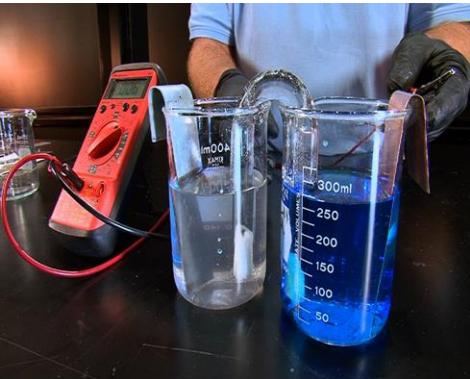


CHAPTER 3:

ELECTROCHEMISTRY

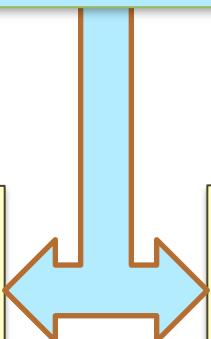


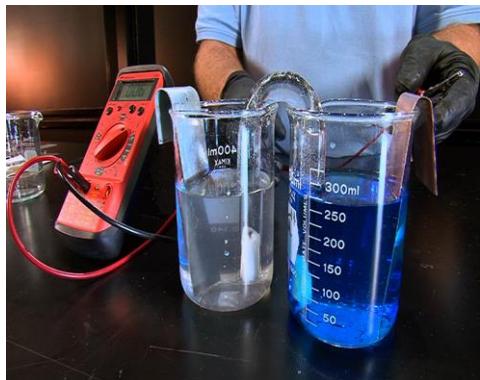
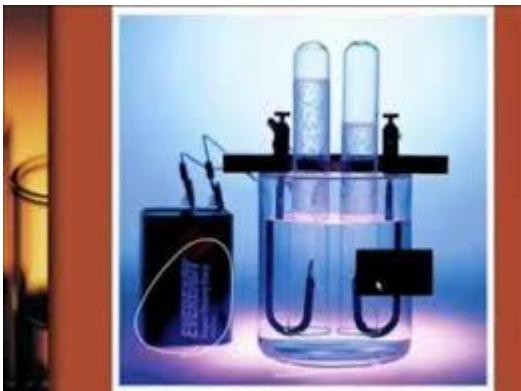
3.0

ELECTROCHEMISTRY

3.1
**Galvanic
Cell**

3.2
**Electrolytic
Cell**





ELECTROCHEMISTRY

3.1 : Galvanic Cell



3.1 GALVANIC CELL

Learning Outcome:

e) Explain hydrogen-oxygen fuel cell (C3)

d) Use the standard reduction /electrode potential values to : (C4)

i) Compare the relative strength of oxidising or reducing agent

ii) Calculate standard cell potential, E°_{cell}

iii) Predict the spontaneity of a redox reaction

c) Construct Standard Reduction/ Electrode Potential Series by using SHE (c3)

f) Write Nernst equation for a given galvanic cell. (C3)

g) Explain the factors that effect cell potential. (C2,C3,C4)

h) Use Nernst equation to determine: (C3)

- i) Cell potential (emf)
- ii) Concentration or partial pressure of a species
- iii) Equilibrium constant (K) when $E_{\text{cell}} = 0$.

i) Predict the spontaneity of cell reaction. (C2,C3)

a) Define : (c1)

- i) Standard reduction/electrode potential
- ii) Standard cell potential, E°_{cell}

Galvanic Cell

b) Describe Standard Hydrogen Electrode (SHE) (c2)

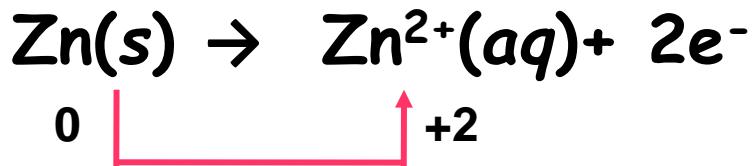
ELECTROCHEMISTRY

- Study of relationship between **chemical change** and **electrical work**

- Two types electrochemistry cells:
 - **Galvanic cell**
(also known as Voltaic cell)

 - **Electrolytic cell**

REDOX: OXIDATION & REDUCTION



OXIDATION

- The loss of electrons
 - Oxidation no. increase
- The oxidation number of Zn increases from 0 to +2
- Zn is the **reducing agent** (species that does the reducing, **giving electrons to the substance being reduced**)

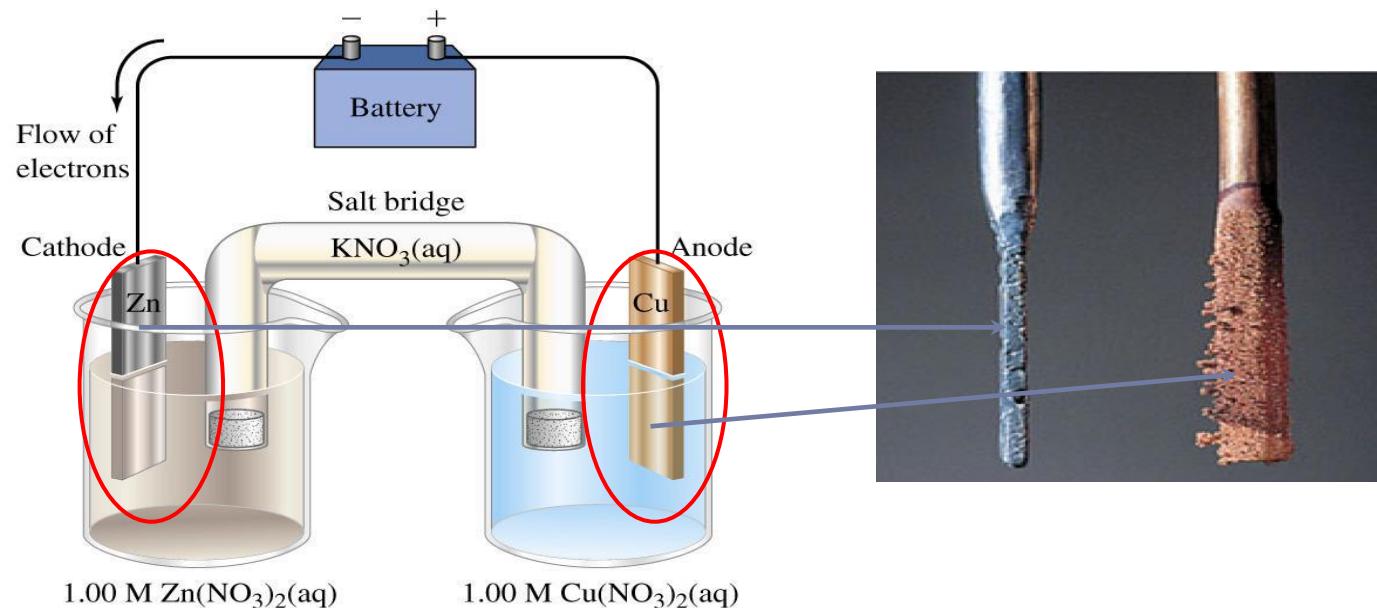
REDUCTION

- The gain of electrons
 - Oxidation no. decrease
- The oxidation number of Cu decreases from +2 to 0
- Cu²⁺ is the **oxidising agent** (species that does the oxidising, **taking electrons from the substance being oxidised**)



ELECTRODES

- Objects that **conduct electricity** between cell and surroundings
- Two electrodes (**anode** and **cathode**) are dipped into an **electrolyte**



TYPES OF ELECTRODES

Types of Electrodes

Active electrode

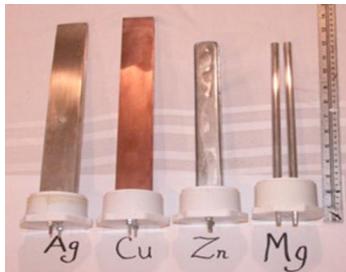
- Involved in half-reaction

EXAMPLE:

zinc (Zn)

copper (Cu)

iron (Fe)



Inactive/Inert electrode

- Do not involve in the half-reaction

EXAMPLE:

graphite (C)

platinum (Pt)





ELECTROLYTE

- Species that can conduct electricity in liquid form (molten) or aqueous solution
- It can be :



- Pure compound.
- EXAMPLE: H_2O , molten salt
- Aqueous solution of salt.
- EXAMPLE: NaCl(aq) , $\text{Na}_2\text{SO}_4(\text{aq})$



GALVANIC CELL/ VOLTAIC CELL

- Use a spontaneous reaction to generate electrical energy
- All batteries contain galvanic cells

The diagram consists of a yellow rectangular box with a red border. Inside the box, the text "Chemical Energy" is positioned on the left, and "Electrical Energy" is positioned on the right. A thick black arrow points from "Chemical Energy" to "Electrical Energy".

Component and Operation of Galvanic cell/ Voltaic Cell

EXAMPLE

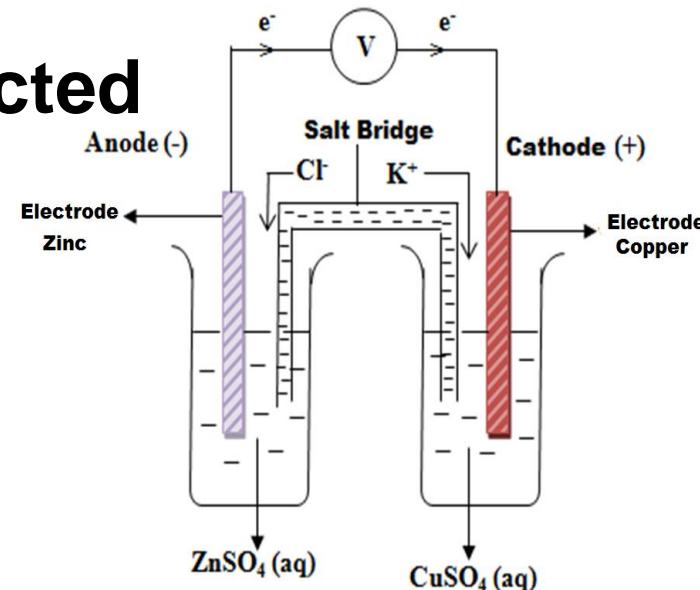
Consists of :

- 1) Zn electrode in an aqueous solution of Zn^{2+}
- 2) Cu electrode in an aqueous solution of Cu^{2+}

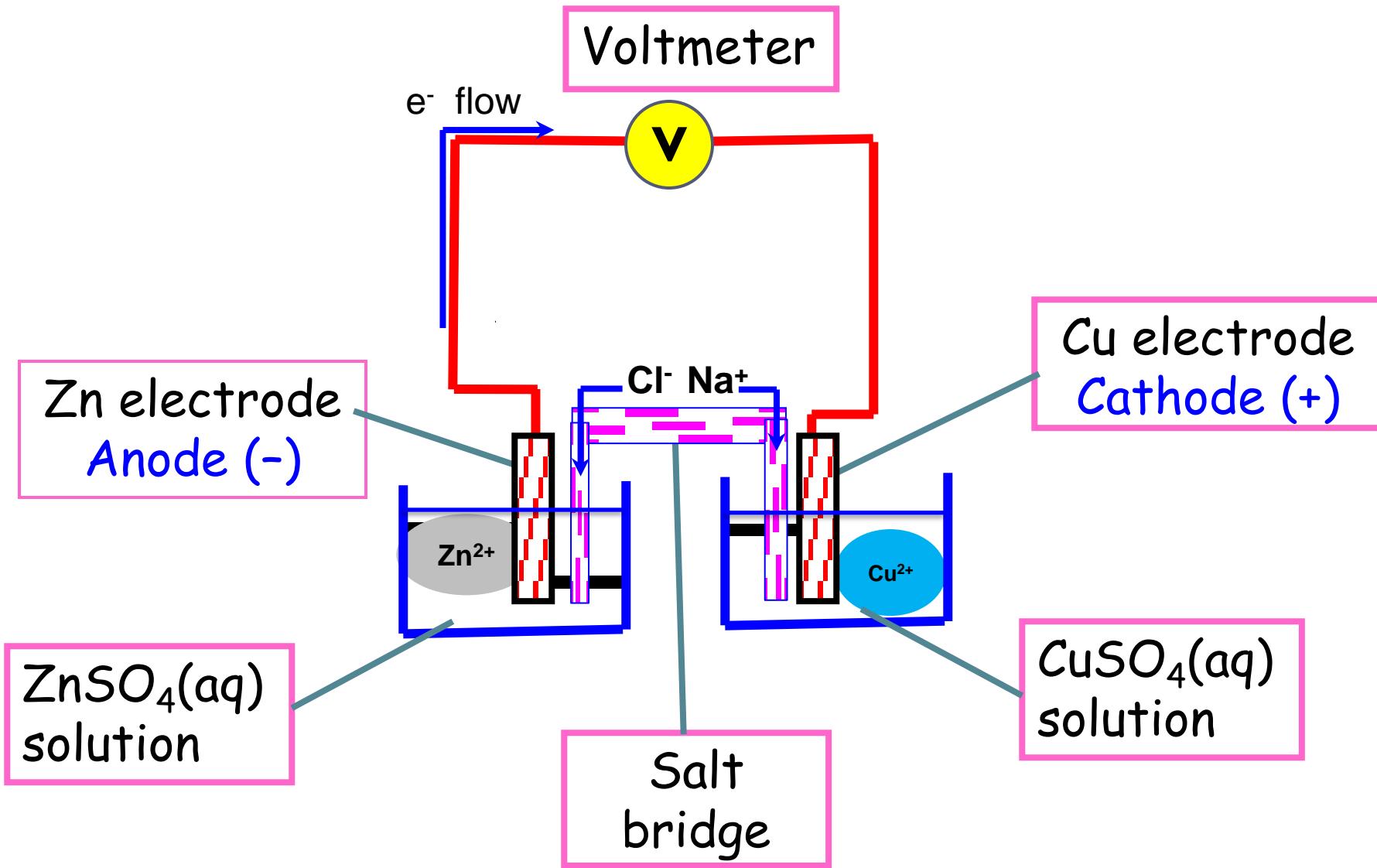
The two electrodes are connected by a wire

The two containers are connected by a salt bridge

A voltmeter is used to detect voltage generated.



Operation of Galvanic cell/ Voltaic cell



What happens at the zinc electrode (anode)?

ANODE

✓ Zn metal (**anode**) immersed in a Zn^{2+} electrolyte (solution of ZnSO_4)

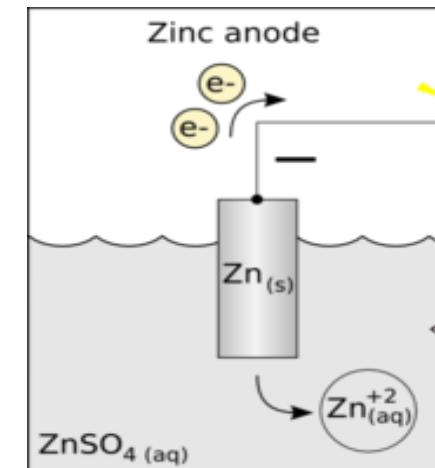
✓ Zn has more tendency to release electrons :



✓ Zn is the negative electrode since it is a source of electrons (**anode**) because **oxidation occur at the electrode**

✓ Zn metal dissolves and the mass of Zn electrode decreases

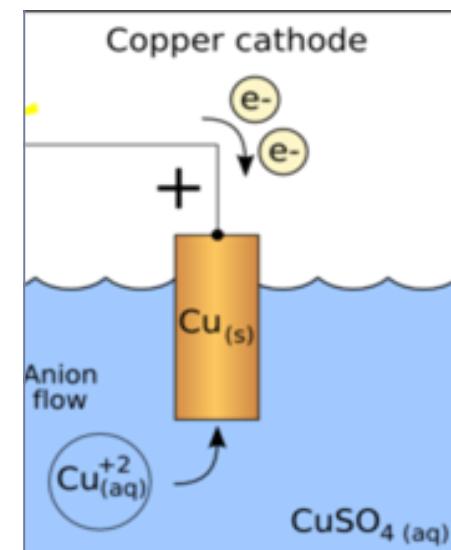
✓ Zn^{2+} ions enter ZnSO_4 solution



What happens at the copper electrode (cathode)?

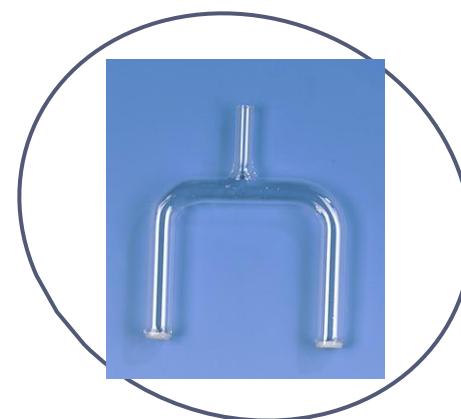
CATHODE

- ✓ Cu metal immersed in a Cu²⁺ electrolyte (CuSO₄ solution)
- ✓ The electrons from the Zn metal moves out through the wire and enter the Cu metal
- ✓ Cu²⁺ ions from the solution accept electrons :
$$\text{Cu}^{2+} \text{ (aq)} + 2\text{e}^- \longrightarrow \text{Cu (s)}$$
- ✓ Cu is the +ve electrode (**cathode**)
- ✓ Reduction occurs at the Cu electrode
- ✓ Cu is deposited at the Cu electrodes
- ✓ The mass of Cu electrode increases



SALT BRIDGE

- Contains a solution of **non reacting ions** such as KCl, KNO₃ and Na₂SO₄.
- Function :
 - i) **to maintain the electrical neutrality of the cell**
 - ii) Acts as a “**liquid wire**” allowing ions to flow and **complete the circuit**



How does the cell maintains its electrical neutrality?

Left Cell (Anode)

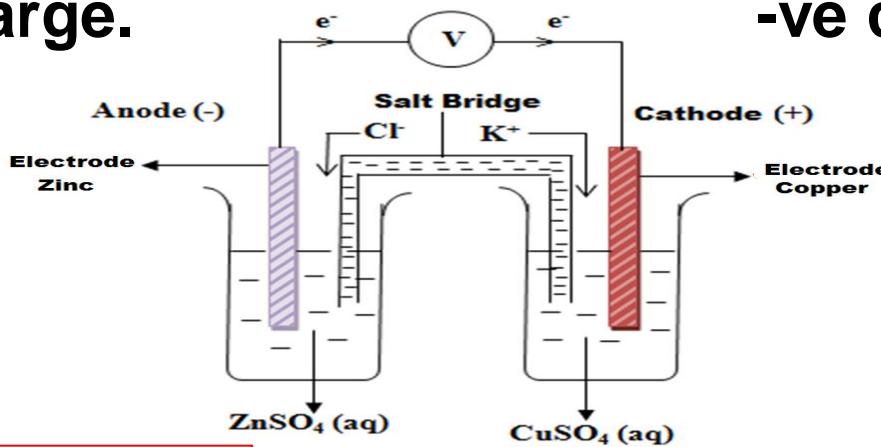


Zn^{2+} ions enter the solution causing an overall excess of +ve charge.

Right Cell (Cathode)



Cu^{2+} ions leave the solution causing an overall excess of -ve charge.

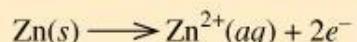
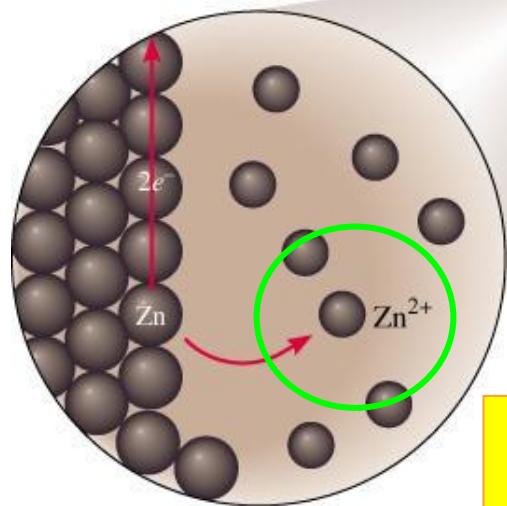


Cl^- ions from salt bridge move into Zn half cell

K^+ ions from salt bridge move into Cu half cell

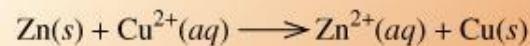
Electrical neutrality is maintained

**anode
oxidation**

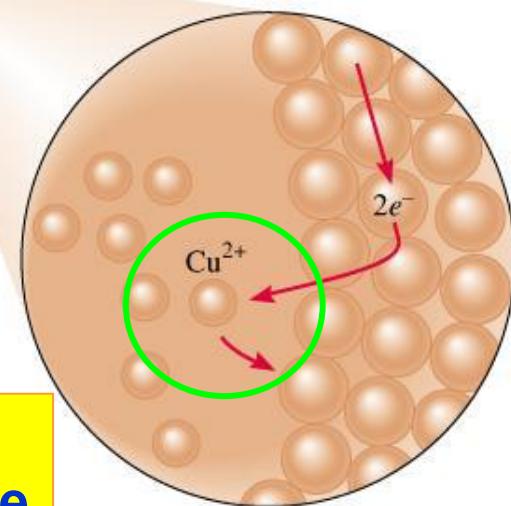


**negative ions
move to anode
half-cell**

Net reaction



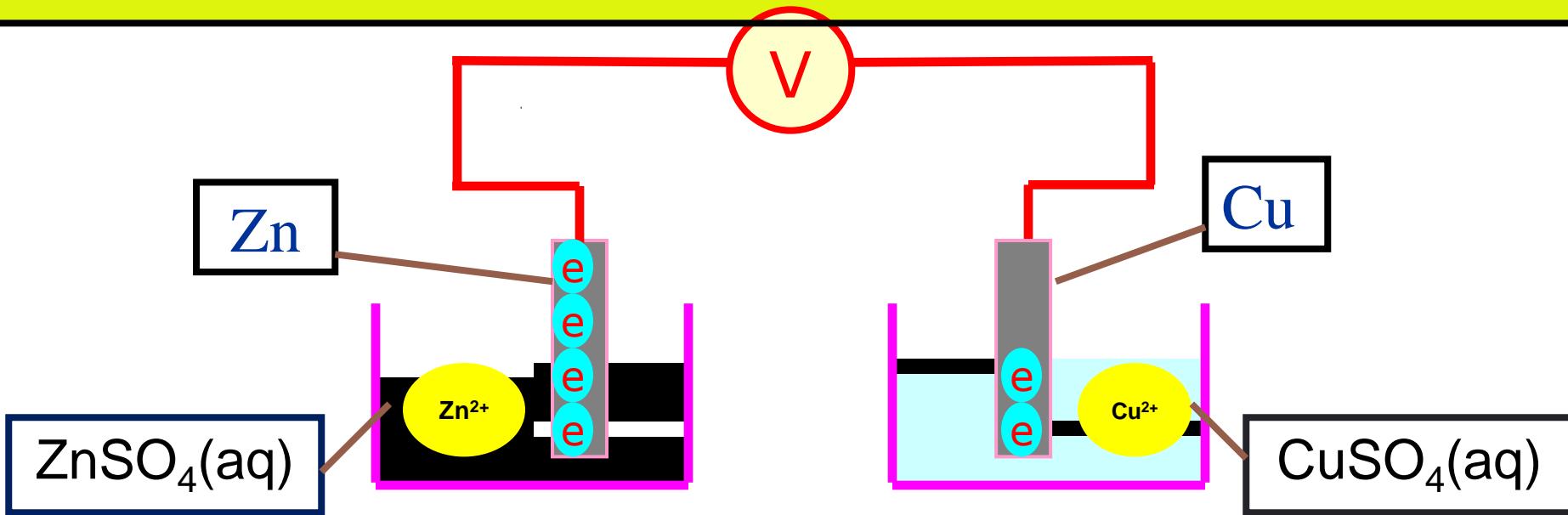
**cathode
reduction**



**positive ions
move to cathode
half-cell**



What happened if there is no salt bridge?



- ☺ As the zinc rod dissolves, the concentration of Zn²⁺ in the left beaker increase.
- ☺ The reaction stops because the nett increase in positive charge is not neutralized.

This excess charge build-up can be reduced by adding a salt bridge.

CELL NOTATION

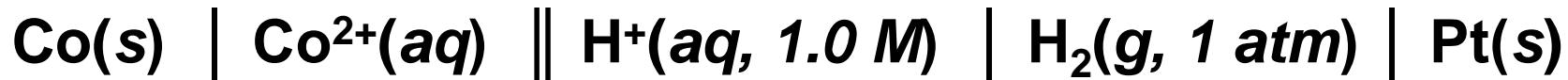
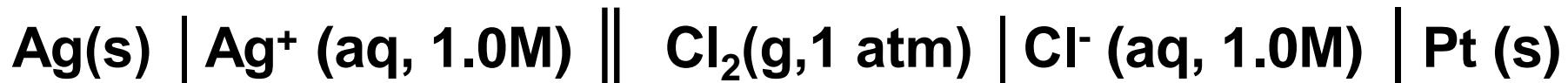
EXAMPLE



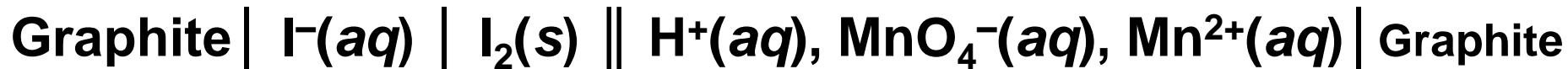
- Anode on the left, cathode on the right
- “|” represent phase boundary
- “||” represent salt bridge
- ✓ Electrodes appear at far right and left of notation

EXAMPLE

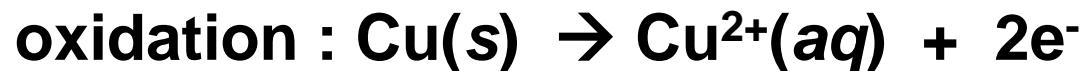
- Use “/” for components that are in different phase



- Use “,” for components that are in same phase



EXAMPLE

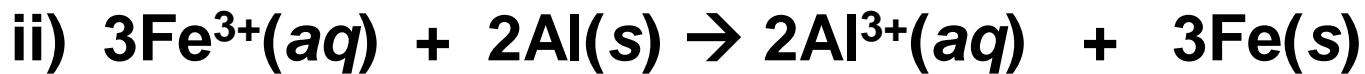


Cell notation:



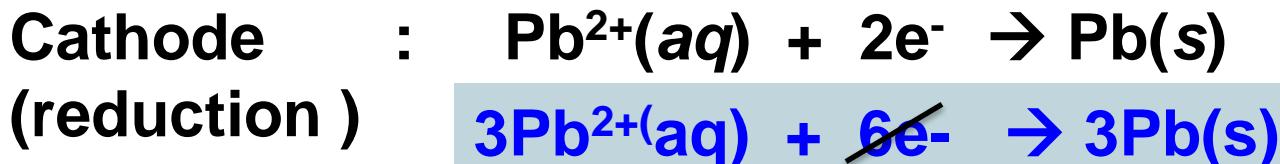
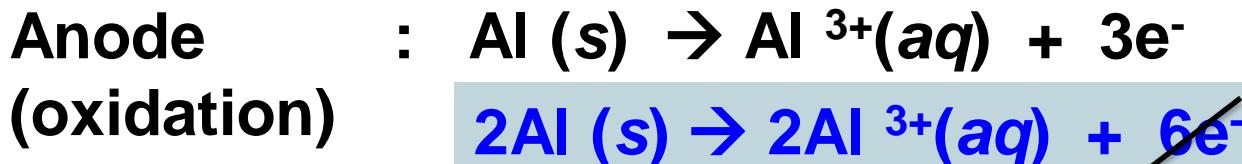
EXAMPLE 1

Write the cell notation for the following redox reactions at standard condition:



EXAMPLE 2

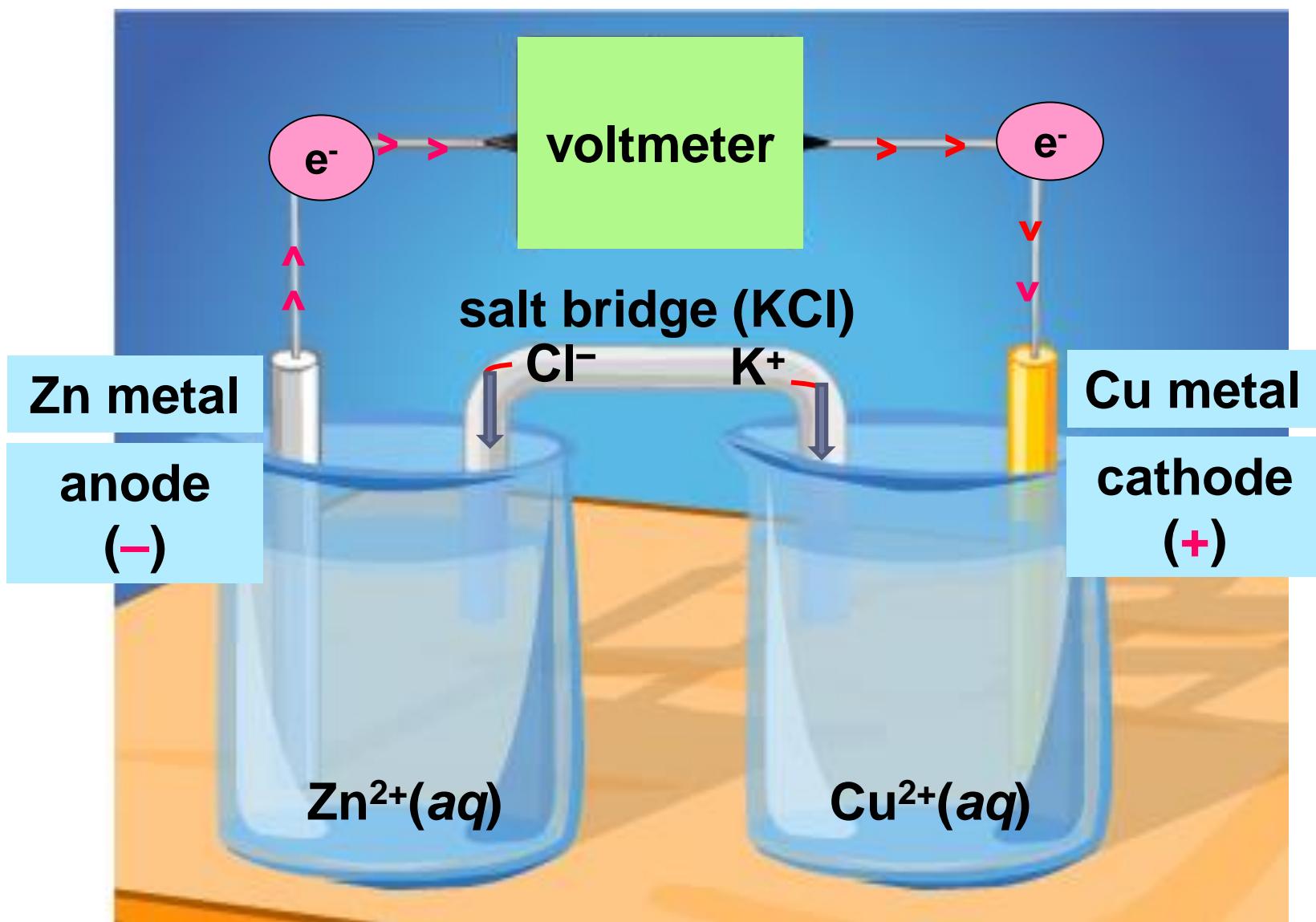
Write the anode and cathode half reactions and overall reactions for the following redox reaction:



STANDARD ELECTRODE POTENTIAL ($E^{\circ}_{\text{half-cell}}$)

A measure of the ability of a half-cell to attract electrons towards it at standard state.

- Standard state: **1 atm for gases**
1 M for solutions
pure solid for electrodes
- The magnitude of the electrode potential depends on the tendency of the metal or non-metal to lose electrons.
- $E^{\circ}_{\text{half-cell}}$ can be E°_{anode} or $E^{\circ}_{\text{cathode}}$



- e⁻ flows from the anode to the cathode because there is a **difference in electrical potential energy** between the electrodes

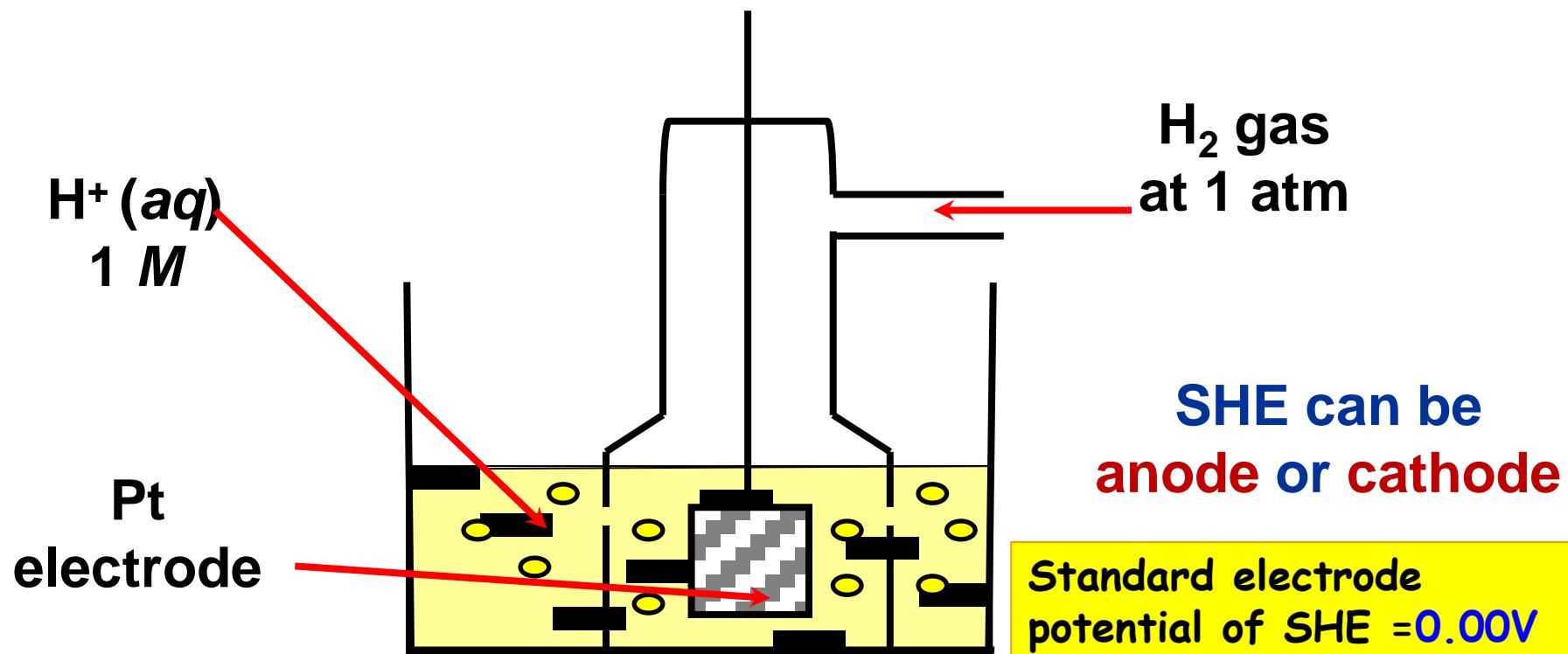
EXAMPLE: Zn / Cu²⁺ cell:



- It is impossible to measure the absolute value of an electrode potential directly.
- The standard hydrogen electrode (SHE) is used as a standard reference to measure the electrode potentials of other half-cells.
- The standard hydrogen electrode, E°_{SHE} = 0.00 V

STANDARD HYDROGEN ELECTRODE (SHE)

Platinum electrode immersed in a 1 M aqueous solution of a strong acid, $\text{H}^+(\text{aq})$ (or $\text{H}_3\text{O}^+(\text{aq})$), through which H_2 gas at 1 atm is bubbled.



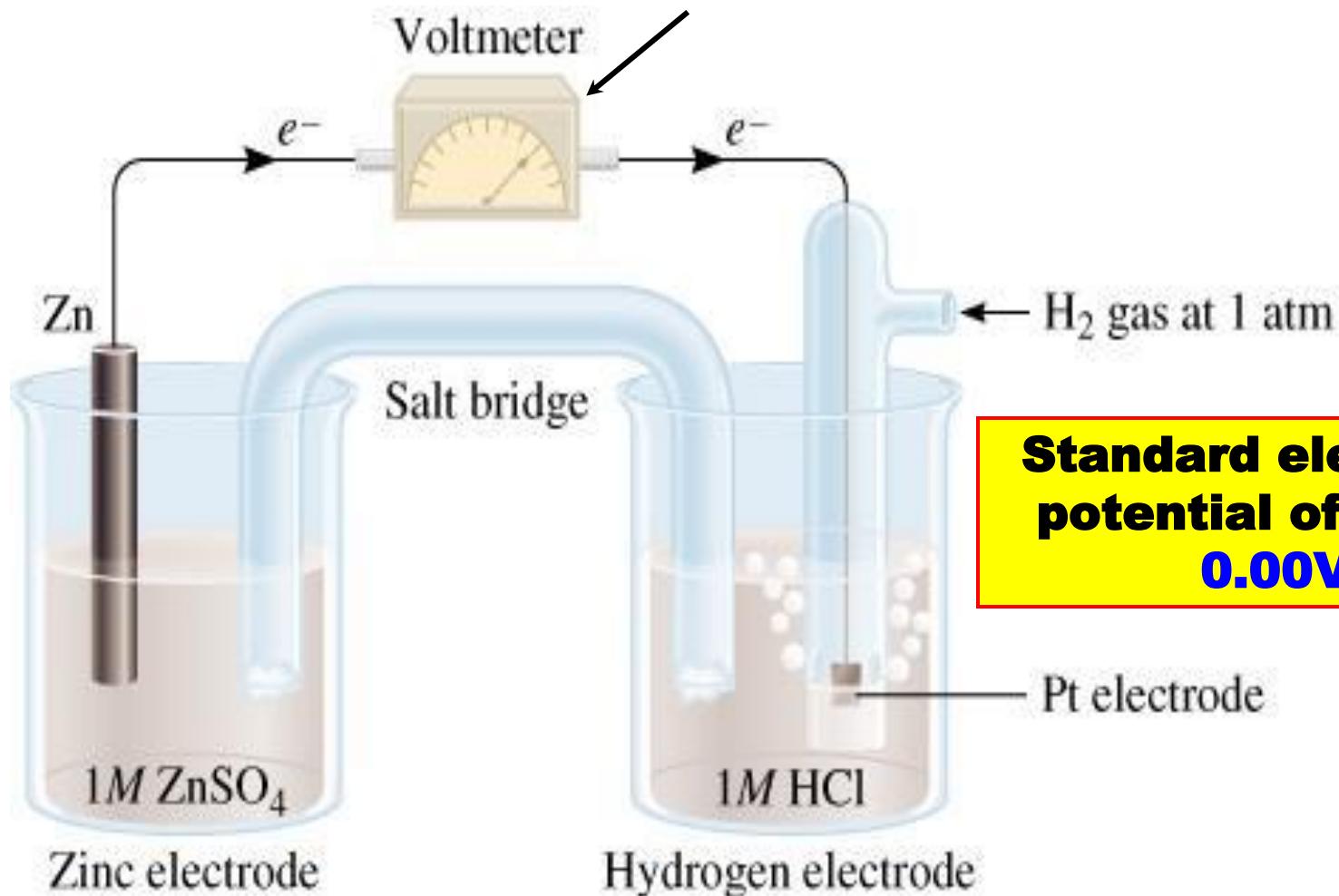
- The standard reduction potential of SHE is assigned exactly 0.00V
- The half-cell equation is given below :



- The direction of the half-reaction of SHE depends on the other half-cell connected to it

EXAMPLE: Determination of the standard reduction potential of Zinc metal (SHE** as cathode)**

$$E^\circ_{\text{cell}} = +0.76$$



EXAMPLE:

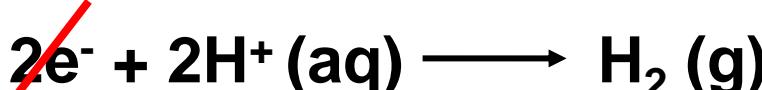


Half-cell equation at:

Anode (oxidation) :



Cathode (reduction):



EXAMPLE: Calculating Standard Reduction Potential of Zn

By using

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$+0.76 \text{ V} = E_{\text{H}^+/\text{H}_2}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$+0.76 \text{ V} = 0.00 \text{ V} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

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

Another method that can be used to calculate standard reduction potential, E_{cell}° :

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + \text{E}_{\text{ox}}^{\circ} \quad \xrightarrow{\text{Change the sign}}$$

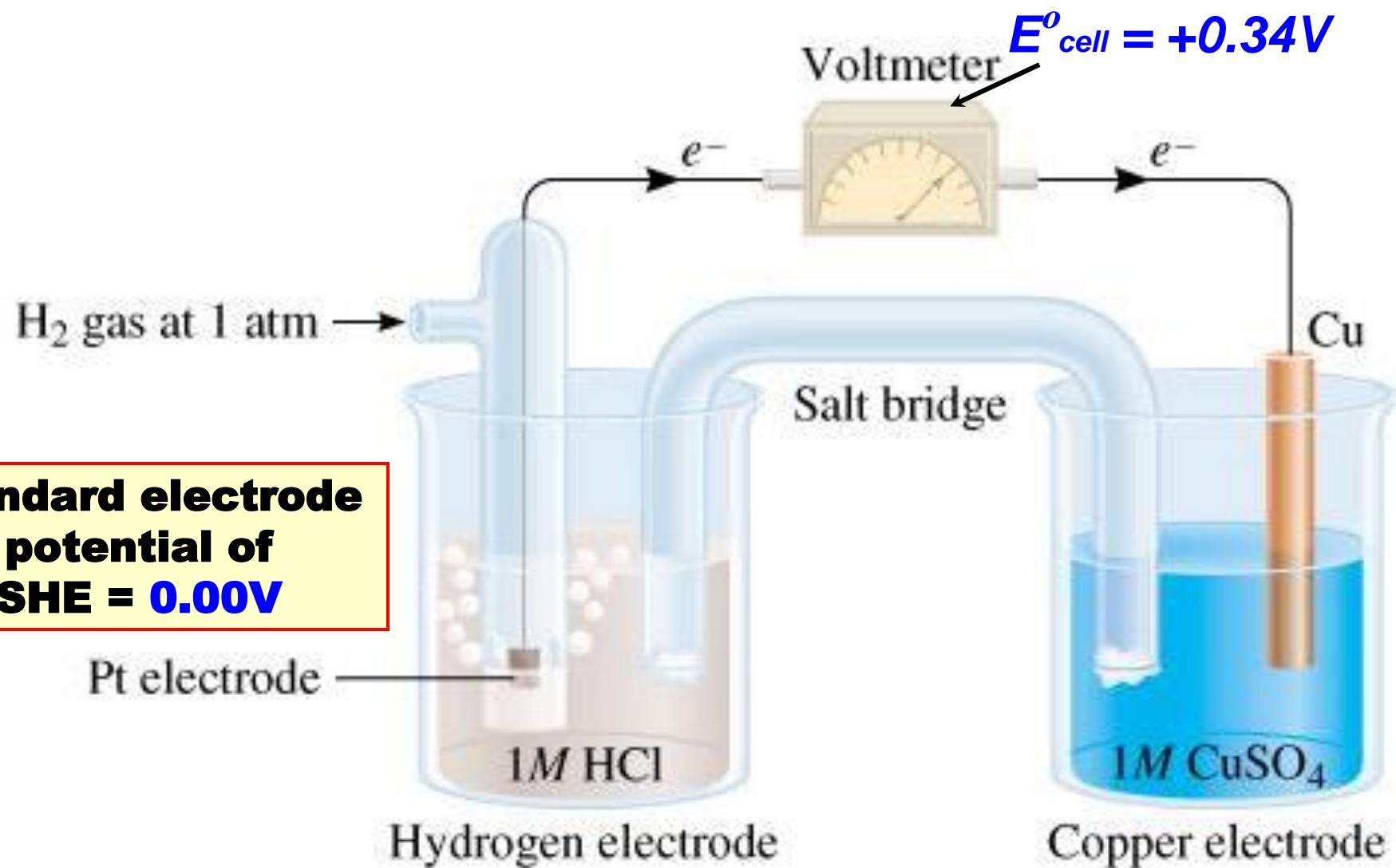
$$+0.76 \text{ V} = E_{\text{H}^+/\text{H}_2}^{\circ} + E_{\text{Zn}/\text{Zn}^{2+}}^{\circ}$$

$$+0.76 \text{ V} = 0.00 \text{ V} + E_{\text{Zn}/\text{Zn}^{2+}}^{\circ}$$

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

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

EXAMPLE: Determination of standard reduction potential of Copper metal (SHE as anode)



EXAMPLE: Pt (s) | H₂ (1 atm) | H⁺ (1 M) || Cu²⁺ (1 M) | Cu (s)

Half-cell equation at:

Anode (oxidation):



Cathode (reduction):



EXAMPLE: Calculating Standard Reduction Potential of Copper

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{H}^+/\text{H}_2}^{\circ}$$

$$+0.34 \text{ V} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - 0.00 \text{ V}$$

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

Another method that can be used to calculate standard reduction potential, E_{cell}[°]:

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ}$$

Change the sign

$$0.34 \text{ V} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + E_{\text{H}_2/\text{H}^+}^{\circ}$$

$$0.34 \text{ V} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - 0.00 \text{ V}$$

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

STANDARD ELECTRODE POTENTIAL TABLE

Each **half-reaction**:

- is written as a **reduction**
- can occur in **either direction**

Standard Reduction Potential (SRP) at 25°C

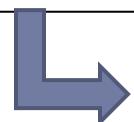
$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.25
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	-0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	-0.31
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Be^{2+}(aq) + 2e^- \rightarrow Be(s)$	-1.85
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	-2.87
$Sr^{2+}(aq) + 2e^- \rightarrow Sr(s)$	-2.89
$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$	-2.90
$K^+(aq) + e^- \rightarrow K(s)$	-2.93
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

at 25°C, the pressure is 1 atm (for gases), and the concentration of electrolyte is 1M.

We can use the value of E° directly from SRP if we use this formula.



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

- Changing the stoichiometric coefficients of a half-cell reaction does not change the value of E°

More positive the E° , higher tendency for reduction (cathode)

More negative the E° , higher tendency for oxidation (anode)

STANDARD CELL POTENTIAL, (E_{cell}°)

- Difference in electrical potential of electrodes measured at a specified temperature (usually 298 K) with all components in their **standard states**
- Also known as **voltage** or **electromotive force (emf)**
- SI unit for Cell Potential
 - **Volt (V)**
 - $1 \text{ V} = 1 \text{ J / C}$
C: Coulomb (SI unit of electrical charge)
- Measured by a voltmeter



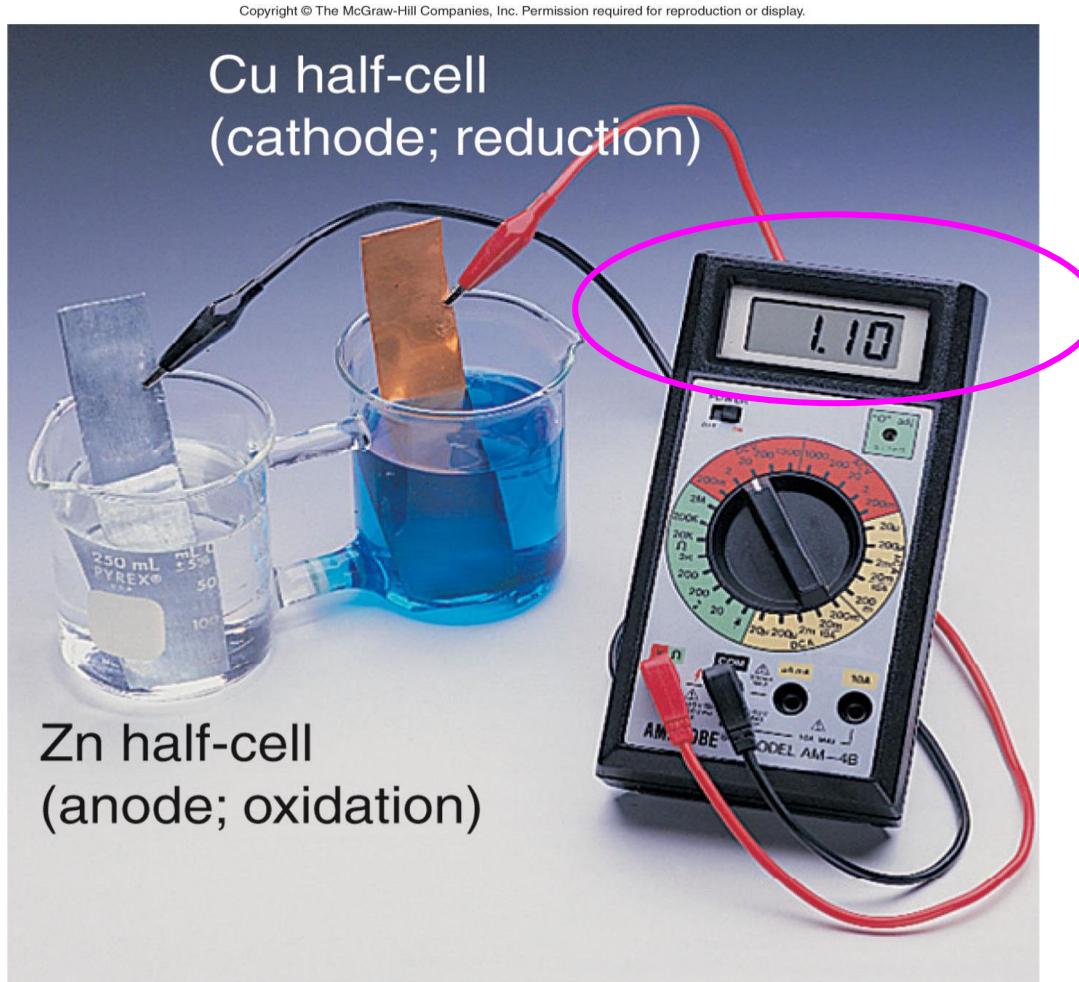
EXAMPLE:



$$E_{\text{cell}}^{\circ} = +1.10\text{ V}$$



$$E_{\text{cell}}^{\circ} = +2.12\text{ V}$$



EXAMPLE 3

Calculate the standard cell potential for the following reaction:



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

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

ANSWER

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

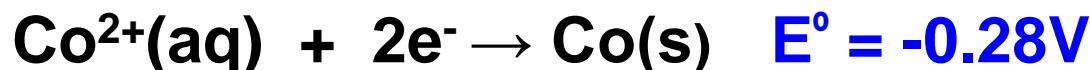
$$= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$= (+0.34 \text{ V}) - (-0.76 \text{ V})$$

$$= 1.10 \text{ V}$$

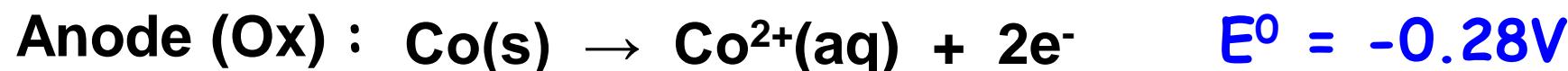
EXAMPLE 4

Calculate the standard cell potential of the following electrochemical cell.



ANSWER

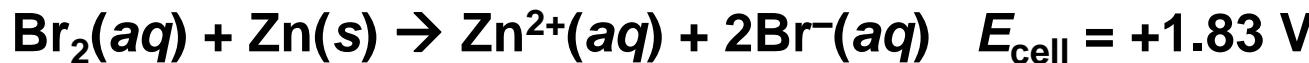
Half-cell equation at:



$$\begin{aligned}E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\&= E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Co}^{2+}/\text{Co}} \\&= (+0.80 \text{ V}) - (-0.28 \text{ V}) \\&= +1.08 \text{ V}\end{aligned}$$

EXAMPLE 5

A voltaic cell houses the reaction between aqueous bromine and zinc metal:



Calculate $E_{\text{Br}_2/\text{Br}^-}$, given $E_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$.

ANSWER

Cathode (Reduction) : $\text{Br}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq}) \quad E_{\text{bromine}}^\circ = ?$

Anode (Oxidation) : $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \quad E_{\text{zinc}}^\circ = -0.76 \text{ V}$

Overall: $\text{Br}_2(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq}) \quad E_{\text{cell}}^\circ = +1.83 \text{ V}$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$= E_{\text{Br}_2/\text{Br}^-}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ$$

$$\begin{aligned} \text{So, } E_{\text{Br}_2/\text{Br}^-}^\circ &= E_{\text{cell}}^\circ + E_{\text{Zn}^{2+}/\text{Zn}}^\circ \\ &= (+1.83 \text{ V}) + (-0.76 \text{ V}) \\ &= +1.07 \text{ V} \end{aligned}$$

RELATIVE STRENGTH OF OXIDIZING AND REDUCING AGENTS

Refer to the list of Standard Reduction Potentials :

Oxidising agent → on the **left side** of the half cell equation

Reducing agent → on the **right side** of the half cell equation

Example:



Oxidising
agent

Reducing
agent

Standard Reduction Potential (SRP) at 25°C

Half-Reaction	$E^\circ(V)$
$\text{F}_2(g) + 2\text{e}^- \rightarrow 2\text{F}^-(aq)$	+2.87
$\text{O}_3(g) + 2\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{O}_2(g) + \text{H}_2\text{O}$	+2.07
$\text{Co}^{3+}(aq) + \text{e}^- \rightarrow \text{Co}^{2+}(aq)$	+1.82
$\text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.77
$\text{PbO}_2(s) + 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2\text{e}^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}$	+1.70
$\text{Ce}^{4+}(aq) + \text{e}^- \rightarrow \text{Ce}^{3+}(aq)$	+1.61
$\text{MnO}_4(aq) + 8\text{H}^+(aq) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}$	+1.51
$\text{Au}^{3+}(aq) + 3\text{e}^- \rightarrow \text{Au}(s)$	+1.50
$\text{Cl}_2(g) + 2\text{e}^- \rightarrow 2\text{Cl}^-(aq)$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}$	+1.33
$\text{MnO}_2(s) + 4\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}$	+1.23
$\text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2(l) + 2\text{e}^- \rightarrow 2\text{Br}^-(aq)$	+1.07
$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3\text{e}^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}$	+0.96
$2\text{Hg}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}(aq)$	+0.92
$\text{Hg}_2^{2+}(aq) + 2\text{e}^- \rightarrow 2\text{Hg}(l)$	+0.85
$\text{Ag}^+(aq) + \text{e}^- \rightarrow \text{Ag}(s)$	+0.80
$\text{Fe}^{3+}(aq) + \text{e}^- \rightarrow \text{Fe}^{2+}(aq)$	+0.77
$\text{O}_2(g) + 2\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2(aq)$	+0.68
$\text{MnO}_4(aq) + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$	+0.59
$\text{I}_2(s) + 2\text{e}^- \rightarrow 2\text{I}^-(aq)$	+0.53
$\text{O}_2(g) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-(aq)$	+0.40
$\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$	+0.34
$\text{AgCl}(s) + \text{e}^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq)$	+0.22
$\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{SO}_2(g) + 2\text{H}_2\text{O}$	+0.20
$\text{Cu}^{2+}(aq) + \text{e}^- \rightarrow \text{Cu}^+(aq)$	+0.15
$\text{Sn}^{4+}(aq) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(aq)$	+0.13
$2\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{H}_2(g)$	0.00
$\text{Pb}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Pb}(s)$	-0.13
$\text{Sn}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Sn}(s)$	-0.14
$\text{Ni}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Ni}(s)$	-0.25
$\text{Co}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Co}(s)$	-0.28
$\text{PbSO}_4(s) + 2\text{e}^- \rightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$	-0.31
$\text{Cd}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cd}(s)$	-0.40
$\text{Fe}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Fe}(s)$	-0.44
$\text{Cr}^{3+}(aq) + 3\text{e}^- \rightarrow \text{Cr}(s)$	-0.74
$\text{Zn}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Zn}(s)$	-0.76
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
$\text{Mn}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Mn}(s)$	-1.18
$\text{Al}^{3+}(aq) + 3\text{e}^- \rightarrow \text{Al}(s)$	-1.66
$\text{Be}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Be}(s)$	-1.85
$\text{Mg}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Mg}(s)$	-2.37
$\text{Na}^+(aq) + \text{e}^- \rightarrow \text{Na}(s)$	-2.71
$\text{Ca}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Ca}(s)$	-2.87
$\text{Sr}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Sr}(s)$	-2.89
$\text{Ba}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Ba}(s)$	-2.90
$\text{K}^+(aq) + \text{e}^- \rightarrow \text{K}(s)$	-2.93
$\text{Li}^+(aq) + \text{e}^- \rightarrow \text{Li}(s)$	-3.05

* For all half-reactions the concentration is 1 M for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

Increasing strength as oxidizing agent

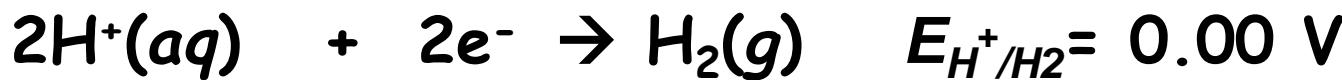
- ❖ All values are relative to hydrogen electrode

- ❖ Strength of oxidizing agent
 - ↗ increase up (more positive)

- ❖ Strength of reducing agent
 - ↗ increase down (more negative)

Increasing strength as reducing agent

EXAMPLE:



Increasing strength as oxidizing agent

The more +ve the value of E° → stronger oxidizing agent

The more -ve the value of E° → stronger reducing agent

Strength of oxidizing agent: $\text{Zn}^{2+} < \text{H}^+ < \text{Cu}^{2+}$

Strength of reducing agent: $\text{Cu} < \text{H}_2 < \text{Zn}$

EXAMPLE 6

Arrange the 3 elements in order of increasing strength of reducing agents



ANSWER



$L < X < Y$

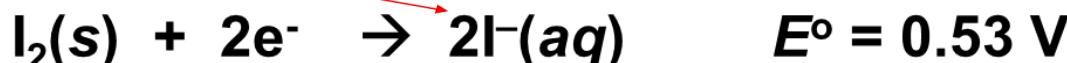
PREDICTING SPONTANEOUS REDOX REACTION USING DIAGONAL RULE

- Under standard-state condition,
- any species on the left side of a given half-cell reaction will react spontaneously with a species that appear on the right of half-cell reaction located below it on the Standard Reduction Potential (SRP) table.
- Steps:

- 1. Write down the two half reactions placing the one with the larger E° up.



- 2. Draw the diagonal from up left pointing to down right

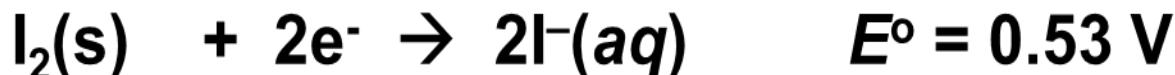


- 3. The species in the up left will react with the species in the products of the down right

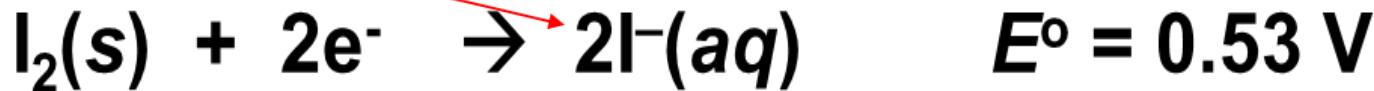
EXAMPLE 7

Predict what will happen if molecular bromine (Br_2) is added to a solution containing Cl^- and I^- at 25°C .

Assume all species are in their standard states.



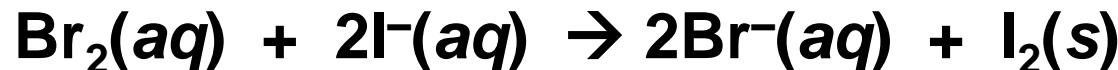
ANSWER



E° of I_2/I^- is more negative ➡ anode (oxidation)

E° of Br_2/Br^- is more positive ➡ cathode (reduction)

Br_2 will react with (oxidize) I^- but will not oxidize Cl^- .



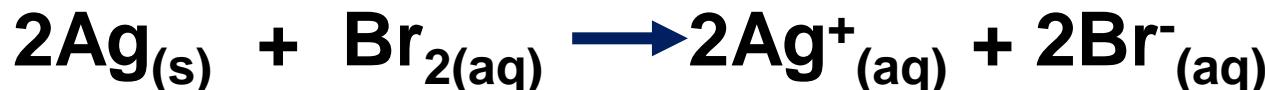
SPONTANEOUS & NON-SPONTANEOUS REACTIONS

- Spontaneous cell reaction when $E_{\text{cell}}^{\circ} > 0$
- Non-spontaneous cell reaction when $E_{\text{cell}}^{\circ} < 0$
- The reaction is at equilibrium when $E_{\text{cell}}^{\circ} = 0$



EXAMPLE 8

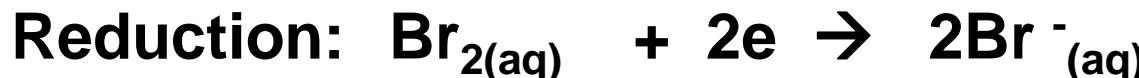
Predict whether the following reactions occur spontaneously :



$$E^{\circ}_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V} \quad E^{\circ}_{\text{Br}_2/\text{Br}^-} = +1.07 \text{ V}$$

ANSWER

Oxidation :



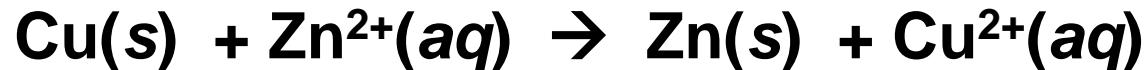
$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= (+1.07 \text{ V}) - 0.80 \text{ V} = +0.27 \text{ V} \end{aligned}$$



The reaction is spontaneous $E^{\circ}_{\text{cell}} > 0$

EXAMPLE 9

Calculate the standard cell potential for the following reaction:

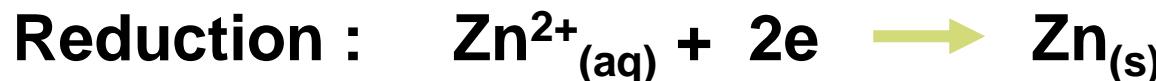


$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

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

Is the reaction spontaneous?

ANSWER



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$= E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} - E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$$

$$= (-0.76 \text{ V}) - (+0.34 \text{ V})$$

$$= -1.10 \text{ V} \quad E_{\text{cell}}^{\circ} < 0$$

So, the reaction is **nonspontaneous**

ELECTROCHEMISTRY

Nernst Equation



Walther Hermann Nernst

1864 - 1941

**German Physical Chemist &
Physicist**

W. Nernst

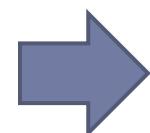
Nernst Equation

Nernst equation can be used to calculate the E_{cell} for any chosen concentration :

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln \frac{[\text{product}]^x}{[\text{reactant}]^y}$$

At 298 K and R = 8.314 J K⁻¹ mol⁻¹, 1 F = 96500 C

$$E_{cell} = E_{cell}^o - \frac{0.0257}{n} 2.303 \log \frac{[\text{product}]^x}{[\text{reactant}]^y}$$



$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log \frac{[\text{product}]^x}{[\text{reactant}]^y}$$

$$Q = \frac{[\text{product}]^x}{[\text{reactant}]^y}$$

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q$$

n = no. of e^- that are involved

Q = reaction quotient

EXAMPLE 1

Consider this electrochemical reaction:



The standard cell potential $E_{\text{cell}}^{\circ} = +0.51 \text{ V}$.

Find the cell potential E_{cell} if the Ni^{2+} concentration is 5.0 M and the Zn^{2+} concentration is 0.050 M.

ANSWER



2 $E_{\text{cell}}^{\circ} = +0.51 \text{ V}$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} \quad n = 2$$

3 $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}$

$$E_{\text{cell}} = (+0.51 \text{ V}) - \left[\frac{0.0592}{2} \log \frac{(0.050)}{(5.0)} \right]$$
$$= +0.57 \text{ V}$$

EXAMPLE 2

An electrochemical cell is represented as,

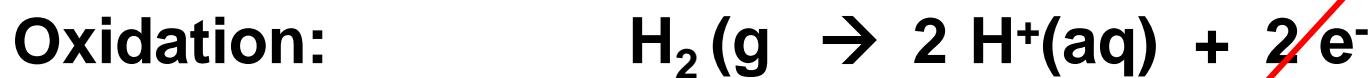


if the value of the cell potential is 1.198V,
determine the concentration of the H^+ solution.

$$E_{\text{H}^+/\text{H}_2}^\circ = 0.00 \text{ V}$$

$$E_{\text{Ag}^+/\text{Ag}}^\circ = + 0.80 \text{ V}$$

ANSWER



② $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
= $(+0.80) - 0.00$
= $+0.80\text{V}$

$$Q = \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 \times P_{\text{H}_2}}$$

n = 2

③ $E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log \left(\frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 \times P_{\text{H}_2}} \right)$

$$+1.198\text{V} = 0.80 - \frac{0.0592}{2} \log \left(\frac{[\text{H}^+]^2}{(1.0)^2 \times (1)} \right)$$

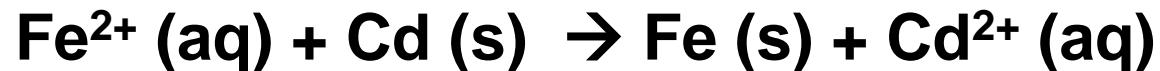
$[\text{H}^+] = 1.9 \times 10^{-7} \text{ M}$

REACTION SPONTANEITY OF A CELL

- The reaction is :
 - 1) At equilibrium when $E_{\text{cell}} = 0$
 - 2) Spontaneous when E_{cell} is positive
 - 3) Nonspontaneous when E_{cell} is negative

EXAMPLE 3

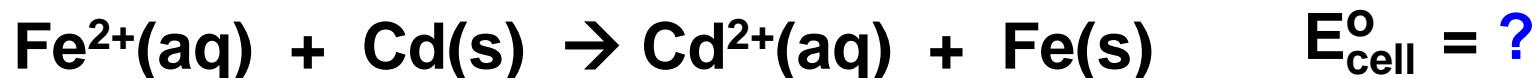
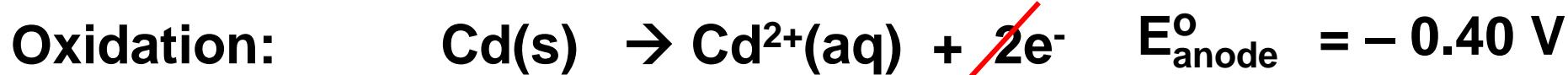
Will the following reaction occur spontaneously at 25°C if $[Fe^{2+}] = 0.60\text{ M}$ and $[Cd^{2+}] = 0.010\text{ M}$?



$$E_{Fe^{2+}/Fe}^{\circ} = -0.44\text{ V}$$

$$E_{Cd^{2+}/Cd}^{\circ} = -0.40\text{ V}$$

ANSWER



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$= E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} - E_{\text{Fe}^{2+}/\text{Fe}}^{\circ}$$

$$= -0.44 \text{ V} - (-0.40 \text{ V})$$

$$= -0.04 \text{ V}$$

From equation, no of electron, n = 2

By using Nernst equation:

$$E_{cell} = E_{cell}^o - \frac{0.0592}{n} \log \frac{[Cd^{2+}]}{[Fe^{2+}]}$$

$$E_{cell} = (-0.04 \text{ V}) - \left(\frac{0.0592}{2} \log \frac{0.010 \text{ M}}{0.60 \text{ M}} \right)$$
$$= +0.013 \text{ V}$$

$E_{cell} > 0$ (E_{cell} is positive)

So, the reaction is spontaneous.

At equilibrium:

- No net reaction occur ($Q=K$)
- $E_{cell} = 0$

$$E_{cell} = E_{cell}^\circ - \frac{0.0592}{n} \log Q$$

$$0 = E_{cell}^\circ - \frac{0.0592}{n} \log K$$

$$E_{cell}^\circ = \frac{0.0592}{n} \log K$$

“dead” battery

- Occurs when the system reaches equilibrium
- No more free energy is released.
The cell can do no more work



EXAMPLE 4

Calculate K for zinc–copper cell.

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

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

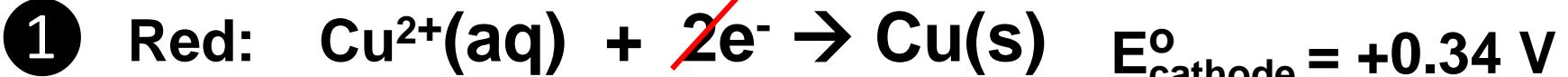
ANSWER



more positive ~~cathode~~ cathode
(reduction)



more negative ~~anode~~ anode
(oxidation)



② $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$$= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}$$

$$= (+0.34 \text{ V}) - (-0.76 \text{ V})$$

$$= +1.10 \text{ V}$$

3 By using Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q \quad n = 2$$

At equilibrium, $Q = K$ and $E_{\text{cell}} = 0$

$$0 = (+1.10 \text{ V}) - \left(\frac{0.0592}{2} \log K \right)$$

$$\log K = \frac{1.10 \times 2}{0.0592} = 37.162$$

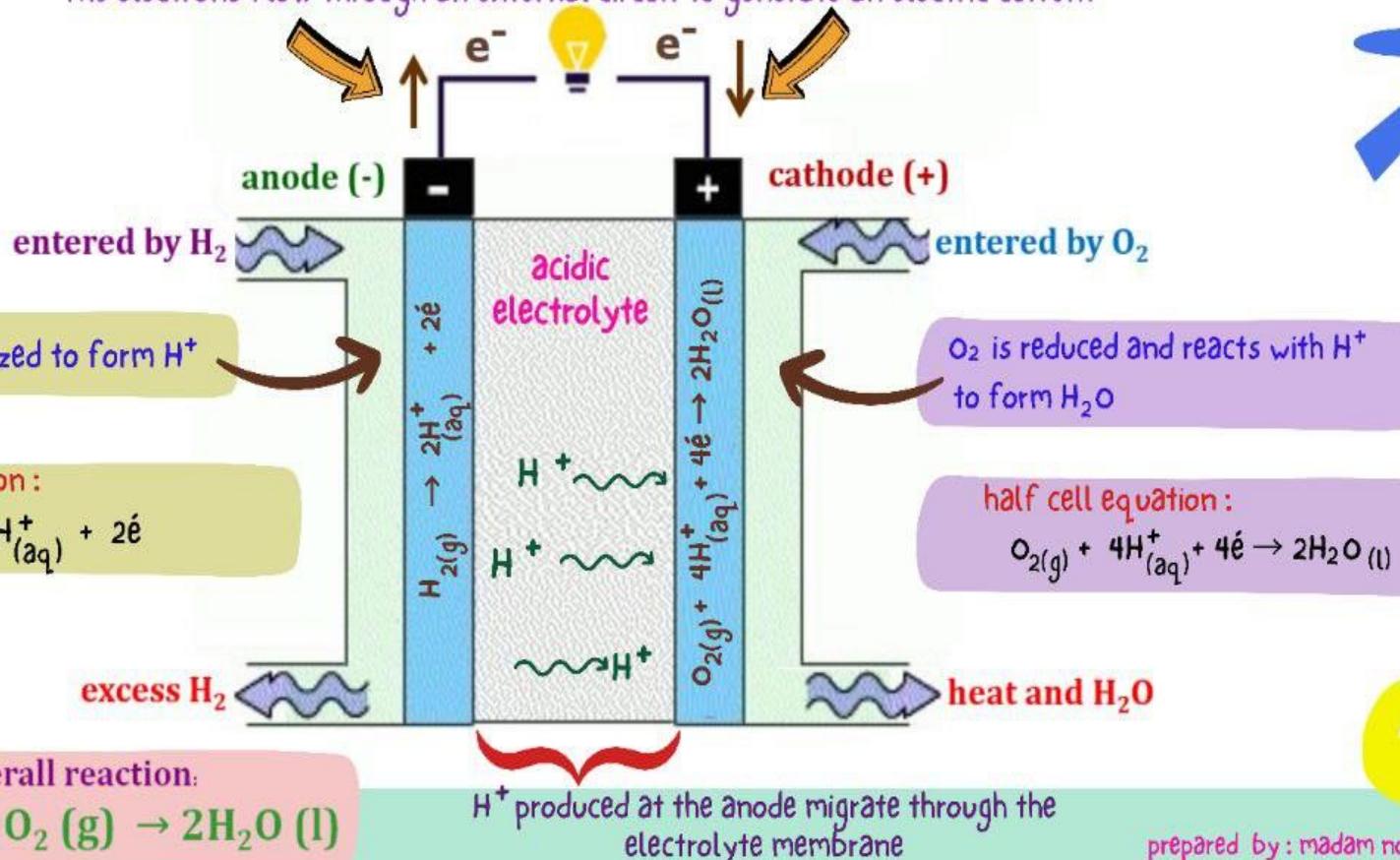
$$K = 1.5 \times 10^{37}$$

Explain hydrogen-oxygen fuel cell.

ACIDIC HYDROGEN-OXYGEN FUEL CELL

Acidic Hydrogen-Oxygen Fuel Cell

The electrons flow through an external circuit to generate an electric current

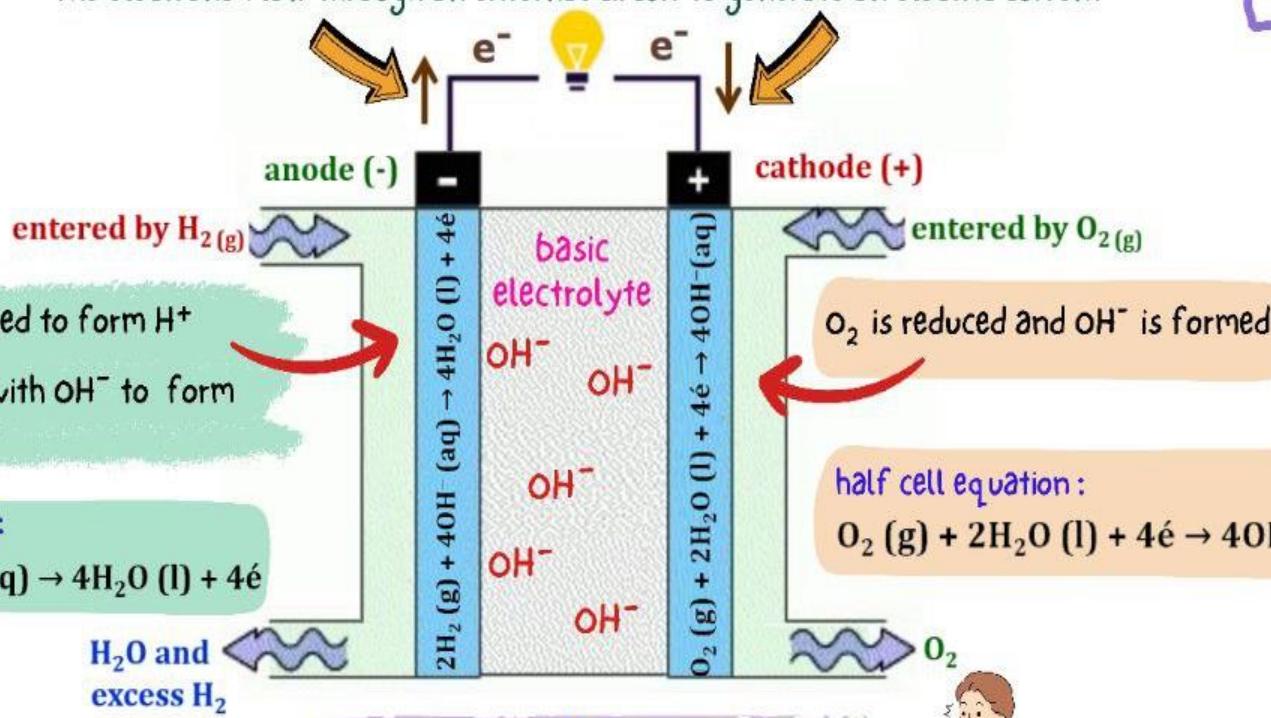


Explain hydrogen-oxygen fuel cell.

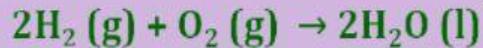
BASIC HYDROGEN-OXYGEN FUEL CELL

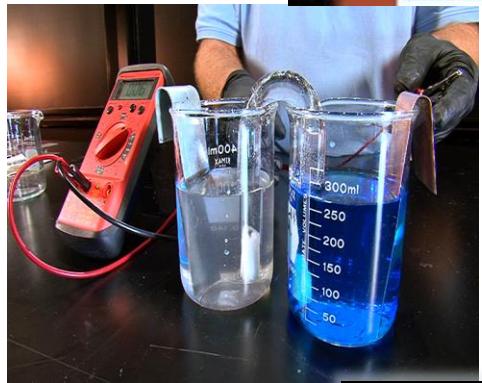
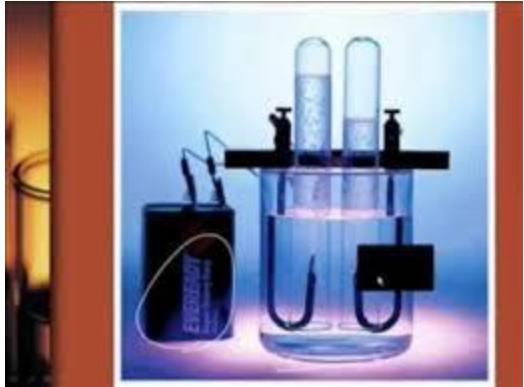
Basic Hydrogen-Oxygen Fuel Cell

The electrons flow through an external circuit to generate an electric current



Overall reaction:





ELECTROCHEMISTRY

3.2: Electrolytic Cell



3.2 ELECTROLYTIC CELL

Learning Outcome:

a) Construct an electrolytic cell (c2)

(b) Explain the operation of an electrolytic cell (c2)

(c) Explain the influence of the factors on selective discharge of a species at the electrode (c2 & c3)

i) Standard reduction potential (SRP) of the species

ii) Concentration of the species

iii) Nature of electrodes (active or inert electrode)

Electrolytic Cell

(f) State Faraday's First Law of electrolysis (c1)

(e) Predict the products of Electrolysis using appropriate examples (c4)

(h) Determine the Faraday's constant experimentally (c3)

(d) Explain the electrolysis of the following electrolytes using inert electrodes (c3 & c4)

i) Molten Salt

ii) Water

iii) Conc. & dilute aqueous NaCl

iv) Aqueous Na_2SO_4

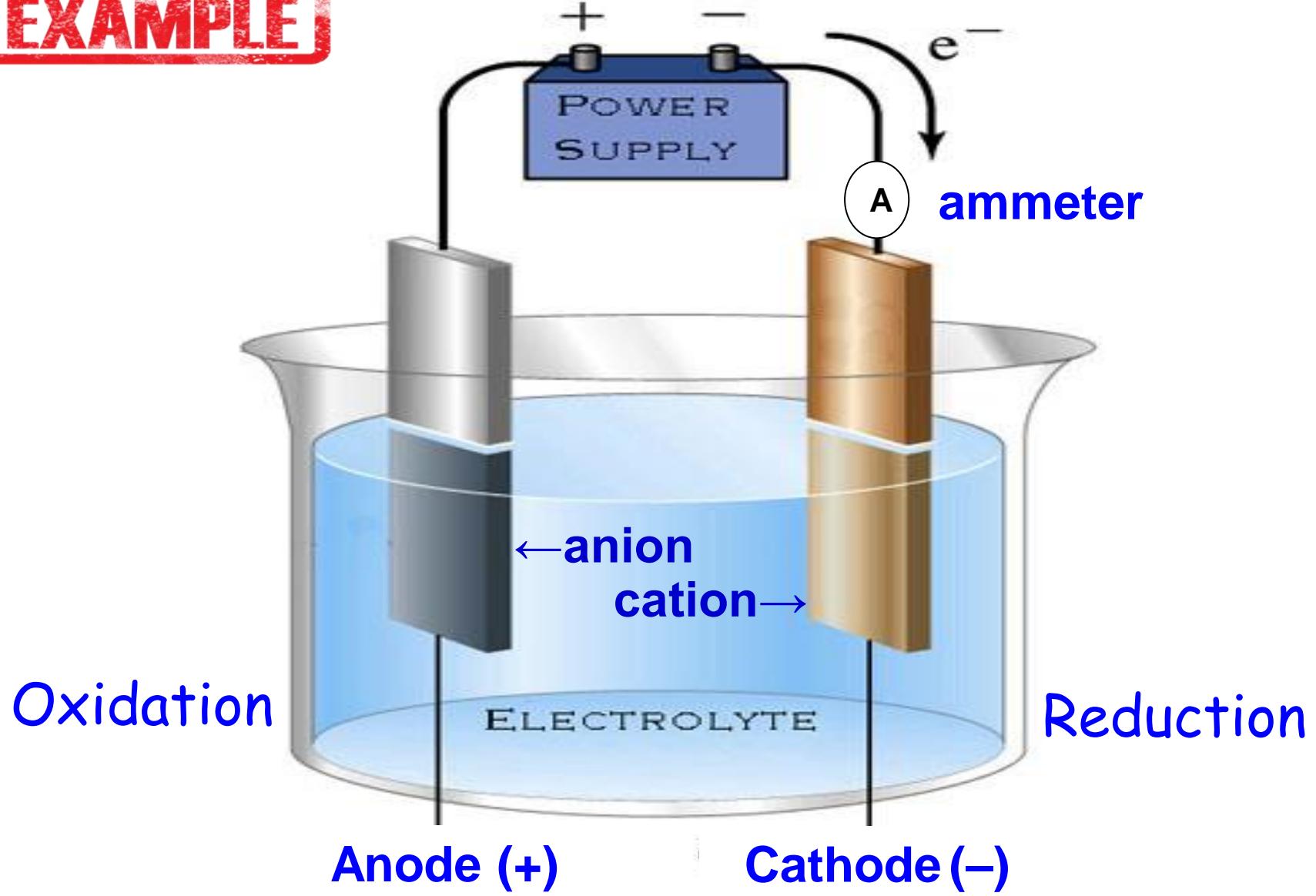
ELECTROLYSIS

- A chemical process that **uses electricity** for a non-spontaneous redox reaction to occur

ELECTROLYTIC CELL

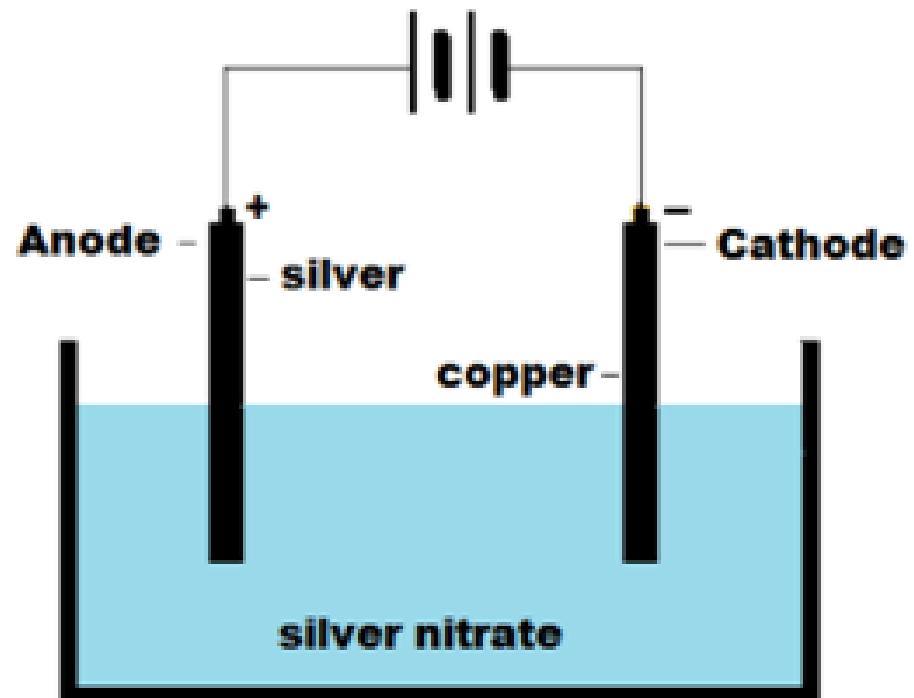
- An **electrolytic cell** is an electrochemical cell that **undergoes a redox reaction when electrical energy is applied.**
- Consists of two electrodes (**anode & cathode**) immersed in an electrolyte and connected to a source of direct current

EXAMPLE

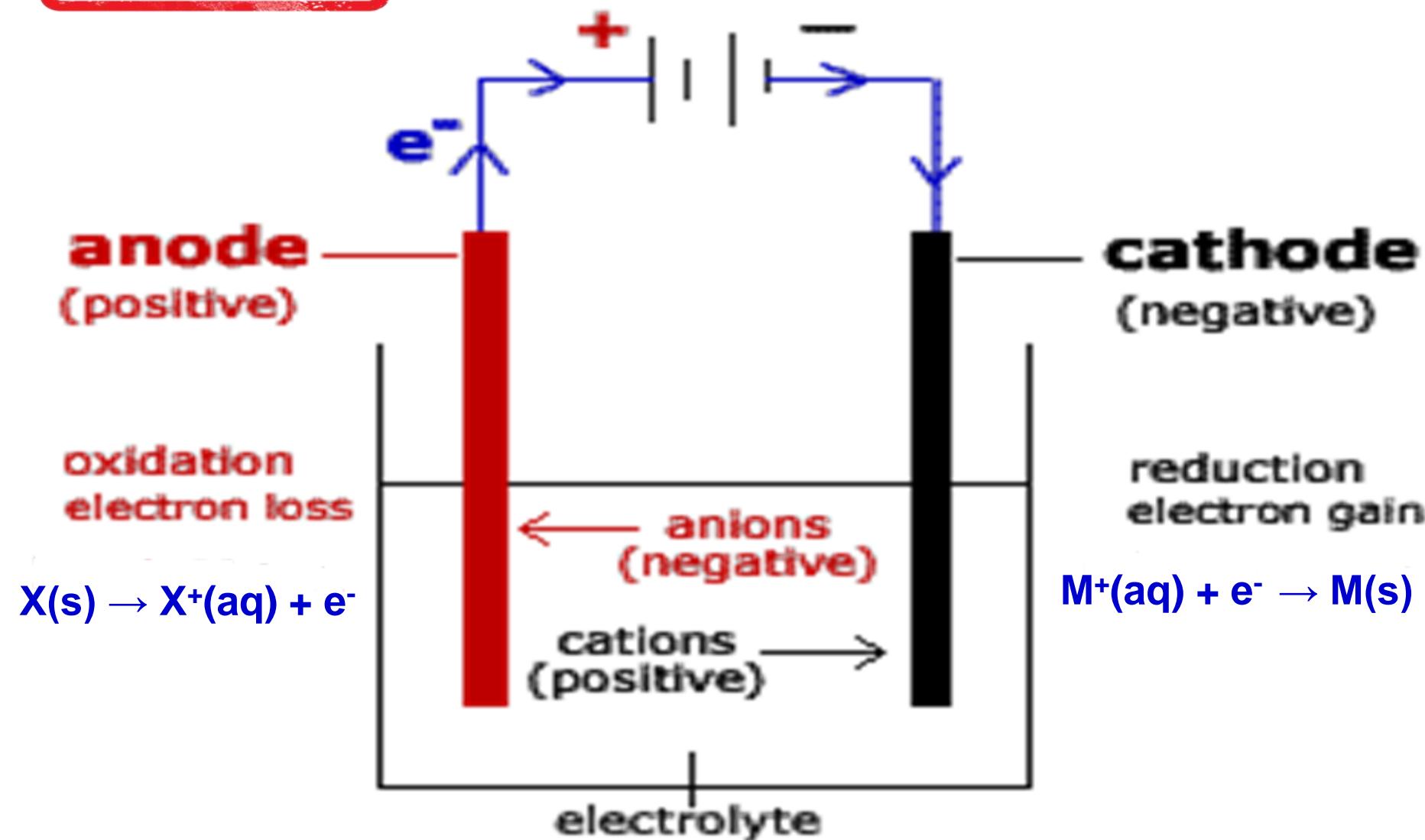


SOURCE OF DIRECT CURRENT

- **Battery** is often used
- **Forces electrons to flow from the anode (+) to cathode (-)**



EXAMPLE



Electrolytic Cell Diagram

How an electrolytic cell operates?

ANODE

- Direct current source supply electrical energy to force the reaction to occur
- negative ions attracted to anode
- ↳ lose e⁻ (oxidation)

CATHODE

- e⁻ travel through the wire from anode (+) to cathode (-)
- positive ions attracted to cathode
- ↳ gain e⁻ (reduction)
- Ions are said to be discharged at the electrodes

Galvanic Cell vs. Electrolytic Cell

Galvanic Cell	Electrolytic Cell
Use a spontaneous reaction to generate electrical energy	Uses electrical energy to drive nonspontaneous reaction
e⁻ generated at anode ☞ negative (-)	e⁻ removes from anode ☞ positive (+)
e⁻ consumed at cathode ☞ positive (+)	e⁻ supplied to cathode ☞ negative (-)
e⁻ flow: from anode (-) to cathode (+)	e⁻ flow: from anode (+) to cathode (-)

FACTORS AFFECTING THE PRODUCTS OF ELECTROLYSIS

- 1 Standard reduction / electrode potential of the species**
- 2 Concentration of the species**
- 3 Nature of electrodes**

STANDARD REDUCTION / ELECTRODE POTENTIAL OF THE SPECIES

- We can use Standard Reduction Potential (SRP) or Electrochemical Series (ECS) to determine anode & cathode.
- When two half-reactions are possible at an electrode:
 - Cathode ↘ reduction (E° more positive)
 - Anode ↗ oxidation (E° more negative)
- In electrolytic cell : ✓ Cation reduced at cathode
✓ Anion oxidized at anode

CONCENTRATIONS OF THE SPECIES

- Affected the discharge of anions only
- Anions with high concentration are preferable to be oxidised

NATURE OF ELECTRODES

- ❖ Affects the ions selected to be discharged at the electrodes
- ❖ Inert electrodes (eg: **graphite, platinum**) are normally use in electrolysis
 - ☞ Do **not involve** in the reaction
- ❖ Active electrodes such as metal (anode) will **dissolve** to form metallic ions, if the electrolyte contains the ions of the same metal





CATIONS : attracted to cathode
(undergo reduction)

1) Active metal: Cations of metal in group (1) and (2), and Al will not be reduced even in high concentration of aqueous solution.

- ☞ E° more negative
- ☞ they are ions of active metal

2) Less active metal: Cations of Au, Ag, Cu, Cr, and Cd will be reduced at cathode.

- ☞ E° more positive

Remember!



ANIONS : attracted to anode (undergo oxidation)

1) Oxoanions : SO_4^{2-} , CO_3^{2-} , NO_3^- and PO_4^{3-} are **not oxidized**

☞ Because the central atom is already in its **highest oxidation state**

2) Halides : I^- , Br^- , Cl^- can be oxidized only at high concentration except for F^- (**very high reactivity**)

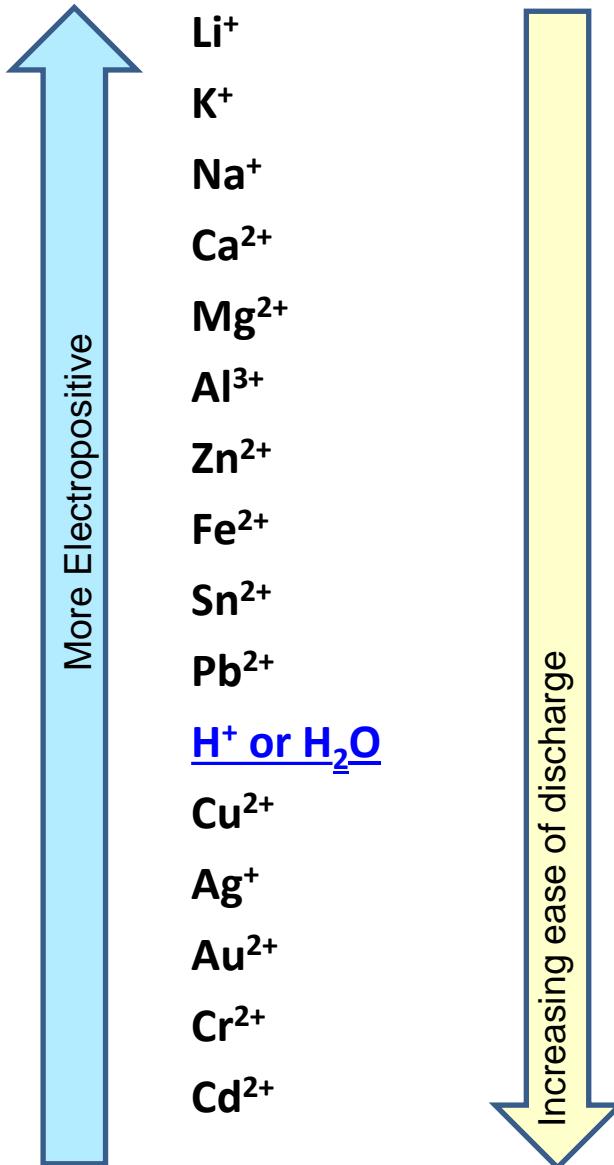
(example concentrated NaCl(aq))

☞ F^- , I^- , Br^- , Cl^- in diluted aqueous solution cannot be oxidized because E° more positive

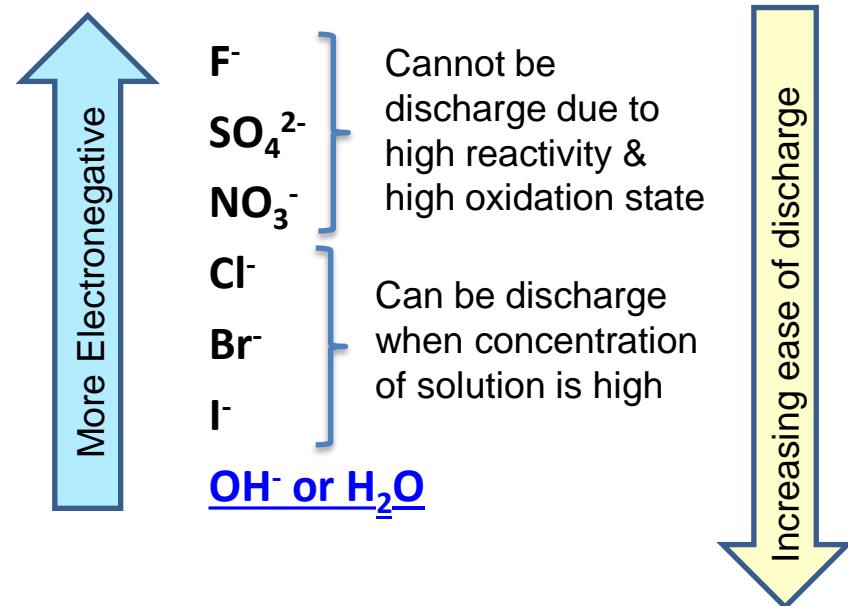
Remember!

ELECTROCHEMICAL SERIES (ECS)

CATHODE : CATION (POSITIVE IONS)



ANODE : ANION (NEGATIVE IONS)



- In electrolytic cell :
 - ✓ Cation **reduced at cathode**
 - ✓ Anion **oxidized at anode**

How
remember
ECS?

<u>Positive Ions</u>		<u>Negative Ions</u>	
K^+	Kalau	F^-	Fahmi
Na^+	Nak	SO_4^{2-}	Sungguh
Ca^{2+}	Kahwin	NO_3^-	Naughty
Mg^{2+}	Mesti	Cl^-	Curi
Al^{3+}	Ada	Br^-	Barang
Zn^{2+}	Zakat	I^-	I
Fe^{2+}	Fitrah	OH^-	Oh
Sn^{2+}	Supaya		
Pb^{2+}	Perkahwinan		
H^+	Hang		
Cu^{2+}	Kekal		
Ag^+	Abadi		

ELECTROLYSIS OF MOLTEN SALTS

- Molten salts contains **cations** and **anions**
- Electrolysis of molten salt requires high temperature

EXAMPLE: Molten sodium chloride, NaCl

Ions present : Na^+ and Cl^-

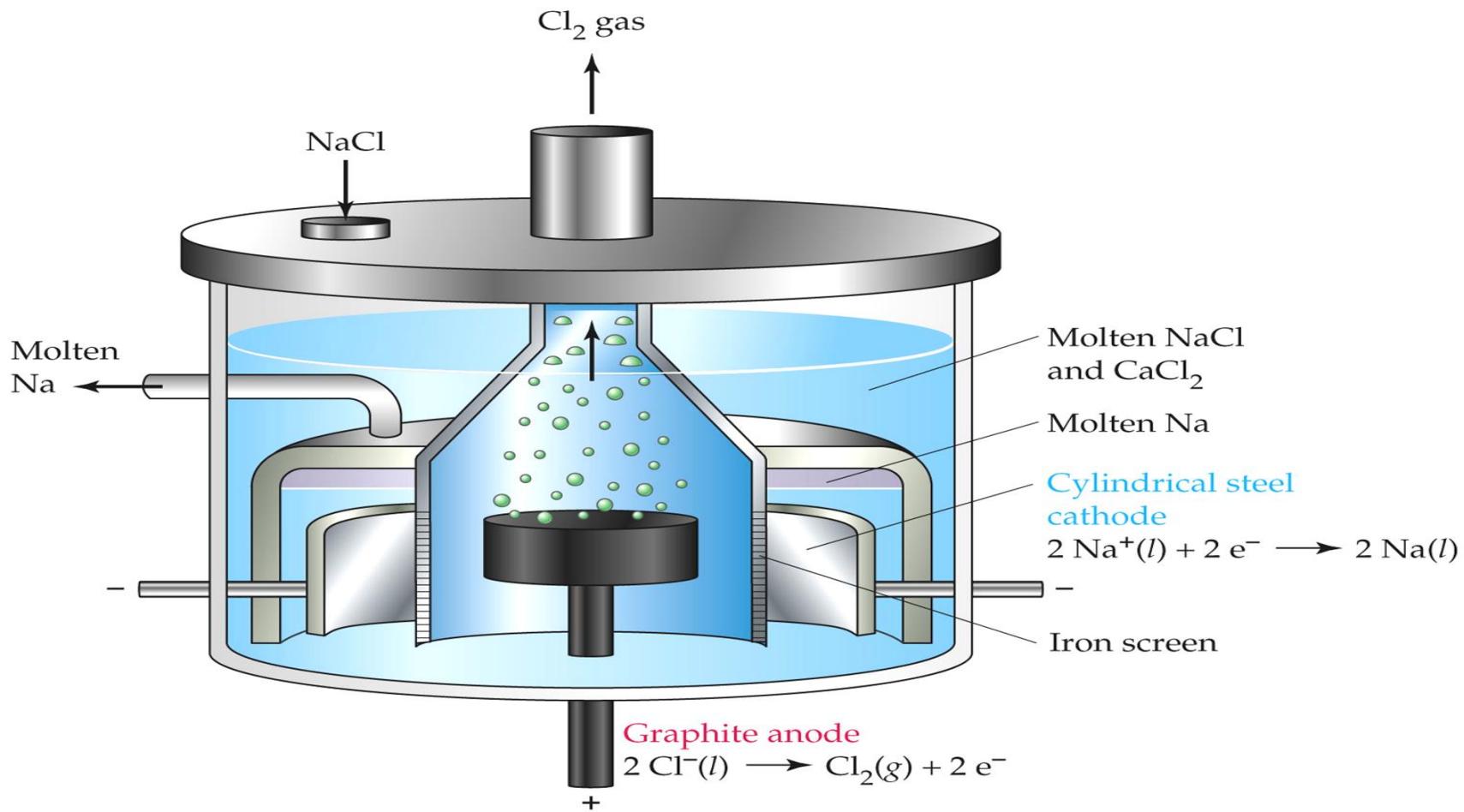


Product formed at cathode : sodium metal (Na) deposited
[liquid at this (high) temperature]

Product formed at anode : chlorine gas (Cl_2) evolved

Application in industry : Electrolysis of molten NaCl

**Electrolysis of molten NaCl is industrially important.
The industrial cell is called ‘Downs Cell’**



EXAMPLE 1

In the electrolysis of molten NaBr,

- (a) What is the product forms at cathode?
- (b) What is the product forms at anode?

ANSWER



Anode (Oxidation):



Cathode (Reduction):

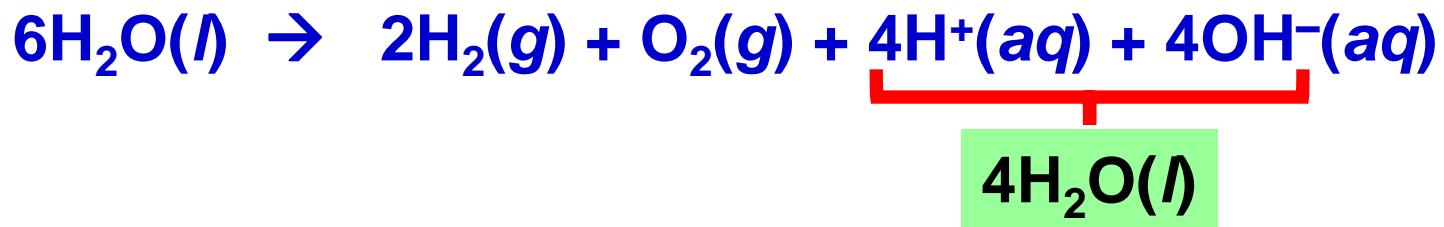
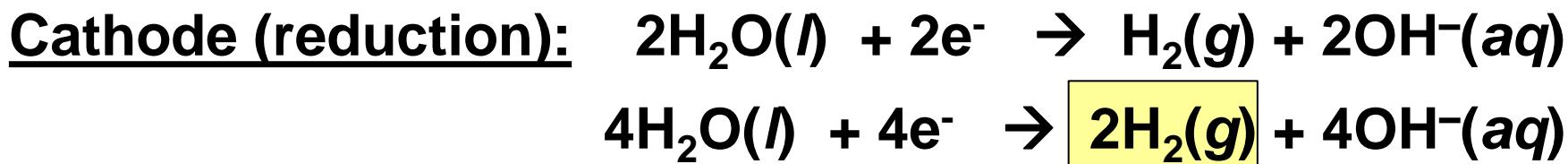


a) Product formed at cathode : sodium metal, $\text{Na}(l)$ deposited

b) Product formed at anode : bromine gas, $\text{Br}_2(g)$ evolved

ELECTROLYSIS OF WATER

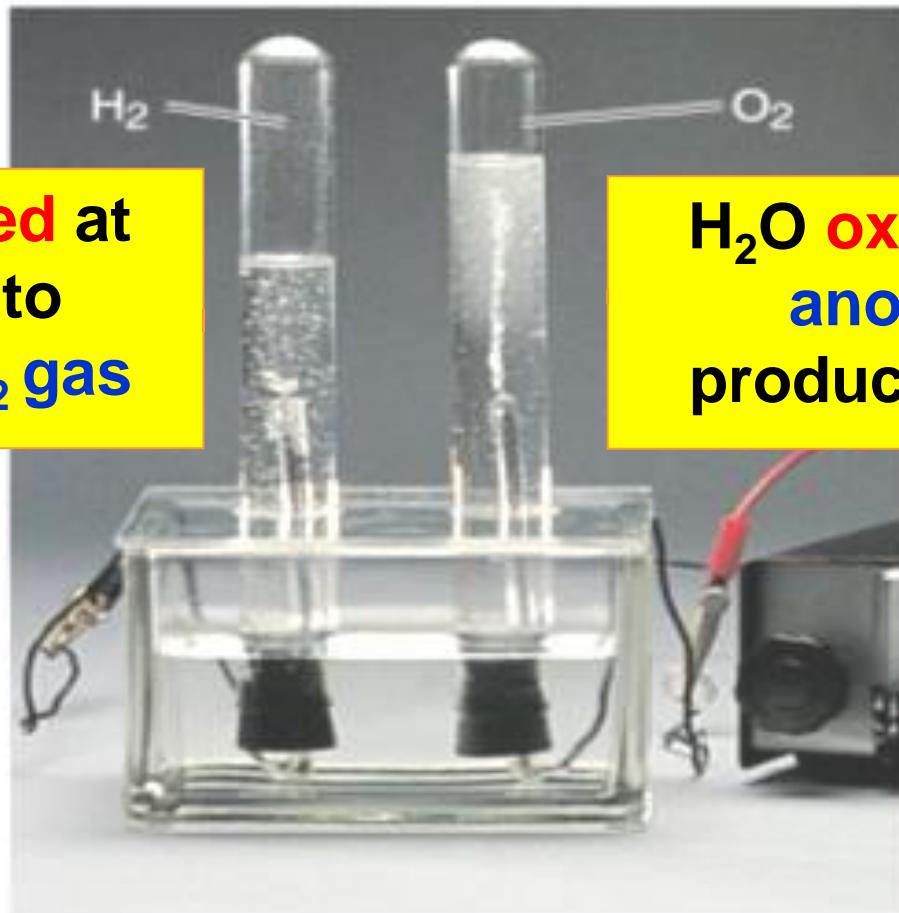
Water is an electro-active substance that may be oxidised or reduced in the process



a) Product formed at cathode : hydrogen gas, H_2 (g) evolved

b) Product formed at anode : oxygen gas, O_2 (g) evolved

ELECTROLYSIS OF WATER



H_2O reduced at
cathode to
produce H_2 gas

H_2O oxidized at
anode to
produce O_2 gas



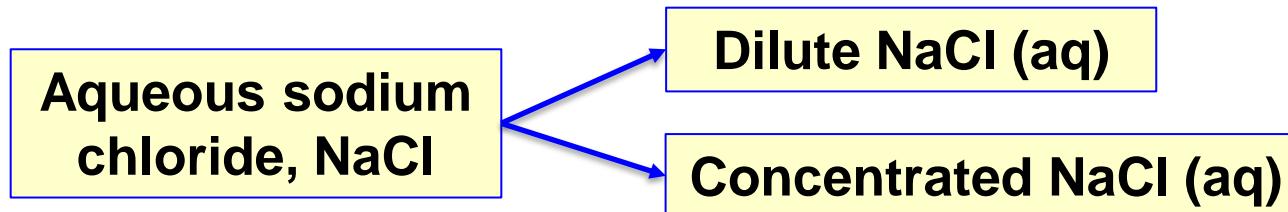
Ratio of H_2 to O_2 = 2 : 1

ELECTROLYSIS OF AQUEOUS SALT

- Aqueous solution of salt are **mixtures** of many species (cations, anions and H₂O)
- We can compare various electrode potentials (E°) to predict electrode **product**
- We can use the electrochemical series by selecting easier to discharge ions.

Electrolysis Of Aqueous NaCl

The **electrolysis of aqueous NaCl depends on the concentration of electrolyte.**



Species present in the solution:

Na^+ , Cl^- and H_2O

During electrolysis,

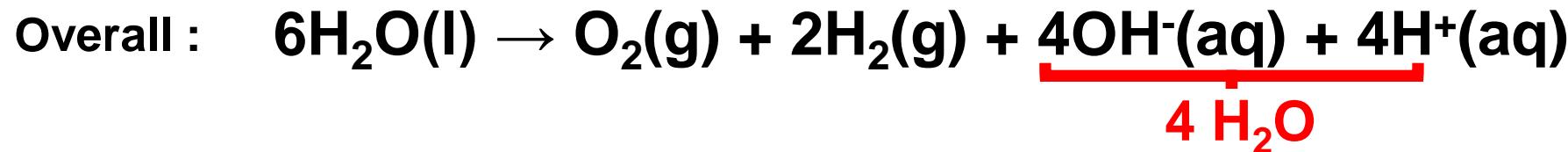
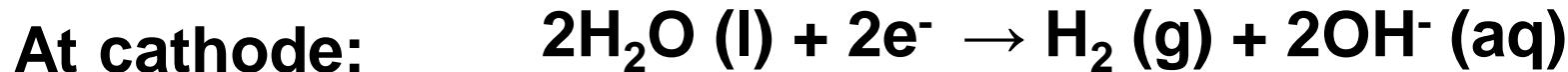
- ✓ the **cathode** attracts Na^+ ion and H_2O molecules
- ✓ the **anode** attracts Cl^- ion and H_2O molecules

Electrolysis of Diluted NaCl solution

Ion Present at Cathode : Na^+ , $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$ will be discharge

Ion Present at Anode : Cl^- , $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$ will be discharge

Reactions involved :

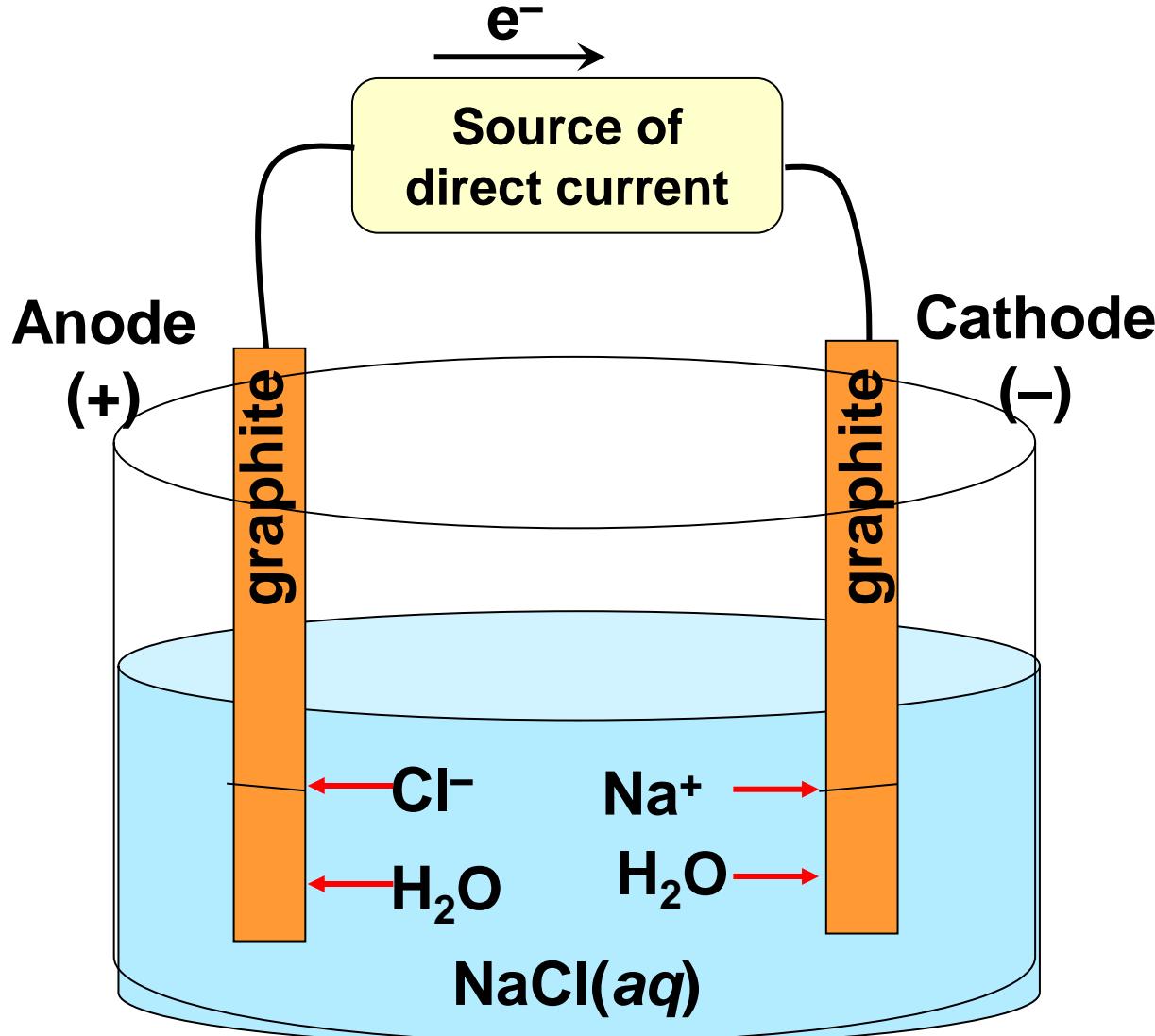


Overall cell equation: $2\text{H}_2\text{O(l)} \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2(\text{g})$

Product formed at cathode : hydrogen gas, $\text{H}_2(\text{g})$ released

Product formed at anode : oxygen gas (O_2) released

Electrolysis of Concentrated NaCl solution



Anode:



Cathode :



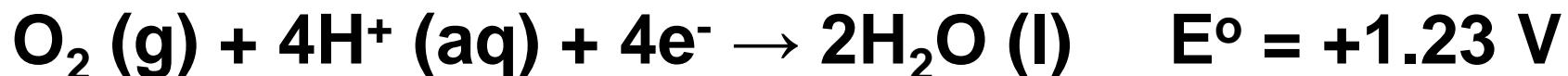
Example : Electrolysis of Concentrated NaCl solution

Cathode :



- ✓ $E^\circ_{\text{Na}^+/\text{Na}}$ is more negative. So, it cannot be reduced.
- ✓ E° for water molecules is more positive.
- ✓ H_2O easier to be reduced.

Anode :



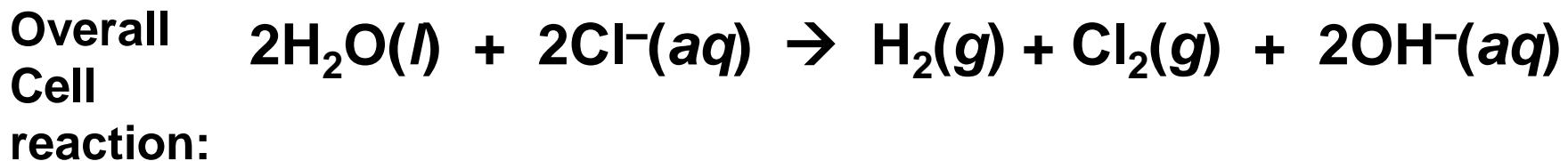
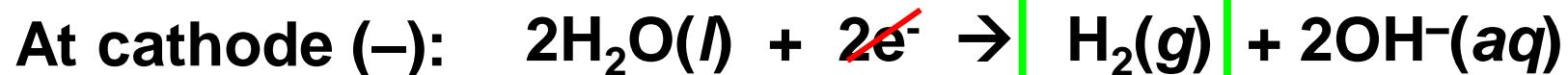
- ✓ In concentrated solution, chloride ions will be oxidised because of its high concentration.

Electrolysis of Concentrated NaCl solution

Ion Present at Cathode : Na^+ , $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$ will be discharge

Ion Present at Anode : Cl^- , $\text{H}_2\text{O} \rightarrow \text{Cl}^-$ will be discharge because concentration of Cl^- is high

Reactions involved :



Product formed:

At cathode : hydrogen gas, $\text{H}_2(g)$ released

At anode : chlorine gas, $\text{Cl}_2(g)$ released

EXAMPLE 3

Predict the electrolysis reaction when an aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes.

Electrolysis of Diluted / Concentrated Na_2SO_4 solution

Ion Present at Cathode : Na^+ , $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$ will be discharge

Ion Present at Anode : SO_4^{2-} , $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$ will be discharge, SO_4^{2-} ions (an oxoanion) are not oxidized because sulphur already at its highest oxidation state (+6).

Equation :



Anode :

O_2 gas is release and the solution become acidic at anode because H^+ ions are formed



Cathode :

H_2 gas is release and the solution become basic at cathode because OH^- ions are formed

Exercise:

1. Predict the electrolysis reaction when a concentrated aqueous solution of KF is electrolysed using graphite electrodes.

2. Predict the electrolysis reaction when a molten of KCl is electrolysed using platinum electrodes.

3. Predict the electrolysis reaction when a aqueous solution of MgBr₂ is electrolysed using graphite electrodes.

4. Predict the electrolysis reaction when a concentrated aqueous solution of NaNO₃ is electrolysed using graphite electrodes.

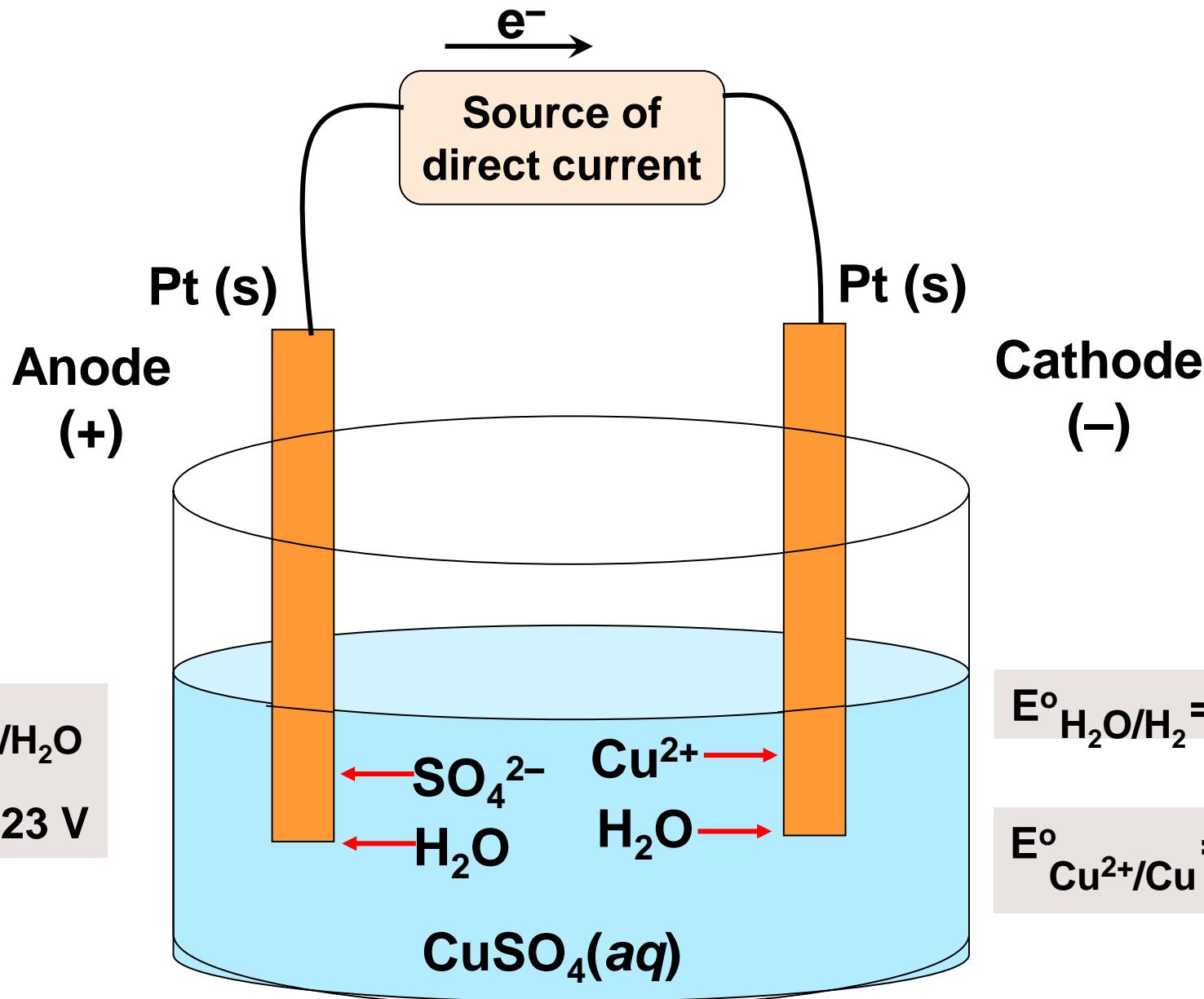
5. Predict the electrolysis reaction when a concentrated aqueous solution of K₂SO₄ is electrolysed using graphite electrodes.

EXAMPLE 4

Predict the electrolysis reaction when an aqueous solution of CuSO_4 is electrolyzed

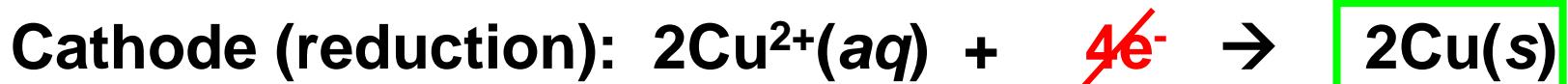
- i) Using platinum electrodes (inert electrodes)
- ii) Using copper electrodes (active electrodes)

Electrolysis of $\text{CuSO}_4(\text{aq})$ using inert electrode (Pt)



EFFECT OF THE NATURE OF ELECTRODES

i) electrolysis of $\text{CuSO}_4(\text{aq})$ using inert electrode (Pt)



Ion Present at Cathode : $\text{Cu}^{2+}, \text{H}_2\text{O} \rightarrow \text{Cu}^{2+}$ will be discharge

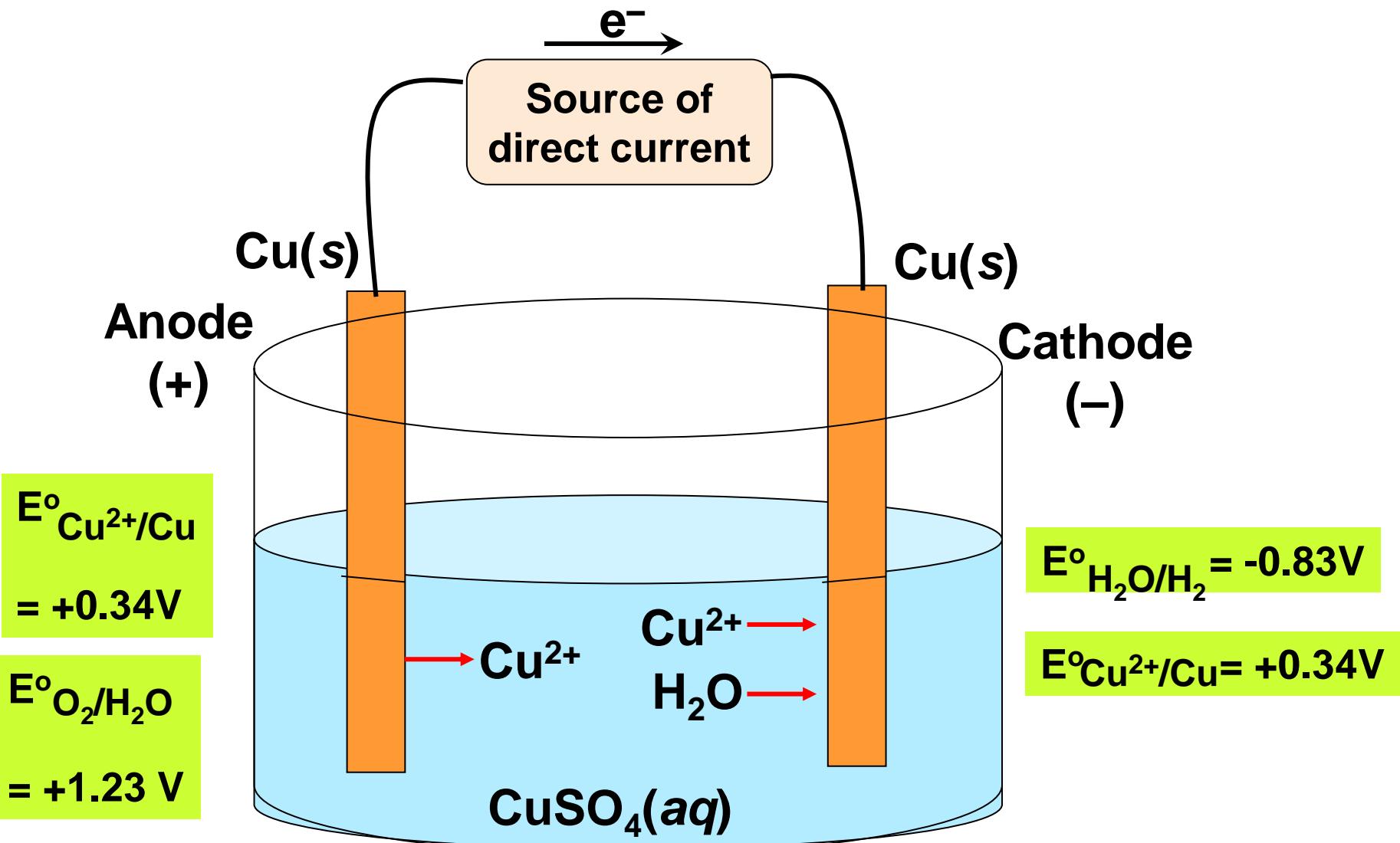
Ion Present at Anode : $\text{SO}_4^{2-}, \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$ will be discharge

Product formed:

At cathode : $\text{Cu}(\text{s})$ deposited

At anode : oxygen gas, $\text{O}_2(\text{g})$ released

Electrolysis of $\text{CuSO}_4(\text{aq})$ using active electrode (Cu)



- This method is used for **purification of metal**

EFFECT OF THE NATURE OF ELECTRODES

ii) electrolysis of $\text{CuSO}_4(\text{aq})$ using active electrode (Cu)



Ion Present at Cathode : $\text{Cu}^{2+}, \text{H}_2\text{O} \rightarrow \text{Cu}^{2+}$ will be discharge

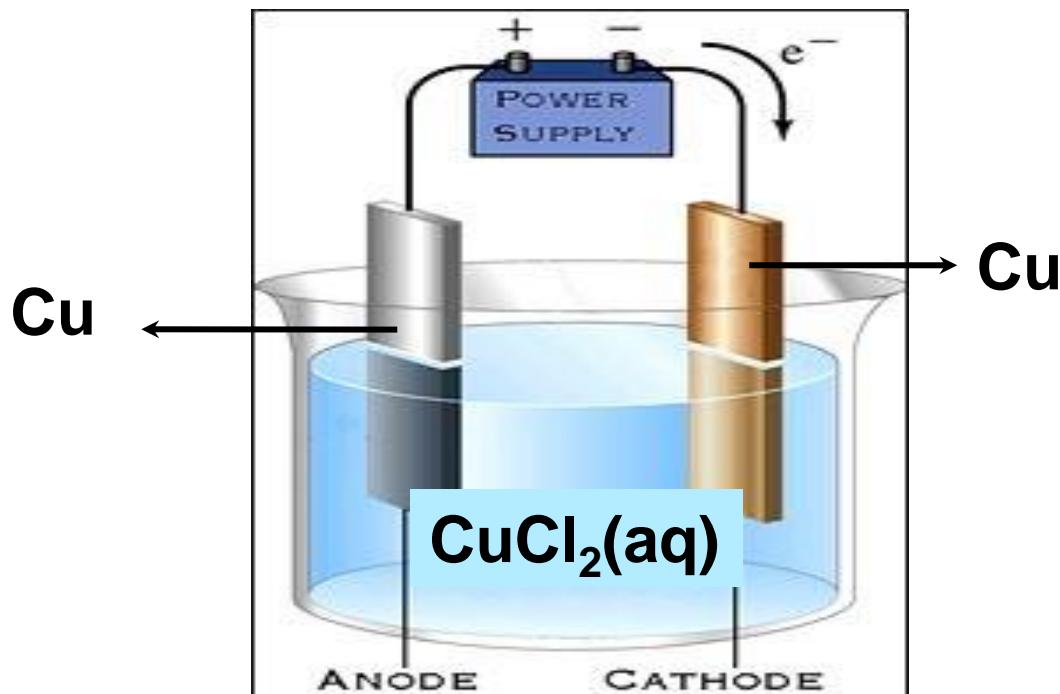
Ion Present at Anode : $\text{SO}_4^{2-}, \text{H}_2\text{O}, \text{Cu}^{2+} \rightarrow \text{Cu}^{2+}$ will be discharge

Product formed:

At cathode: Copper, Cu(s) deposited. Mass of Cu electrode increase.

At anode: Formation of Cu^{2+} ion. Mass of Cu electrode reduced.

EXAMPLE 5



From the figure above, predict the electrode reactions and the overall reaction when the anode and cathode is made of copper in aqueous solution of CuCl_2 electrolyte.

ANSWER



Ion Present at Cathode : Cu^{2+} , $\text{H}_2\text{O} \rightarrow \text{Cu}^{2+}$ will be discharge

Ion Present at Anode : Cl^- , H_2O , $\text{Cu}^{2+} \rightarrow \text{Cu}^{2+}$ will be discharge

Copper is transferred from anode to the cathode through the solution as Cu^{2+} .

The concentration of CuSO_4 remains unchanged.

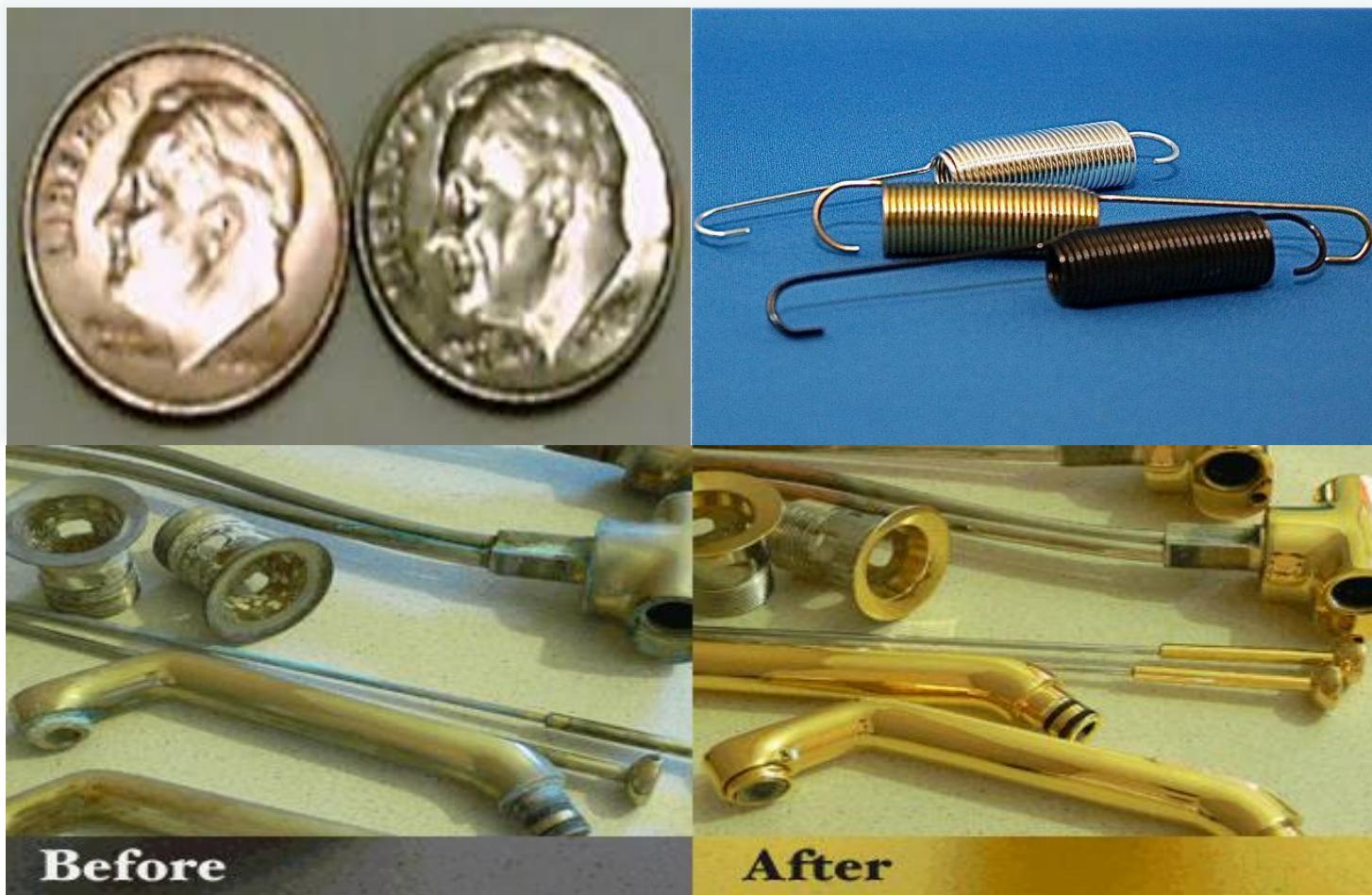
Product formed:

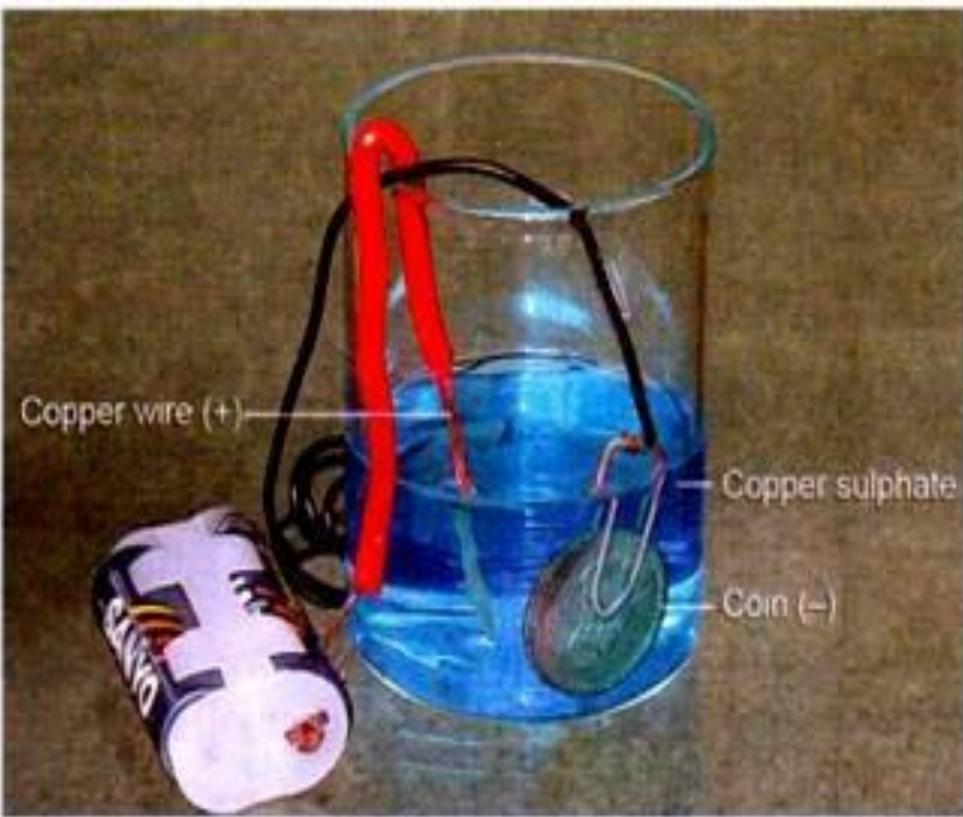
At cathode: Copper, Cu(s) deposited. Mass of Cu electrode increase.

At anode: Formation of Cu^{2+} ion. Mass of Cu electrode reduced.

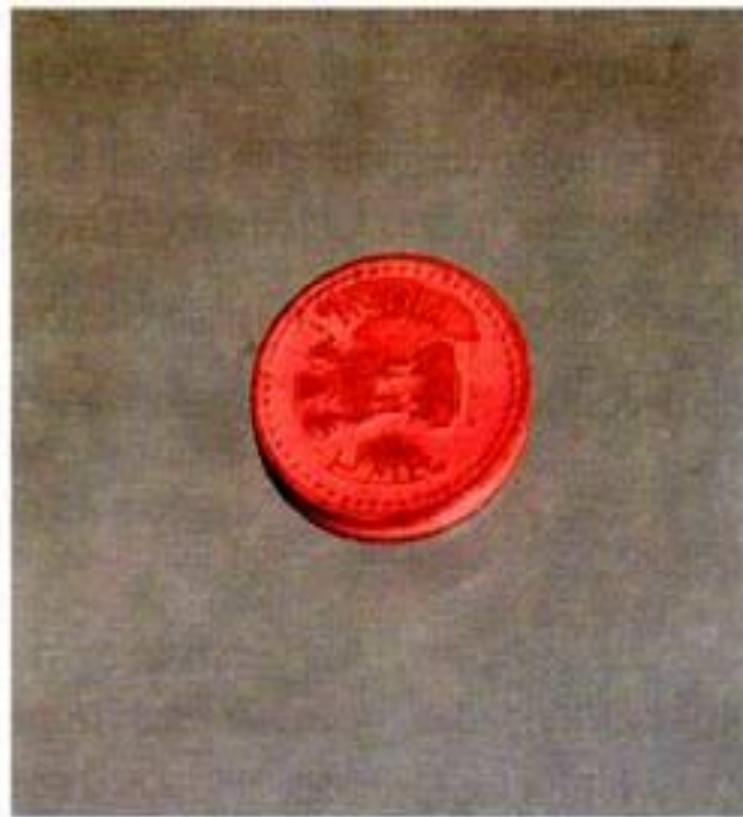
ELECTROCHEMISTRY

ELECTROLYSIS IN INDUSTRIES





(a)

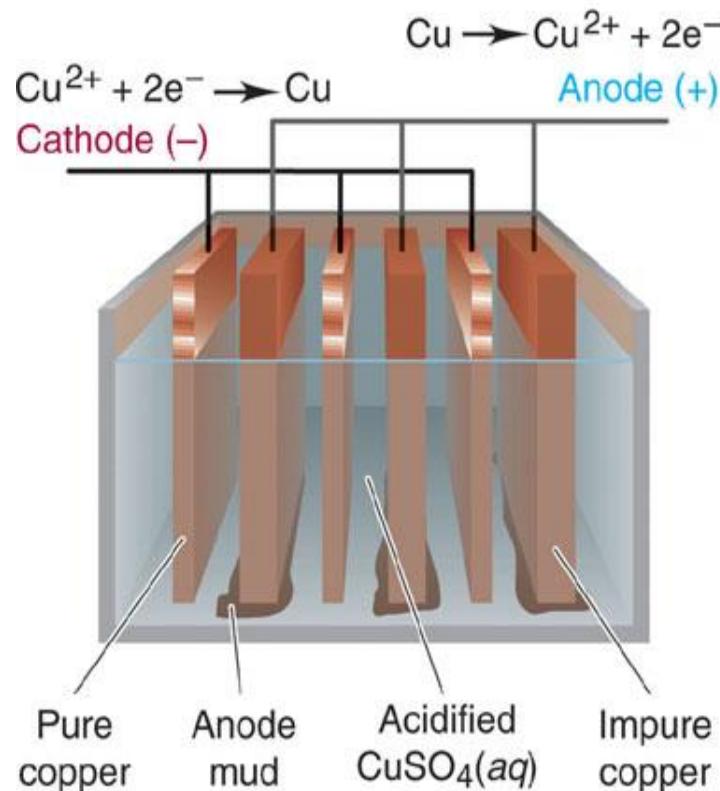


(b)

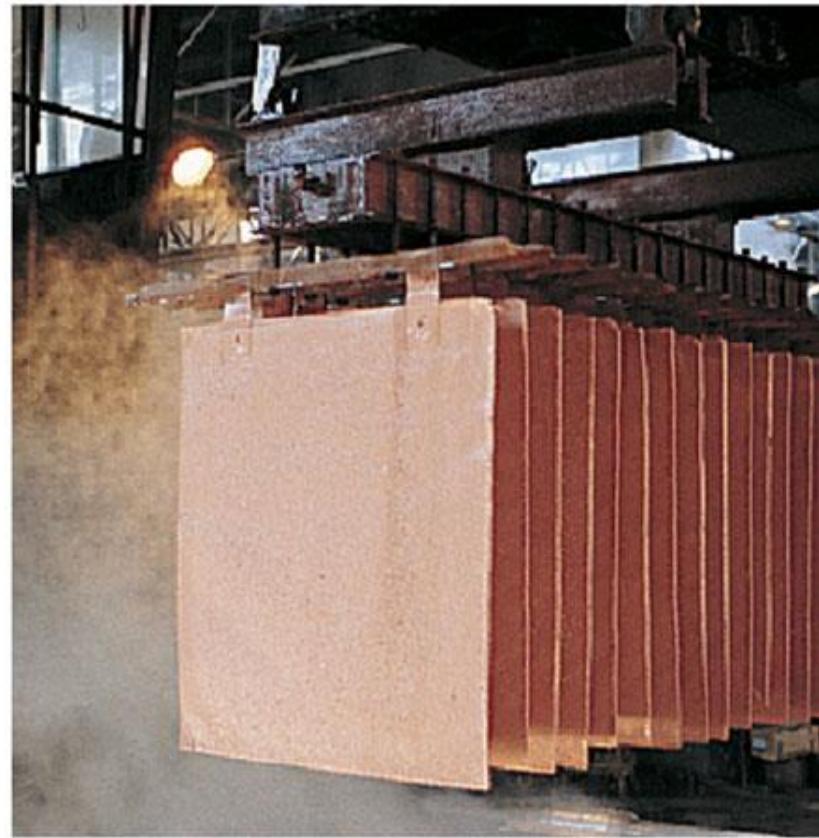
- The item to be plated is the **cathode** in an **electrolytic cell**



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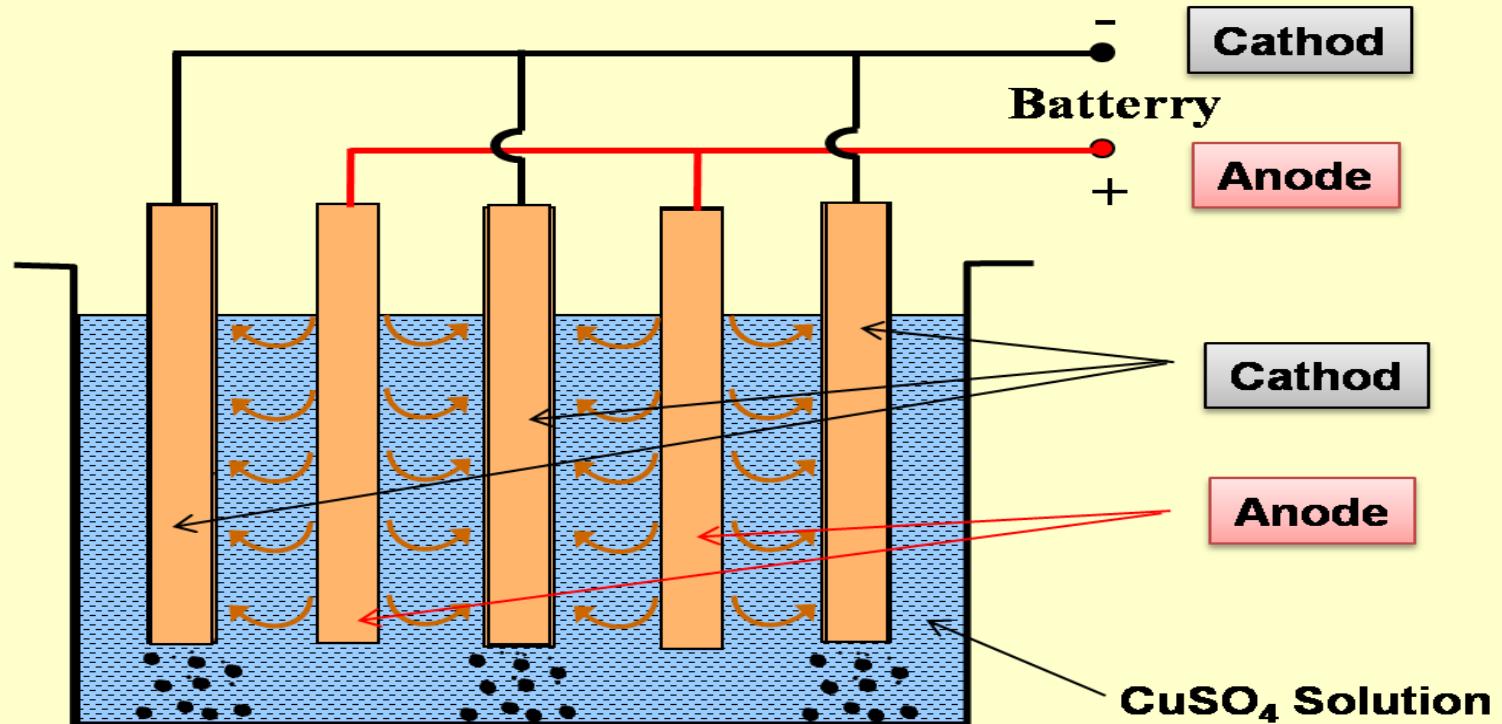


A



B

The electrorefining of copper. The item to be refined is **anode**

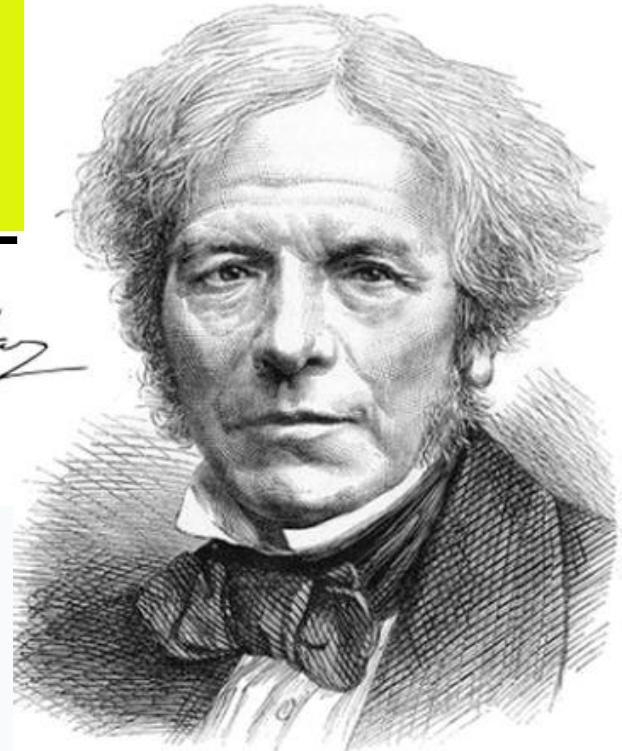


Purification of copper

Purification of metals

QUANTITATIVE ASPECTS OF ELECTROLYSIS

Faraday
1791-1867



In the 1834:

- Michael Faraday developed the quantitative treatment of electrolysis
- He observed that the amount (mass) of substance produced at an electrode by electrolysis depends on the quantity of charge passed through the cell

FARADAY'S FIRST LAW

FARADAY'S FIRST LAW OF ELECTROLYSIS

- “The mass of an element liberated on an electrode during electrolysis is directly proportional to the quantity of electrical charge, Q , which passes through the solution of an electrolyte.”
- Amount of substance produced at each electrode is directly proportional to quantity of electrical charge flowing through the cell
- If m is the mass or amount of a substance deposited or liberated and I is the current in amperes, which passes for ‘ t ’ seconds, then according to the law:

$$m \propto Q$$

$$Q = It$$

$$m \propto I \times t$$

Q = quantity of electrical charge

I = current

t = time

QUANTITY OF ELECTRICAL CHARGE (Q)

The unit of the **quantity of electrical charge, Q** is called **coulomb (C)**.

Coulomb (C) is the quantity of charge passed when **one ampere (A) of current** passes for **one second**.

According to Faraday's 1st Law:

$$Q = It$$

Charge(Q) = Current(I) x time(t)

Unit: Coulomb(C) Ampere(A) second (sec)

The larger unit of the **quantity of electrical charge** is called **Faraday (F)**. Also known as **Faraday constant**.

$$1 \text{ mol e}^- = 1 F = 96500 \text{ C}$$

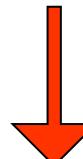
GIVEN:

Current (A) & time (s)



Find the product of current & time

Charge (C)



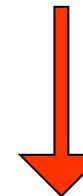
Divide by the Faraday constant

No. of moles of e^-



Use coefficients in the balanced equation to find mole ratio

No. of moles of product



Use molar mass or the ideal gas equation

Grams (g) @ liters (L)
of product

FIND:

EXAMPLE 6

An aqueous solution of CuSO_4 is electrolysed using a current of 0.150 A for 5 hours. Calculate the **mass of copper** deposited at cathode.

Molar mass for Cu = 63.5 g/mol

ANSWER

1 $Q = I \times t$ (time in sec)

$$Q = (0.150 \text{ A}) \times (5 \times 60 \times 60) \text{ s}$$

$$Q = 2700 \text{ C}$$



$$\begin{aligned} 2 \text{ mol of e}^- &= 2F = 2(96500 \text{ C}) \\ &= 193000 \text{ C} \end{aligned}$$

3 193000 C produces 1 mol of Cu

$$\begin{aligned} \text{So, } 2700 \text{ C produces: } &\frac{2700 \text{ C} \times 1 \text{ mol Cu}}{193000 \text{ C}} \\ &= 0.01399 \text{ mol Cu} \end{aligned}$$

4 Mass of copper deposited = $0.01399 \text{ mol} \times 63.6 \text{ g/mol}$

$$= 0.8897 \text{ g}$$

EXAMPLE 7

A technician is plating a faucet with 0.86 g of Cr from an electrolytic bath containing aqueous $\text{Cr}_2(\text{SO}_4)_3$.

If 12.5 min is allowed for the plating, how much current needed?

Molar mass of Cr = 52.0 g/mol.

ANSWER

$$\text{Mol} = \frac{\text{Mass (g)}}{\text{Molar mass (g/mol)}}$$

$$\begin{aligned}\text{Mole of Cr} &= \frac{0.86 \text{ g}}{52.0 \text{ g/mol}} \\ &= 0.0165 \text{ mol Cr}\end{aligned}$$



$$3 \text{ mole of } e^- = 3F = 3 \times 96500 \text{ C} = 289500 \text{ C}$$

1 mol Cr needs: 289500 C

So, 0.0165 mol Cr needs: $\frac{0.0165 \text{ mol} \times 289500 \text{ C}}{1 \text{ mol}}$
= 4776.8 C

$$Q = I \times t$$

$$Q = 4776.8 \text{ C}$$

$$t = 12.5 \text{ min} \times 60 \text{ sec/min} = 750 \text{ sec}$$

$$I = \frac{Q}{t} = \frac{4776.8}{750} = 6.4 \text{ A}$$

EXAMPLE 8

Electrolysis of molten $MgCl_2$ is the final production step in the isolation of magnesium from seawater by the Down process.

Assuming that 35.6 g of Mg metal forms,

- (a) How many moles of electrons are required?**
- (b) How many coulombs are required?**
- (c) How many amps (ampere) are required to produced this amount in 2.50 h.**

(Molar mass of Mg = 24.3 g/mol)

ANSWER

$$\text{Mol of Mg} = \frac{35.6 \text{ g}}{24.3 \text{ g/mol}} \\ = 1.465 \text{ mol Mg}$$



1 mol Mg needs = 2 mol electrons

$$\text{So, } 1.465 \text{ mol Mg needs} = \frac{1.465 \cancel{\text{mol}} \times 2 \text{ mol electrons}}{1 \cancel{\text{mol}}} \\ = 2.93 \text{ mol electrons}$$

(b) $1 \text{ mol e}^- = 1 \text{ F}$

$$2.93 \text{ mol electrons} = 2.93 \times 1 \text{ F}$$

$$= 2.93 \text{ F}$$

$$1\text{F} = 96500 \text{ C}$$

$$\text{So, } 2.93 \text{ F} = 2.93 \times 96500 \text{ C}$$

$$= 2.83 \times 10^5 \text{ C}$$

(c) $Q \text{ (charge)} = I \text{ (current)} \times t \text{ (time in sec)}$

$$t = 2.5 \cancel{\text{hr}} \times 3600 \text{ sec/}\cancel{\text{hr}}$$

$$= 90000 \text{ sec}$$

$$\text{Current (I)} = \frac{Q}{t} = \frac{2.83 \times 10^5}{9000 \text{ sec}}$$

$$= 31.4 \text{ A}$$