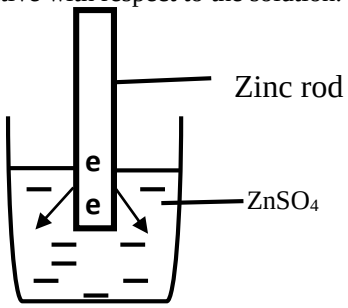
ELECTROCHEMICAL CELLS

ELECTRODE POTENTIAL (E)

-Is the potential difference between an element and an aqueous solution of its ions, when it is in equilibrium with its ions.

Consider a metal dipped into a solution of its ions, e.g. ***a Zinc rod dipped in a solution of zinc ions*** such as zinc sulphate. Two processes may occur;

- Metal atoms may ionize leaving a buildup of electrons on the metal surface, metal becomes ***negatively charged.***
  $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$
- Metal ions from a solution may take up electrons from the rod of the metal; discharged as metal atoms; metal becomes **positively charged**.
  $Zn^{2+}(aq) + 2e \longrightarrow Zn(s)$
  Because of different rates at which the above process occur, and the high electro positivity of the zinc metal, tendency to ionize outweigh the tendency to gain electrons; electrons accumulate on its surface, becomes more negative with respect to the solution.



STANDARD ELECTRODE POTENTIAL (SEP) , E^{θ}

-Is the electrode potential value of an electrode when the electrode is dipped in a solution of 1M concentration of its ions, at a standard temperature of 25°C and a pressure of one atmosphere.

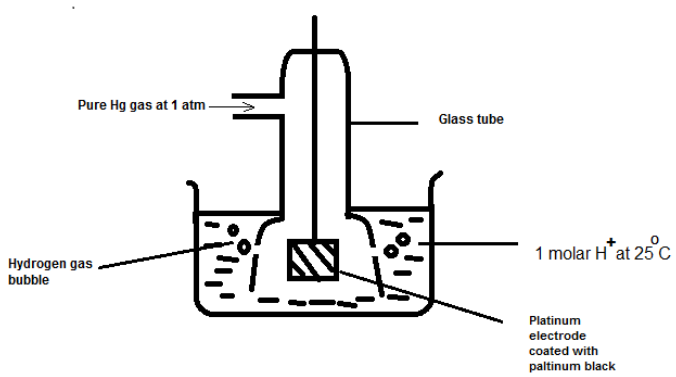
-It's impossible to measure electrode potential of an isolated electrode, and assign an absolute potential to it, but **only differences in potential are measurable**.

-Can only be measured relatively to the standard hydrogen electrode(SHE); whose potential difference is arbitrarily taken as 0.0v; it does not exert is own potential with respect to the solution.

Guiding question. Explain why it's not possible to measure standard electrode potential absolutely, **UNEB 2002(2) no. 4a(ii)**

STANDARD HYDROGEN HALF CELL/ STANDARD HYDROGEN ELECTRODE (SHE)

-Consists of a piece of Platinum foil; coated with platinum black; suspended in a 1M solution of hydrogen ions, with hydrogen gas bubbling over platinum surface at 25^0C and a pressure of one atmosphere.



-Hydrogen gas is adsorbed on the platinum, and an equilibrium is established between the adsorbed layer of hydrogen gas, and aqueous hydrogen ions in solution.

$\frac{1}{2} H_2(g) \rightleftharpoons H^+(aq) + e$

-Cell notation of SHE ***$Pt, H_2(g)/2H^+(aq)$ $E^{\theta} = 0.0V$***

Importance of platinized platinum

-Allows hydrogen gas to be adsorbed on its surface, bringing hydrogen molecules in contact with hydrogen ions.

-Its covering by a loosely deposited layer of finely divided platinum, allows to catalyse the formation of an equilibrium between the $H_2(g)$ and H^+ by increasing surface area over which the equilibrium is established

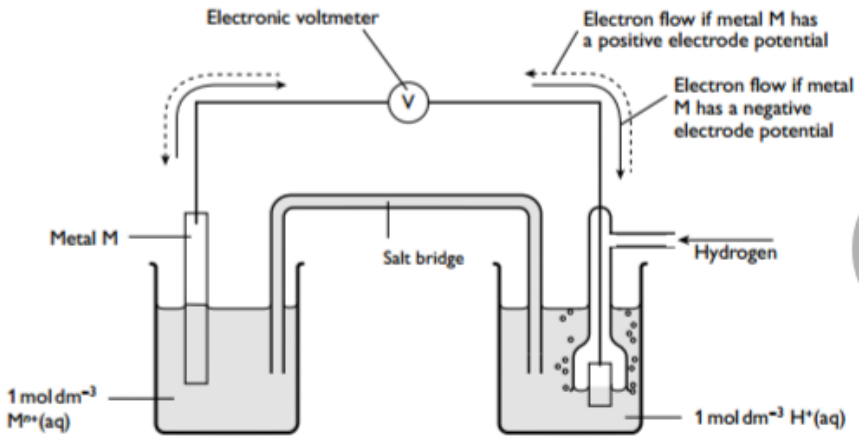
-Acts as an inert metal connection to the H2/H+ system (no tendency for platinum to form ions itself)

Guiding questions

1.Describe a standard hydrogen half -cell. **UNEB 2002(2) No.4b**

MEASUREMENT OF STANDARD ELECTRODE POTENTIALS

-In measuring and comparing electrode potentials, same standard conditions with which the potential of the platinum electrode in a standard hydrogen electrode is obtained, is chosen i.e. (i) All solutions have a concentration of 1M (ii) pressure of 1 atmosphere for any gases involved (iii) Temperature,25℃ (298K).



Procedure

- The electrode whose electrode potential is to be determined, consisting of a **metal rod** immersed in **1M solution of its ions** is connected to **right** of the **standard hydrogen electrode** across a voltmeter, with the two solutions connected by means of a **salt bridge.**

-The standard hydrogen electrode consisting of **hydrogen gas** bubbled over platinized platinum, immersed in a 1 M hydrochloric acid.

- Maximum potential difference (e.m.f) between the electrodes of the two half cells is read using a potentiometer or a high- resistance voltmeter, and since the electrode potential due to the SHE is **0.0V**, the potential registered by the voltmeter/potentiometer is the standard electrode potential of the metal electrode.

NOTE ***The standard hydrogen electrode must always be on the left.***

Guiding questions.

1.Describe briefly how the standard electrode potential of copper electrode can be determined. (**Include half -cell equations at different electrodes, overall cell equation and cell diagram)**

2.Describe with the aid of a labelled diagram how the standard electrode potential of a zinc electrode can be determined. **UNEB 2007 (2) NO.4a**

3. UNEB 1997(2) NO. 4a, UNEB 2002(2) NO. 4a.

4.Draw a well labelled diagram to show how the standard electrode potential could be determined for $Pb^{2+}(aq)/Pb(s)$ electrode. **JJEB 2012(2) No.1a**

5.(a)Standard electrode potentials, E^{θ}, are measured relative to a standard reference electrode. What is the standard reference electrode and what is its potential?

(b) State **three** conditions which must apply when values of E^{θ} are being determined.

(c.) What is the function of the salt bridge, stating its composition? **NEAB**

FACTORS AFFECTING MAGNITUDE OF STANDARD ELECTRODE POTENTIAL

-Sublimation energy / atomization energy.

The higher the sublimation energy, the lower the negative value of electrode potential because it becomes difficult to convert the solid metal into gaseous atoms.

-Ionization energy

The higher the ionization energy, the lower the negative value of the electrode potential because it is difficult to convert gaseous atoms to gaseous ions.

-Hydration energy

The greater the hydration energy, the higher the negative value of electrode potential because the gaseous ions are easily hydrated in aqueous solution

-Concentration

Increase in concentration of aqueous ion, makes the electrode potential for all metal ion/ metal systems more positive, because reduction of these ions is then more likely to occur (half- cell becoming a better oxidising agent). Conversely, electrode potentials become less positive when concentration is reduced e.g.Standard electrode potential of copper is +0.34V, but electrode potential of 0.1M $Cu^{2+}(aq)/Cu(s)$ is only +0.31V.

-Temperature.

-Nature of the metal

Guiding questions.

1.Discuss the factors which affect the value of standard electrode potentials **UNEB 2002(2) NO.4a(iii)**
2 State **two** factors which affect the magnitude of standard electrode potential. **KASSHIPA (1) NO 13a(ii)**

ARRANGEMENT OF EMF CELLS (STANDARD CELL POTENTIALS)

E.m.f of a cell is a **combination of two electrode potentials or half cells**.
Conventionally;

- Electrochemical cell is made up of two half cells; the left hand half -cell and right hand half - cell.
- Half-cell undergoing oxidation should be on the left; electrons thus flow from left to the right hand half-cell.
- Oxidation occurs at the anode; reducing agents are found at the anode. More negative/less positive electrode form the anode; i.e. anode is always on the left hand side of the cell.
- Reduction occurs at the cathode; oxidizing agents are found at the cathode. More positive/ less negative electrode forms the cathode.i.e. cathode is always on the right hand side of the cell.
- Given two electrode potentials; both positive, the less positive one becomes the electron donor (anode) constituting the left hand electrode e.g.
  Cu^{2+} (aq) /Cu(s) E^{θ} = + 0.34 Ag^{+} (aq) / Ag(s) E^{θ} = + 2.34V
  Copper being less positive occupies the left hand electrode
- Given two electrode potentials; one positive and the other negative, the one negative constitutes the left hand electrode.
- Given two electrode potentials; both negative, the more negative one constitutes the left hand electrode
- Standard electrode potentials are always recorded as **standard reduction potentials;** reactions are written with the reduced species on the right i.e. **Oxidized species + ne ⇌ reduced species**

Standard electrode potential for metal/metal ion half cells

Oxidized species + ne ⇌ reduced species	**E^{θ}/V**
$K^{+}_{(aq)}$ + e ⇌ K(s)	-2.92
Ca^{2+}(aq) + 2e ⇌ Ca(s)	-2.87
$Mg^{2+}_{(aq)}$ + 2e ⇌ Mg(s)	-2.37
$Al^{3+}_{(aq)}$ + 3e ⇌ Al(s)	-1.66
$Zn^{2+}_{(aq)}$ + 2e ⇌ Zn(s)	-0.76
$Fe^{2+}_{(aq)}$ +2e ⇌ Fe(s)	-0.44
$2H^{+}_{(aq)}$ + e ⇌ H_2(s)	0.00
$Cu^{2+}_{(aq)}$ + 2e ⇌ Cu(s)	+0.34
$Ag^{+}_{(aq)}$ + e ⇌ Ag(s)	+ 0.84

CELL NOTATION/CELL DIAGRAM

- Is the convenient short hand notation for writing down cell formed by connecting two half cells.
-cell is represented by inserting appropriate species in the following scheme.
Reduced form/oxidized form//oxidized form/ reduced form or **electrode/solution // solution/electrode**
- For half- cell systems not involving a metal electrode e.g. a standard Fe^{3+}(aq) / Fe^{2+}(aq), ***platinum electrode*** is inserted in the scheme.

Symbols used in cell diagrams

Symbol	**Description**
/	Represents change in phase between aqueous ions, gas and solid metal (**phase boundary**)
//	Salt bridge between two half cells
- - -	Porous partition between two half cells
,	Separates species in the same phase.
Pt	Platinum electrode; used when one of the half cells or both does involve a metal electrode

Example.

1.The equations for some redox reactions are shown below.

$2H^{+}$(aq) + $2Fe^{2}$ (aq) ⇌ $H_{2(g)}$ +$2Fe^{3+}$(aq)

$Br0^{-}_{3}$(aq) + 3Zn(s) +6OH^{-} (aq) +3H_2O(l) ⇌3$Zn(OH)^{2-}_{4(aq)}$ +Br^{-}(aq)

For each reaction, write the ;

(a)half- cell reactions taking place at the,

(i).anode (ii) cathode

(b) cell notation for the cell made by combining the electrode for each half cell.

Solution

(a) **(i) At** anode. Zn(s) + $4OH^{-}$(aq) ⟶ $Zn(OH)^{2-}_{4(aq)}$+2e

Fe^{2+}(aq) ⟶ Fe^{3+}(aq) + e

(ii) At cathode $2H^{+}$(aq) +2e ⟶ $H_{2(g)}$

$Br0^{-}_{3}$(aq) + 3H_2O(l) +6e ⟶ Br^{-}(aq) +6OH^{-}(aq)

(b). Pt(s)/ Fe^{2+}(aq),Fe^{3+}(aq) // H^{+}(aq) / $H_{2(g)}$ /Pt(s)

Zn(s)/ OH^{-}(aq), $Zn(OH)^{2-}_{4(aq)}$ // $Br0^{-}_{3}$(aq) , Br^{-}(aq) ,OH^{-}(aq) /Pt(s)

APPLICATION OF STANDARD ELECTRODE POTENTIALS

(i). **Determining e.m.f of the cell.**

From the given standard reduction potentials, e.m.f is calculated using;

$E^\theta_{cell} = E^\theta_{right\ hand\ side} - E^\theta_{left\ hand\ side}$ or $E^\theta_{cell} = E^\theta_{reduction} - E^\theta_{oxidation}$ or $E^\theta_{cell} = E^\theta_{cathode} - E^\theta_{anode}$.

Examples

1. Calculate the e.m.fs of the following half cells and write the overall cell reaction

   a) $Na^+_{(aq)} / Na_{(s)}$ $E^\theta = -2.71v$
   $\frac{1}{2}F_{2\,(g)} / F^-_{(aq)}$ $E^\theta = +2.87v$

   b) $Zn^{2+}_{(aq)}/Zn_{(s)}$ $E^\theta = -0.76v$
   $Ni^{2+}_{(aq)}/Ni_{(s)}$ $E^\theta = -0.25v$

   c) $Cu^{2+}/ Cu_{(s)}$ $E^\theta = +0.34v$
   $Ag^+_{(aq)}/ Ag_{(s)}$ $E^\theta = +0.80v$

   d) $Zn^{2+}_{(aq)} / Zn_{(s)}$ $E^\theta = -0.76V$
   $Cu^{2+}_{(aq)} / Cu_{(s)}$ $E^\theta = +0.34V$

solutions

a) Emf of a cell = $E^\theta_{right} - E^\theta_{left}$
= 2.87− (−2.71)
= **+5.58V**

Half -cell reactions;
At Anode; $Na_{(s)} \longrightarrow Na^+_{(aq)} + e$ $E^\theta = +2.71v$
At Cathode; $\frac{1}{2}F_{2\,(g)} + e \longrightarrow F^-_{(aq)}$ $E^\theta = +2.87v$
Overall cell reaction; $\mathbf{Na_{(s)} + \frac{1}{2}F_{2\,(g)} \longrightarrow Na^+_{(aq)} + F^-_{(aq)}}$ $\mathbf{E^\theta = +5.58v}$

b) Emf of a cell = $E^\theta_{right} - E^\theta_{left}$
= (−0.25) – (−0.76)
= **+ 0.51V**

Half -cell reactions;
At Anode; $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\bar{e}$ $E^\theta = +0.76v$
At Cathode; $Ni^{2+}_{(aq)} + 2e \longrightarrow Ni_{(s)}$ $E^\theta = -0.25v$
Overall cell reaction; $\mathbf{Zn_{(s} + Ni^{2+}_{(aq)} \longrightarrow Zn^{2+} + Ni_{(s)}}$ $\mathbf{E^\theta = +0.51V}$

(c) Emf of a cell = $E^\theta_{right} - E^\theta_{left}$
= (+0.80 − +0.34)
= **+0.46V**

Half- cell reactions;
At Anode; $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e$ $E^\theta = -0.34V$
At Cathode; $2Ag^+_{(aq)} + 2e \longrightarrow 2Ag_{(s)}$ $E^\theta = +0.80v$
Overall cell reaction;
$\mathbf{Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}}$ $\mathbf{E^\theta = +0.46V}$

(d)Emf of a cell = $E^\theta_{right} - E^\theta_{left}$
= (0.34 − - 0.76)v
= **+ 1.10V**

Half- cell reactions
At Anode; $Zn(s) \longrightarrow Zn^{2+}_{(aq)} + 2e$ $E^\theta = +0.76V$
At cathode; $Cu^{2+}(aq) + 2e \longrightarrow Cu\ (s)$ $E^\theta = +0.34V$
Full cell reaction;
$\mathbf{Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}_{(aq)} + Cu\ (s)}$ $\mathbf{E^\theta = +1.10V}$

2. The standard electrode potential of some systems are given below.

Electrode	**E^θ (V)**
$Cr^{3+}(aq)/ Cr^{2+}(aq)$	- 0.402
$MnO^-_4(aq) / Mn^{2+}(aq)$	+ 1.52

(a)Write the convention of the cell formed when the electrodes are coupled
(b)Write an equation for the cell reaction
(c.) Determine the standard cell potential of the cell

Solution.

(a)$Pt_{(s)}/Cr^{2+}_{(aq)}, Cr^{3+}_{(aq)}// MnO^-_{4\ (aq)}, Mn^{2+}(aq)/Pt_{(s)}$

(b)Left hand half- cell reaction. $(Cr^{2+}_{(aq)} \longrightarrow Cr^{3+}_{(aq)} + e)\ 5$ $E^\theta = +0.402V$

Right hand half-cell reaction $MnO^-_{4\ (aq)} + 8H^+_{(aq)} + 5e \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$ $E^\theta = +1.52V$

Overall cell reaction

$\mathbf{5Cr^{2+}_{(aq)} + MnO^-_{4\ (aq)} + 8H^+_{(aq)} \longrightarrow 5\ Cr^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4H_2O_{(l)}}$ $\mathbf{E^\theta = 1.922V}$

(c.) Emf of a cell = $E^\theta_{right} - E^\theta_{left}$
= +1.52 − − 0.402
= 1.922V

Note. In combining half- cell equations, one or both may be multiplied by integers to balance the electrons, BUT the electrode potential values are not affected because they don't depend on how many times the reaction occurs.

3.The standard electrode potentials of two half cells are given in the table below.

Half cell	**E^θ (V)**
$HCl(aq)/ H_2(g)$	0.00
$CdSO_{4(aq)} / Cd(s)$	-0.40

(a).Write the cell notation for the cell formed by combining the two half cells
(b).Write the ionic equation for the
(i) reaction at the cathode (ii)reaction at the anode (iii)Overall cell reaction
(c.) Calculate the e.m.f of the cell. **UNEB 2013(1) NO 7**

Solution

(a) $Cd(s)/ Cd^{2+}(aq) // H^+(aq)/H_{2(g)} / Pt(s)$

(b) (i) $2H^+(aq) + 2e \longrightarrow H_{2(g)}$ (ii) $Cd(s) \longrightarrow \mathbf{Cd}^{2+}(aq) + 2e$ (iii) $Cd(s) + 2H^+(aq) \longrightarrow Cd^{2+}(aq) + H_{2(g)}$

(c.) Emf of a cell = $E^\theta_{right} - E^\theta_{left}$ = 0.00-(-0.40)= **+0.40V**

Lawrence Arum Bronsted . Email. Lawry50@gmail.com watsap +256700523500 .

4.Given two half- cell reactions

$Cr_2O^{2-}_{7\,(aq)} + 14H^+_{(aq)} + 6e \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O\ (l)$ $\quad E^\theta = +1.33V$

$\frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e \longrightarrow H_2O\ (l)$ $\quad E^\theta = +1.23V$

a) Write the equation for the reaction between dichromate ion and water

b) Calculate the value of E^θ for the reaction between dichromate ions and water

Solution

(a). Anode reaction. $(H_2O(l) \longrightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e)3$ $\quad E^\theta = -1.23V$

Cathode reaction. $Cr_2O^{2-}_{7\,(aq)} + 14H^+_{(aq)} + 6e \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O\ (l)$ $\quad E^\theta = +1.33V$

Overall cell reaction. . $\mathbf{Cr_2O^{2-}_{7\,(aq)} + 8H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)}\ \frac{3}{2}O_{2(g)} + 4H_2O\ (l)}$

(b). Emf of a cell = $E^\theta_{\text{cathode}} - E^\theta_{\text{anode}}$

= +1.33-1.23= **+0.1V**

5. The standard electrode potentials for some systems are given below;

$Mn^{3+}_{(aq)}/Mn^{2+}_{(aq)}$ $\quad E^\theta = +1.5\ V$

$V^{3+}_{(aq)} / V^{2+}_{(aq)}$ $\quad E^\theta = -\ 0.26\ V$

(a) Write the convention for cell formed by combining the two systems

(b) Write down the overall equation for the cell reaction

(c) Calculate the emf of the cell. **UNEB 2001(1)8c Modified**.

solution

(a)$Pt(s)/V^{2+}_{(aq)}, V^{3+}_{(aq)} // Mn^{3+}_{(aq)}, Mn^{2+}_{(aq)}/Pt(s)$

(b)$Mn^{3+}_{(aq)} + V^{2+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + V^{3+}_{(aq)}$

(c)Emf of a cell = $E^\theta_{\text{right}} - E^\theta_{\text{left}}$ = (+1.5 – (-0.26) = **+ 1.76V**

6. The standard electrode potentials for some half cells are shown below;

$Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}$ $\quad E^\theta = +0.76V$

$I_{2(aq)} / I^-_{(aq)}$ $\quad E^\theta = +0.54V$

(a) (i)Write the cell convention for the combined cell

(ii)(The equation for the overall cell reaction

(b)Calculate the overall electrode potential for the cell. **UNEB 2005 (1) No 1(a, b)**

Solution

a)(i)$Pt(s)/I^-_{(aq)}, I_{2(aq)} // Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)}/Pt(s)$

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

(b.) Emf of a cell = $E^\theta_{\text{right}} - E^\theta_{\text{left}}$

= (+0.76V – 0.54V)

= **+ 0.22V**

Activity

1.The standard oxidation electrode potentials for some half cells reactions are given below.

$Fe^{2+}_{(aq)}/Fe^{3+}_{(aq)}$ $\quad E^\theta = -0.76V$

$I^-_{(aq)} / I_{2\,(aq)}$ $\quad E^\theta = -0.54V$

Write the

(a) cell notation for the cell formed when the half cells are combined.

(b) Equation for the reaction taking place at the (i) anode (ii) cathode

(c) Calculate the e.m.f of the cell.

2.Electrode potentials for some half cells are given below.

Half cell	**E^θ (V)**
$Fe^{2+}(aq), Fe^{3+}(aq)/Pt$	- 0.771
$Cr^{3+}(aq)$, (aq) $Cr_2O^{2-}_{7\,(aq)}, H^+(aq)/Pt$	-1.33

Write the (a) cell notation for the cell formed when the half cells are combined. (b) equations for half cells reaction (c.) equation for overall cell reaction.

(d) Calculate the emf of the cell.

3. Given the following redox electrode potentials.

$MnO^-_4(aq) / Mn^{2+}(aq)$ $\quad E^\theta = +1.52V$ $\quad S_2O_8^{2-}(aq) / SO_4^{2-}(aq)$ $\quad E^\theta = +2.01V$. (a) Write the;

(i) Cell notation if the two electrodes are connected by a salt bridge

(ii) Overall equation for the cell reaction

(b) Calculate the emf of the cell.

4. The table below shows some values for standard electrode potentials.

Electrode reaction	E^{θ} (V)
$Fe^{2+}_{(aq)} + 2e \rightleftharpoons Fe_{(s)}$	-0.44
$H^{+}(aq) + e \rightleftharpoons \frac{1}{2} H_2(g)$	0.00

(a). Calculate the em.f of the cell
(b) State which would be the positive electrode
(c.) Write an equation to show overall reaction in the cell
(d) Write down the cell diagram that represents the overall reaction in the cell.

5.The standard reduction potentials for hydrogen peroxide and iron (iii) oxide to iron(II) ions are +1.77V and +0.76V respectively.
(a) . Write the half- cell equations to show the reduction processes
(b) Write the (i) cell convention for the combined cell (ii) equation for overall cell reaction
(c.) Calculate the e.m.f of the cell in b(i)

(i)Predicting the feasibility of a redox reaction

For a redox reaction to be spontaneous/ feasible; occuring without input of energy from external source, e.m.f of the cell should be ***positive***, giving a ***negative value of Gibb's free energy***.

$\Delta G^{\theta} = -nFE^{\theta}_{cell}$

Where n = number of electrons transferred in the electrode reaction; F = Faraday's constant(96500C)
E^{θ} = e.m.f of a cell

Example

1. The following are half cells of some reaction;

$Ag^{+}_{(aq)} / Ag^{+}_{(s)}$ $E^{\theta} = +0.799V$
$Cd^{2+}_{(aq)} / Cd_{(s)}$ $E^{\theta} = -0.402V$

(a) Write the convention of the cell formed when the electrodes are coupled.
(b) Determine the standard cell potential of the cell
(c) Hence predict the spontaneity of the reaction

Solution

(a) $Cd_{(s)} / Cd^{2+}_{(aq)} // Ag^{+}_{(aq)} / Ag_{(s)}$
(b) Emf of a cell = $E^{\theta}_{right} - E^{\theta}_{left}$
$= 0.799 - (-0.402)$
$= \mathbf{+ 1.201V}$
(c) $Cd\ (s) \longrightarrow Cd^{2+}_{(aq)} + 2e$
$(Ag^{+}_{(aq)} + \bar{e} \longrightarrow Ag_{(s)}) \times 2$
$Cd_{(s)} + 2Ag^{+}\ (aq) \longrightarrow Cd^{2+}_{(aq)} + 2Ag\ (s)$
$\Delta G^{\theta} = -nFE^{\theta}$
$= -2 \times 96500 \times 1.201$
$\mathbf{\Delta G^{\theta} = -231793J}$; ***Negative value of Gibb's free energy; gives a spontaneous reaction***

2.The equations for some half –cell reactions are given below.

$Cd^{2+}_{(aq)} + 2e \longrightarrow Cd\ (s)$ $E^{\theta} = -0.44V$
$H_2O_{2(aq)} + 2H^{+}(aq) + 2e \longrightarrow 2H_2O(l)$ $E^{\theta} = +1.77V$

(a).Write the;
(i) cell notation for the cell formed by combining two half cells.
(ii) equation for the overall cell reaction
(b) Calculate the e.m.f of the cell.
(c.)State whether the reaction is feasible or not. Give a reason for your answer.

Solution

(a). (i). $Cd_{(s)} / Cd^{2+}_{(aq)} // H_2O_{2(aq)}, H^{+}(aq) / H_2O(l) / Pt_{(s)}$
(ii) $H_2O_{2(aq)} + 2H^{+}(aq) + Cd\ (s) \longrightarrow Cd^{2+}_{(aq)} + 2H_2O(l)$
(b). Emf of a cell = $E^{\theta}_{right} - E^{\theta}_{left}$
$= 1.77-(0.44) = \mathbf{+2.21V}$
(c.) Feasible; because standard electrode potential of the cell is positive.

Guiding questions.

1. The convention of the cell is given below.

$Pt/\ )Fe^{2+}_{(aq)}, Fe^{3+}_{(aq)} // MnO^{-}_{4\ (aq)}, Mn^{2+}(aq), H^{+}(aq) / Pt$

(a). Write the equations for the half cell reaction at the (i) anode (ii) cathode
(b). Write the overall equation for the cell reaction.
(c.) The electrode potentials for the system $Fe^{2+}_{(aq)} / Fe^{3+}_{(aq)}$ and $Mn^{2+}(aq) / MnO^{-}_{4\ (aq)}$ are -0.76V and -1.51V respectively. Deduce whether the reaction in (b) is feasible or not and give a reason for your answer.**1998(1) 8**.

Lawrence Arum Bronsted . Email. Lawry50@gmail.com watsap +256700523500 .

2. The standard electrode potentials for some half cells are shown below.

$Fe^{3+}_{(aq)} + e \longrightarrow Fe^{2+}_{(aq)}$ $E^\theta = +0.76V$

$ClO_4^-(aq) + 2H^+(aq) + 2e \longrightarrow ClO_3^-(aq) + H_2O(l)$ $E^\theta = 1.20V$

(a) Write the cell notation of the cell made when half cells above are connected via a salt bridge.

(b) (i). Write the overall cell equation

(ii) Calculate the emf of the cell

(c.) State whether the reaction is feasible or not. Give a reason for your answer. **UNASSE 2011(1) No1**

3. The following are the half- cell reactions at the electrodes.

$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e$ $E^\theta = -0.13V$

$VO^{2+}(aq) + 2H^+(aq) + e \longrightarrow V^{3+}(aq) + H_2O(l)$ $E^\theta = XV$

(a) Write the overall cell equation.

(b) Calculate the value of X, if the emf of the cell is +0.67V.

(c) Explain the feasibility of the cell. **KASSHIPA 2012(1) 13. Part of question**

4.The e.m.f cell $Fe(s) / FeCl_{2(aq)} // FeCl_{3(aq}, Fe^{2+}(aq)/ Pt$. has a standard emf of +1.211V.

(a). Write down equations for the cell above at (i) cathode (ii) anode

(b). If the standard reduction potential of the anod is -0.44V, what is the electrode potential for the cathode?

(c.) Calculate the standard free energy change for the reaction, state whether the reaction is feasible or not?

5. **UNEB 2007(1) No1, 2005 (1) No 1**.

(iii) **Determination of the value of the equilibrium constant, Kc**

$\Delta G = -2.303RT\log Kc$

But $\Delta G = -nFE^\theta$

$\Rightarrow -nFE^\theta = -2.303RT\log Kc$

$nFE^\theta = 2.303RT\log Kc$

$\log Kc = \frac{nFE\theta}{2.303RT}$

$$\mathbf{Kc = \log^{-1}\left(\frac{nFE^\theta}{2.303RT}\right)}$$

Note ***Between emf values greater then +0.6V (where reaction goes to completion) and more negative than -0.6V(where reaction does not go to completion at all) the system is in equilibrium.***

(iv) Selecting a good oxidizing and reducing agent

-A strong oxidizing agent; accepts electrons easily, has a more positive/less negative value of electrode potential e.g. metal ion lower in the electrochemical series

-A strong reducing agent loses electrons easily/readily; forming positively charged ion; has a more negative / less positive value of electrode potential e.g. metal ions in the electrochemical series.

ELECTROCHEMICAL SERIES

Is the arrangement of standard electrode potentials of redox systems in an increasing order.

Half- cell reaction	**E^θ(V)**
$Li^+_{(aq)} + e \rightleftharpoons Li(s)$	−3.04 **(strongest reducing agent)**
$K^+_{(aq)} + e \rightleftharpoons K(s)$	− 2.92
$Na^+(aq) + e \rightleftharpoons Na(s)$	- 2.71
$Mg^{2+}_{(aq)} + 2e \rightleftharpoons Mg(s)$	- 2.38
$Al^{3+}(aq) + 3e \rightleftharpoons Al(s)$	- 1.66
$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	- 0.76
$Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$	− 0.13
$2H^+(aq) + 2e \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}_{(aq)} + 2e \rightleftharpoons Sn^{2+}_{(aq)}$	+0.15
$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	+0.34
$Fe^{3+}_{(aq)} + e \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77
$Ag^+(aq) + e \rightleftharpoons Ag(s)$	+0.80
$2Br_{2(l)} + 2e \rightleftharpoons 2Br^-_{(aq)}$	+1.07
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6\bar{e} \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O$	+1.33 **(strongest oxidizing agent)**

Example.

1.The electrode potential of some half- cell reactions are shown below;

A. $Fe^{3+}_{(aq)} + e \rightleftharpoons Fe^{2+}_{(aq)}$ $E^\theta = +0.77V$

B. $Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$ $E^\theta = -0.76V$

C. $MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e \rightleftharpoons Mn^{2+}(aq) + 4H_2O$ $E^\theta = +1.51V$

D. $MnO_4^- + e \rightleftharpoons MnO_4^{2-}$ $E^\theta = +0.56V$

E. $Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$ $E^\theta = +0.34V$

F. $MnO_4^-(aq) + 4H^+_{(aq)} + 5e \rightleftharpoons MnO_{2(aq)} + 2H_2O(l)$ $E^\theta = +2.264V$

State the species which is the best.

i. Reducing agent **(Zn(s))** **(ii)** Oxidizing agent **(MnO_4^- in F)**

2.Given the following electrode potentials;

$Na^{+}_{(aq)} + e \longrightarrow Na\ (s)$ $\quad E^{\theta} = -2.71V$

$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu\ (s)$ $\quad E^{\theta} = +0.337V$

$Zn^{2+}_{(aq)} + 2e \longrightarrow Zn\ (s)$ $\quad E^{\theta} = -0.763V$

$Ag^{+}_{(aq)} + e \longrightarrow Ag\ (s)$ $\quad E^{\theta} = +0.799V$

Arrange the electrodes in order of reducing power starting with the least reducing. **UNEB 1996(1) 3(a)**

$Ag^{+}_{(aq)}$ / $Ag_{(s)}$, $Cu^{2+}_{(aq)}$ /Cu(s), $Zn^{2+}_{(aq)}$ /Zn(s), $Na^{+}_{(aq)}$/Na(s)

TYPES OF ELECTRODES

(a) Metal – Metal ion electrode;

For example; Zn / $Zn^{2+}_{(aq)}$, Cu(s)/Cu^{2+}(aq) etc

(b) Gas electrode;

-consists of gas at a given temperature and pressure, bubbled over an inert electrode, platinum dipped into a solution of its ions

- Platinum (i) provides an area over which the gas dissolves (ii) acts as a catalyst.

Eg (i) Pts (s), $Hg_{(g)}$/ $H^{+}_{(aq)}$ or $\quad H^{+}(aq) / H_2(g)$, Pt(s) $\quad$ Pt(s), F_2 (g) / $F^{-}_{(aq)}$ $\quad$ or $\quad F^{-}_{(aq)}/F^{2}(g)$, Pts

(c.) Metal – metal insoluble salt electrode

-Consists of a piece of metal coated with an insoluble salt of that metal; whole setup then immersed in solution of salt with common anion to that of insoluble salt.e.g.

Electrode.	**Reaction**
(i) Ag(s), AgCl(s) / Cl^{-}(aq)	$AgCl(s) \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}(aq)$; $Ag^{+}_{(aq)} + e \longrightarrow Ag(s)$ $\quad$ $AgCl(s) + e \longrightarrow Ag(s) + Cl^{-}(aq)$
(ii) Pb(s) ,$PbSO_4$(s) /$SO^{2-}_{4}(aq)$	$PbSO_{4(s)} \rightleftharpoons Pb^{2+}(aq) + SO^{2-}_{4}$ (aq); $Pb^{2+}(aq) + 2e \longrightarrow Pb(s) + SO^{2-}_{4}$ (aq) $\quad$ $PbSO_{4(s)} + 2e \longrightarrow Pb(s) + SO^{2-}_{4}$ (aq
(iii)Cu(s), $CuCO_{3(s)}$/ CO^{2-}_{3} (aq)	$CuCO_3(S) \longrightarrow Cu^{2+}(aq) + CO^{2-}_{3}$ (aq); Cu^{2+} (aq) + 2e $\longrightarrow$ Cu(s) $\quad$ $CuCO_3(S) + 2e \longrightarrow Cu(s) + CO^{2-}_{3}$ (aq)

Examples.

1.The standard electrode potentials for the system Ag(s) / AgCl(s) // $CuCl_2$(aq) / Cu(s) are + 0.223V and + 0.34V respectively. Calculate the e.m.f of the cell.

$E^{\theta}_{cell} = E^{\theta}_{right} - E^{\theta}_{left} = 0.34 - 0.223 =$ **+0.117V**

2. The standard electrode potentials for the system Ag(s) / AgCl(s) // $CuCl_2$(aq) / Cu(s) are + 0.223V and + 0.34V respectively.

(a). Write the equations for the half- cell reactions that take place at the,

(i) anode (ii) cathode

(b). Write the overall equation for the cell reaction

(c.) Calculate the ,

(i) e.m.f of the cell (ii) standard free energy of the cell

(d) State whether the reaction is feasible or not. Give a reason for your answer.

(d)Ion – Ion half -cell electrode (Redox electrode)

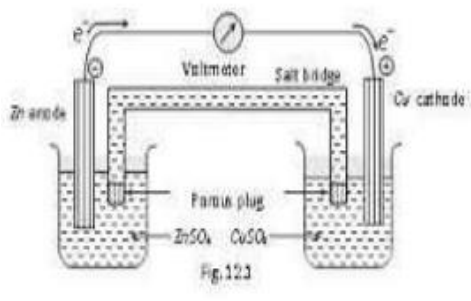
-Consists of an inert metal, platinum immersed in solution containing ions of some elements in two oxidation state

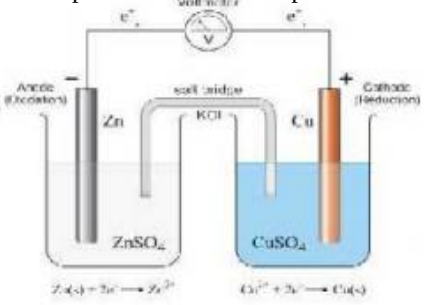
e.g. (i) Pt(s) / $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$ OR $Fe^{3+}_{(aq)}$, $Fe^{2+}_{(aq)}$ / Pt(s) (ii) Pt(s) / $Cr^{2+}_{(aq)}$, $Cr^{3+}_{(aq)}$

DANIELL CELL:

-Constructed by dipping two metal electrodes, in solutions of their salts.

-The two solutions with their corresponding electrodes form separate half cells, are connected and separated by a salt bridge, made from filter paper soaked in potassium nitrate or potassium chloride solution.





-Zinc dissolves from Zinc rod leaving electrons behind on the Zinc giving it a **negative potential** (**anode**)

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

-Cu^{2+} from $CuSO_4$ (aq) solution accept electrons, become deposited on the copper rod giving it a **positive potential**(**cathode**)

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

-Flow of electrons from Zinc rod to the copper rod constitute of current which flows in the opposite direction i.e from copper metal to Zinc metal.

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

Cell notation. $Zn_{(s)} / Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)} / Cu(s)$

Significance of the salt bridge

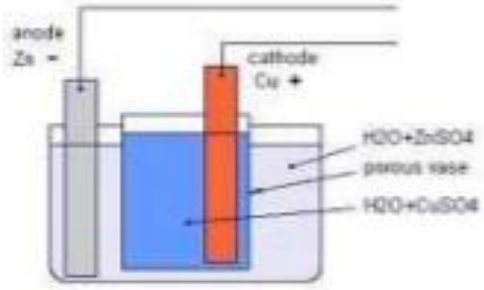
-Completes the circuit by allowing electrons flow from cell to another.

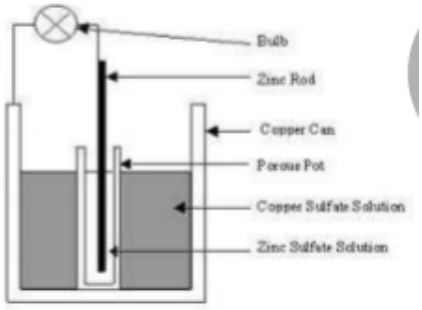
-Prevent excessive mixing of the two electrolytes, by keeping them separate.

-Provides cations and anions which replenishes those consumed at the electrodes.

NOTE. Salt bridge is some Daniel cells is replaced with a (i) porous partition or (ii) rigid porous pot i.e

(i).**With porous pot**.





(ii) **With a porous partition**.



Guiding questions

1.(a) Draw a fully labelled diagram of a Daniell cell, and show the direction in which electrons flow in the external circuit when it is used to generate electricity.

(b) Write equations for the reactions at each electrode when the cell produces an electric current.

GALVANIC CELL/VOLTAIC CELL

Is an electrochemical cell in which redox reactions cause an electric current to flow in an external circuit, where useful work can be done.

Divided into (a) Batteries (b) Fuel cells.

(A)**Batterie**s

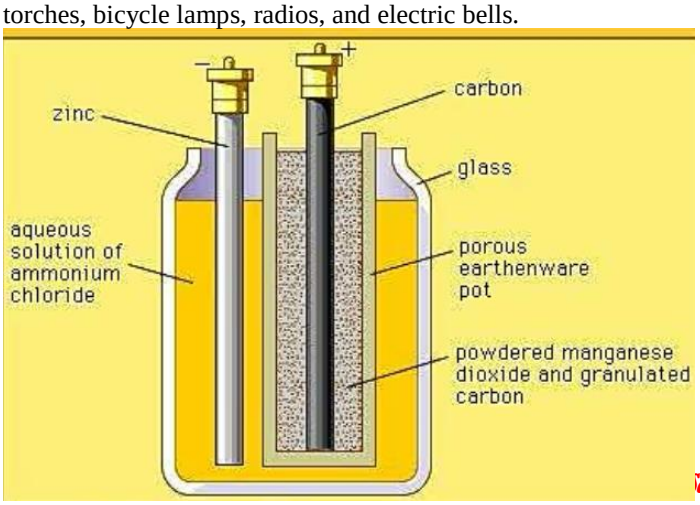
-Consists of two types (i) primary cells and (ii) secondary cells ; each having two electrodes in contact with an electrolyte.

-Electrons flow in the electrodes, with ions flowing in the electrolyte.

(i) **Primary cells (Dry cells)**

-Are galvanic cells which can be used once only, and cannot be recharged.

-Most common example is the **leclanche dry cell**, used in a wide range of small electrical appliances such as torches, bicycle lamps, radios, and electric bells.



-Consists of a negative Zinc terminal; and a positive carbon rod terminal; surrounded by a mixture of powdered charcoal and Manganese (IV) Oxide; with ammonium chloride paste as electrolyte.

-Manganese(IV)oxide oxidizes hydrogen produced at the cathode to water; preventing bubbles of the gas from coating carbon terminal, which would otherwise reduce its efficiency.

-When is use, casing is eaten away as zinc is oxidized to Zinc(II) ions ; paste oozes through the outer card board.

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

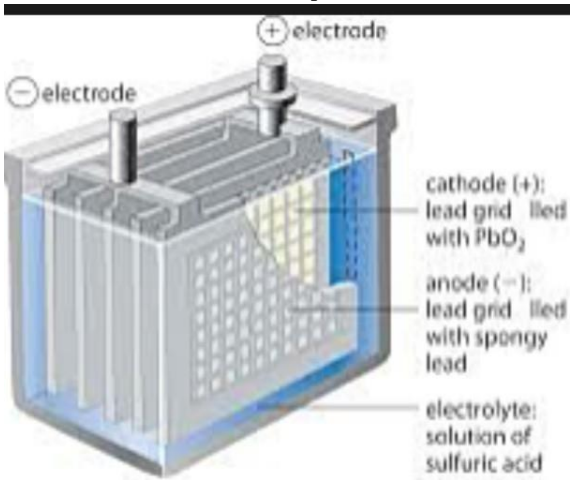
Cathode $2NH_4^+(aq) + 2e \longrightarrow NH_3(g) + H_2(g)$

NB Ammonium chloride paste is replaced by (i) zinc chloride electrolyte (**Heavy duty type**) (ii) Concentrated Potassium hydroxide electrolyte **('long life' alkaline type**)

(ii) **Secondary cells (accumulators)**

-Are galvanic cells which can be recharged after use

-Most common example is the **Lead acid accumulators**; used in vehicles to power the starter motor.



-Consists of six 2V cells connected in series; with each cell comprising of a negative lead plate terminal(anode) and a positive lead(IV)oxide –coated plate terminal(cathode) both dipping in dilute sulphuric acid, electrolyte;

-During discharge process (operating state of cell),

At Anode $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4\ (s) + 2e$

At cathode. $PbO_2(s) + 2H^+(aq) + SO_4^{2-}(aq) + 2e \longrightarrow PbSO_4\ (s) + H_2O(l)$

-The battery is charged by passing a direct electric current at the cathode and anode; electrode processes above are reversed producing lead and lead (IV)oxide.

NB. (i)Sulphuric acid is formed during discharge; getting used up during charging.

(ii) Since sulphuric acid is much denser than water; state of battery can be assessed by measuring the density of the battery acid with a hydrometer.

Question.

1.Some electrode potentials of electrode reactions of an accumulator cell are given below. $MnO_{4\,(aq)}^- + 8H^+_{(aq)} + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)\ E^\theta = +1.52V$

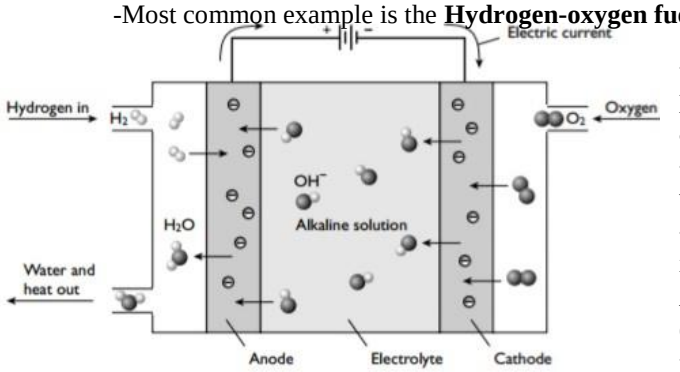
$SO_4^{2-}(aq) + 2H^+(aq) + 2e \longrightarrow SO_3^{2-}(aq) + H_2O(l)\ E\theta = +0.20V$

(a). Write the overall cell reaction between $MnO_{4\,(aq)}^-$/ $H^+_{(aq)}$ and sulphite ions, and determine the emf of the cell (b) Why was water preferred to dilute sulphuric acid when charging?

(B) **FUEL CELLS**

-Are voltaic cells that covert chemical energy from the combustion of fuels such as Hydrogen, hydrocarbon and alcohols directly to electrical energy.

-Most common example is the **Hydrogen-oxygen fuel cell**.



-Consists of a negative terminal, porous carbon coated with Nickel; and positive terminal, porous carbon coated with nickle and nickle(II) oxide; acting as a catalyst on the surface of the terminals.

-Hydrogen is passed into negative compartment of the cell ; and oxygen into the positive compartment.

-Under pressure, the two gases diffuse through the porous carbon terminals into the warm potassium hydroxide solution between them.

Anode reaction. $2H_{2(g)} + 4OH(aq) \longrightarrow 4H_2O(l) + 4e$

Cathode reaction $O_{2(g)} + 2H_2O(l) + 4e \longrightarrow 4OH^-_{(aq)}$

NB. Differ from dry cells and lead acid accumulators in having a steady supply of reactants from which to produce electric current.

DIFFERENCES BETWEEN ELECTROLYTIC CELL AND EMF CELLS

Electrolytic cell	**Emf cell**
Electric current is externally supplied	Electric current is internally generated
Converts electrical energy to chemical energy	Converts chemical energy to electrical energy
Oxidation occurs at positive electrode	Oxidation occurs at negative electrode

Question.

State **two** ways in which an electrolytic cell differs from the e.m.f cell**. UNEB 1997(P2) 4C**