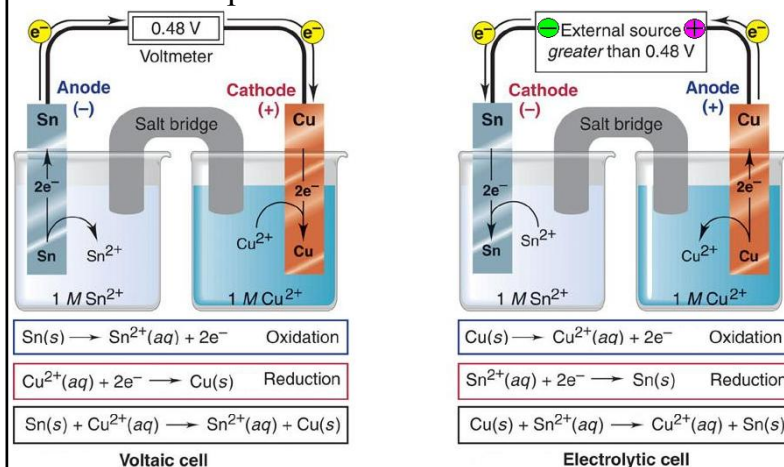
Example: Galvanization of Fe by coating it with Zn

$$E^\circ_{Zn} = -0.76\text{ V}$$



21.7 Electrolytic Cells and Electrolysis

- **Electrolytic cells** – use external electrical source to drive a non-spontaneous reaction



- **Electrolytic cells** act in reverse (non-spontaneous) direction compared to galvanic cells
 - $E^\circ_{\text{cell}} < 0$ and $\Delta G > 0$ (non-spontaneous reaction)
 - The **anode is positive** and the **cathode is negative**
- There are some **similarities** between **electrolytic** and **galvanic** cells
 - **Oxidation** is always on the **anode** and **reduction** is always on the **cathode**
 - Electrons always flow from anode toward cathode

Cell Type	ΔG	E_{cell}	Electrode		
			Name	Process	Sign
Voltaic	<0	>0	Anode	Oxidation	–
			Cathode	Reduction	+
Electrolytic	>0	<0	Anode	Oxidation	+
			Cathode	Reduction	–

- **Electrolysis** – the passage of electrical current through an electrolyte by applying external voltage (the process in electrolytic cells)
 - Electrolysis causes a non-spontaneous reaction (often a splitting of a substance to its elements)
 - The applied voltage must be greater than the cell potential of the reverse spontaneous reaction
 - The electrolyte can be a molten salt or an aqueous electrolyte solution
 - Salt bridges are often not necessary
 - During electrolysis the **cations** are attracted to the **cathode** (negative) and the **anions** are attracted to the **anode** (positive)