Electrochemistry

CHE 3053

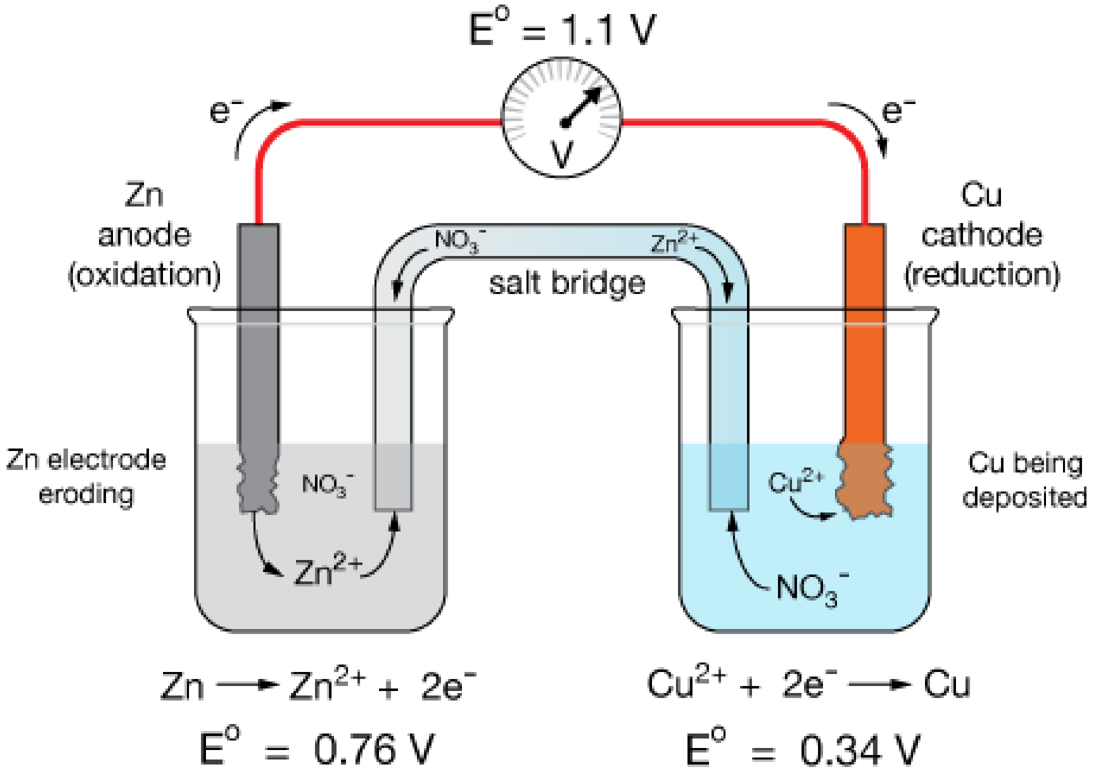
EMF & Electrolysis

Ahmad Alakraa

Danial Cell

Spontaneous

Galvanic



$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^0 = -0.76\,V$ ✗

$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = +0.34\,V$ ✓ cathode

$Zn \rightarrow Zn^{2+} + 2e^- \qquad E^0 = +0.76\,V$ ✓ anode

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$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \qquad E^0 = +1.1\,V$

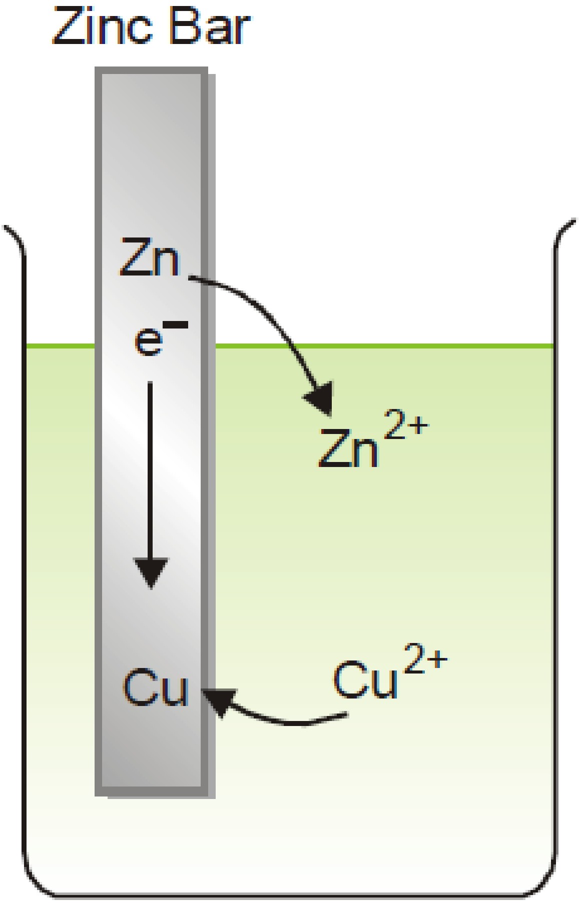
Irreversible electrochemical Cells

- Cells whose cell reactions can not be reversed when an external emf (E_{ext}) greater than its capacity (E_{cell}) is applied.

- It does not obey thermodynamic conditions of reversibility.

Electricity Production

- When a bar of zinc is dipped in a solution of copper sulphate, Zn ions are dissolved and copper metal is deposited on the bar.



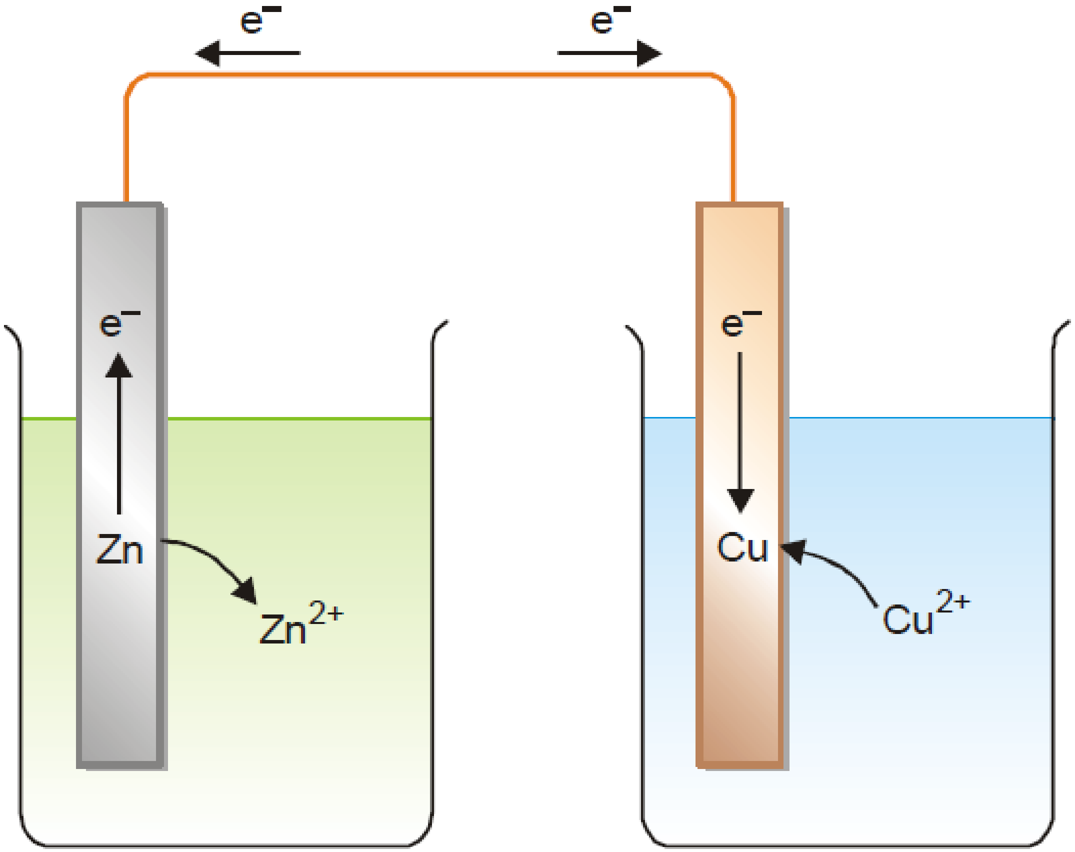
$Zn \leftrightarrow Zn^{2+} + 2e^-$ **Oxidation**

$Cu^{2+} + 2e^- \leftrightarrow Cu$ **Reduction**

$Zn + Cu^{2+} \leftrightarrow Zn^{2+} + Cu$

- As both half-reactions occurred on the same electrode, no **useful electricity** can be obtained although it is a galvanic process.
- This is very similar to the case of **corrosion**.

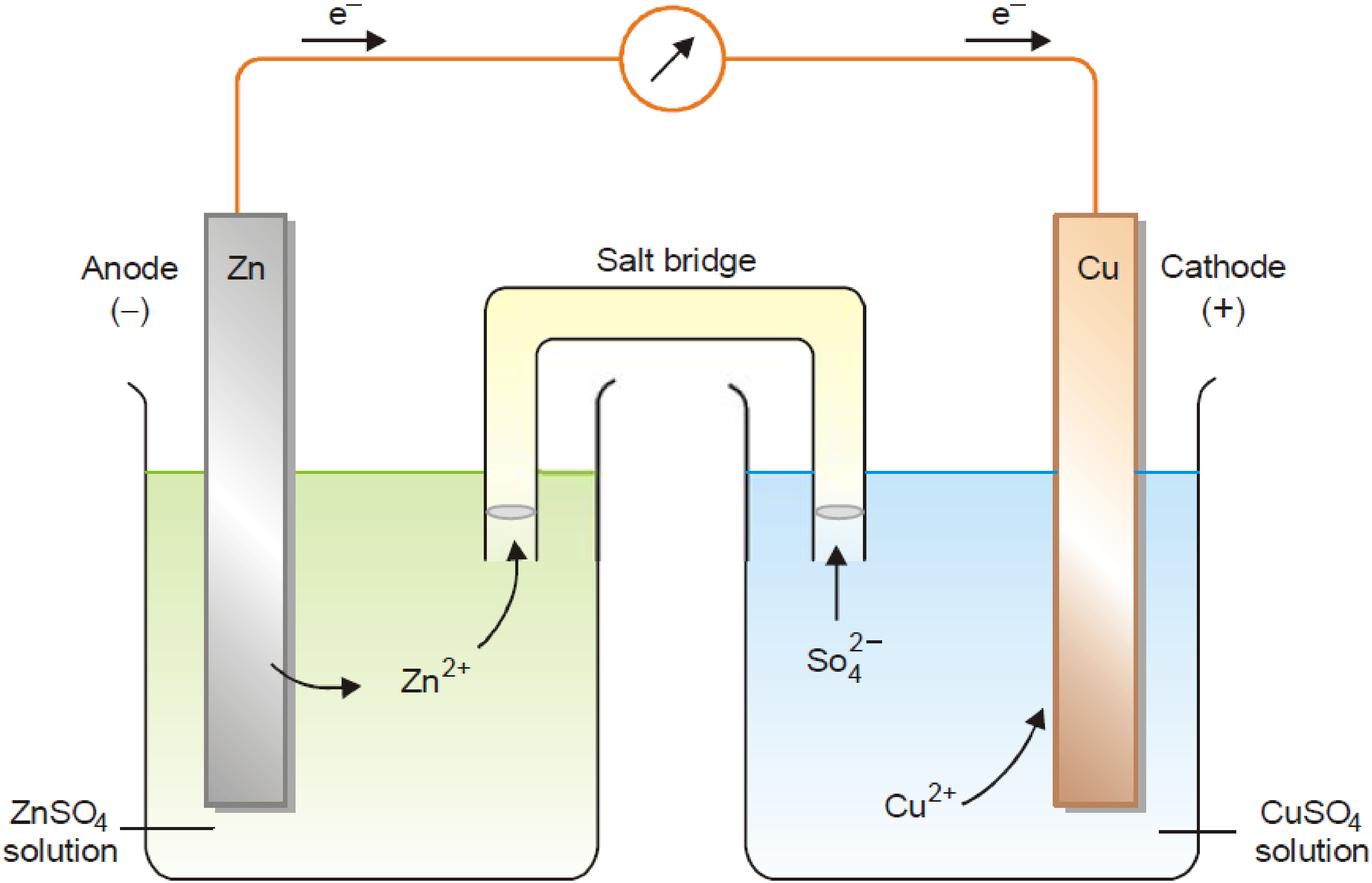
Two compartment cells /no salt bridge



- e's flow (electricity) through the wire for an instant and then stop because of the charge build up in the two compartments. e's flow from the anode (becomes +Ve) to cathode (becomes –Ve)

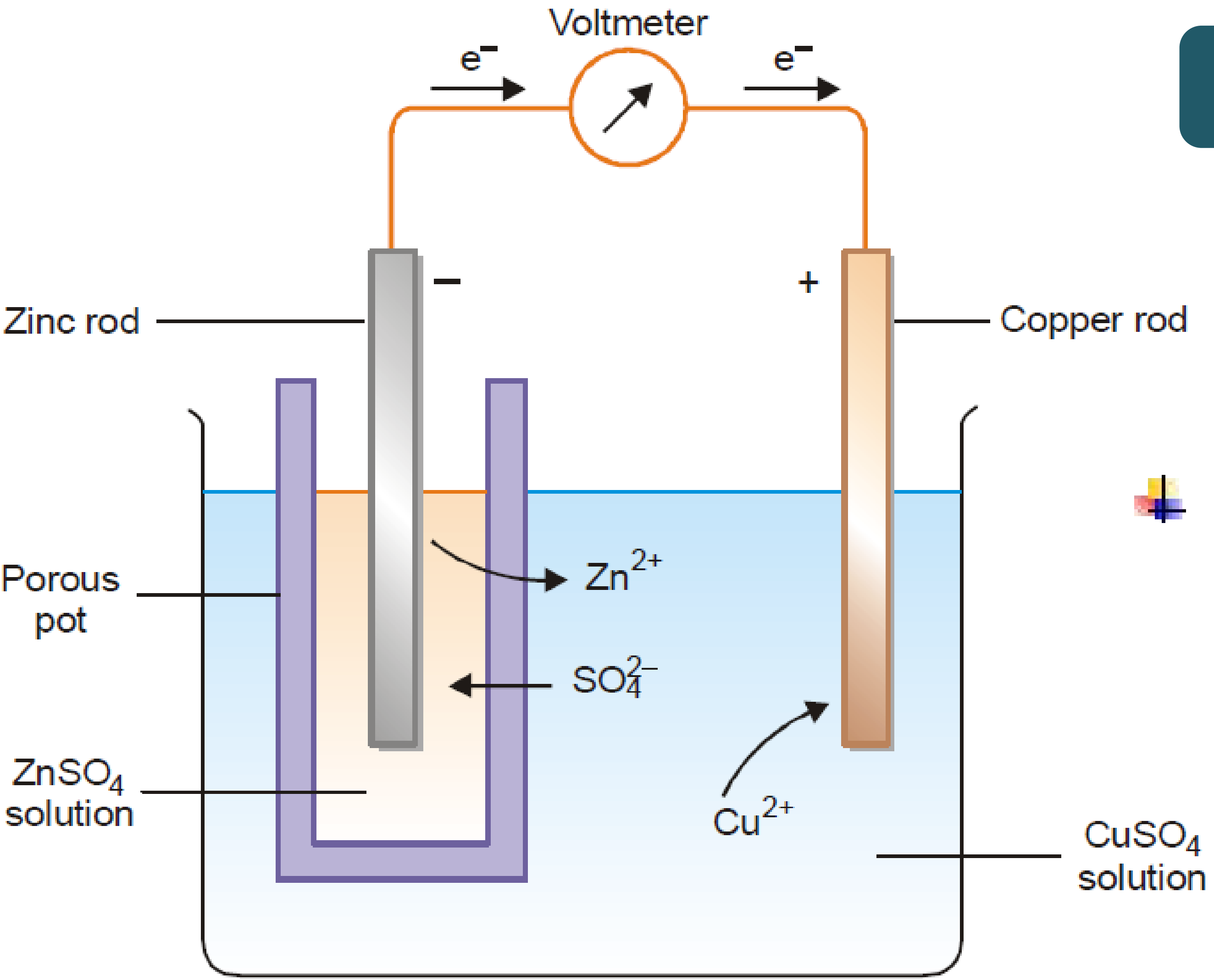
Voltaic/Galvanic Cells

The cell operates till either Zn or Cu^{2+} is completely used up.



$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ $E^0_{cell} = 1.1\ V$

Daniel Cell



- The salt-bridge has is replaced by a porous pot.

Cell diagram

$$Zn(s)\,|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(s)$$

Cell Diagram or Representation

- is an abbreviated symbolic depiction of an electrochemical cell
- A single **vertical line** (|) represents a phase boundary between metal electrode and ion solution (**electrolyte**).
- The metal electrode in **anode** half-cell is on **left**, while in **cathode** half-cell is on **right** of metal ion.
- A double vertical line (| |) represents the **salt bridge**, **porous partition** or any other means permitting ion flow while preventing the electrolyte from mixing.
- Anode half-cell is written on the left and cathode half-cell on the right.

Daniel Cell

Salt Bridge

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

Anode Half-Cell

Cathode Half-Cell

- The symbol for an inert electrode, like the **platinum electrode** is often enclosed in a bracket.

Inert Electrode

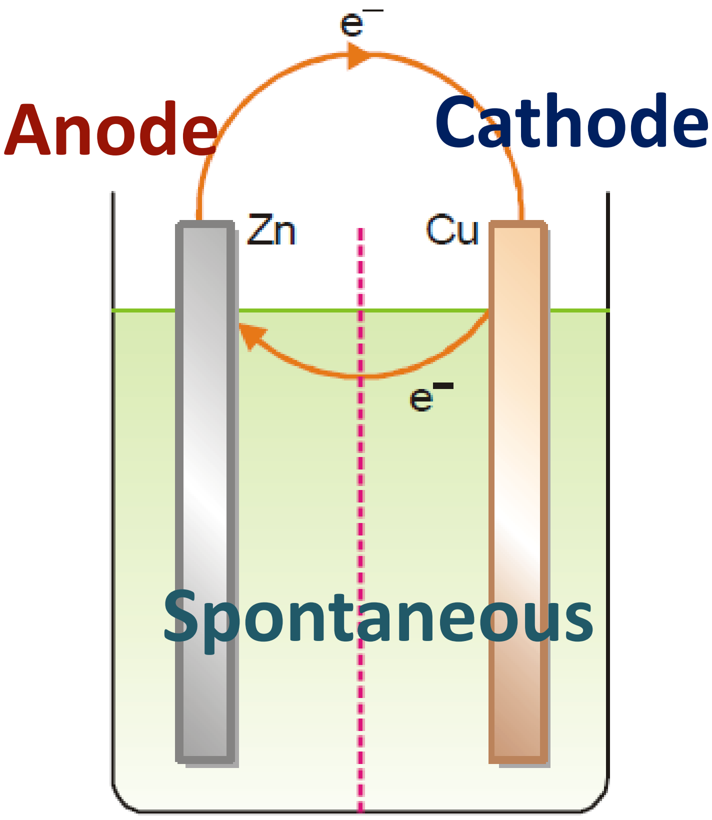
$$Mg \mid Mg^{2+} \parallel H^{+} \mid H_2(Pt)$$

- The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1 V and is represented as

$$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu \qquad E = +1.1\ V$$

Convention in the sign of emf

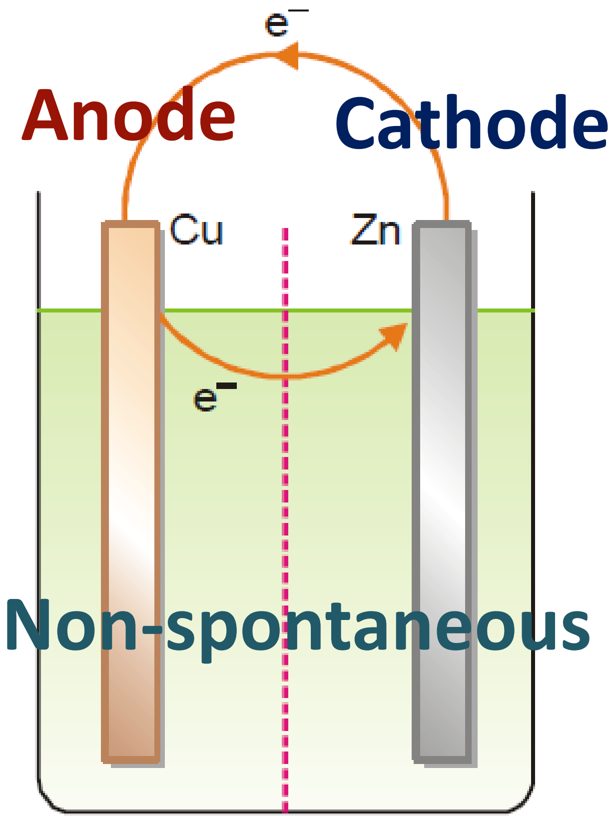
Zn | $ZnSO_4$ || $CuSO_4$ | Cu	E = + 1.1 V
Cu | $CuSO_4$ || $ZnSO_4$ | Zn	E = – 1.1 V



Anode **Cathode**

Spontaneous

E = + 1.1V



Anode **Cathode**

Non-spontaneous

E = – 1.1V

–Ve E indicates the **infeasibility** of the given direction.

Electrodes/Electrolyte

- The electrode (**Pole**) at which **oxidation** occurs is called the **anode**; the electrode at which **reduction** occurs is called the **cathode**.

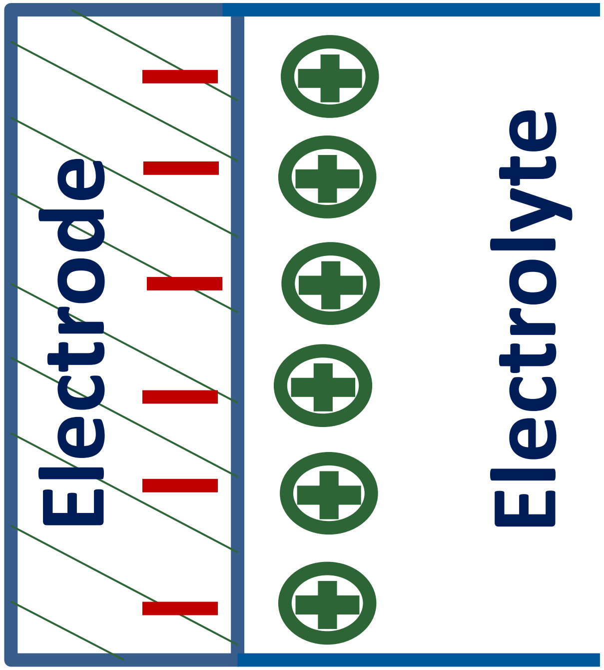
- The cathode and anode are **usually** made of metals or carbon (i.e., **1st class conductors**) and they may be or may not be involved in the reactions.

- The solution between electrodes is composed of a **polar solvent** (mostly **water**) and at least one chemical (called **Electrolyte**) that ionizes to produce ions in solution.

Electrical double layer (DL)

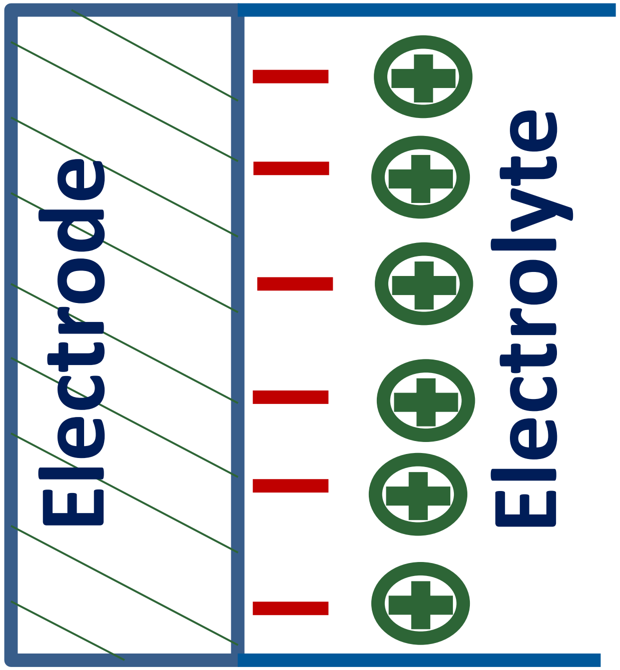
Ionization

- results in excess e⁻s at the electrode surface and hydrated +Ve ions that are attracted electrostatically to the –Ve charges at the electrode surface forming the DL.



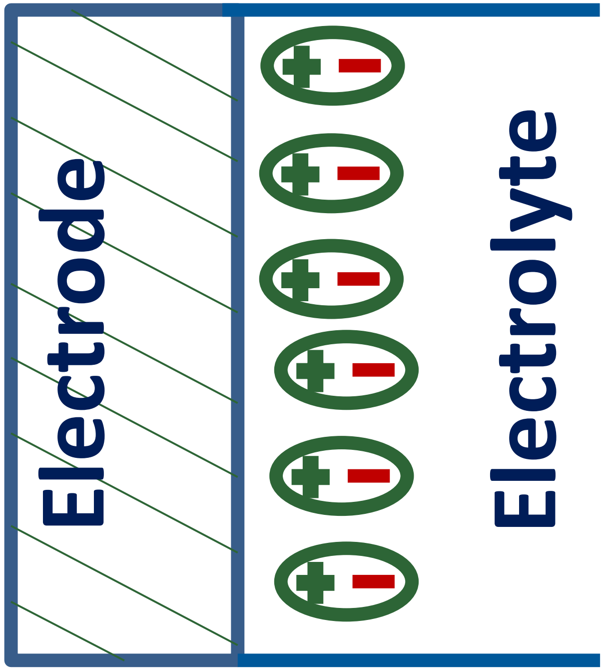
Specific adsorption

- of non-hydrated –Vely charged anions e.g., Cl $^{-}$, SCN $^{-}$ (chemisorption) producing –Ve charges at the electrode surface that attract +Vely charged hydrated cations to a distance of closest approach, hence, forming the DL .



Adsorption of oriented dipoles

- as water and that occurs in the direction of the electric field.

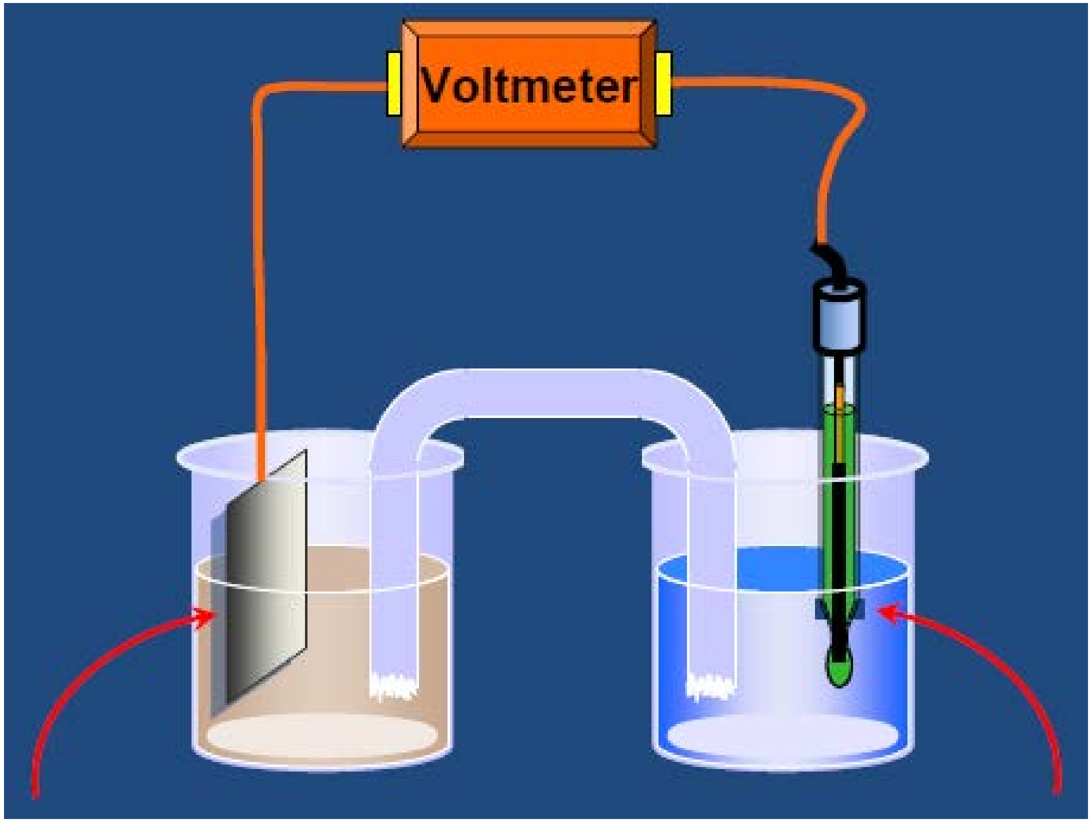


Electric field

- The distance of closest approach is ≈ 5 A°.
- The charge separation inducts a potential drop across the DL ≈ 1V.
- The potential field is therefore equal:

$$\frac{d\emptyset}{dx} \approx \frac{1\ \mathrm{V}}{5\times10^{-8}\ \mathrm{cm}} \approx 2\times10^{7}\ \mathrm{Vcm}^{-1}$$

Potential Measurement



Working Electrode

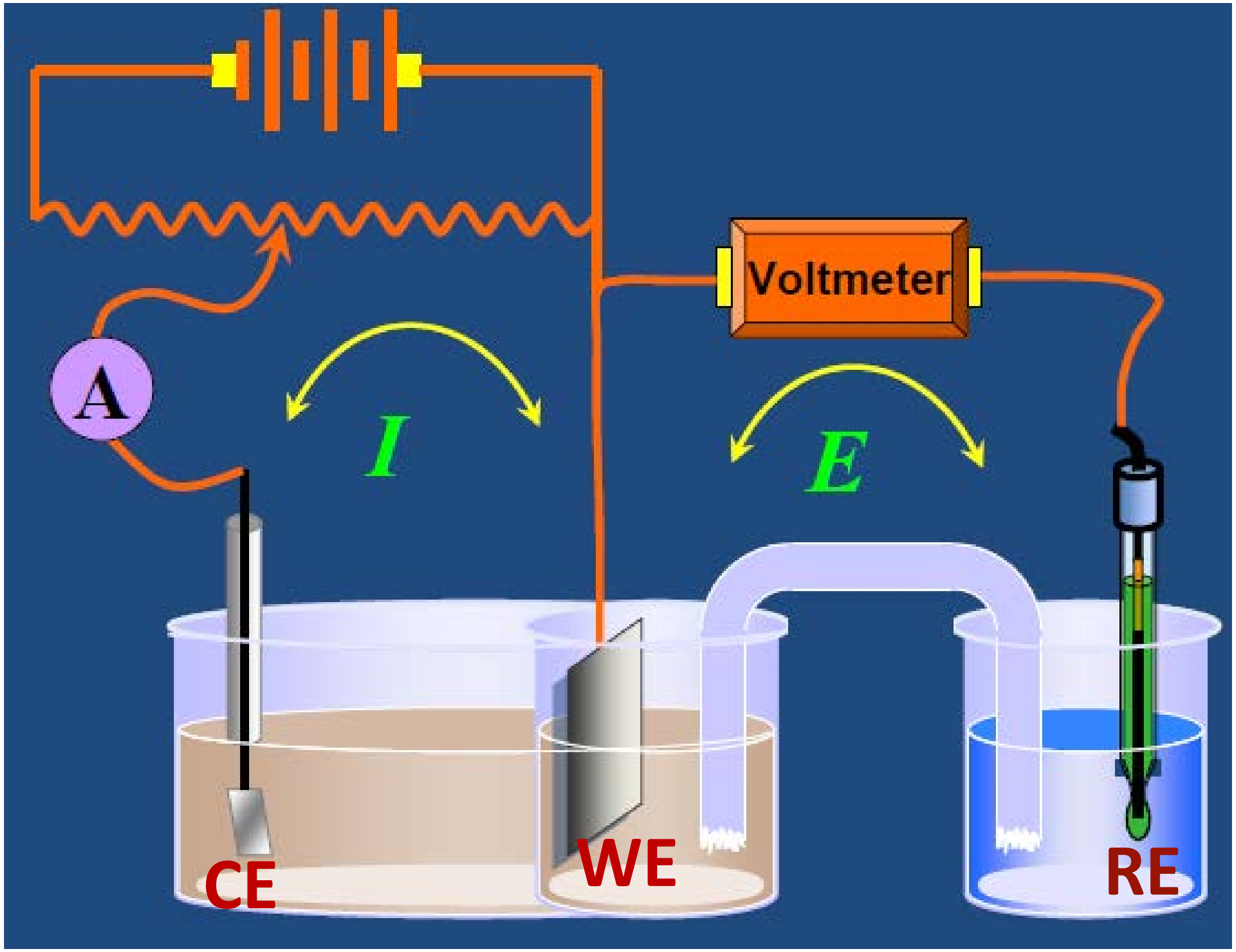
- The electrode under consideration

$$E = E_{\mathrm{WE}} - E_{\mathrm{RE}}$$

Reference Electrode

- Its potential is practically constant
- Electron transfer through its interface is extremely fast

Three-electrode cells



CE: counter (Auxiliary) electrode: completes the circuit to measure the current without impeding its passage, e.g., **Pt sheet**.

Polarizable Electrodes

- is a hypothetical electrode featured with no **faradaic current** flow (no net DC current between the two sides of the electrical double layer) when the electrode potential is varied.

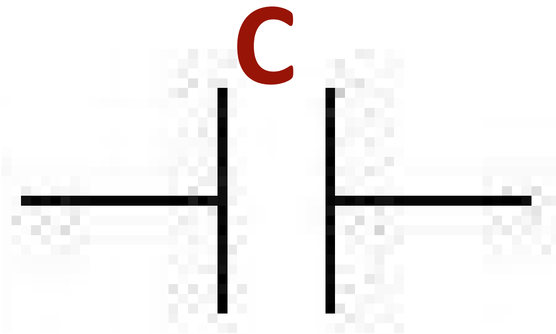
- usually can be used as **Working** or **Counter** electrodes.

- It has a very high polarization or charge transfer resistance.

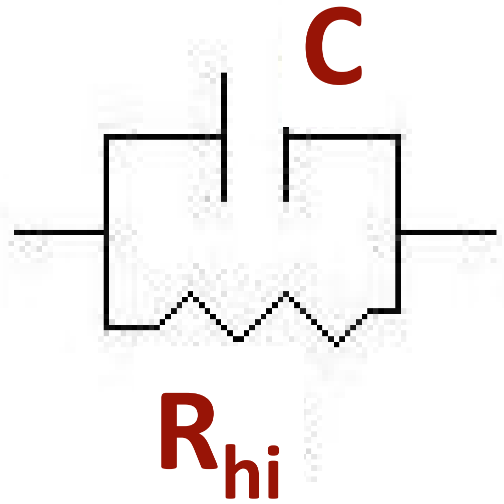
- Each electrode (Pt, Au, GC) has a potential window satisfying this feature.

Polarizable electrodes- Equivalent circuits

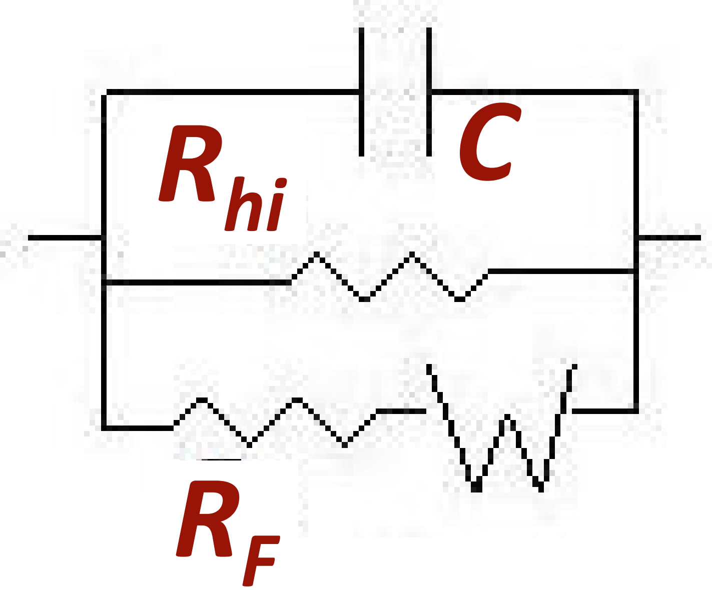
- An ideal polarizable electrode can be represented by a capacitor (condenser) in equivalent circuit.



- In reality, an extremely weak current flows at an actual polarizable electrode. Hence, a high resistance (R_{hi}) is connected in parallel with the capacitor



- If a redox species coexisted at the **polarizable** electrode, another redox reaction would occur and Faraday current would flow. In this case, a potential depending variable resistance (R_F) should be added to the equivalent circuit in parallel. Furthermore, the effect of the species diffusion should be included, and a Warburg Impedance element is connected to Faraday resistance (R_F) in equivalent circuit.



Non-Polarizable Electrodes

- is a hypothetical electrode for which once the electrode potential is changed, the **Faraday current** flows out.
- has almost a zero polarization resistance and infinitely large exchange current density & infinitely fast electrode reaction. It behaves as an electrical short.
- Its potential is almost fixed regardless the reactions it participates in.
- They can be used as **Reference** electrodes (SHE, SCE, Ag/AgCl, ..etc.).

Electricity

- **Electricity** is conducted through the cell by
  - Electrons in the electrodes and wires, and
  - Ions in solution.

- Species undergoing oxidation at the anode is called **anolyte**

- Species undergoing reduction at the cathode is the **catholyte**.

Cell potential

- A galvanic cell consists of an oxidizing agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment.

- The "**pull**," or **driving force**, on the electrons is called the cell potential (**E_{cell}**), or the electromotive force (**emf**) of the cell.

- The unit of electrical potential is the **volt** (abbreviated V), which is defined as 1 joule of work per coulomb of charge transferred.

Electromotive Force

- The "pull," or driving force, inspiring the electron transfer.
- The electrical energy permitting the transfer of a given charge.

STANDARD REDUCTION POTENTIALS AT 25°C (298 K)

Stogner oxidizing agent

Weaker oxidizing agent

Reduction Half-reaction	E° (V)
$F_2 + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	1.21
$Br_2 + 2e^- \longrightarrow 2Br^-$	1.09
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	0.56
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
$\mathbf{2H^+ + 2e^- \longrightarrow H_2}$	**0.00**
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.40
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$H_2 + 2e^- \longrightarrow 2H^-$	−2.23
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.37
$Na^+ + e^- \longrightarrow Na$	−2.71
$Li^+ + e^- \longrightarrow Li$	−3.05

Weaker reducing agent

Stronger reducing agent

Oxidizing / Reducing Ability

TABLE 18.1 › Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathcal{E}^\circ$ (V)	Half-Reaction	$\mathcal{E}^\circ$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

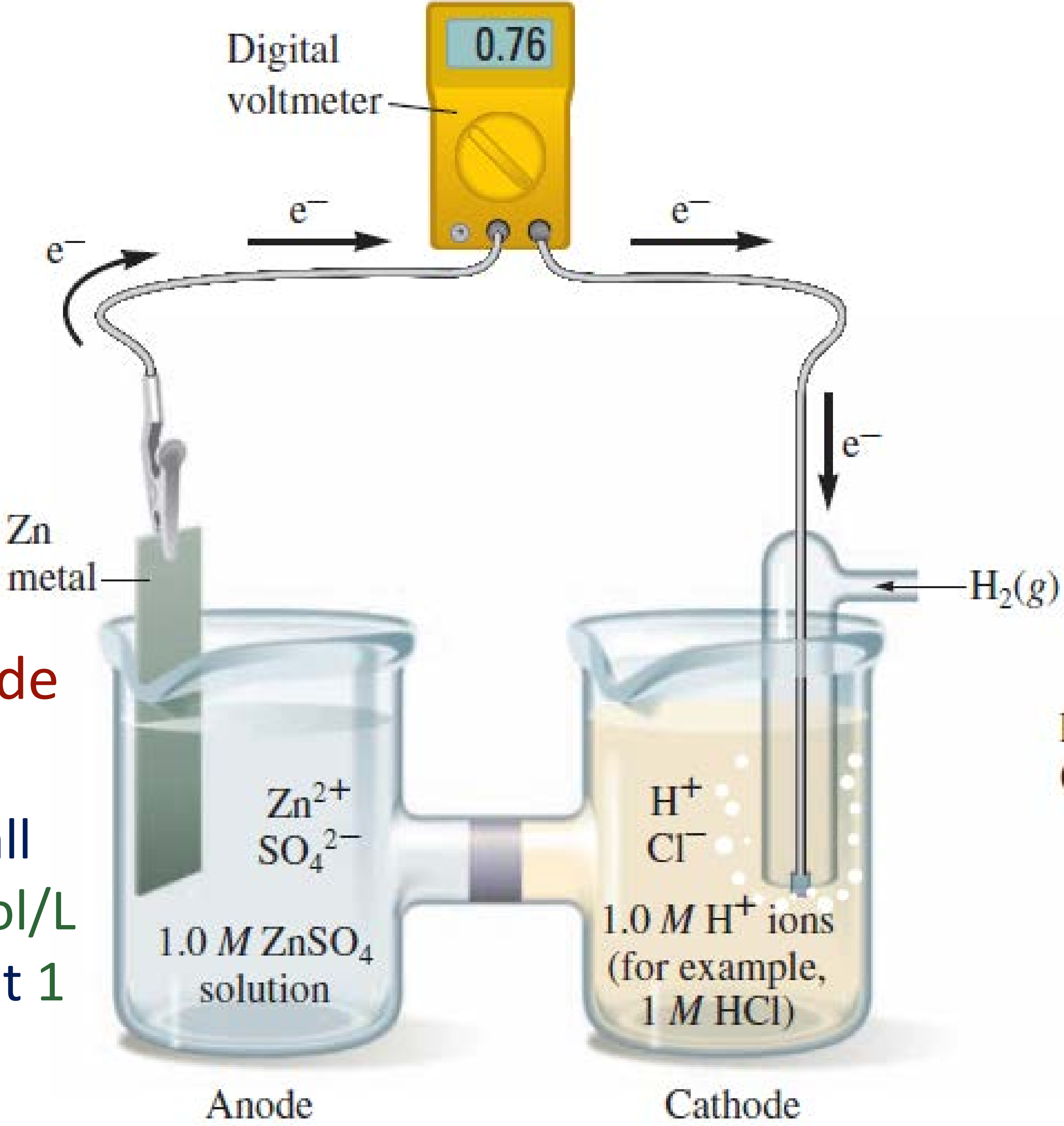
↑ **Reduction tendency increase**

↓ **Oxidation tendency increase**

Example

Standard electrode Potential

Potential when all solutes are at 1 mol/L and all gases are at 1 atm.



Example

$$2H^+(aq.) + Zn\ (s) \longrightarrow Zn^{2+}(aq.) + H_2\ (g)$$

Reduction/Cathode

$$2H^+(aq.) + 2e^- \longrightarrow H_2\ (g) \qquad E^0 = 0.0\ V$$

$$Zn^{2+}(aq.) + 2e^- \longrightarrow Zn\ (s) \qquad E^0 = -0.76\ V$$

$$Zn\ (s) \longrightarrow Zn^{2+}(aq.) + 2e^- \qquad E^0 = 0.76\ V$$

Oxidation /Anode

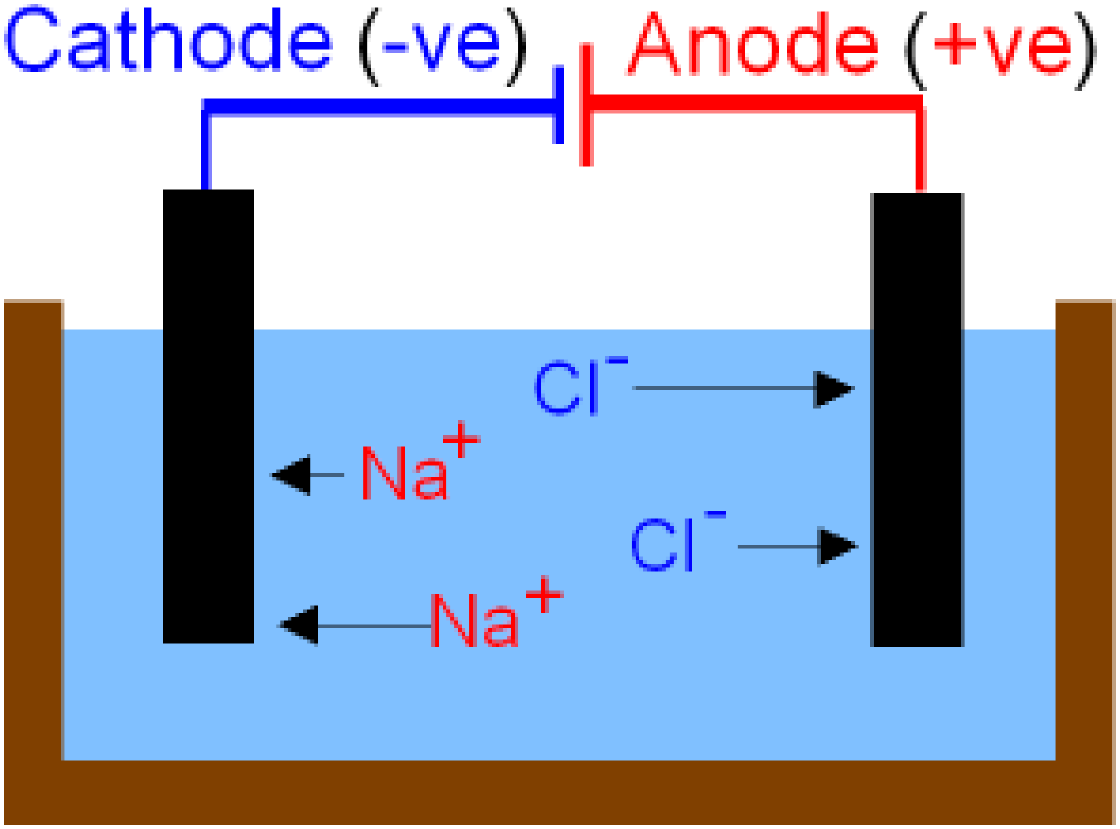
$$2H^+(aq.) + Zn\ (s) \longrightarrow Zn^{2+}(aq.) + H_2\ (g)\ E^0_{cell} = 0.76\ V$$

$$E^0_{cell} = E^0_{H^+ \rightarrow H_2} + E^0_{Zn \rightarrow Zn^{2+}}$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

Employing red. pot.

Electrolysis of molten NaCl



Non-Spontaneous/Electrolytic

$$2NaCl\ (l) \rightleftharpoons 2Na(s) + Cl_2\ (g)$$

Spontaneous/Galvanic

$$\mathrm{Na^{+} + e^{-} \longrightarrow Na} \qquad E^{0} = -2.71\ \mathrm{V}$$

$$\mathrm{Cl_2 + 2e^{-} \longrightarrow 2Cl^{-}} \qquad E^{0} = 1.36\mathrm{V}$$

Spontaneous/Galvanic

$$\mathrm{2Na + Cl_2 \longrightarrow 2Na^{+} + 2Cl^{-}} \qquad E^{0}_{\mathrm{cell}} = +4.07\ \mathrm{V}$$

Non-Spontaneous/Electrolytic

$$\mathrm{2Na^{+} + 2Cl^{-} \longrightarrow 2Na + Cl_2} \qquad E^{0}_{\mathrm{cell}} = -4.07\ \mathrm{V}$$

Electrolysis Condition in contrast to Galvanic cells

- ☐ In molten NaCl, the strongest reducing agent (**Cl⁻**, having the highest reduction E⁰) will undergo oxidation. The strongest oxidizing agent (**Na⁺**) will be reduced. If aqueous NaCl was used instead, **H⁺** ions would undergo reduction instead of Na⁺, because it is a stronger oxidizing agent.

$$Na^+ + e^- \longrightarrow Na \qquad E^0 = -2.71\ V$$ Redn./Cath.

$$2H^+ + 2e^- \longrightarrow H_2 \qquad E^0 = 0\ V$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad E^0 = 1.36\ V$$

$$2Cl^- \longrightarrow Cl_2 + 2e^- \qquad E^0 = -1.36\ V$$ Oxidation/Anode

$$2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2 \qquad E^0_{cell} = -4.07\ V$$

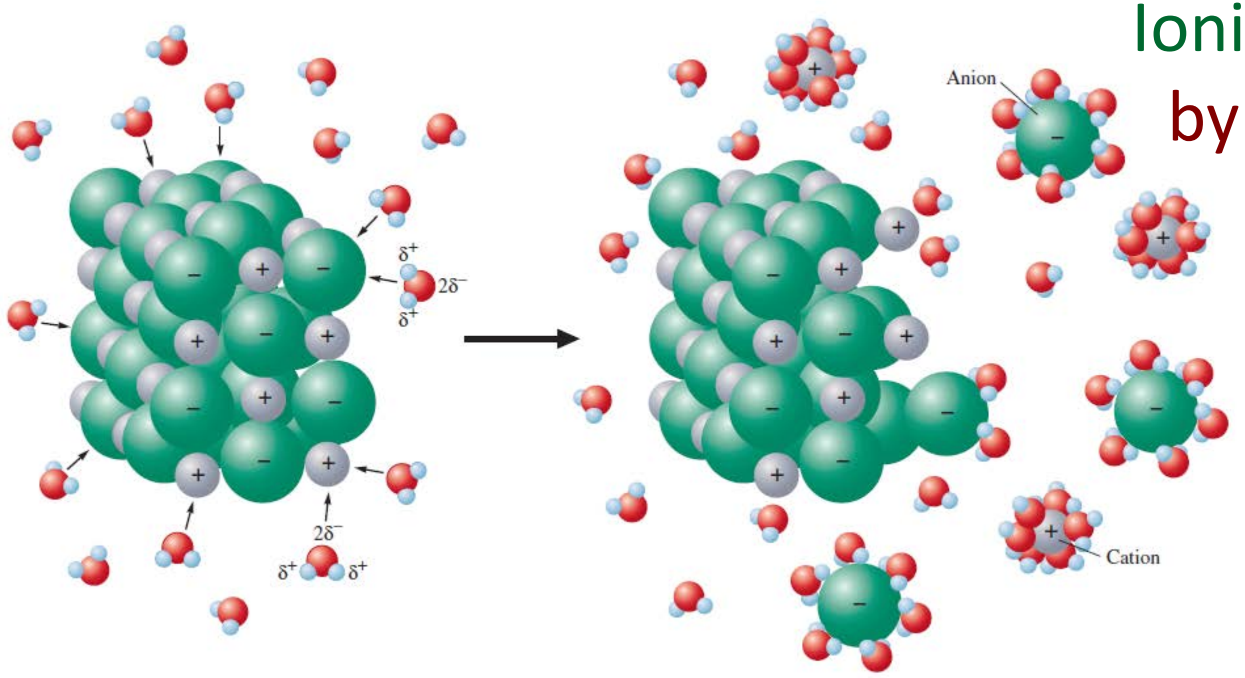
Electrolysis

Solution

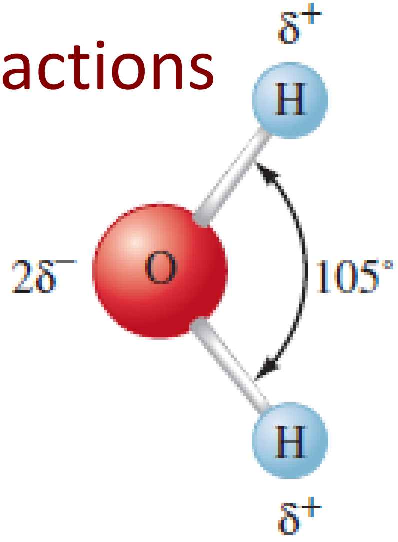
- is a homogeneous mixture of two or more components.
- The component whose phase retains ($1£7) is called "Solvent" and the other component whose phase disappears is called "Solute".
- If all components are in the same phase, the one in greatest amount will be the "Solvent" and other components are "Solutes".
- Solutions, in which water is the solvent are called aqueous solutions.
- The polarity in **H_2O** is responsible of its great ability to dissolve several compounds.

Hydration in Aqueous Solutions

- When water dissolves an ionic solid, the “positive ends” of water molecules are attracted to the negatively charged anions and the “negative ends” are attracted to the positively charged cations. This process is called “hydration”.

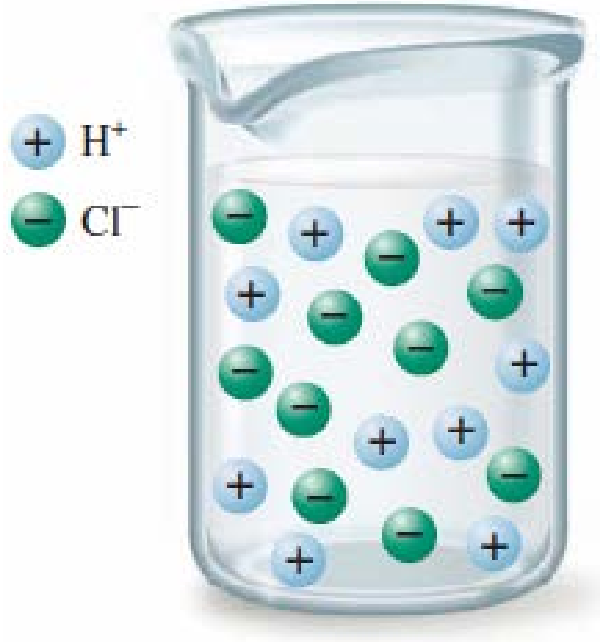


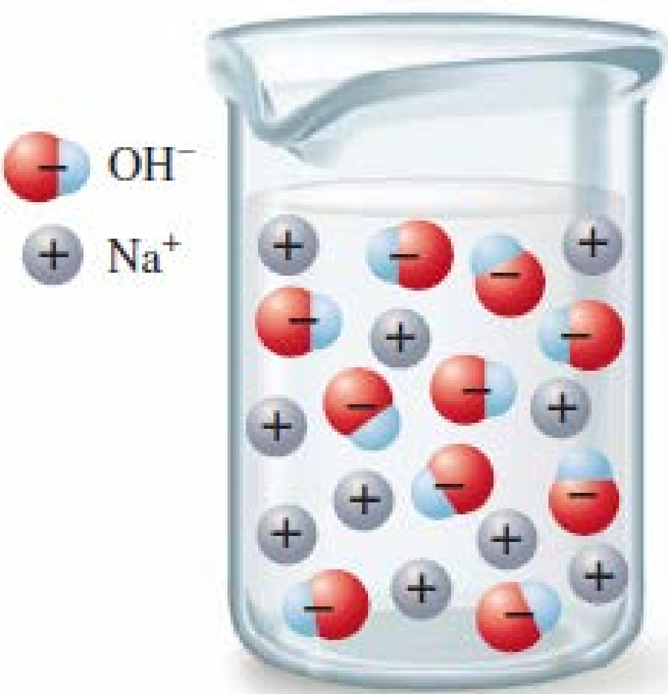
Ionic forces are replaced by stronger water–ion interactions

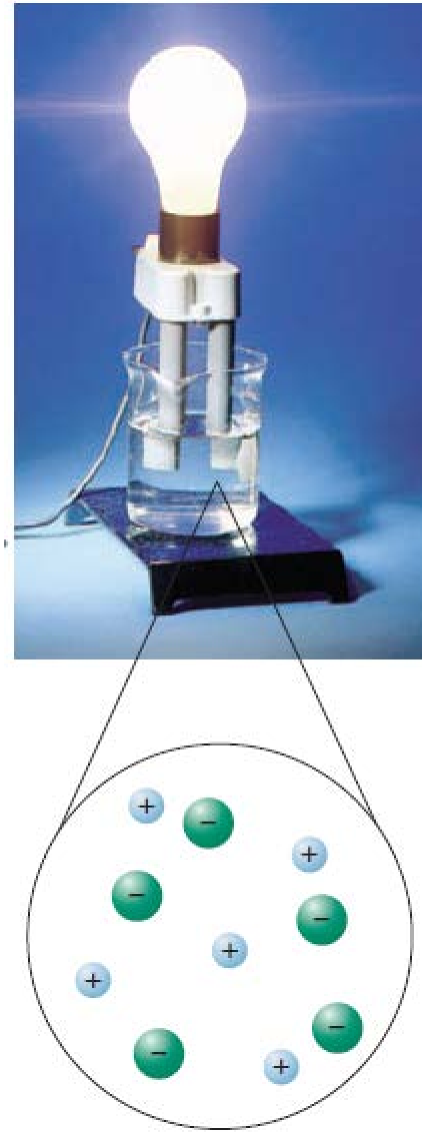


Strong Electrolyte

Substances that are completely ionized (i.e., conduct electricity efficiently) when they are dissolved in water. Examples include soluble salts, strong acids, and strong bases.

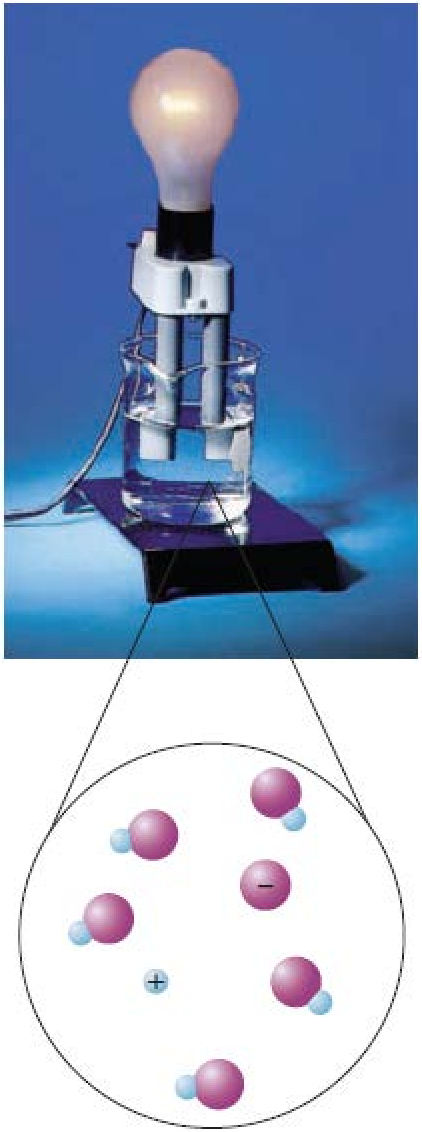






Weak Electrolyte

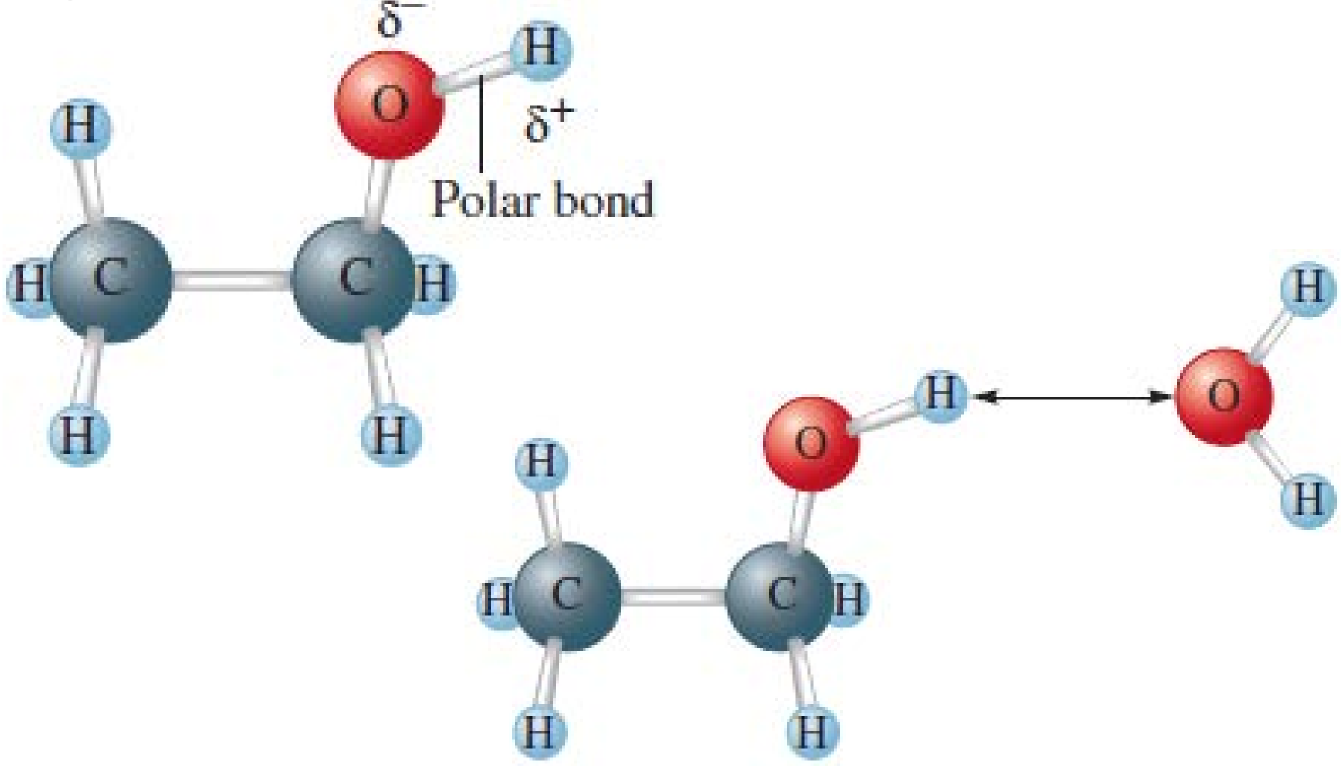
- Substances that exhibit a small degree of ionization in water (i.e., conduct only a small current).
- They produce relatively few ions when dissolved in water.
- Examples include weak acids (acetic acid) and weak bases (ammonia).

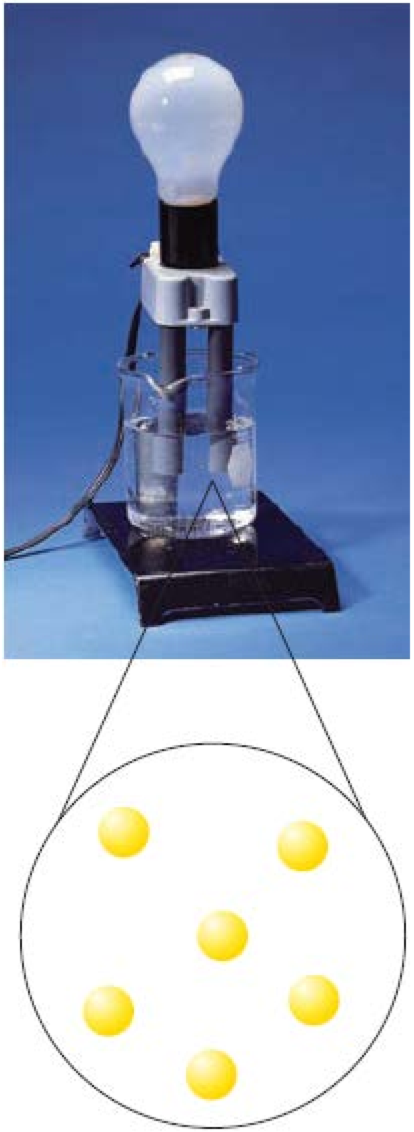


$$HC_2H_3O_2(aq.) + H_2O(l) \leftrightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

Nonelectrolyte

- Substances that dissolve in water but do not produce any ions (i.e., non conductors for electricity).
- Examples include ethanol and glucose





Electrolytes and Electrolysis

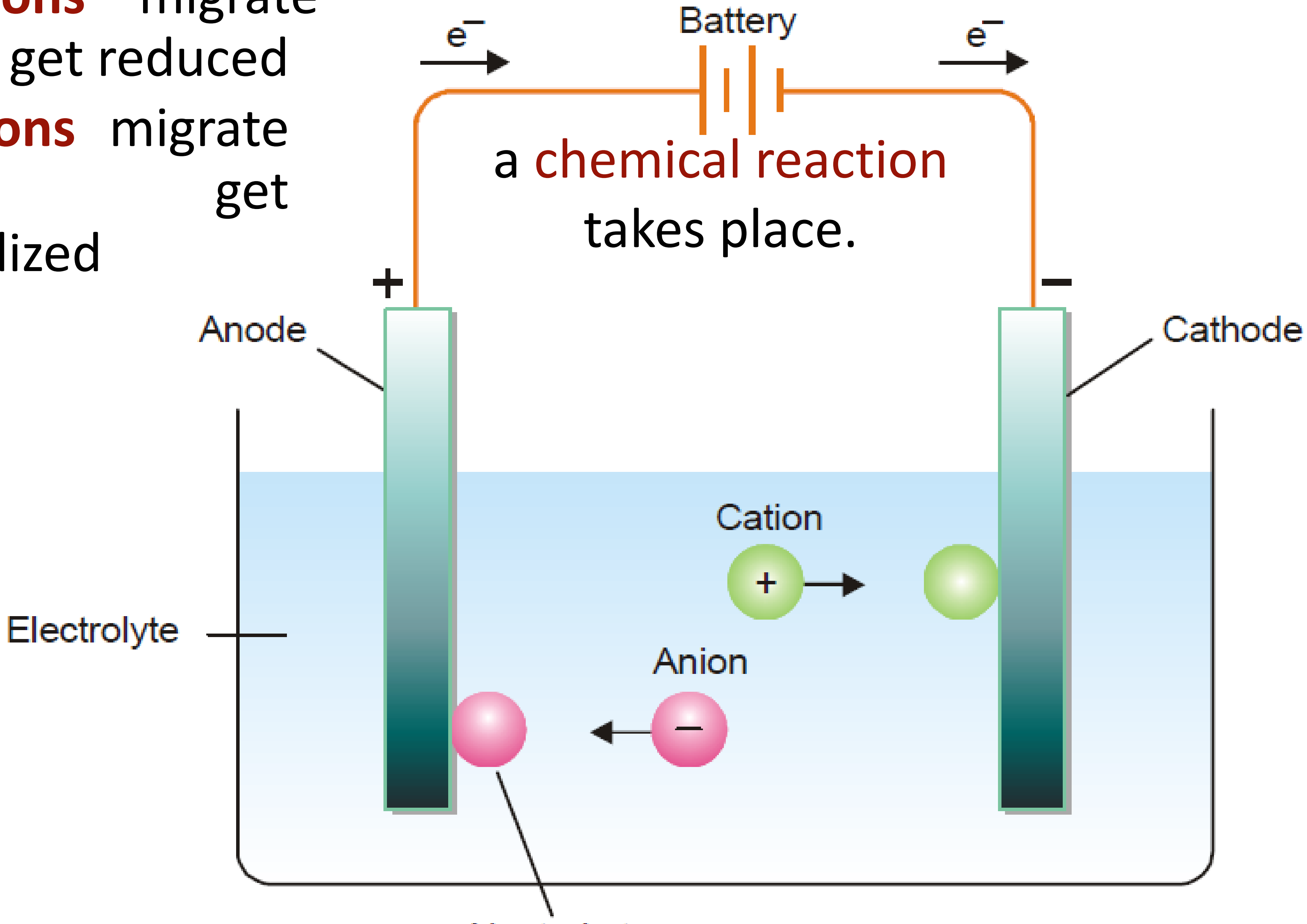
- An **electrolyte** invariably undergoes chemical decomposition as a result of the passage of electric current through its solution; a phenomenon termed as “**electrolysis**” (lyo = breaking).

- **Electrolysis** is carried in a cell containing an electrolyte in which two electrodes are dipped and connected outside to a **battery**.

- The electrode connected to the positive terminal of the battery attracts the negative ions (**anions**) and is called **anode**. The other electrode connected to the negative end of the battery attracts the positive ions (**cations**) and is called **cathode**.

Mechanism of Electrolysis

- **Cations** migrate and get reduced
- **Anions** migrate and get oxidized



a chemical reaction takes place.

Electrolysis of HCl

$$2HCl \xrightarrow{H_2O} 2H^+ + 2Cl^-$$

$$H^+ + e^- \xrightarrow{\text{Cathode}} H$$ **Reduction**

$$H + H \xrightarrow{\text{Cathode}} H_2$$ **Combination**

$$Cl^- \xrightarrow{\text{Anode}} Cl + e^-$$ **Oxidation**

$$Cl + Cl \xrightarrow{\text{Anode}} Cl_2$$ **Combination**

$$2H^+ + 2Cl^- \xrightarrow{\text{Electrolysis}} H_2 + Cl_2$$ **Overall**

Electrical Units

- A **Coulomb** (C): is a unit quantity of electricity. It is the amount of electricity which will deposit 0.001118 g of silver from a 15 % solution of silver nitrate in a coulometer.
- An **Ampere** (A): An ampere is a unit rate of flow of electricity. It is that current which will deposit 0.001118 g of silver in one second. In other words, an **ampere** is a current of one coulomb per second.
- An **ohm** (Ω): is a unit of electrical resistance. It is the resistance offered at 0^oC to a current by a column of mercury 106.3 cm long of about $1\ mm^2$ cross-sectional area and weighing 14.4521 g.
- A **volt** (V) is a unit of electromotive force. It is the difference in electrical potential required to send a current of 1A through a resistance of 1 Ω.

Faraday’s 1st law of electrolysis

- The amount (or mass, m) of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity, Q which passes through the electrolyte solution.

$$\boxed{m \propto Q} \Rightarrow \boxed{Q = It} \Rightarrow \boxed{m \propto It} \Rightarrow \boxed{m = ZIt}$$

Z is a constant known as the **Electrochemical Equivalent** of the substance (electrolyte)

- Z is the amount of a substance deposited by 1A current passing for 1s (i.e., 1C).

Faraday's 2nd law of electrolysis

- When the same quantity of electricity, Q passes through solutions of different electrolytes, the amounts (or mass, m) of the substances liberated at the electrodes are directly proportional to their electrochemical **equivalents**.

- **F**: is the quantity of electricity, Q required to liberate one **gram-equivalent** of a substance.

1F = $(1.6\times10^{-19}$ C/e$)$ $(6.023\times10^{23}$ e/mole e's$)$

Faraday (1F = 96,485.3 C/mol e's)

F vs. Ion’s Valency

- Quantity of electricity, Q required to liberate 1 mol of a substance depends on its ion’s valency.

Q required to deposit 1 mol of Ag^+, Cu^{2+} and Al^{3+} are

$$Q_{Ag^+} = 1F \text{ per 1 mol of } Ag^+ \qquad Ag^+ + e^- \rightarrow Ag$$

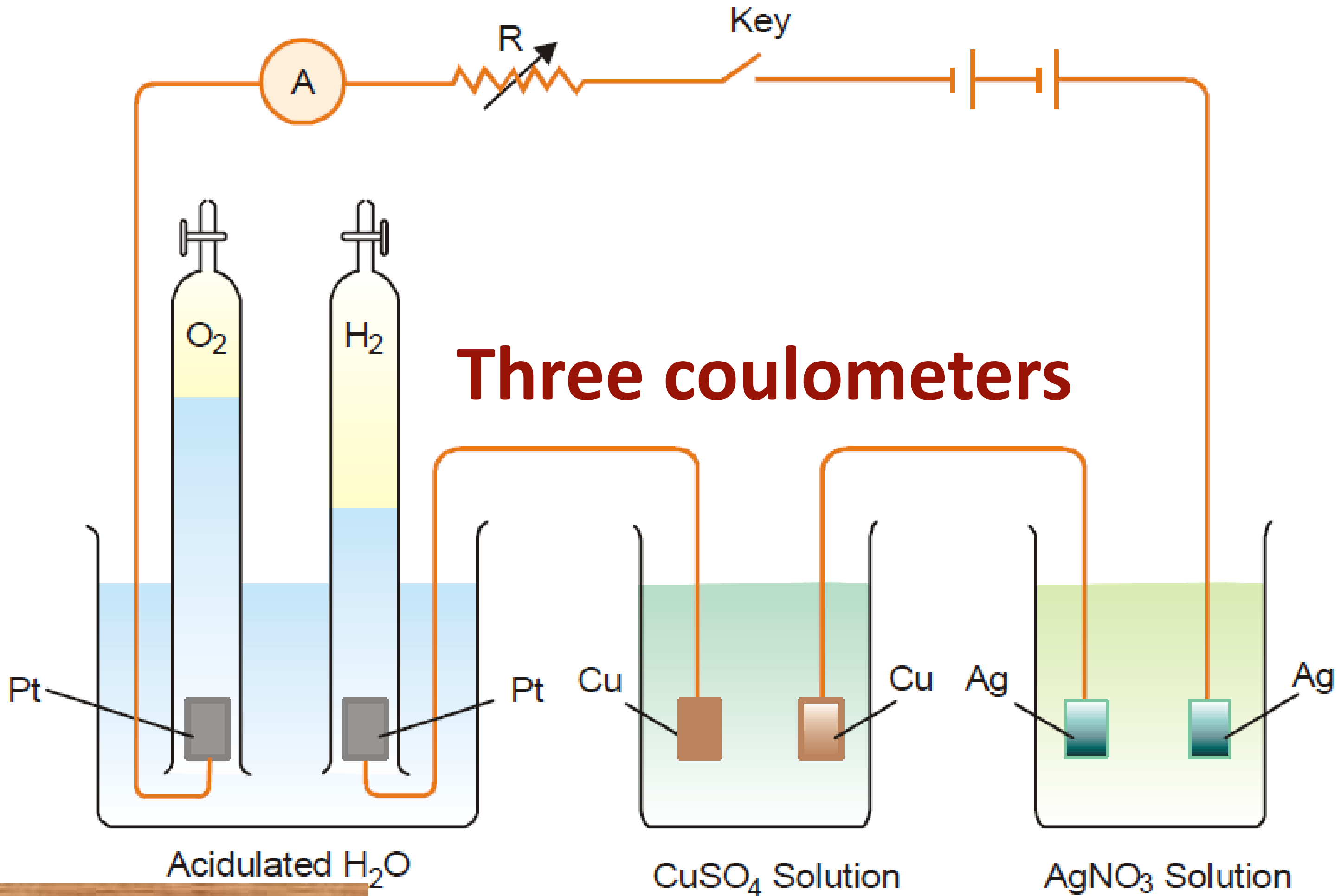
$$Q_{Cu^{2+}} = 2F \text{ per 1 mol of } Cu^{2+} \qquad Cu^{2+} + 2e^- \rightarrow Cu$$

$$Q_{Al^{3+}} = 3F \text{ per 1 mol of } Al^{3+} \qquad Al^{3+} + 3e^- \rightarrow Al$$

$$Q_{M^{n+}} = nF \text{ per 1 mol of } M^{n+}$$

- The quantity of electricity in 1F is 1 mol of electrons. 1F = 96,500 C/mol e’s

- Masses of the substances deposited on the electrodes are proportional to their chemical equivalents (Eq. mass).



Three coulometers

$2H^+ + 2e^- \rightarrow H_2$

$Cu^{2+} + 2e^- \rightarrow Cu$

$Ag^+ + e^- \rightarrow Ag$

For any quantity of electricity passed for the same time

$$\frac{m_{H_2}}{m_{Cu}} = \frac{\text{Eq. mass}_{H_2}}{\text{Eq. mass}_{Cu}} = \frac{1.0}{31.78}$$

$$\frac{m_{Cu}}{m_{Ag}} = \frac{\text{Eq. mass}_{Cu}}{\text{Eq. mass}_{Ag}} = \frac{31.78}{107.88}$$

For $Q = 1$,

$$m_{H_2} = 0.00001036\text{ g}$$

$$m_{Cu} = 31.78 \times 0.00001036 = 0.0003292\text{ g}$$

$$m_{Ag} = 107.88 \times 0.00001036 = 0.001118\text{ g}$$

Problem

- 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper?

Solution

$$\mathbf{Cu^{2+} + 2e^{-} \rightarrow Cu}$$ **Reduction**

$$\boxed{\mathbf{m = ZIt}}$$

$$0.1978\ \mathrm{g} = Z(0.2\ \mathrm{A})\left(50\ \mathrm{min} \times \frac{60\ \mathrm{s}}{1\ \mathrm{min}}\right)$$

$$\boxed{\mathbf{Z = 3.297 \times 10^{-4}\ g\ C^{-1}}}$$

Problem

- What current strength in amperes will be required to liberate 10 g of iodine from potassium iodide solution in one hour? Atomic mass of I = 127 g/mol.

Solution

$2I^- \rightarrow I_2 + 2e^-$ **Oxidation**

Calculation of Z →

2 × 127 g I_2 is liberated by 2F (2 mol e^-) = 2 × 96,500 C

Simply,

127 g I_2 (1 g eqvt) is liberated by → **96,500 C**

10 g I_2 is liberated by → **Q**

$$\boxed{Q = 10\ \mathrm{g\ I_2} \times \frac{96500\ \mathrm{C}}{127\ \mathrm{g\ I_2}} = 7.6 \times 10^3\ \mathrm{C}}$$

However,

$$\boxed{Q = It}$$

$$\boxed{Q = 7.6 \times 10^3\ \mathrm{C} = I \times 1\mathrm{h} \times \frac{60\ \mathrm{min}}{1\ \mathrm{h}} \times \frac{60\ \mathrm{s}}{1\ \mathrm{min}}}$$

$$\boxed{I = 2.11\ \mathrm{A}}$$

Faraday's General Formula

Combining 1st and 2nd law gives:

$$\boxed{\mathbf{m} = \frac{\mathbf{Q}}{\mathbf{F}} \times \frac{\mathbf{M_m}}{\mathbf{n}} = \frac{\mathbf{ItM_m}}{\mathbf{nF}}}$$

m : mass of the electroactive substance (g).

Q: charge (C) required for deposition

F : Faraday's constant ≈ 96500 C/mol of e^-

M_m: molar mass of the electroactive species (g/mol)

n : no. of e^- involved (mol^{-1} of electroactive substance)

I: current density passed (A)

t: time of the process (s)

$\frac{M_m}{n}$ = Equivalent mass

Units

$$M^{n+} + ne^{-} \rightarrow M$$

$$\boxed{m = \frac{Q}{F} \times \frac{M_m}{n} = \frac{ItM_m}{nF}}$$

$$\boxed{m(g_M) = \frac{Q\ (C) \times M_m\ \left(\frac{g_m}{mol_M}\right)}{n\left(\frac{mol_{e^-}}{mol_M}\right) \times F\left(\frac{C}{mol_{e^-}}\right)}}$$

Problem

- An electric current is passed through three cells in series containing respectively solution of copper sulphate, silver nitrate and potassium iodide. What masses of silver and iodine will be liberated while 1.25 g of copper is being deposited?

Solution

As they are connected in series, same Q will be passed

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

$$Ag^{+} + e^{-} \rightarrow Ag$$

$$2I^{-} \rightarrow I_2 + 2e^{-}$$

$$\boxed{m(g_{Cu}) = \frac{Q_{Cu}(C) \times M_m\left(\frac{g_{Cu}}{mol_{Cu}}\right)}{n\left(\frac{mol_{e^-}}{mol_{Cu}}\right) \times F\left(\frac{C}{mol_{e^-}}\right)}}$$

$$\boxed{1.25(g_{Cu}) = \frac{Q_{Cu}(C) \times 63.4(\frac{g_{Cu}}{mol_m})}{2\left(\frac{mol_{e^-}}{mol_{Cu}}\right) \times 96500(\frac{C}{mol_{e^-}})}}$$

$$\boxed{Q_{Cu} = 3805\ C}$$

$$\boxed{Q_{Cu} = Q_{Ag} = Q_{I_2}}$$

$$\boxed{m(g_{Ag}) = \frac{3805\ C \times 108\left(\frac{g_{Ag}}{mol_{Ag}}\right)}{1\left(\frac{mol_{e^-}}{mol_{Ag}}\right) \times 96500\left(\frac{C}{mol_{e^-}}\right)} = 4.26\ g_{Ag}}$$

$$m\left(g_{I_2}\right) = \frac{3805\ \text{C} \times 254\left(\frac{g_{Ag}}{mol_{Ag}}\right)}{2\left(\frac{mol_{\ e^-}}{mol_{Ag}}\right) \times 96500\left(\frac{\text{C}}{mol_{\ e^-}}\right)} = 5.0\ g_{I_2}$$

Another Solution

One may utilize that at constant Q

$$m \propto \text{Equivalent mass} = \frac{M_m}{n}$$