CHAPTER 9: ELECTROCHEMISTRY

9.1 Galvanic Cell
9.2 Nernst Equation
9.3 Electrolitic Cell

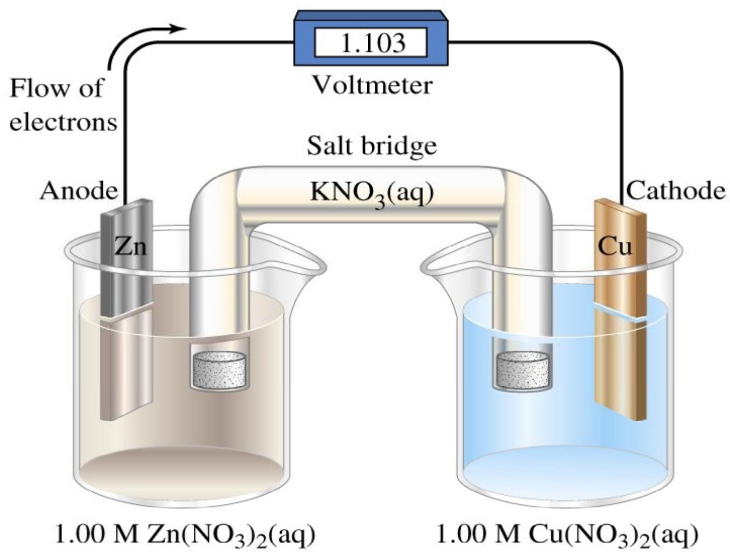
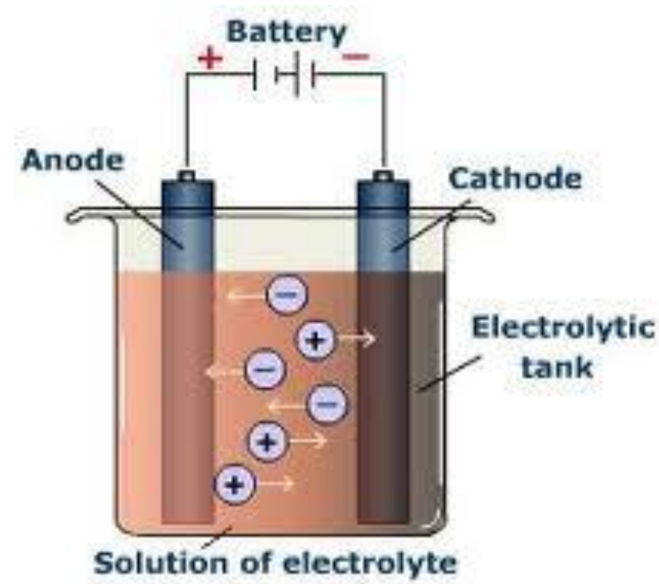
Electrochemistry

Is the study of the relationship between ___________ ______ and _________ ______.

Electrochemical processes involved are :

One type of reaction cannot occur without the other.

Electrochemical Cells

GALVANIC CELL	ELECTROLYTIC CELL
	

Definition

Spontaneous reaction	A reaction that has a natural tendency to occur and does not require an energy input for it to occur. Example: Galvanic cell & rusting of iron
Non-spontaneous reaction	A reaction that cannot happen naturally and needs an energy input to help it to occur. Example: Photosynthesis & electrolytic cell

CHAPTER 9: ELECTROCHEMISTRY
9.1 Galvanic Cell

Electrochemistry

At the end of this topic, students should be able to:

a) Define: oxidation, reduction & redox reaction
b) Explain electrode potential for a metal immersed in a corresponding metal ions solution
c) Sketch and describe the components and operation of a voltaic/galvanic cell
d) Write half-cell equations and the overall cell reaction equation

REDOX Reaction

- Reaction involving both oxidation & reduction occur at the same time

REDUCTION

- _____ of electron
- Oxidation no. __________
- Reaction at _________

Example:

OXIDATION

- _____ of electron
- Oxidation no. __________
- Reaction at ______

Example:

Electrode	Conductor (carbon rod or metal) that allows electrons to pass through it.
Anode	Electrode at which ________ occurs.
Cathode	Electrode at which ________ occurs.

Remember….
RED CAT
= REDuction at CAThode

EXAMPLE:

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

Cu is __________ to Cu^{2+}

Ag^{+} is _________ to Ag.

Reducing agent: _____

Oxidising agent: _____

The _________ ______ is reduced, and the ________ ______ is oxidised.

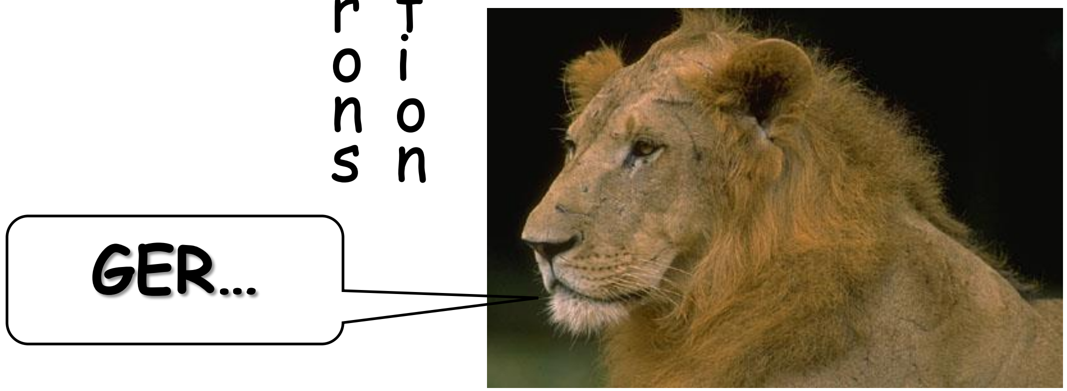
Oxidising agent (oxidant): species that undergoes reduction or gains electrons.

Reducing agent (reductant): species that undergoes oxidation or donates electrons.

LEO the lion says GER!

Lose
Electrons
Oxidation

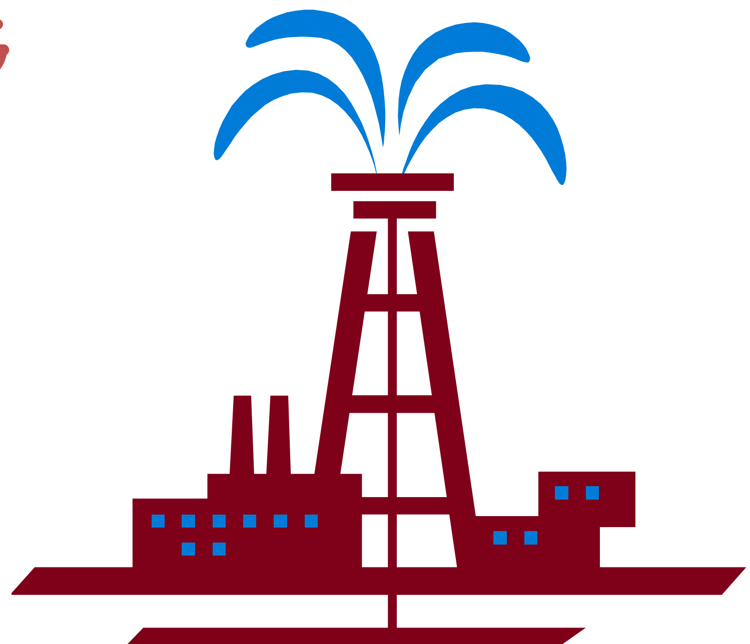
Gain
Electrons
Reduction



OIL RIG

Oxidation
Is
Lose

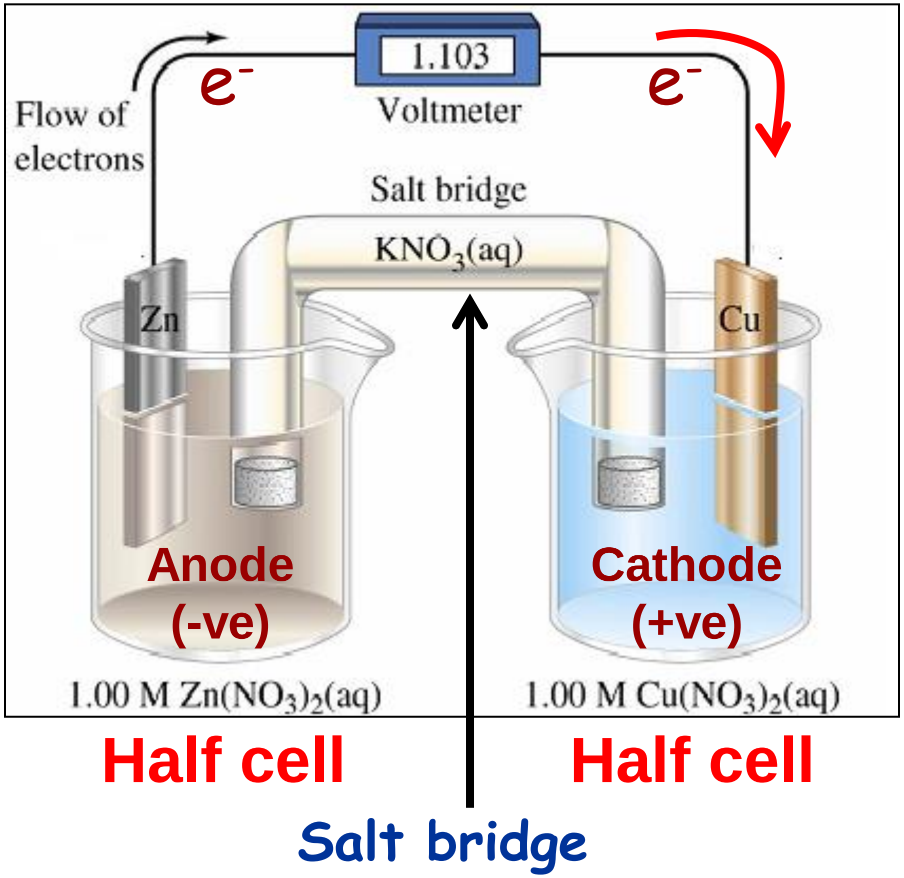
Reduction
Is
Gain



Galvanic / Voltaic Cell

Electron moves from the ______ **to the** ________

- A **half-cell** consists of an __________ immersed in a solution of ions.



Anode: electrode at which ___________ occurs

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

Cathode: electrode at which ___________ occurs

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

Cations (K^+) migrate to the cathode; **anions (NO_3)** move to the anode

Half Cell Equations & Overall Reaction

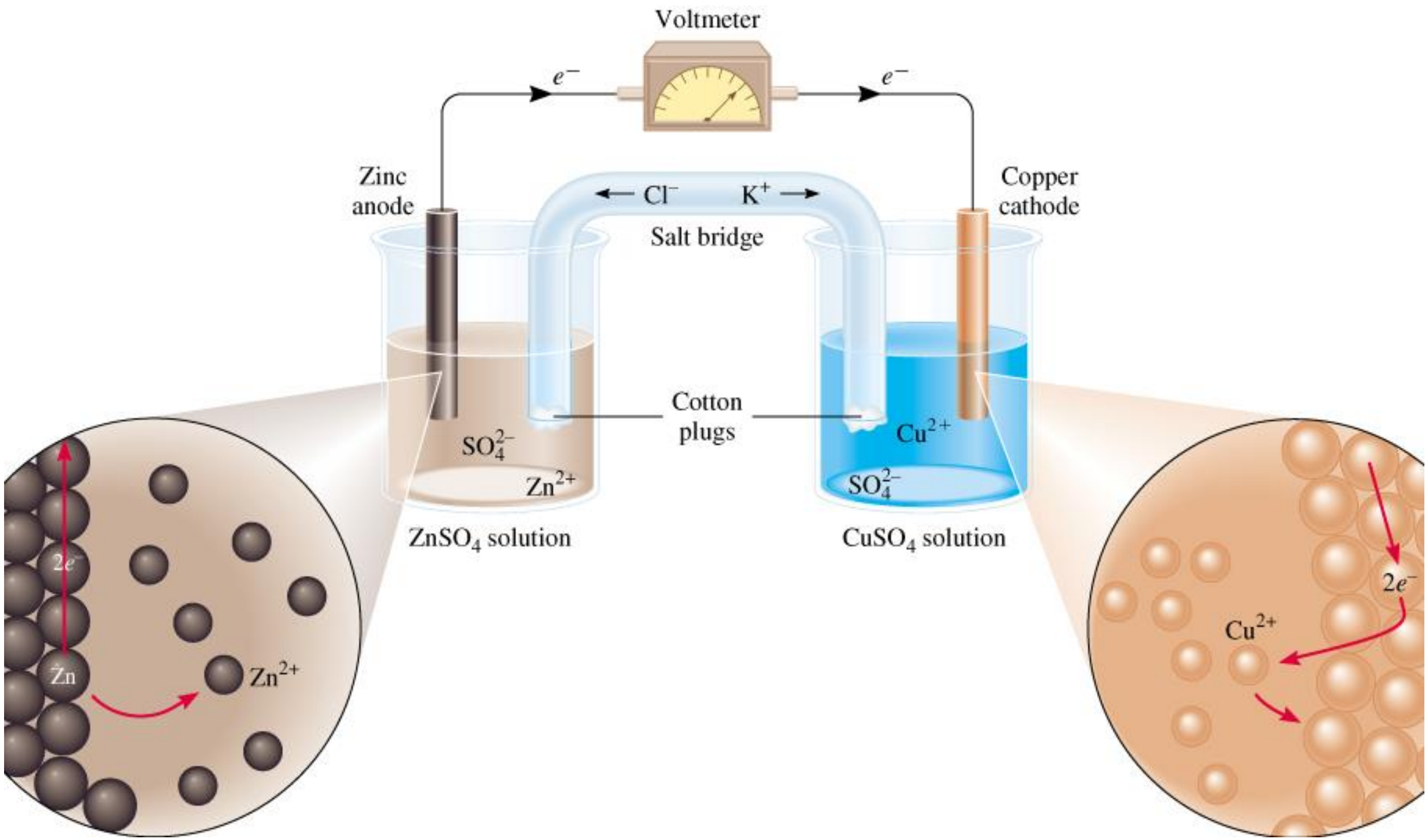
anode :
(oxidation)

cathode :
(reduction)

} Half-cell reactions

Overall cell reaction :

Zn electrode vs Cu electrode



What happens at the zinc electrode ?

What happens at the zinc electrode ?

What happens at the zinc electrode ?

- Zinc is ___________________ than copper.
- Tendency to release electrons: Zn > Cu.

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

- Zinc electrode dissolves.
- Oxidation occurs at the Zn electrode.
- Zn^{2+} ions enter $ZnSO_4$ solution.
- Zn is the _______ electrode since it is a source of electrons => ______ .

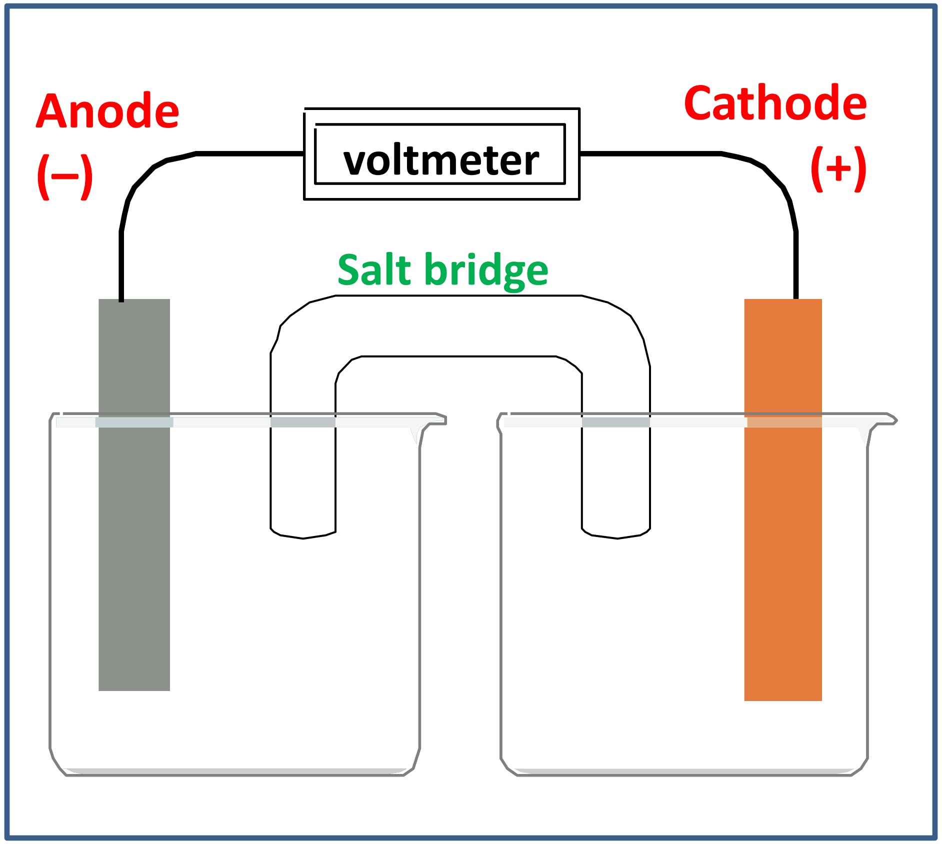
What happens at the copper electrode ?

- The electron from the Zn metal moves out through the wire enter the Cu metal
- Cu^{2+} ions from the solution accept electrons.

$$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$$

- Copper electrode is deposited.
- Reduction occurs at the Cu electrode.
- Cu is the _________ electrode => _________

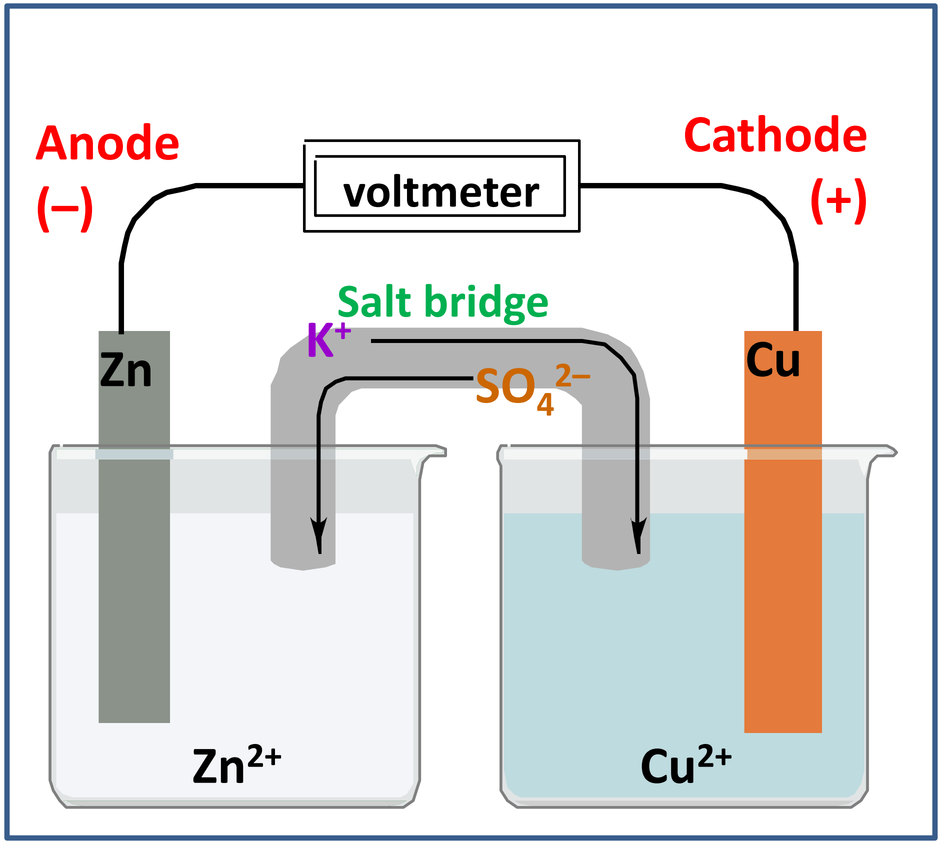
Salt Bridge



- U tube containing an inert electrolyte.
- Example: ______ , ______ , ______ or ______.
- Suspended in a gel.
- Not react with the electrode nor with the ions in the cell.

Salt Bridge

Example: Saturated K_2SO_4



Functions:

a) to __________ the electrical circuit by permitting the ions to flow through it.

b) to maintain ____________ ____________ in electrolytes.

c) to __________ physically the anode compartment and the cathode compartment so that no metallic element will be deposited on the anode

How does the cell maintains its electrical NEUTRALITY?

Left Cell

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Zn^{2+} ions enter the solution.

Causing a net excess of +ve charge.

Right Cell

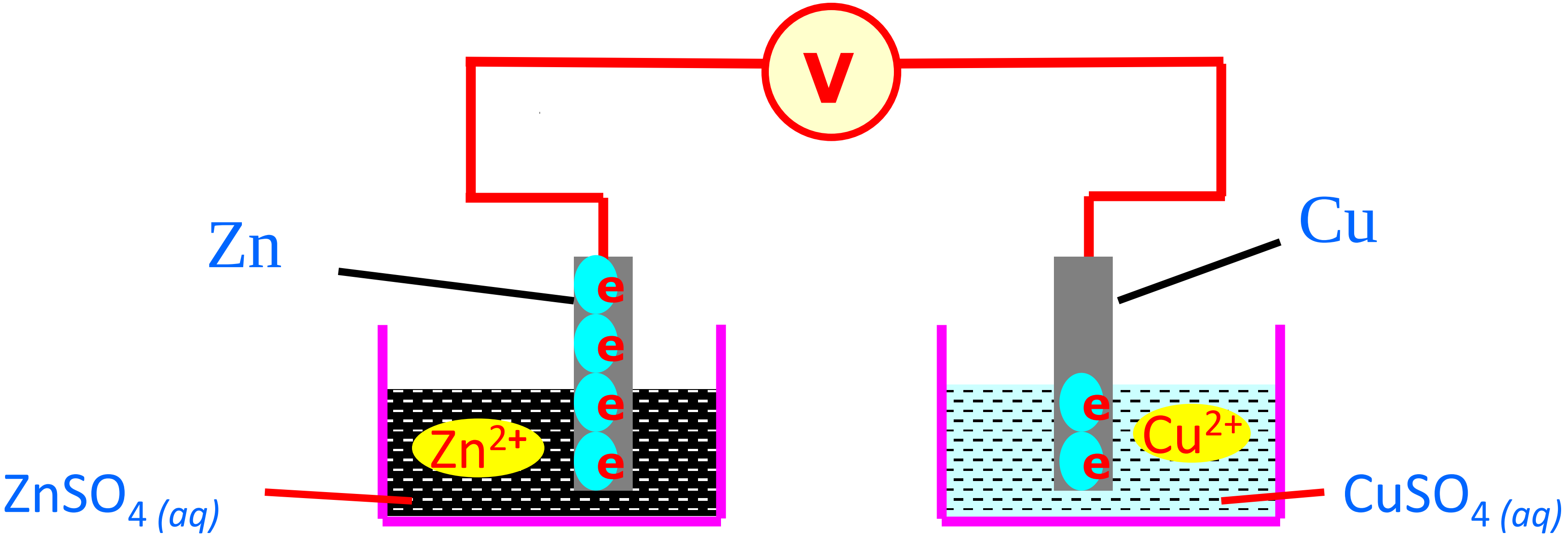
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Cu^{2+} ions leave the solution.

Causing an overall excess of -ve charge.

Electrical neutrality is maintained

What happened if there is no salt bridge?



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

Writing the Cell Notation /Cell Diagram

Electrode (s) | Electrolyte || Electrolyte | Electrode (s)

Writing the Cell Notation

Overall cell reaction : $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

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

Note: Ion with lower oxidation no. are written next to electrode

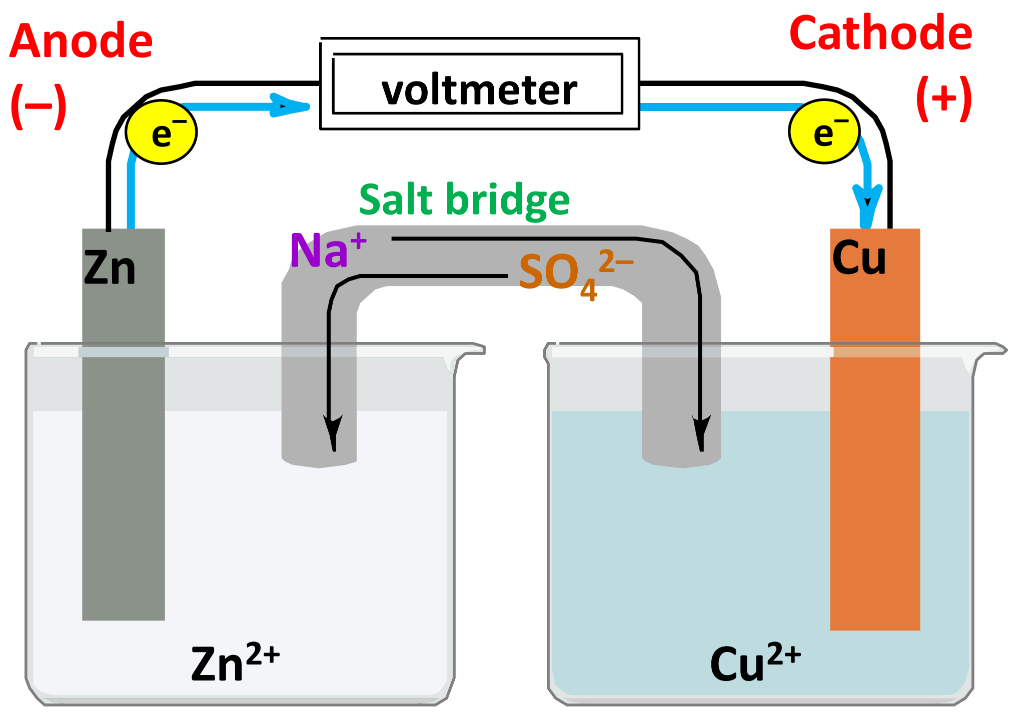
Electron is flowing from anode to cathode…

REMEMBER "2R" – Right for Reduction

&

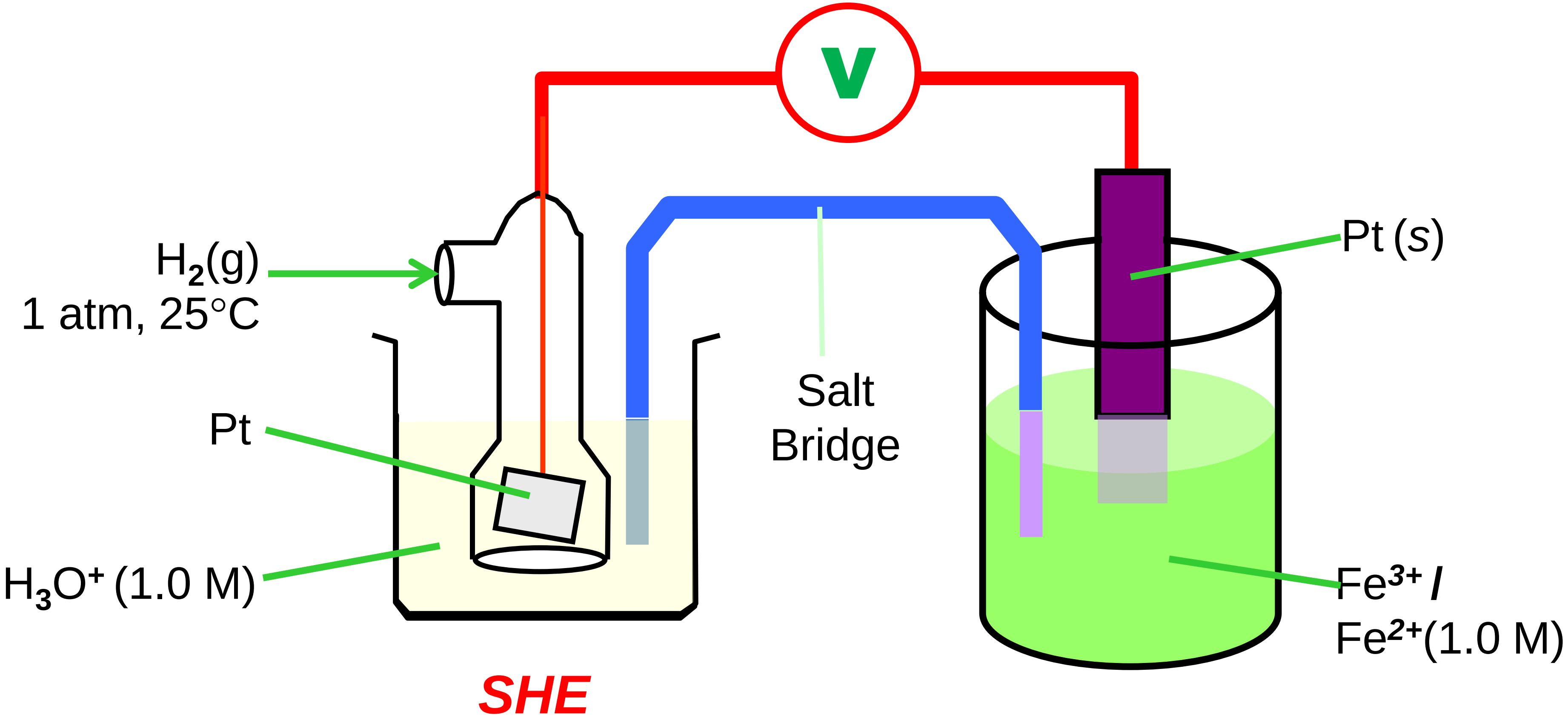
"RED CAT" – REDuction at CAThode

EXAMPLE 1:



Cell notation:

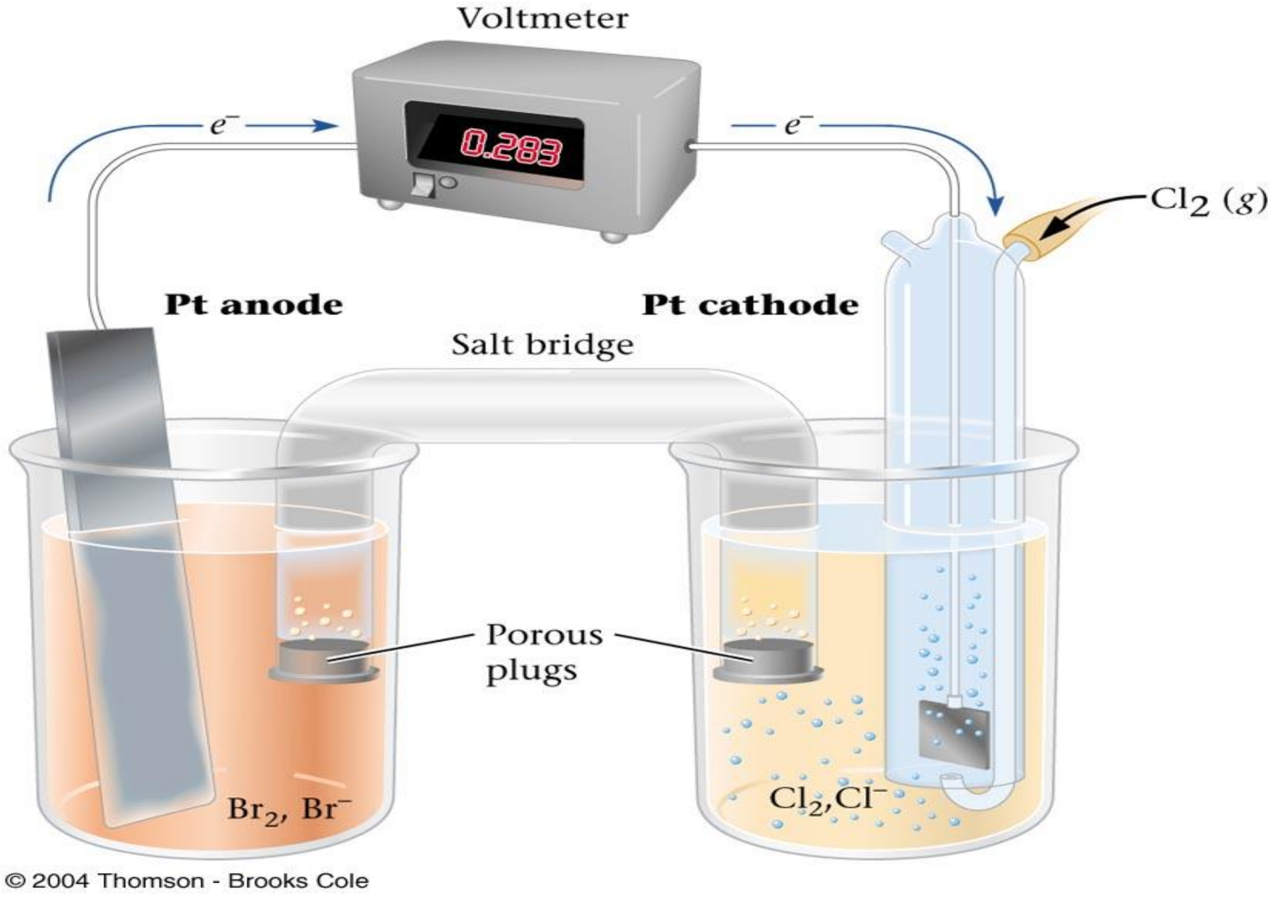
EXAMPLE 2:



Cell notation:

Note: Pt is used as the electrode if the element does not exist as solid at 25°C (Cl_2, O_2) or is a non-conductor (I_2).

EXAMPLE 3:



Cell notation:

Note: For galvanic cells involving gases, an additional vertical line is present and written next to the electrode

Keep in Mind !

1) Phases of the reactants and products must be indicated. Concentration of ion or pressure of gas must be specified if it is known.

2) / -- represents phase boundary within a half-cell
Use comma between two species of the same phase.

3) // -- designates the salt bridge connecting two half-cells

4) *OIL* : *Oxi*dation is on the *L*eft

REG : *Red*uction is on the *R*ight

5) *Solid conductors* (metal rods) must be at both ends of a cell notation

Exercise :

For the cell below, write the anode and cathode reaction and also net cell reaction.

1. $Al_{(s)} | Al^{3+}_{(aq)} || Sn^{4+}_{(aq)}, Sn^{2+} (aq) | C (s)$

Solution:

2. $Pt_{(s)} \mid Cu^{+}_{(aq)}, Cu^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$

Solution:

Exercise :

Write the cell notation for the galvanic cell below:

a) $2Fe^{3+}{}_{(aq)} + 2I^{-}{}_{(aq)} \rightarrow I_{2\,(aq)} + 2Fe^{2+}{}_{(aq)}$

b) $Mg_{(s)} + Sn^{2+}{}_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + Sn_{(s)}$

EXERCISE :

Write the cell notation for a voltaic cell that consists of a copper electrode immersed in 1.0 M $Cu(NO_3)$ solution and a silver electrode immersed in 1.0 M $AgNO_3$ solution. The copper electrode is the anode.

SUMMARY

- **Galvanic cell**: chemical $E \rightarrow$ electrical E
- **Electrolytic cell**: electrical $E \rightarrow$ chemical E
- Flip equation, change the sige of $E°$
- Multiply the equation, no change in $E°$
- Cell notation: anode // cathode

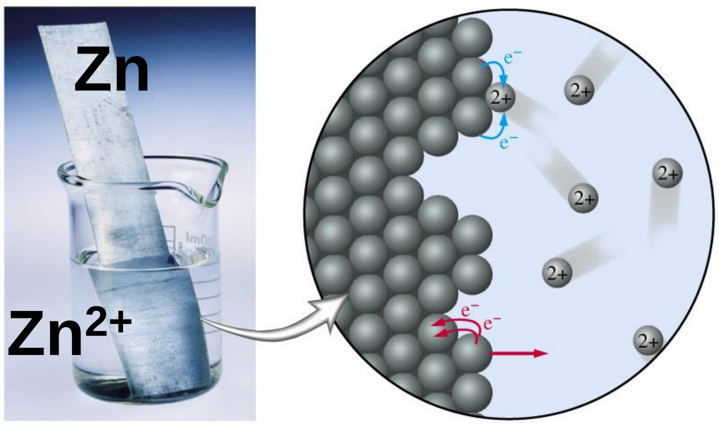
Electrochemistry

At the end of this topic, students should be able to:

a) Define: oxidation, reduction & redox reaction
b) Explain electrode potential for a metal immersed in a corresponding metal ions solution
c) Sketch and describe the components and operation of a voltaic/galvanic cell
d) Write half-cell equations and the overall cell reaction equation
e) Write cell notation for a Galvanic cell

Electrode Potential

A Zn plate immersed in its ions solution



$$\mathbf{Zn(s)} \rightleftharpoons \mathbf{Zn^{2+}}(aq) + 2\mathbf{e}$$

- Zn metal loses **e,**
  Zn^{2+} gains electrons
- Equilibrium between
  Zn and Zn^{2+}

The **electrical potential difference** produced between the electrode and the solution in a half cell is called ***electrode potential*** of the metal.
~ cannot be measured

Electrode Potential

The electrode potential is also known as **reduction potential.**

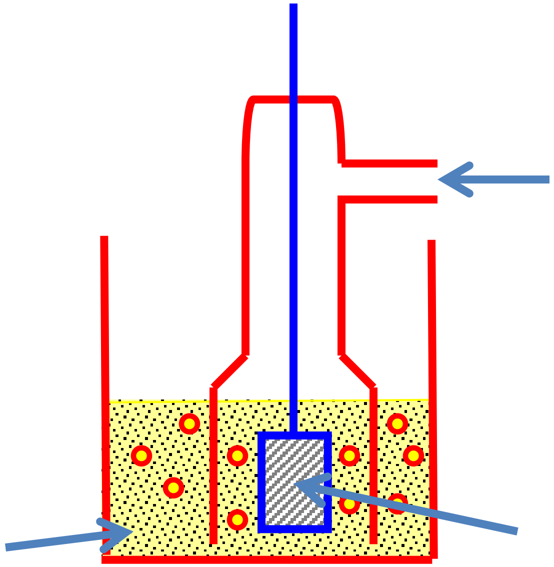
The half cell is connected to a **standard hydrogen electrode** (SHE) which is **used as a standard or reference electrode** to measure the electrode potential of any half cell.

The standard conditions for the measurements:

a. The concentrations of aqueous ions are 1.0 M
b. All gas pressures are fixed at 1 atm
c. The temperature is 25°C (289K)

Standard Hydrogen Electrode, SHE

SHE consists of **H_2 (g, 1 atm)**, bubbling around a platinum electrode which is immersed in **1.0 M** solution of **H^+** solution **at 25°C**.



E° = ???

The standard reduction of SHE is 0.00 V

- The half cell equation:

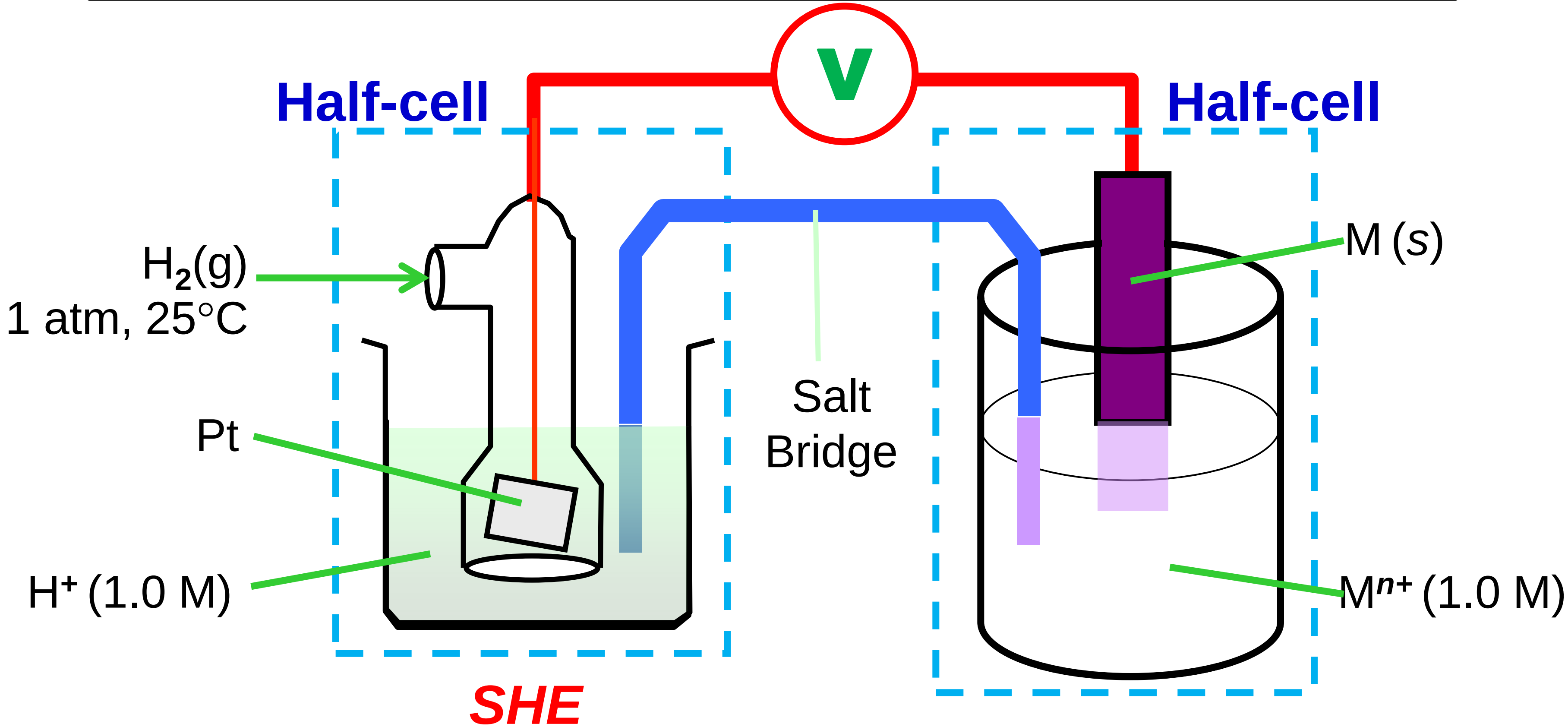
$$2H^+_{(aq)}\,(1M) + 2e \rightleftharpoons H_{2(g\,,\,1\,atm)} \qquad E° = 0$$

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

- The cell notation for SHE is either:

In either case, E^0 of SHE remains 0.00 V

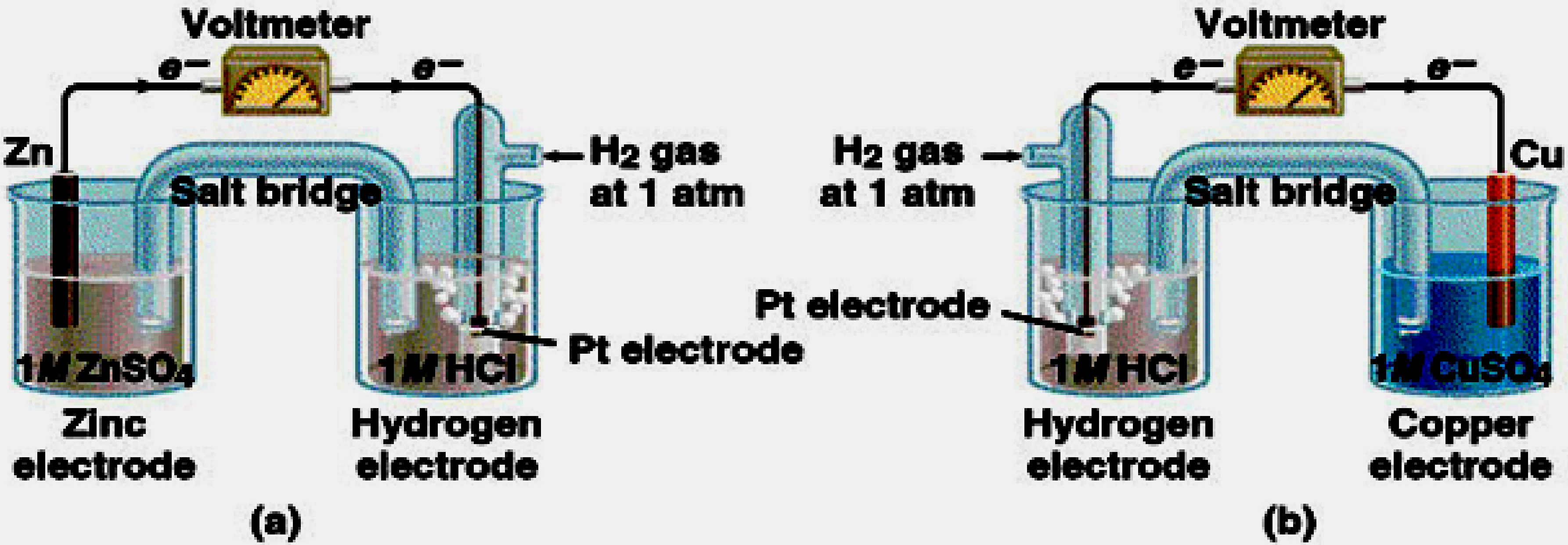
Standard Electrode Potential



Standard electrode (reduction) potential (*SRP*) of element M: -

- The potential difference produced when a half-cell of an element M – ions M^{n+} (electrode) is connected to a hydrogen half-cell at standard-state conditions

Cells Operating under Standard-State Conditions



$|| \; H^+_{\,(aq)} \;|\; H_{2\,(g)} \;|\; Pt_{\,(s)}$

$Pt_{\,(s)} \;|\; H_{2\,(g)} \;|\; H^+_{\,(aq)} \; ||$

Standard Reduction Potential

REDUCTION HALF-REACTION	E° (Volt)
$Na^+ + e^- \rightleftharpoons Na$	-2.71
$Mg^{2+} + 2\ e^- \rightleftharpoons Mg$	-2.37
$Al^{3+} + 3\ e^- \rightleftharpoons Al$	-1.66
$Zn^{2+} + 2\ e^- \rightleftharpoons Zn$	-0.76
$Fe^{2+} + 2\ e^- \rightleftharpoons Fe$	-0.44
$Sn^{2+} + 2\ e^- \rightleftharpoons Sn$	-0.14
$Pb^{2+} + 2\ e^- \rightleftharpoons Pb$	-0.13
$2\ H^+ + 2\ e^- \rightleftharpoons H_2$	+0.00
$Sn^{4+} + 2\ e^- \rightleftharpoons Sn^{2+}$	+0.15
$Cu^{2+} + 2\ e^- \rightleftharpoons Cu$	+0.34
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80

***** All written in reduction form.***

$E°$ = **Standard *Electrode* Potential**

= **Standard *Reduction* Potential**

$E°$ = **+ve**

$\Rightarrow$ **Forward** reaction predominates

E°cell

At standard state conditions:

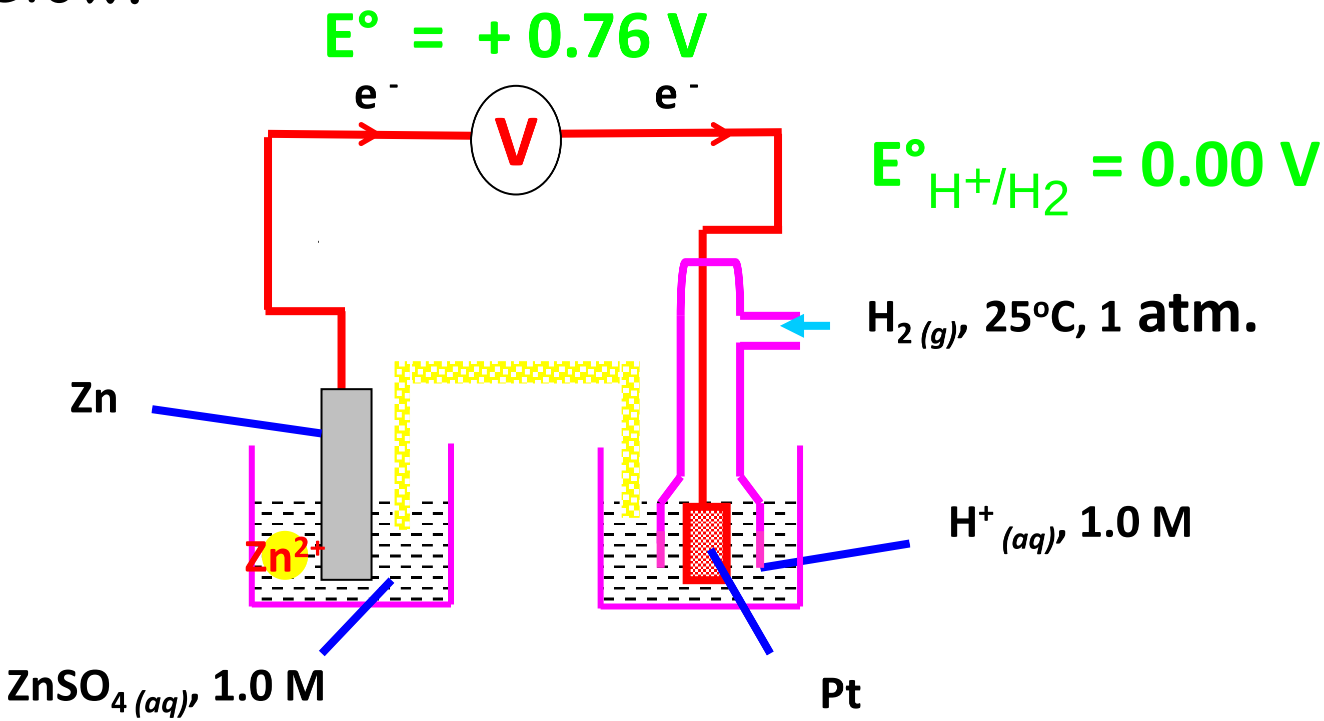
- Temperature: **25°C**
- Pressure of gas: **1.0 atm**
- Solute concentration: **1.0 M**

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

$E°_{cell}$ = cell potential / cell voltage / cell emf (electromotive force)

Example 1:

Standard reduction potential of zinc half cell is measured by setting up the electrochemical cell as below.



Anode :

Cathode :

$Zn(s) \mid Zn^{2+}(1\,M) \parallel H^{+}(1\,M) \mid H_2(1\text{ atm}) \mid Pt(s)$

Anode: $Zn(s) \rightarrow Zn^{2+}(1\,M) + 2e^-$

Cathode: $2H^+(aq, 1\,M) + 2e^- \rightarrow H_2(g, 1\,atm)$

Cell reaction:

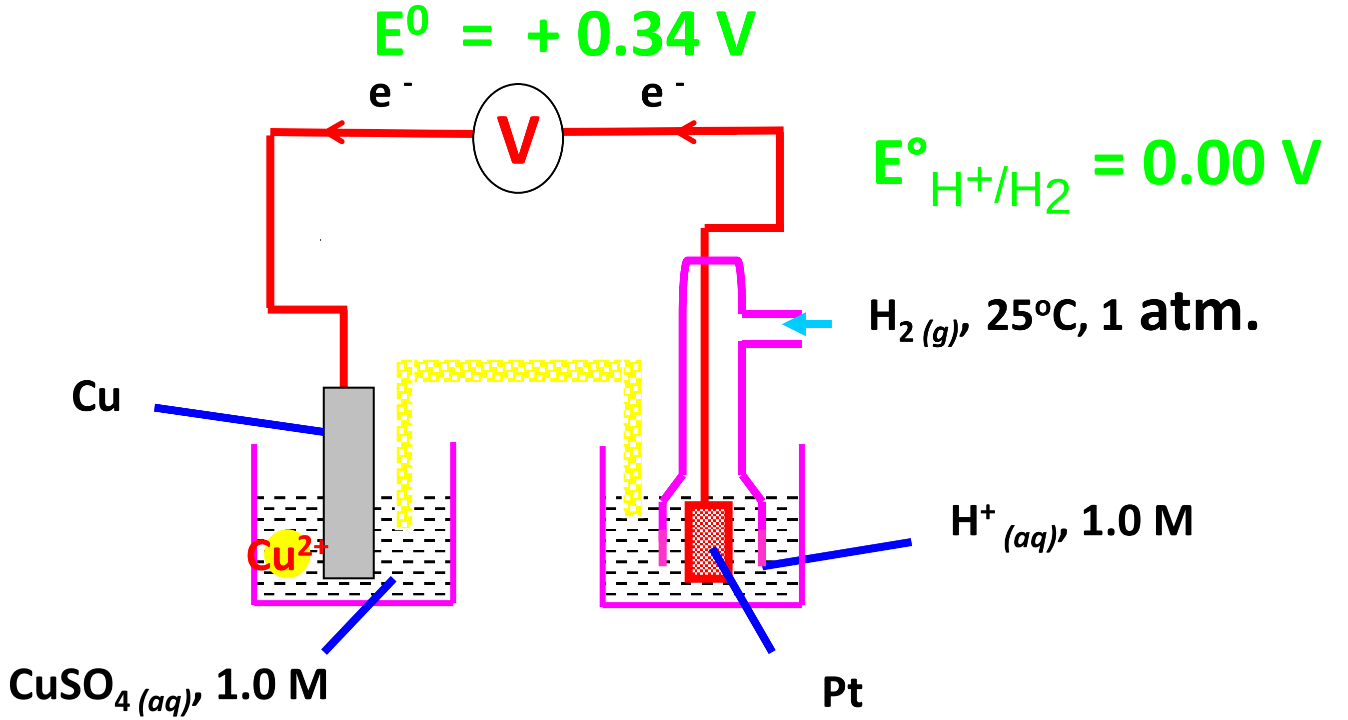
$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{cell} = E^o_{H^+/H_2} - E^o_{Zn^{2+}/Zn}$$

∴ Standard reduction potential: $Zn^{2+} + 2e^- \rightarrow Zn$ $E^0 = -0.76$ V

Example 2:

Standard reduction potential of copper half cell is measured by setting up the electrochemical cell as below.



Anode:

Cathode:

$Pt\ (s)\ |\ H_2\ (1\ atm)\ |\ H^+\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$

Anode: $H_2\ (1\ atm) \rightarrow 2H^+ + 2e^-$

Cathode: $Cu^{2+}\ (1\ M) + 2e^- \rightarrow Cu\ (s)$

Cell reaction:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{H^+/H_2}$$

∴ Standard reduction potential: $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = -0.76\ V$

NOTE 1:

- The ***sign of E^o changes*** when the reaction is reversed.

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

$F_{2(g)} + 2e^- \rightarrow 2\,F^-_{(aq)}$ $\quad E^o = +2.87$ V

NOTE 2:

- Changing the stoichiometric coefficients of a half-cell reaction ***does not change*** the value of E^o

$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$ $\qquad E^o = -1.68$ V

Example 3:

$Cl_{2\,(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$ $E^0_{Cl_2/Cl^-} = +1.36\ V$

$\frac{1}{2}Cl_{2\,(g)} + e^- \rightarrow Cl^-_{(aq)}$

$2Cl_{2\,(g)} + 4e^- \rightarrow 4Cl^-_{(aq)}$

$2Cl^-_{(aq)} \rightarrow Cl_{2\,(g)} + 2e^-$

NOTE 3:

- Indications of the sign of E°.

Oxidant + *n*e$^-$ $\rightleftharpoons$ Reductant

$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$ $E^o = +1.36\ V$

$Br_{2(l)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$ $E^o = +1.07\ V$

+ve *E*^{o} $\Rightarrow$ favours the **forward** reaction

$\Rightarrow$ Cl_2 tends to **accept e**; more electronegative

$\Rightarrow$ Cl_2 is easier to be reduced; stronger oxidising agent

$\Rightarrow$ Cl^- is difficult to be oxidised; more stable

The strength of oxidising agents:

The strength of reducing agents:

Example 4:

$Ni^{2+}{}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ $E^0 = -0.25\ V$

$Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $E^0 = +0.34\ V$

$Ag^+{}_{(aq)} + e^- \rightarrow Ag_{(s)}$ $E^0 = +0.80\ V$

Oxidation agent → left of the half cell equation

Reduction agent → right of the half cell equation

The more -ve the value of E^0 →

The more +ve the value of E^0 →

NOTE 4:

REDUCTION HALF-REACTION	E^o (Volt)
$Na^+ + e^- \rightleftharpoons Na$	-2.71
$Mg^{2+} + 2\ e^- \rightleftharpoons Mg$	-2.37
$Al^{3+} + 3\ e^- \rightleftharpoons Al$	-1.66
$Zn^{2+} + 2\ e^- \rightleftharpoons Zn$	-0.76
$Fe^{2+} + 2\ e^- \rightleftharpoons Fe$	-0.44
$Sn^{2+} + 2\ e^- \rightleftharpoons Sn$	-0.14
$Pb^{2+} + 2\ e^- \rightleftharpoons Pb$	-0.13
$2\ H^+ + 2\ e^- \rightleftharpoons H_2$	+0.00
$Sn^{4+} + 2\ e^- \rightleftharpoons Sn^{2+}$	+0.15
$Cu^{2+} + 2\ e^- \rightleftharpoons Cu$	+0.34
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80

The more positive the value of E^o, the more likely the substance is reduced (cathode).

Likewise, the more negative the value, the more likely the substance is oxidised (anode).

Example 5:

$Cu^{2+}{}_{(aq)}$ + 2e → $Cu_{(s)}$ E^o_{red} = + 0.34 V

$Zn^{2+}{}_{(aq)}$ + 2e → $Zn_{(s)}$ E^o_{red} = - 0.76 V

The more positive the half-cell's electrode potential, more easier to accept electrons.

Tendency for reduction ↑ (cathode)

Standard reduction potential of Cu half-cell is more positive compared to zinc.

Copper half-cell becomes ________.

Zinc half-cell becomes ________.

EXERCISE 1:

Calculate the standard cell potential of the following electrochemical cell.

$$Co\,(s)\ |\ Co^{2+}(aq)\ ||\ Ag^{+}(aq)\ |\ Ag(s)$$

$$Ag^{+}(aq) + e^{-} \rightarrow Ag\,(aq) \qquad E^{0} = +\,0.80V$$

$$Co^{2+}(aq) + 2e^{-} \rightarrow Co\,(s) \qquad E^{0} = -\,0.28V$$

Answer:

EXERCISE 2:

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

$$X^{3+} + 3e^{-} \rightarrow X \qquad E^{0} = -1.66\ V$$

$$Y^{2+} + 2e^{-} \rightarrow Y \qquad E^{0} = -2.87\ V$$

$$L^{2+} + 2e^{-} \rightarrow L \qquad E^{0} = +0.85\ V$$

Answer:

Uses of standard electrode potential (SRP)

- Determine the electron flow direction, anode and cathode
- Determine species being reduced (oxidant) and species being oxidised (reductant) – *refer NOTE 3 & Example 4*
- Build up the electrochemical series
- Calculate the cell potential ($E°_{cell}$)
- Predict the stability of ions
- Predict the spontaneity of a reaction

Predicting spontaneity of redox reaction

E° cell +ve → The FORWARD rxn is **spontaneous**

E° cell – ve → The FORWARD rxn is NON-spontaneous

But the REVERSE rxn is spontaneous

E° cell = 0 → The rxn is at **EQUILIBRIUM**

Example 6:

Predict whether the following reactions occur spontaneously or non-spontaneously.

$$Zn + Sn^{4+} \rightarrow Sn^{2+} + Zn^{2+}$$

$$[E^o_{Sn^{4+}/Sn^{2+}} = +0.15V, E^o_{Zn/Zn^{2+}} = +0.76V]$$

Answer:

Enhancement 1:

Predict : Spontaneous or non-spontaneous reaction?

$$Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \rightarrow Pb_{(s)} + Cl_{2\,(g)}$$

$E^{\circ}_{Pb2+/Pb} = -\ 0.13\ V$ $E^{\circ}_{Cl2/Cl-} = +1.36\ V$

Answer:

Enhancement 2:

A cell consists of silver and tin in a solution of 1 M silver ions and tin (II) ions. Determine the spontaneity of the reaction and calculate the cell voltage of this reaction. *[$E^\circ_{Ag+/Ag}$ = + 0.80 V, $E^\circ_{Sn/Sn2+}$= + 0.14 V]*

Answer:

Enhancement 3:

The cell diagram is
Zn (s) / Zn^{2+} (1M) // Fe^{3+} (1M), Fe^{2+} (1M) / Pt (s)

i) Label A to E in figure 1

ii) State the direction of electrons flow in the external circuit

iii) Write the half-cell equations and overall equation

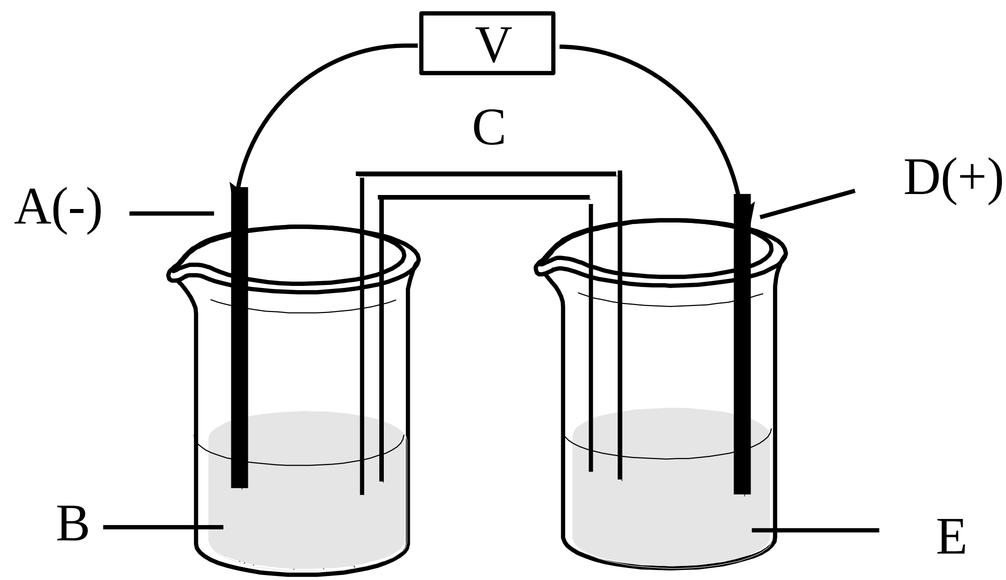


Figure 1

Enhancement 4:

Aluminium will displace tin from solution according to the equation,

$$2\,Al\,(s) + 3\,Sn^{2+}\,(aq) \longrightarrow 2\,Al^{3+}\,(aq) + 3\,Sn\,(s)$$

i) If this was the cell reaction in a galvanic cell, what is the anode?

ii) Write the individual half-cell reactions.

iii) Write the cell notation.

Enhancement 5:

(a) Define standard cell potential.

(b) A voltaic cell is built from nickel and silver half-cells under standard conditions.

$$Ni^{2+}(aq) + 2e \longrightarrow Ni(s) \quad E^o = -0.23\ V$$

$$Ag^{+}(aq) + e \longrightarrow Ag(s) \quad E^o = +0.80\ V$$

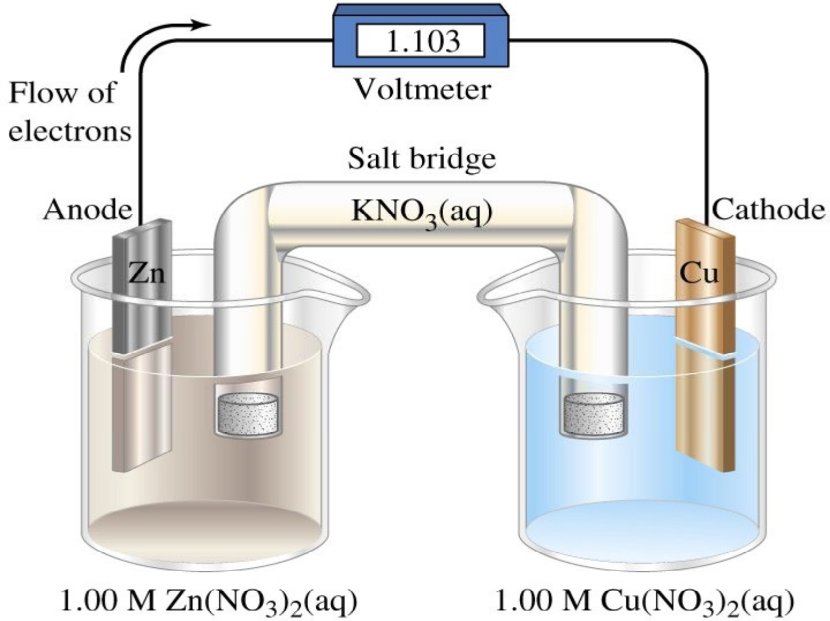
i) Write the cell notation.

ii) Write the reactions of the half cells and the overall cell reaction.

iii) Deduce the reducing agent in the voltaic cell.

iv) Calculate the standard cell potential.

Enhancement 6:



Describe what would you expect to see happening to both electrode compartments after a period of time? Account for your answer.

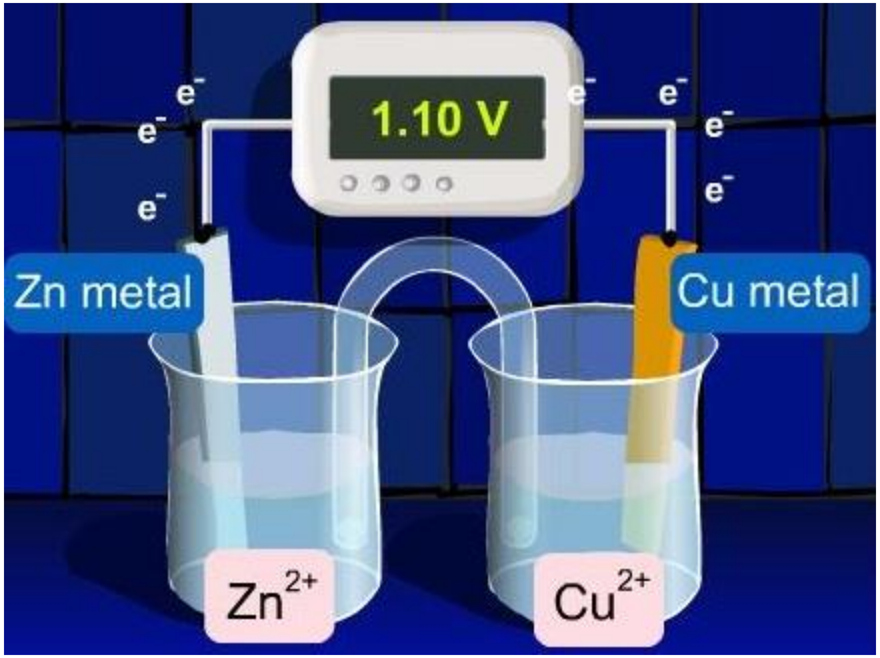
Enhancement 7:

Determine the anode and cathode from a given

(a) Set of Standard Electrode (reduction) Potentials, $E°$

$E^{o}_{Cd/Cd^{2+}} = + 0.46\ V$

$E^{o}_{Cr^{3+}/Cr} = - 0.74\ V$



(b) Cell diagram

(c) Overall cell equation