Chapter 13:

Electrochemistry

The area of chemistry that deals with the interconversion of electrical energy and chemical energy is electrochemistry.

$$\textit{chemical energy} \underset{\textit{electrolysis}}{\overset{\textit{elctrochemical cell}}{\rightleftharpoons}} \textit{electricity}$$

In electrochemical cell, redox reactions occur, the energy released by this spontaneous reaction is converted to electricity.

ELECTROLYSIS

electricity is used to drive a non spontaneous reaction.

Electric energy is used to decompose an electrolyte to its elements.

For example:

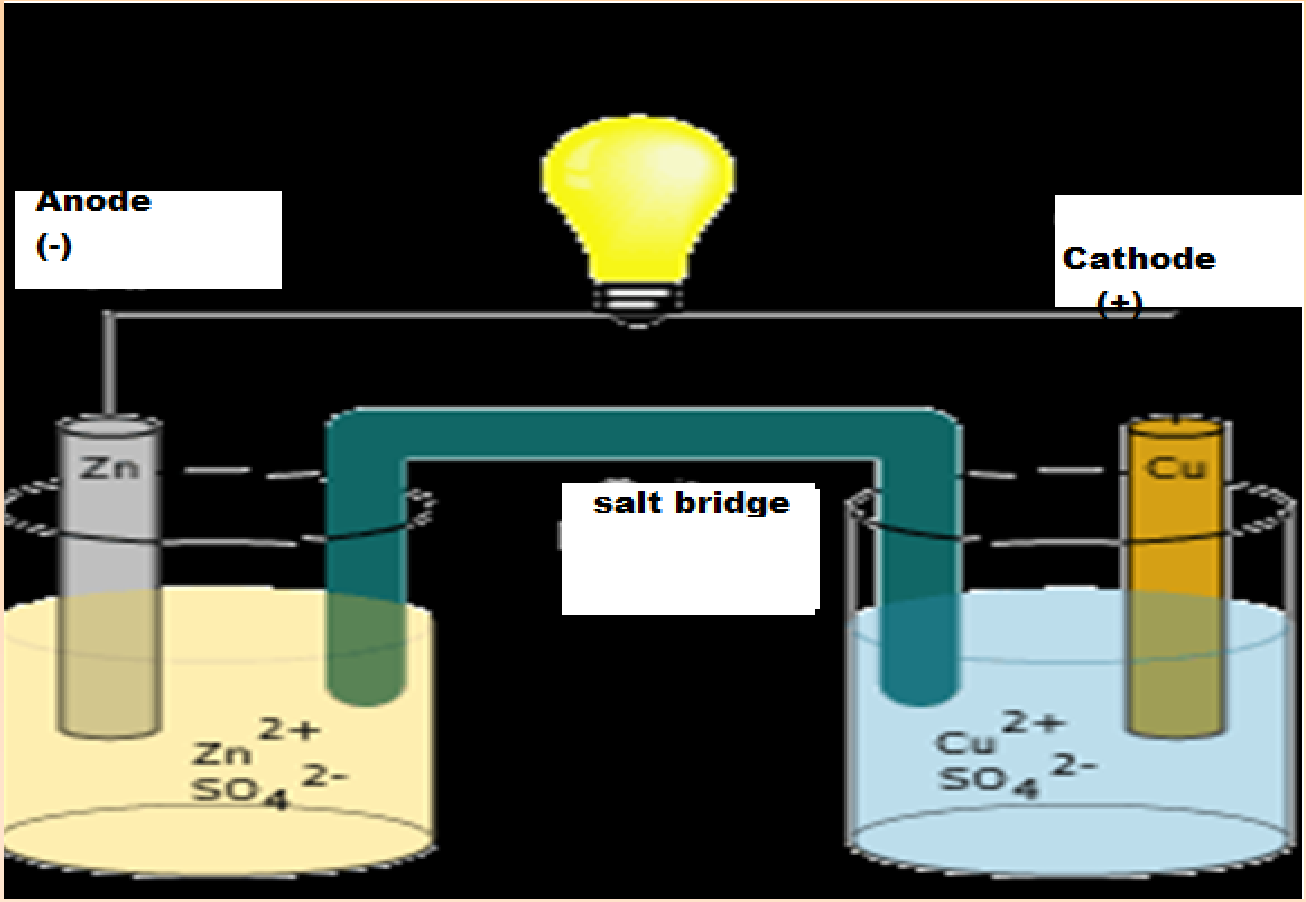
$$2H_2O(l) + electricity \longrightarrow 2H_2(g) + O_2(g)$$

GALVANIC CELL

The experimental apparatus for generating electricity by a spontaneous reaction is called a galvanic cell or voltaic cell.

The cell first constructed by the Italian scientists Luigi Galvani and Alessandro Volta.

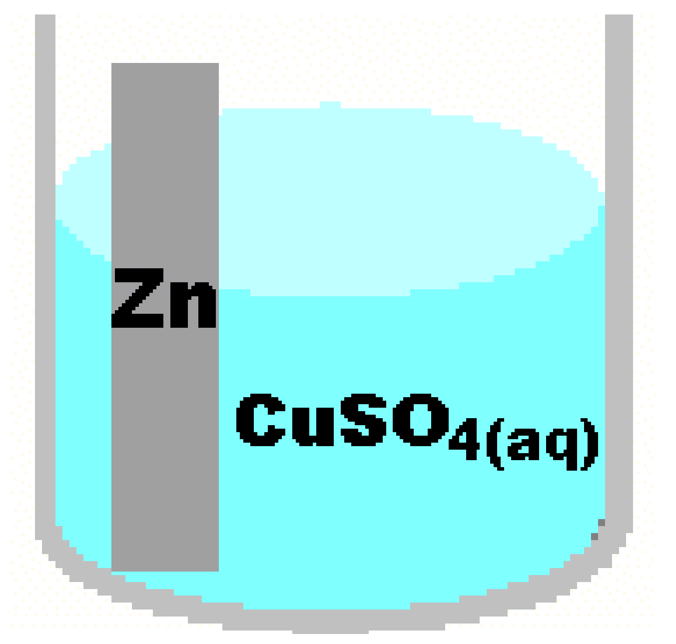
A galvanic cell



What happens when zinc electrode is place in copper(II) sulphate solution?

When zinc metal placed in $CuSO_4$ solution, following reaction take place:

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)} + \text{heat energy}$$



Half equations of reaction takes place are:

Oxidation: $Zn_{(s)} \rightarrow Zn^{2+} + 2e$

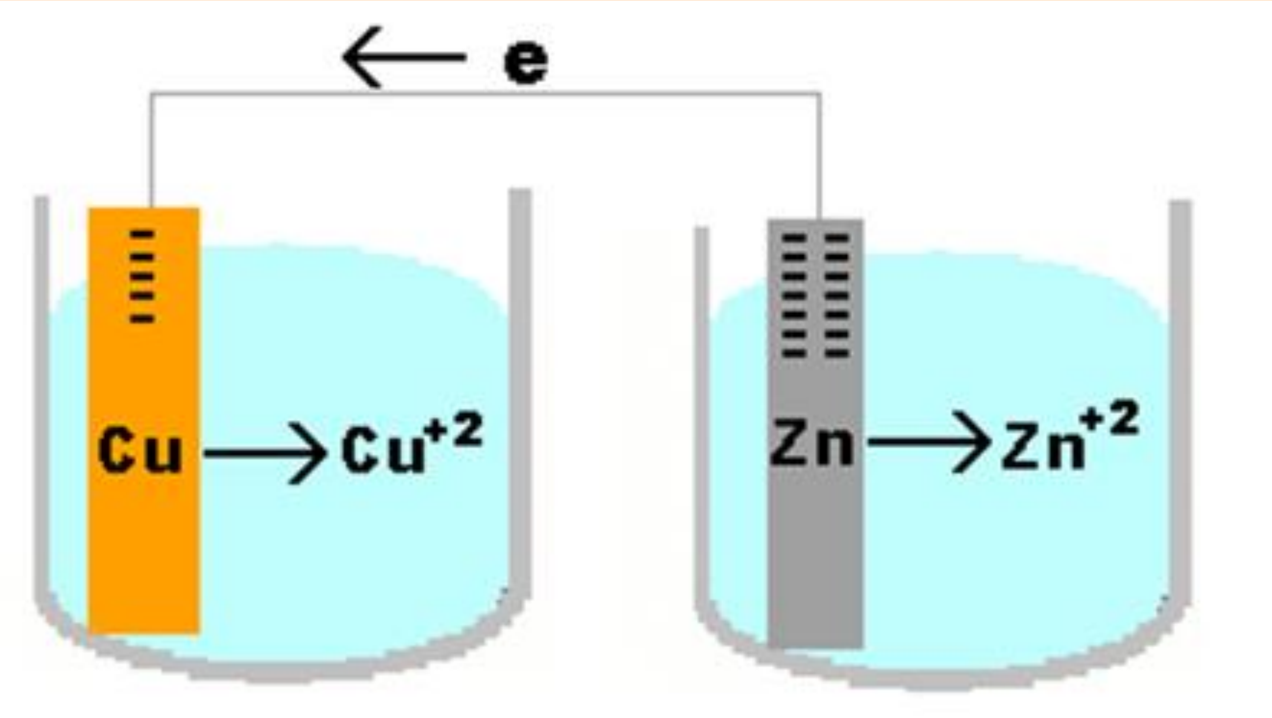
Reduction: $Cu^{2+} + 2e \rightarrow Cu$

Overall ionic equation is:

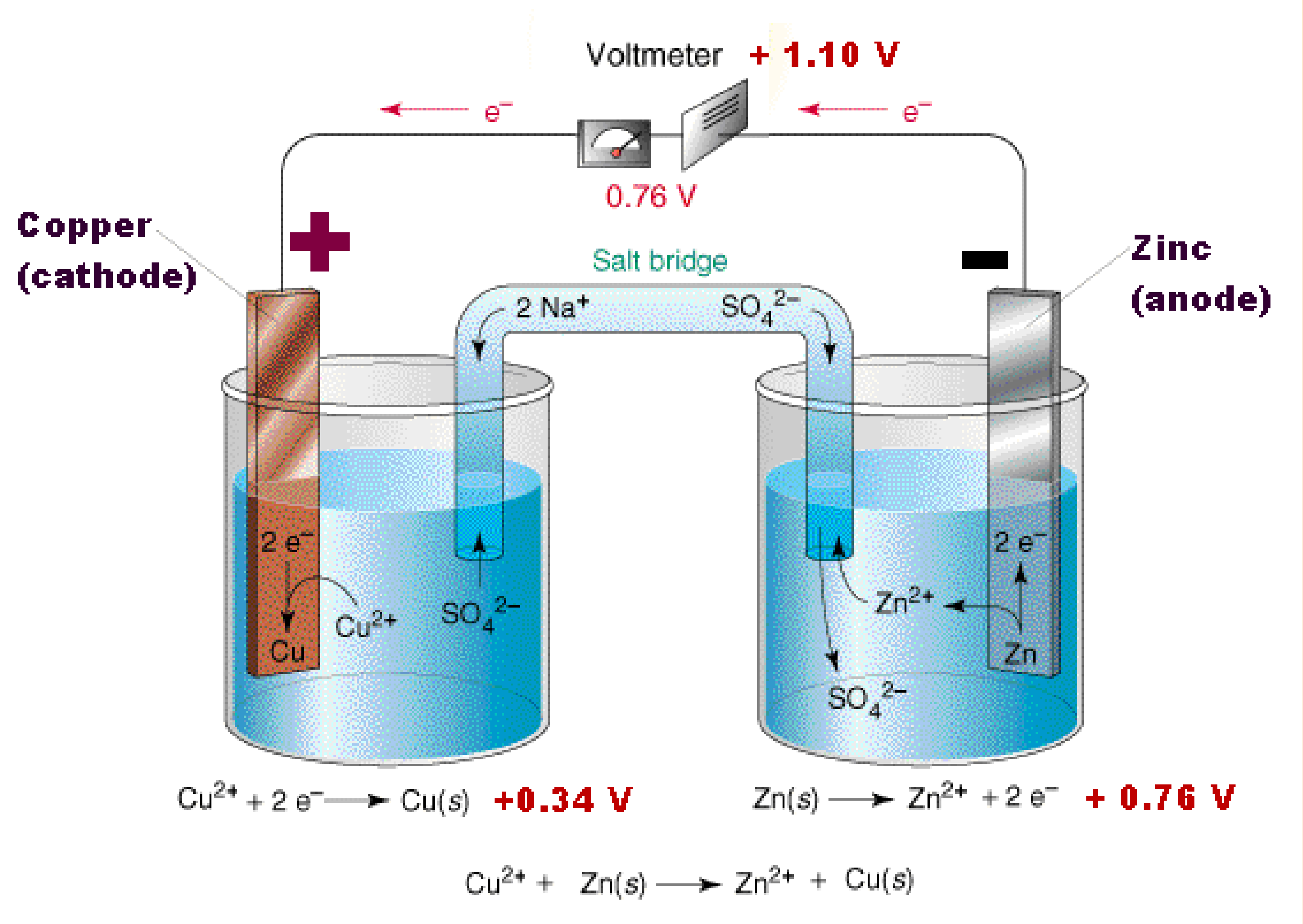
$$Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$$

Zinc electrode will dissolves and reddish brown solid of copper is form.

When each metal is dipped in their aqueous solution Electrons will not flow in the following apparatus:



But if reaction carried out in the apparatus shown in Figure (Cu/Zn system), electrons are transferred from Zn to Cu^{2+} through a wire producing electrical energy.



The salt bridge is necessary to complete the circuit and maintain charge neutrality.

The e.m.f of cell is 1.10V

ELECTRODE POTENTIAL

When a piece of magnesium is immersed in a solution of its ions.

The reaction takes place is as follows:

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

A dynamic equilibrium will be established when the rate magnesium ions are leaving the surface is exactly equal to the rate at which they are joining it again.

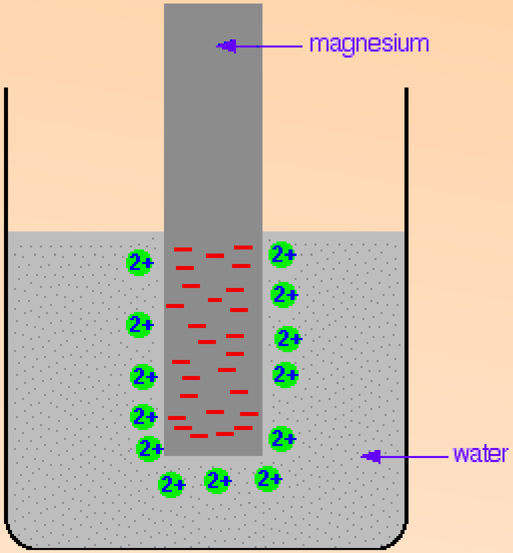
Note:

By convention, all these equilibria are written with the electrons on the left-hand side of the equation.

Example:

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

A STATE OF DYNAMIC EQUILIBRIUM BETWEEN MG METAL & ITS IONS

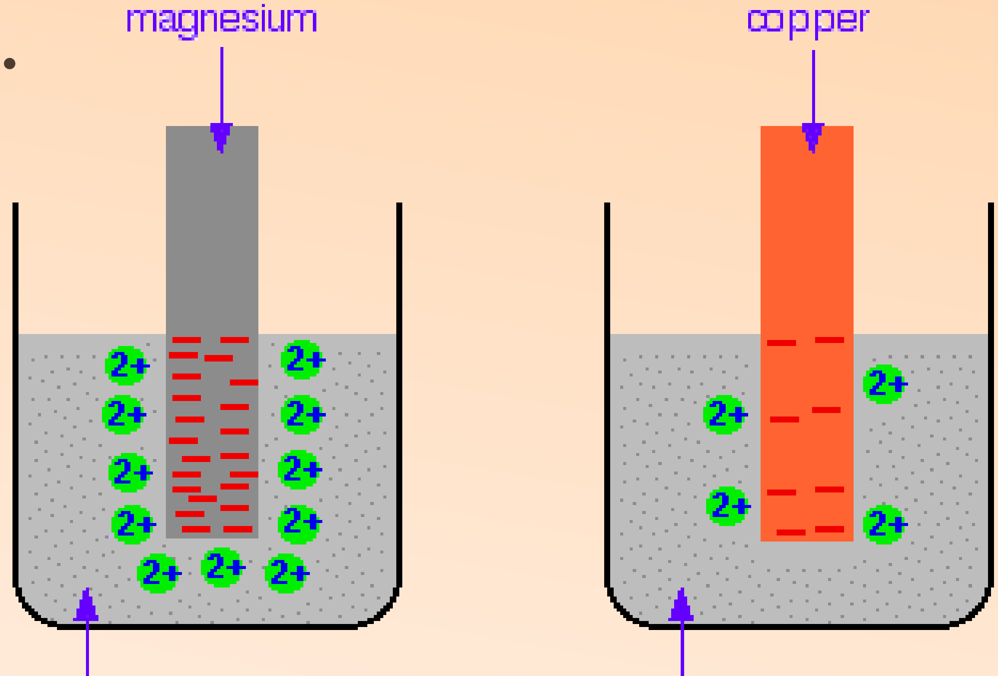


How would this be different if you used a piece of copper instead of a piece of magnesium?

Copper is less reactive, so forms its ions less readily.

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

A dynamic equilibrium is achieves with less charge on the metal, and fewer ions in solution.



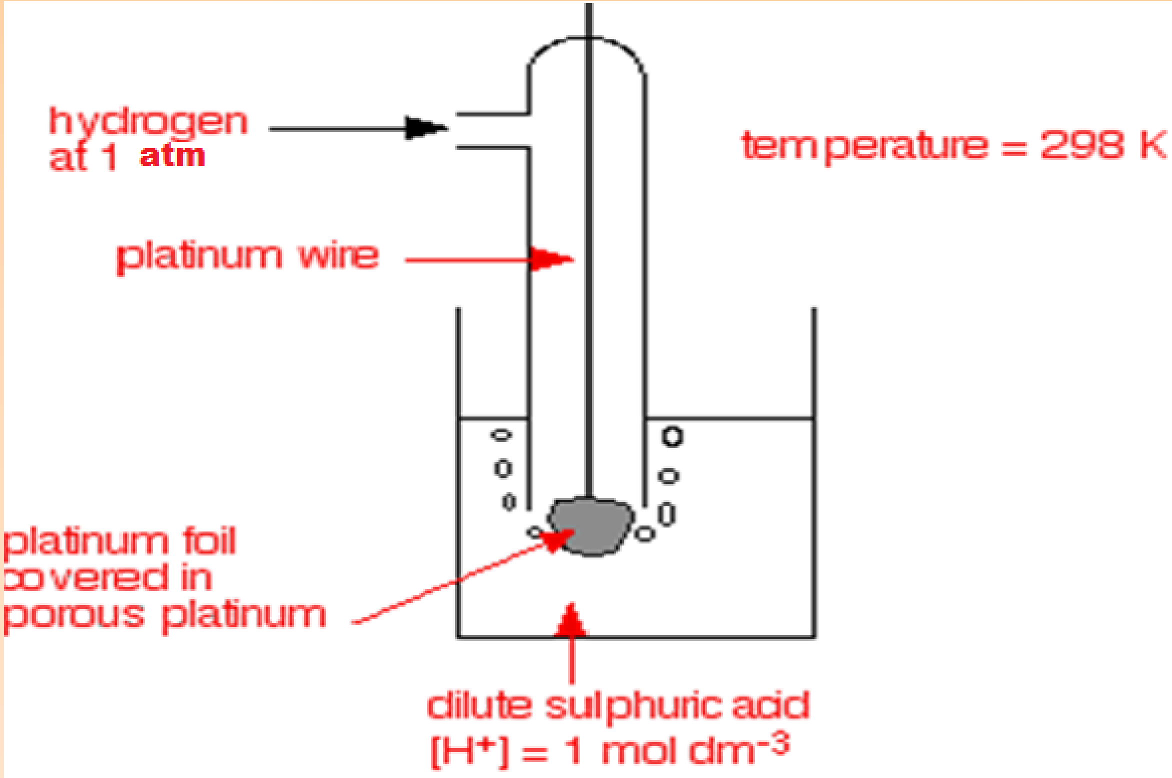
Therefore the position of the magnesium equilibrium lies further to the left than that of the copper equilibrium.

Means that magnesium sheds electrons and forms ions more readily than copper does.

But we can’t measure the absolute voltage between the metal and the solution.

So, we compare the voltage with a ***reference electrode*** called a standard hydrogen electrode.

THE STANDARD HYDROGEN ELECTRODE (S.H.E)



Standard hydrogen electrode (S.H.E)

Hydrogen gas, 1 atm is bubbled into 1 mol/L hydrochloric acid at 25°C.

The platinum electrode has two function.

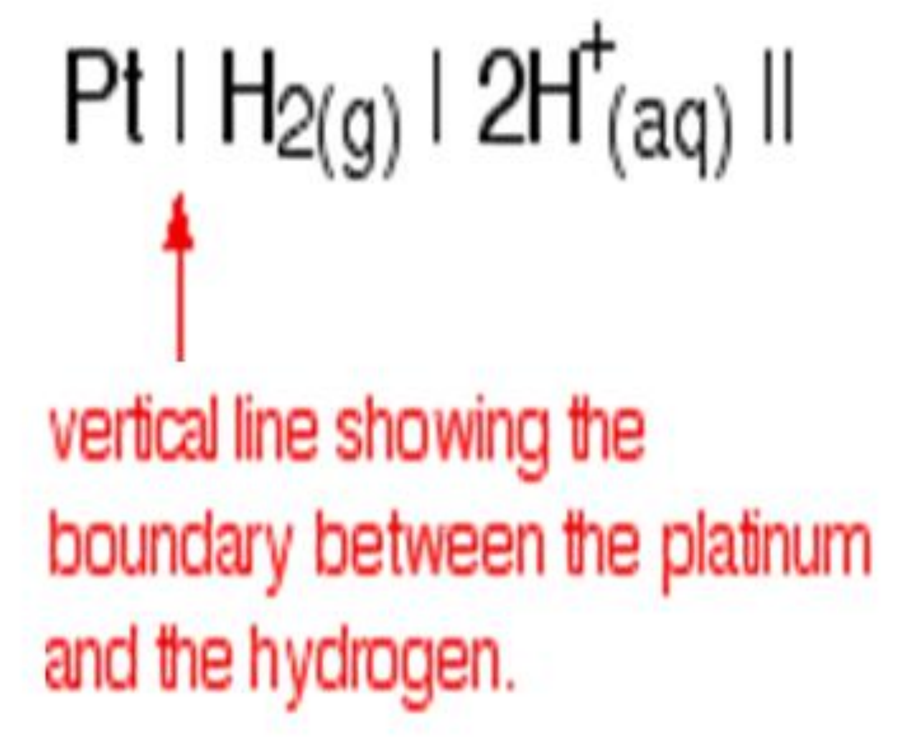
(a) it provides a surface on which the dissociation of hydrogen molecules can take place:

$H_2 \rightarrow 2H^+ + 2e$ where $\varphi° = 0$ V

(b) as an electrical conductor to the external circuit.

The potential for the reduction of H^+ is taken to be zero. $2\,H^+ + 2e \rightarrow H_2$ where $\varphi° = 0$ V

The hydrogen electrode also can be represented as:



$Pt \mid H_{2(g)} \mid 2H^{+}_{(aq)} \parallel$

vertical line showing the boundary between the platinum and the hydrogen.

Note:

1. concentration of solution used is 1 mol/L. According to Le Chatelier's principle, increase concentration of ions will shift equilibrium to right, favour the reduction process.
2. Temperature of solution is 25°C as position of equilibrium is affected by temp.

Thus electrode potential depend on:

(i) nature of the metal

(ii) Temperature and pressure

(iii) Concentration of ions.

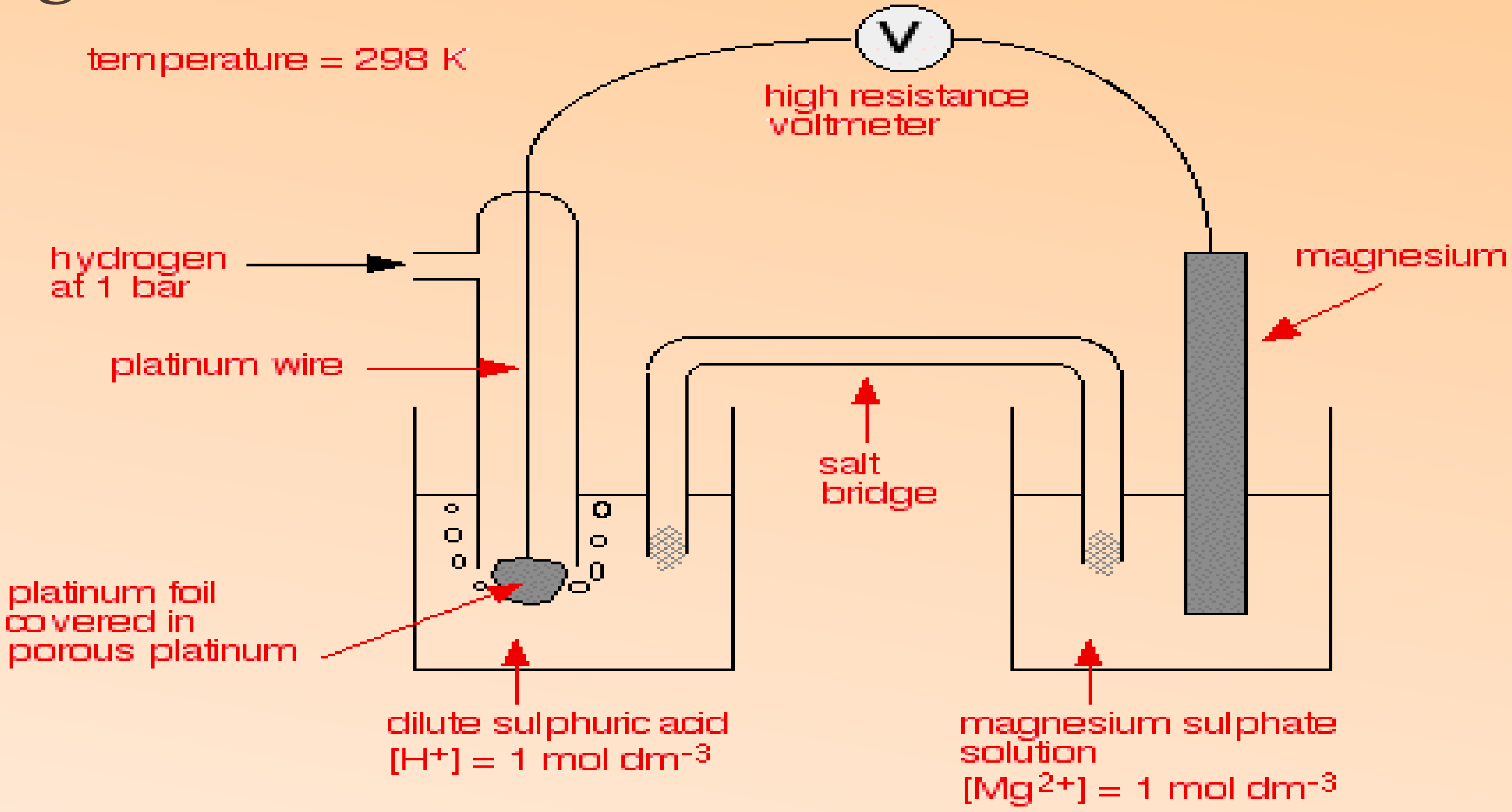
USING THE STANDARD HYDROGEN ELECTRODE(SHE)

The standard hydrogen electrode is attached to the electrode system you are investigating.

For example, a piece of magnesium in a solution containing magnesium ions.

Example 1:

To measure the standard electrode potential of magnesium.



CELLS AND HALF CELLS

The whole of this set-up is described as a ***cell***.

Each of the two beakers and their contents are described as ***half cells***.

STANDARD ELECTRODE POTENTIALS

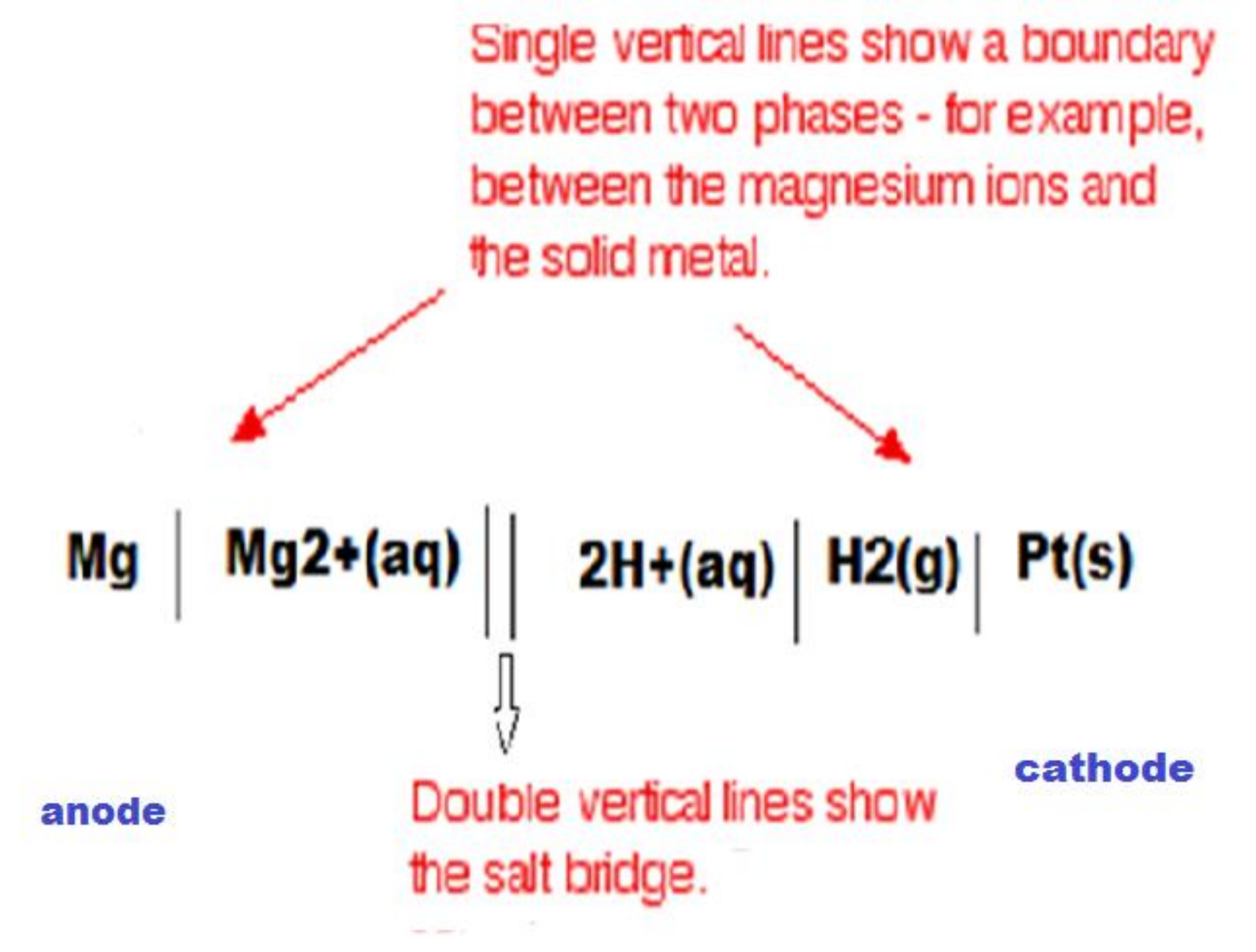
By convention , half cell potentials are tabulated as standard electrode potentials or standard reduction potentials, $\varphi°$. (see table 13.1)

Here are a few typical standard electrode potentials :

Half reaction	$\varphi°$ (V)
$Mg^{2+} + 2\,e \rightleftharpoons Mg$	- 2.37
$Zn^{2+} + 2\,e \rightleftharpoons Zn$	- 0.76
$Cu^{2+} + 2e \rightleftharpoons Cu$	+ 0.34
$Ag^{+} + e \rightleftharpoons Ag$	+ 0.80

Cell diagram:

A quick way of drawing a cell



Single vertical lines show a boundary between two phases - for example, between the magnesium ions and the solid metal.

$\mathrm{Mg} \mid \mathrm{Mg2{+}(aq)} \parallel \mathrm{2H{+}(aq)} \mid \mathrm{H2(g)} \mid \mathrm{Pt(s)}$

Double vertical lines show the salt bridge.

ELECTRODE NAMES

For **BOTH** electrochemical cells **AND** electrolytic cells,

Cathode is the site of reduction.

Anode is the site of oxidation.

$E^\circ_{cell} = \varphi^\circ_{(cathode)} - \varphi^\circ_{(anode)}$

or

$= \varphi^\circ_{+} - \varphi^\circ_{-}$

$= 0 - (-0.76)$

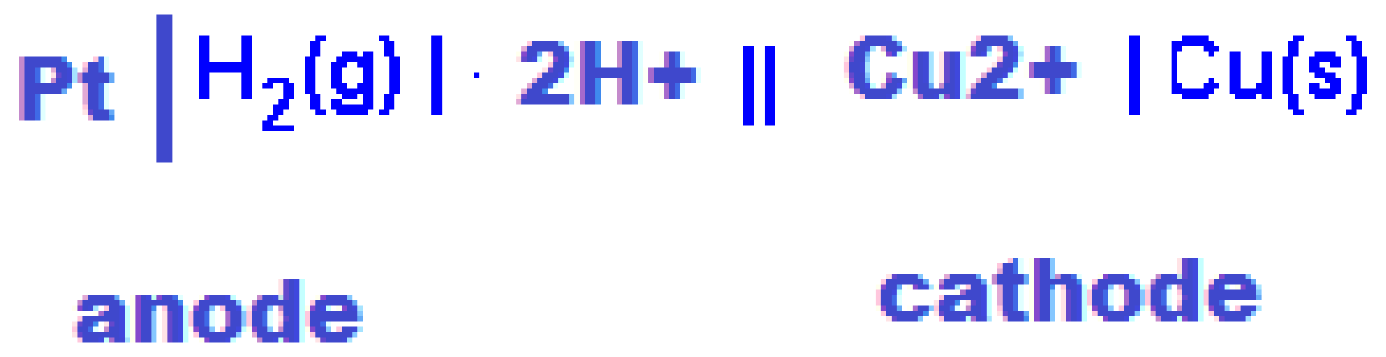
$= +0.76$ (V)

The e.m.f of a cell measured under standard conditions is given the symbol $\mathbf{E^\circ_{cell}}$.

The superscript"°" denotes standard state conditions.

φ° is the standard reduction potential or the voltage associated with a reduction reaction at an electrode when solutes are 1 mol/L and pressures of all gases are 1 atm.

Example 2: to measure the standard electrode potential of copper.



$\mathrm{Pt}\ |\ \mathrm{H_2(g)}\ |\ \mathrm{2H+}\ ||\ \mathrm{Cu2+}\ |\ \mathrm{Cu(s)}$

anode

cathode

$$E^\circ_{cell} = \varphi^\circ_{(cathode)} - \varphi^\circ_{(anode)}$$

or

$$= \varphi^\circ_{+} - \varphi^\circ_{-}$$

$$= 0.34 - 0$$

$$= +0.34\ (V)$$

IMPORTANT NOTES ON STANDARD ELECTRODE POTENTIALS:

1. The φ° values apply to the half-cell reactions as read in the forward direction.

   $Zn^{2+} + 2e \rightleftharpoons Zn \qquad \varphi° = -0.76$

Sign changes when the half cell is written as oxidation process.

For example:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e \qquad \varphi° = +0.76V$

2. The more +ve φ° value, the greater tendency for the substance to be reduced.

A + ve value of φ° indicates that the half cell should proceed spontaneously from left to right.

For example:

$$F_2(g)+2e \rightleftharpoons 2F^-(aq) \qquad \varphi^\circ=+2.87V$$

$$Cl_2(g)+2e \rightleftharpoons 2Cl^-(aq) \qquad \varphi^\circ=+1.36V$$

$$I_2(g)+2e \rightleftharpoons 2I^-(aq) \qquad \varphi^\circ=+0.53V$$

$$2H^+(aq)+2e \rightleftharpoons H_2(g,1atm) \qquad \varphi^\circ=0V$$

Means that :

fluorine has the highest + ve φ° value among

all half-cell reactions, so F_2 is the strongest

oxidising agent because it has the greatest

tendency to be reduced.

- A – ve value of φ° indicates that the reverse reaction occurs spontaneously.

$$Na^{+}(aq)+e \rightleftharpoons Na(s) \qquad \varphi^{\circ}=-2.71\ V$$

$$Zn^{2+}(aq)+2e \rightleftharpoons Zn(s) \qquad \varphi^{\circ}=-0.76\ V$$

These substances are more readily oxidized than hydrogen.
sodium has higher –ve value, so it is more readily oxidised than zinc.
So, Na is a stronger reducing agent than Zn.

3.changing the stoichiometric coefficients of a half-cell reaction does not affect the value of φ° because the value of φ° is unaffected by the size of the electrodes or the amount of solutions present.

For example:

$I_2(s) + 2e \rightarrow 2\, I^-(aq) \qquad \varphi^\circ = 0.53\ V$

$2I_2(s) + 4e \rightarrow 4\, I^-(aq) \qquad \varphi^\circ = 0.53\ V$

APPLICATION OF STANDARD ELECTRODE POTENTIAL

1. Predict relative strength of oxidising agent and reducing agent.

Example 1 :

$\varphi^\circ_{Fe^{3+}/Fe^{2+}} = 0.77 \text{ V}$

$\varphi^\circ_{Ce^{4+}/Ce^{3+}} = 1.61 \text{ V}$

Therefore Ce^{4+} is a stronger oxidising agent than Fe^{3+}.

Example 2 :

Given that

$$Ca^{2+}(aq) + 2e \rightleftharpoons Ca(s) \qquad \varphi^{\circ} = -2.87\ V$$

$$Be^{2+}(aq) + 2e \rightleftharpoons Be(s) \qquad \varphi^{\circ} = -1.85\ V$$

So calcium metal, Ca is a stronger reducing agent than beryllium, Be.




Given that

$Cu^{2+}(aq)+2e \rightleftharpoons Cu(s) \qquad \varphi^{\circ}=+0.34\ V$

$MnO_4^-(aq)+8H^+ +5e \rightleftharpoons Mn^{2+}(aq)+4H_2O(l) \quad \varphi^{\circ}=1.51\ V$

$Br_2(l)+2e \rightleftharpoons 2Br^-(aq) \qquad \varphi^{\circ}=1.07\ V$

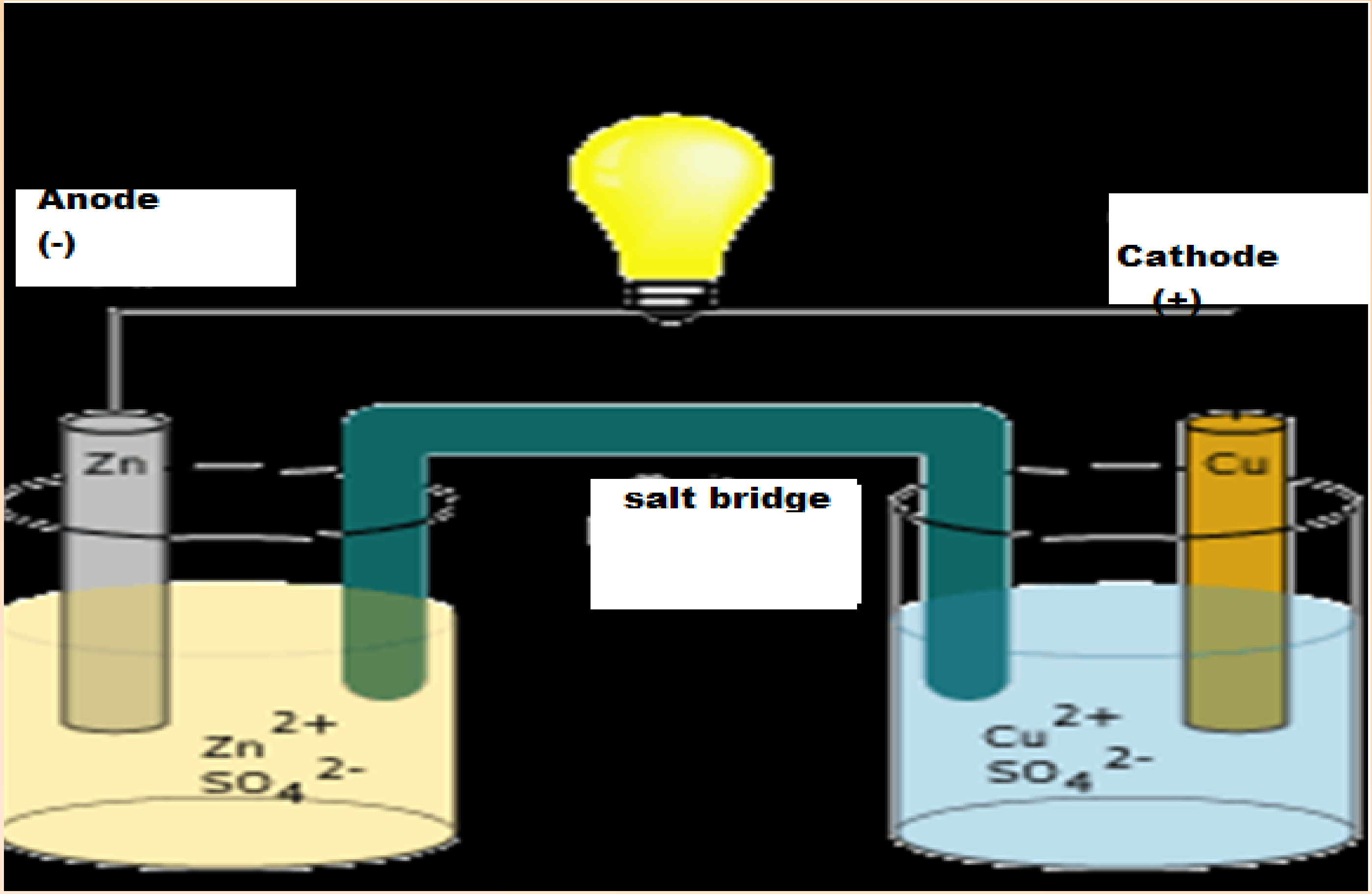
$Zn^{2+}(aq)+2e \rightleftharpoons Zn(s) \qquad \varphi^{\circ}=-0.83\ V$

Relative strength as oxidising agent is

$MnO_4^- > Br_2 > Cu^{2+} > Zn^{2+}$

2. To calculate e.m.f of a cell.

Example 1: Zn-Cu cell



The cell diagram is $Zn(s) | Zn^{2+} \| Cu^{2+} (aq) | Cu(s)$

By convention, the standard emf of the cell,

$$E_{cell} = \varphi^{\circ}_{(cathode)} - \varphi^{\circ}_{(anode)}$$

$$= 0.34 - (-0.76)$$

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

Example 2: Cu-Ag cell

E.m.f of cell can be calculate using half reaction equation and their electrode potential.

Copper is more reactive than Ag, it donate electron and then oxidise to Cu^{2+} ,Ag^{+} ion in solution accept electron and reduces to Ag.

Half equations of reaction take place are :

$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e \quad \varphi^\circ = -\ 0.34\ v$

oxidation, Cu act as anode

$2Ag^{+} + 2e \rightarrow 2Ag(s) \qquad \varphi^\circ = +\ 0.80\ v$

Reduction , Ag acts as cathode

Overall equation of reaction is

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

The e.m.f of cell :

$$E_{cell} = 0.80 + (-\ 0.34) = 0.46\ (v)$$

Example 3 : lead-acid battery

Half equations of reaction are:

At cathode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \rightarrow$
$PbSO_4 + 2\ H_2O \qquad \varphi° = 1.70\ v$

At anode:

$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e \quad \varphi° = 0.31\ v$

Overall equation of rxn:

$Pb + PbO_2(s) + 2\ H_2SO_4(aq) \rightarrow 2\ PbSO_4(s) + 2\ H_2O(l)$

$E_{cell} = 1.70 + 0.31 = 2.01(v)$

3. To predict spontaneity of redox reaction, where the reducing agent and oxidising agent are separated from each other, or in a beaker.

Example 1:

Given: $\varphi°(Fe^{2+}/Fe) = -0.41$ V

$\varphi° (Ni^{2+}/Ni) = -0.25$V

Will the following reaction occur spontaneously?

$$Fe^{2+} + Ni \rightarrow Fe + Ni^{2+}$$

Based on the given equation, e.m.f of cell is

oxidation: $Ni \rightarrow Ni^{2+} + 2e$ $\varphi° = 0.25$ V

reduction: $Fe^{2+}(aq) + 2e \rightarrow Fe$ $\varphi° = -0.44$ V

$E_{cell} = 0.25 + (-0.44) = -0.19$ (V)

As < 0, the reaction is non-spontaneous.

OR we say that the reaction will proceed from right to left.

i.e

$Fe + Ni^{2+} \rightarrow Fe^{2+} + Ni$

Example 2:

Given that

$\varphi°(MnO_4^-/Mn^{2+}) = 1.51$ V

$\varphi°\ (H_2O_2/H_2O) = 1.71$V

$\varphi°(O_2/\ H_2O_2) = 0.68$ V

Q: write a balance ionic equation for the reaction that is likely to occur when MnO_4^- and H_2O_2 are mixed in acidic condition.

Half equations of reaction are

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+} + 4H_2O(l) \quad \varphi^\circ = 1.51\ V$$

$$H_2O_2(aq) \longrightarrow O_2(g) + 2H^+(aq) + 2e \qquad \varphi^\circ = -0.68\ V$$

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

$E_{cell} = 1.51 + (-\ 0.68\ ) =\ 0.83\ (V)$

As $E_{cell} > 0$, the reaction will occurs spontaneously.

UEC PAST YEAR QUESTIONS

Uec 09-2

A primary cell is represented by:

$Ni(s) / Ni^{2+}(aq) // Cu^{2+} (aq) /Cu (s)$

(a) Draw a labeled sketch of the primary cell showing anode and cathode, flow of electron, salt bridge and electrolyte; (1%, 1%)

(b) Write a balanced equation for the overall cell reaction; (1%)

(c) Calculate the standard electromotive force of the cell. (1%) Ans: 0.57 V

Uec 09-8 .

(a)Describe briefly the electrochemical purification of copper. (5%)

(b)Use standard electrode potential to explain the following: (3%)

The electrolysis of dilute NaCl(aq) produces mainly oxygen gas at the anode, whereas the electrolysis of concentrated NaCl(aq) produces mainly chlorine gas.

Standard reduction potentials

$Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$ $\varphi^\circ = +1.36$ V

$O_2(g) + 2H_2O(l) + 4e(aq) \rightarrow 4\,OH^-(aq)$ $\varphi^\circ = 0.40$ V

Ans for (b):

When dilute NaCl is electrolyzed, as the reduction electrode potential of OH^- ion is lower than Cl^- ion, therefore OH^- ion is oxidised to O_2 at anode . The equation of reaction is:

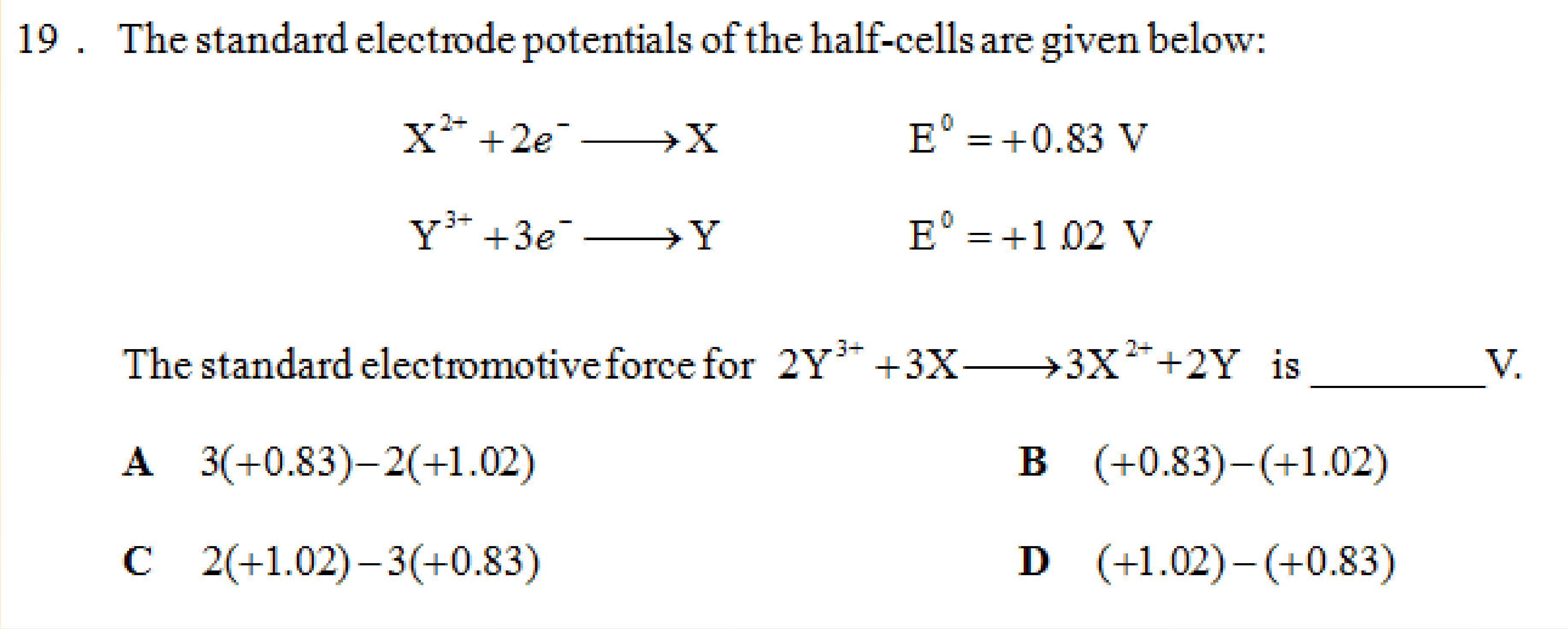
$4\,OH^-(aq) \rightarrow O_2\,(g) + 2\,H_2O(l) + 4e$

When conc. NaCl is electrolyzed, concentration of Cl^- ion is high, so, Cl^- ion is oxidised to Cl_2 and evolved at anode.

$2Cl^-(aq) \rightarrow Cl_2\,(g) + 2e$

(c) It is estimated that 0.5 g of silver is needed to be electroplated onto worn silver trophy. Calculate the time required to achieve this when a current of 0.20 A passes through the electrolysis cell.

Uec 10-19



19 . The standard electrode potentials of the half-cells are given below:

$$X^{2+} + 2e^{-} \longrightarrow X \qquad E^{0} = +0.83\ \text{V}$$

$$Y^{3+} + 3e^{-} \longrightarrow Y \qquad E^{0} = +1.02\ \text{V}$$

The standard electromotive force for $2Y^{3+} + 3X \longrightarrow 3X^{2+} + 2Y$ is ________ V.

A $3(+0.83) - 2(+1.02)$

B $(+0.83) - (+1.02)$

C $2(+1.02) - 3(+0.83)$

D $(+1.02) - (+0.83)$

Ans: D

06-20

Given that:

$Mg^{2+}(aq) + 2e^{`} \rightarrow Mg(s) \qquad E^{o} = -2.38\ V$

$Cu^{2+}(aq) + 2e^{`} \rightarrow Cu(s) \qquad E^{o} = +0.34\ V$

Then the standard e.m.f. of the cell

$Mg(s) / Mg^{2+}(aq) \| Cu^{2+}(aq) / Cu(s)$ is ____V.

A. +2.72 B. –2.72 C. +2.04 D. +1.36

Ans: A

07-19. The standard electrode potentials of four electrodes are shown as below:

(Note: The elements are represented by the letter M, N, P and Q.)

If the standard electromotive force (E°) of a primary cell is 1.2 V, what are the two electrodes of the primary cell?

$\varphi^{o}{}_{P^{+}/P} = -0.3V;$

$\varphi^{o}{}_{N^{2+}/N} = +0.3V;$

$\varphi^{o}{}_{M^{+}/M} = +0.9V;$

$\varphi^{o}{}_{Q^{2+}/Q} = -0.9V;$

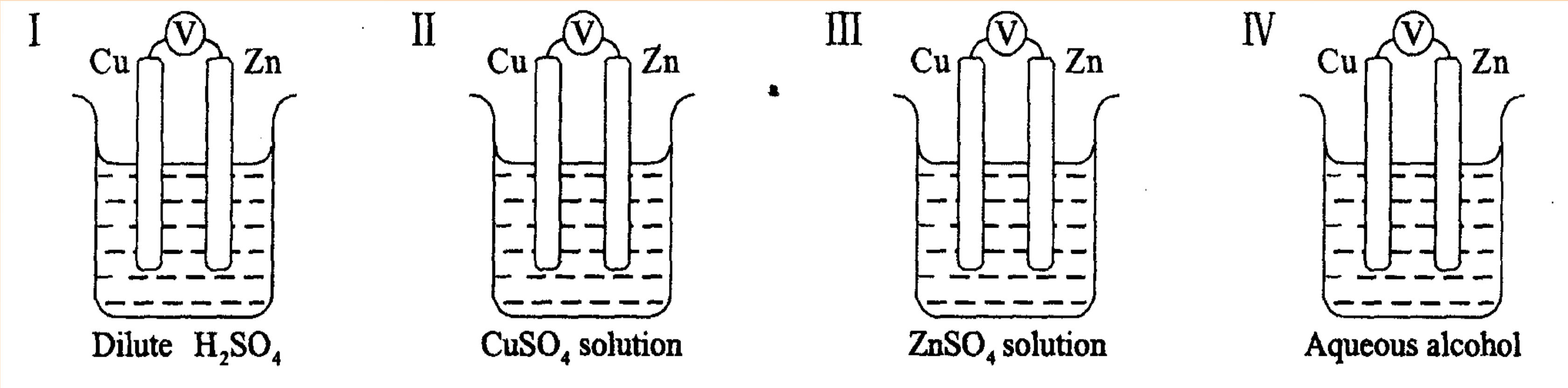
Ans: 07-19

As $E_{cell} = \varphi^{\circ}_{(cathode)} - \varphi^{\circ}_{(anode)}$

So, possible chemical cell could be M-P cell where M is cathode and P is anode.

Another cell is N-Q cell where N is cathode and Q is anode.

07-20. Which of the following devices can form a primary cell to produce electric current?



A. I,II B. I,III C. II, III D. III, IV

Ans: A

The End...

Thank you =]