ELECTROCHEMICAL CELLS

Electrochemistry

1. Redox reactions involve the transfer of electrons from one reactant to another
2. Electric current is a flow of electrons in a circuit

Many reduction-oxidation reactions occur spontaneously, giving off energy.

- Other reduction-oxidation reactions are non-spontaneous, requiring energy.

- Galvanic/Voltaic Cells
- Spontaneous reactions occur
- Electrolytic Cells
- Non-spontaneous reactions occur

Volta

A shocking experience!

While Volta is known and remembered for his contribution to the study of electrochemistry, not all his experimental methods bear repeating!

> I introduced into my ears two metal rods with rounded ends and joined them to the terminals of the apparatus. At the moment the circuit was completed I received a shock in the head—and began to hear a noise—a crackling and boiling. This disagreeable sensation, which I feared might be dangerous, has deterred me so that I have not repeated the experiment. *Alessandro Volta*

ELECTROCHEMICAL CELLS

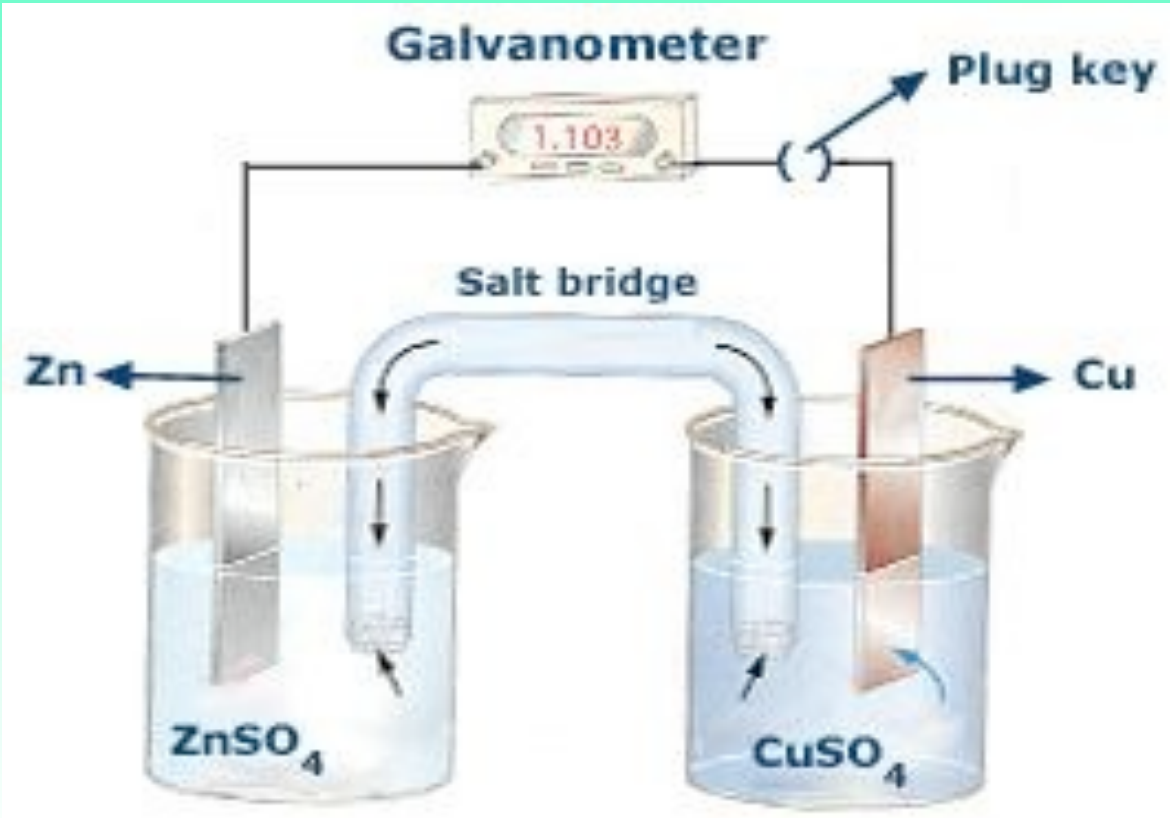
Batteries operate by allowing electrons to spontaneously flow (electrical current) from the reducing agent to the oxidizing agent.

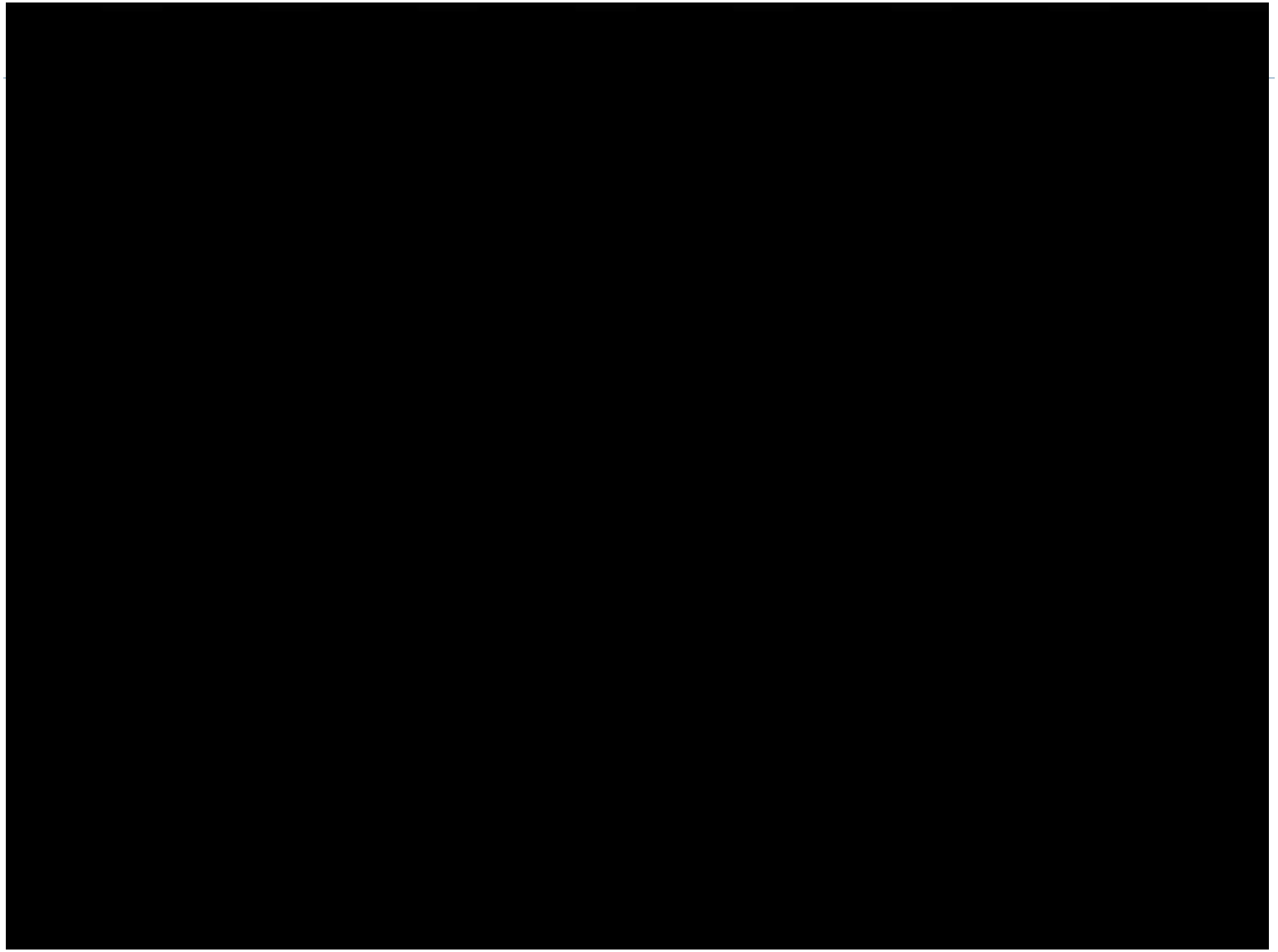
A current will continue to flow until the cell reaches equilibrium.

NOTE: A reducing agent is oxidized, and an oxidizing agent is reduced

ELECTROCHEMICAL CELLS

A galvanic (voltaic) cell may be created using aqueous solutions of good electrolytes (substances which conduct an electric current when dissolved in water)

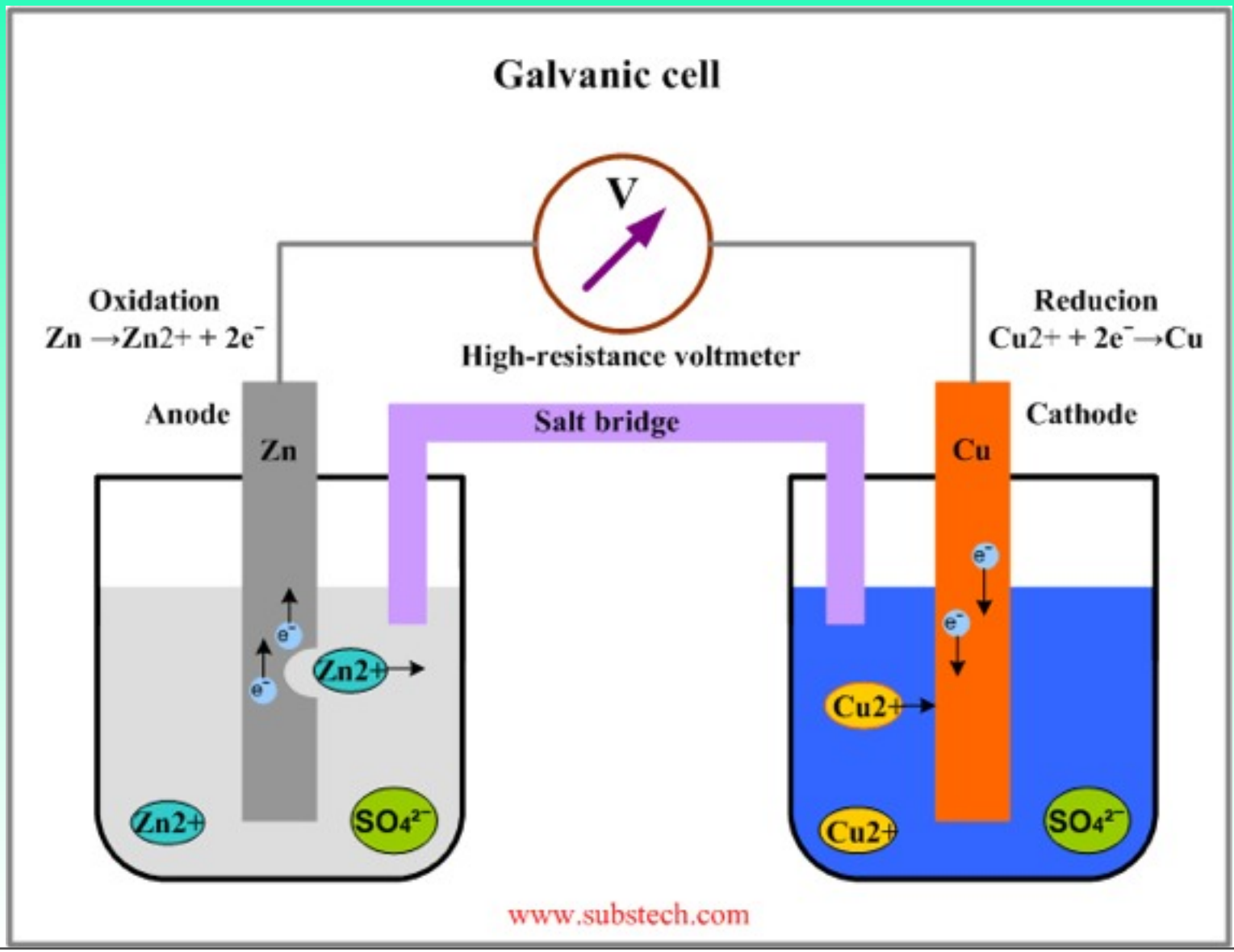




$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$

Reduction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Oxidation: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$



ELECTROCHEMICAL CELLS

The half-reactions occur in each of the separate beakers.

electrodes – metal pieces which allow electrical conduction

Since positive metal ions are formed, the solution must have the same metal as the electrode

Q: Which metal is placed into which solution?

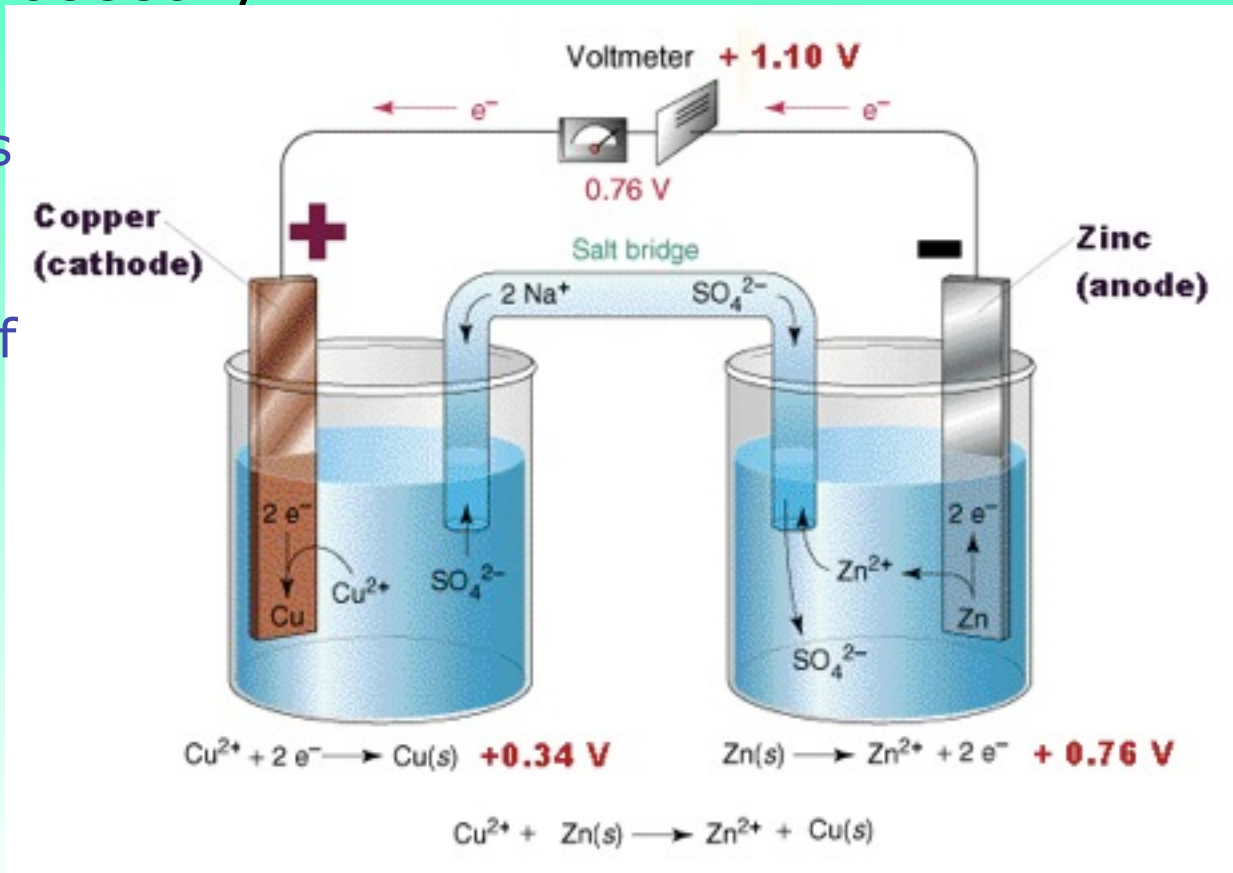
ELECTROCHEMICAL CELLS

salt bridge – a U-shaped tube containing a strong electrolyte solution

Q: Why is this necessary?

To prevent the build-up in each beaker of excess positive or negative charges that can interfere with the flow of electrons.

The contents of both beakers remain electrically neutral even as the concentrations of reactant and products change during the reaction



ELECTROCHEMICAL CELLS

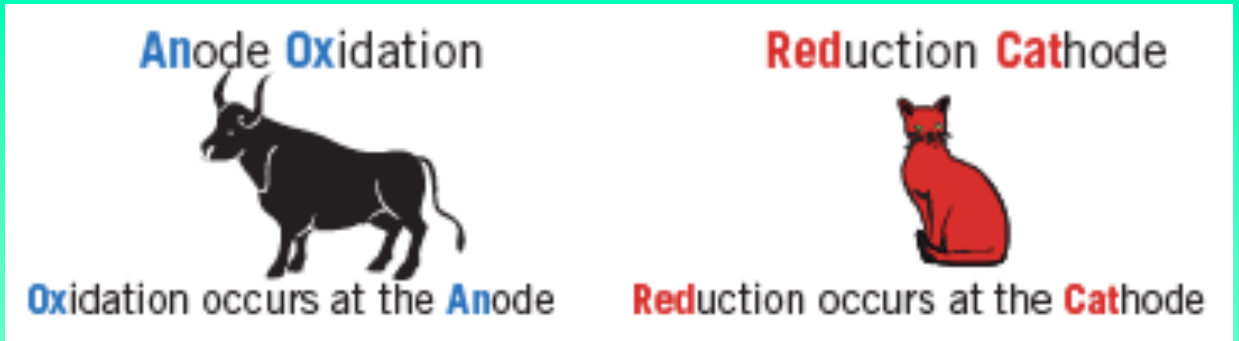
Classical definitions (always true):

anode – electrode which attracts anions (-)

cathode – electrode which attracts cations (+)

Electrons flow from the _____ to the _____.

ELECTROCHEMICAL CELLS



For a galvanic cell:

anode – electrode where oxidation reaction occurs

– negative electrode

cathode – electrode where reduction reaction occurs

– positive electrode

ELECTROCHEMICAL CELLS

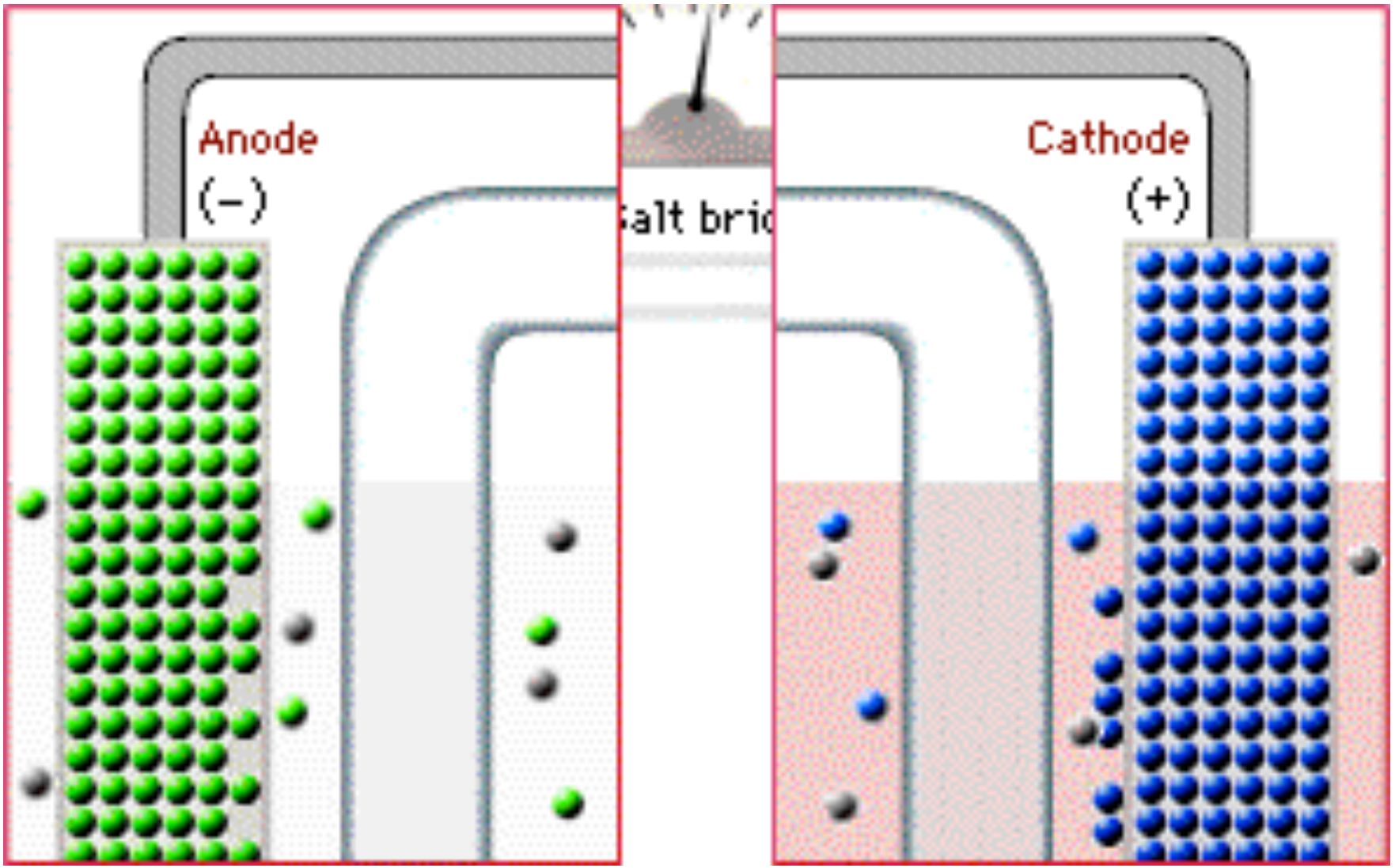
A counter-current flow must occur in the opposite direction as electron flow.

Q: Why?

The build-up of charge on each side can stop the flow of electrons.

What is moving in this counter current flow?

Anions. Anions flow to the anode.


Anode
(–)
alt bri
Cathode
(+)

ELECTROCHEMICAL CELLS

A short-hand notation can also represent a full diagram of a galvanic cell.

anode | electrolyte || electrolyte | cathode

|| = salt bridge

$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

Try it!

2. Write the oxidation half-reaction, the reduction half-reaction, and the overall cell reaction for each of the following galvanic cells. Identify the anode and the cathode in each case. In part (b), platinum is present as an inert electrode.

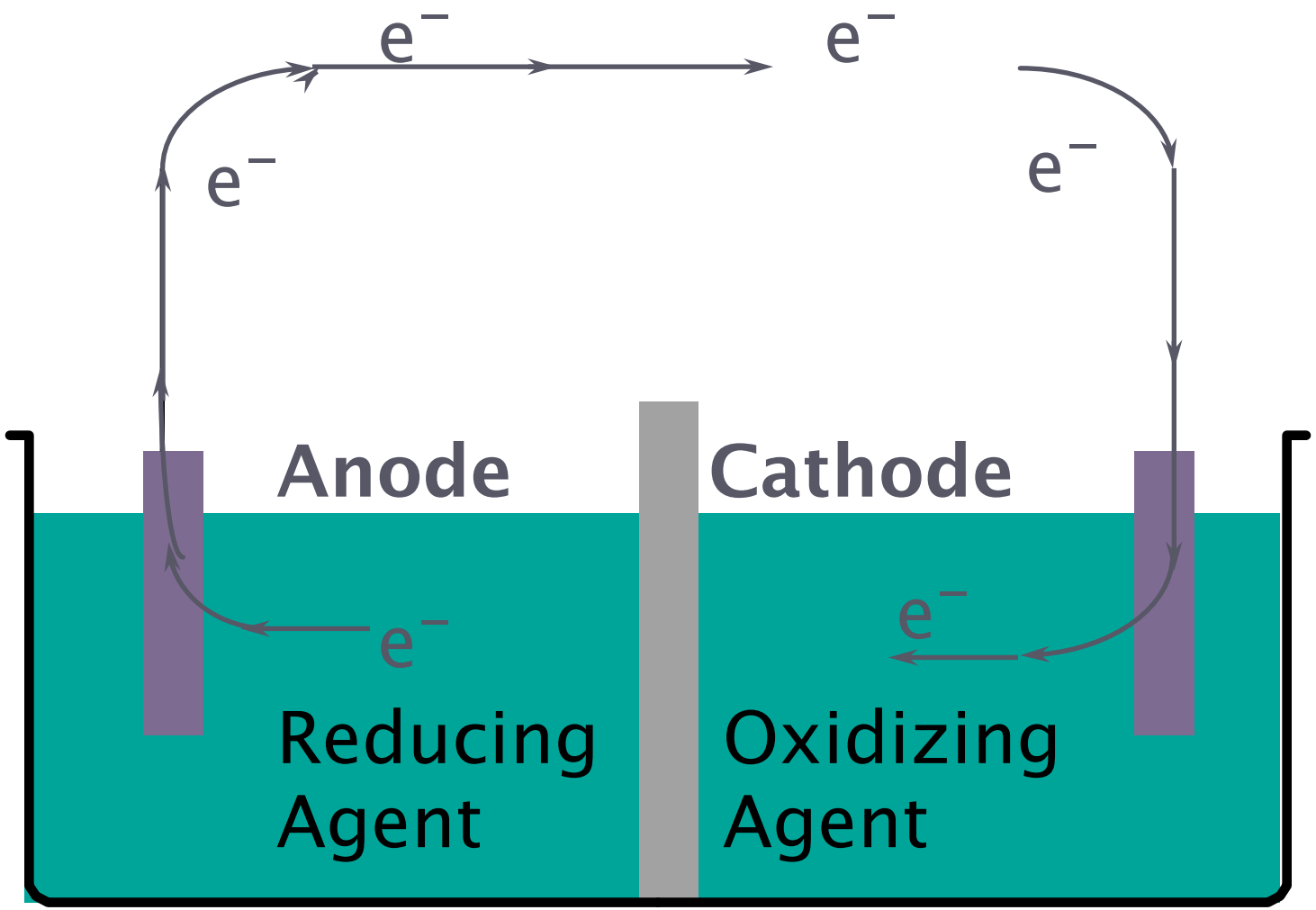
(a) $Sn_{(s)} \mid Sn^{2+}_{(aq)} \parallel Tl^{+}_{(aq)} \mid Tl_{(s)}$

(b) $Cd_{(s)} \mid Cd^{2+}_{(aq)} \parallel H^{+}_{(aq)} \mid H_{2(g)} \mid Pt_{(s)}$

- anode | cation of anode || cation of cathode | cathode

- Oxidation: $Sn \rightarrow Sn^{2+} + 2e^-$
- Reduction: $Tl^+ + 1e^- \rightarrow Tl$
- Overall: $Sn + 2Tl^+ \rightarrow Sn^{2+} + 2Tl$
- Anode: Sn, Cathode: Tl

Summary of Galvanic Cell



Summary of Galvanic Cells

The **ANODE...**	The **CATHODE...**
supplies electrons to the external circuit (wire)	**accepts electrons** from the external circuit (wire)
is the **negative** pole of the battery	is the **positive** pole of the battery
is the site of **OXIDATION**	is the site of **REDUCTION**
is written on the **left hand side** if the convention is followed	is written on the **right hand side** if the convention is followed
is the half-cell with the **lowest** electrode potential	is the half-cell with the **highest** electrode potential

ELECTROCHEMICAL CELL POTENTIAL

CELL POTENTIAL

Each half-reaction is associated with an E° value.

E° - standard half-cell potential at SATP

All reactions are compared to the H_2 electrode which has an E° value of 0.0 V.

CELL POTENTIAL

Combining two half-reactions provide a voltage potential value of a full cell. The magnitude of the value indicates its ability to do electrical work.

$$\Delta E^\circ_{(cell)} = E^\circ_{(cathode)} + E^\circ_{(anode)}$$

$\Delta E^\circ_{(cell)} > 0$, the reaction is spontaneous

$\Delta E^\circ_{(cell)} < 0$, the reaction is not spontaneous

CELL POTENTIAL

Example #1

Can aluminum foil immersed in an electrolyte solution be used to restore the lustre to silverware?

Show the balanced chemical equation for this reaction.

$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$ $\quad E^\circ = +1.66V$

$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$ $\quad E^\circ = +0.80V$ x 3

$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$ $\quad E^\circ = +1.66V$

$3Ag^+_{(aq)} + 3e^- \rightarrow 3Ag_{(s)}$ $\quad E^\circ = +0.80V$

$Al_{(s)} + 3Ag^+_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3Ag_{(s)}$ $\quad E^\circ = +2.46V$

DOES NOT CHANGE.
3 times more electrons does not mean 3 times more likely to flow.

Since the voltage is positive, the reaction is spontaneous.

.: aluminum foil can restore the lustre to silver

CELL POTENTIAL

Rules when manipulating half-reactions:

1. When the reaction is reversed, the sign of E° is also reversed.

2. When the reaction is multiplied by a factor, the E° value is NOT affected.

CELL POTENTIAL

Why is the E° not affected by multiplication factors?

Voltage is a measure of how quickly electrons are transferred in a redox reaction. Molar concentration does not affect how quickly electrons flow.

CELL POTENTIAL

Example #2

When silver metal is placed in 1.0 M HCl, there is no observable reaction. However, when Mg metal is placed in the same HCl solution, the metal oxidizes and H_2 is produced. Explain.

$2Ag_{(s)} \rightarrow 2Ag^{+}_{(aq)} + 2e^{-}$ $\quad E^\circ = -0.80V$

$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$ $\quad E^\circ = 0.00V$

$2H^{+}_{(aq)} + 2Ag_{(s)} \rightarrow H_{2(g)} + 2Ag^{+}_{(aq)}$ $\quad E^\circ = -0.80V$

Since negative, the reaction will not occur spontaneously

$Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^{-}$ $\quad E^\circ = +2.37V$

$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$ $\quad E^\circ = 0.00V$

$2H^{+}_{(aq)} + Mg_{(s)} \rightarrow H_{2(g)} + Mg^{2+}_{(aq)}$ $\quad E^\circ = +2.37V$

Since positive, the reaction will occur

QUANTITATIVE ANALYSIS

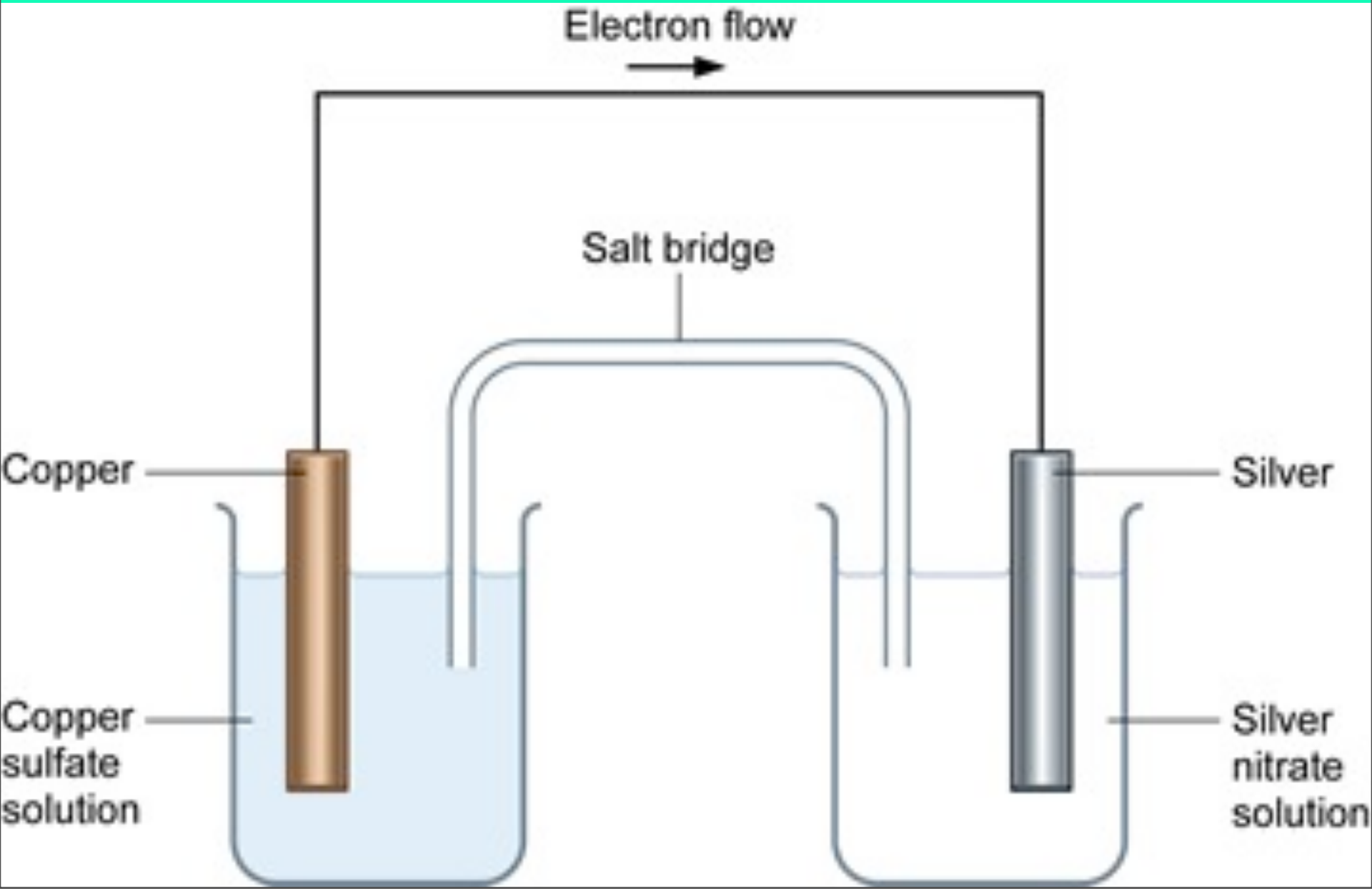
QUANTITATIVE ANALYSIS

Sketch an electrochemical cell made of copper and silver half-cells.

a)Label:

- anode / cathode
- positive / negative electrodes
- direction of e^- flow in external circuit
- direction of flow in salt bridge

QUANTITATIVE ANALYSIS



QUANTITATIVE ANALYSIS

b) What is the net ionic equation and the standard cell potential for the overall reaction?

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ $\quad E^\circ = -0.34V$

$2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$ $\quad E^\circ = +0.80V$ x 2

$Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$ $\quad E^\circ = +0.46V$

QUANTITATIVE ANALYSIS

c) Which electrode loses mass? gains mass? How much of each?

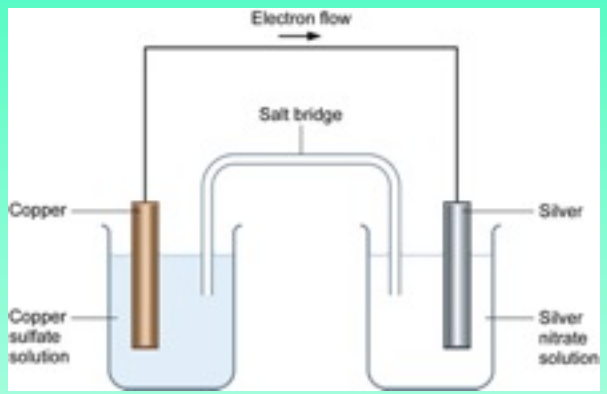
As the cell discharges, the silver electrode increases in mass and the copper electrode decreases in mass

The electrodes will not change equally in mass as the molar ratios of the elements involved are different.

QUANTITATIVE ANALYSIS

d) If the change in mass of the silver electrode was 2.15g, what was the change in mass of the copper electrode?

Since silver electrode is at the cathode, it gained 2.15g



$$n_{Ag} = \frac{m}{M}$$

$$= \frac{2.15g}{107.880g/mol}$$

$$= 0.019929551mol$$

$$Cu_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

$$\frac{2 \text{ mol Ag}}{1 \text{ mol Cu}} = \frac{0.019929551mol \text{ Ag}}{x}$$

$$x = 0.00996 \text{ mol Cu}$$

$$m_{Cu} = n \times M$$

$$= 0.00996mol \times 63.54g/mol$$

$$= 0.633g$$

.: 0.633g of copper was lost