Electrochemical cells

When a strip of metal is placed in a solution of its ions, the metal atoms tend to ionize; cations dissolve in solutions while electrons remain on the metal surface. For instance, a divalent metal, M, ionizes as follows
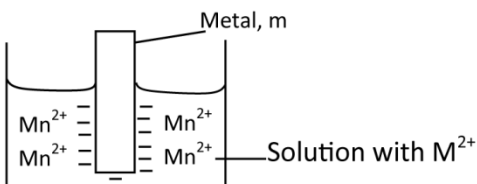
$M(s) \leftrightarrow M^{2+}(aq) + 2e$

Fig. 4.1

The attraction of the metal rod (containing negative charge) and the solution (containing positive charges) causes a potential difference called **electrode potential.**

The metal dipped into it's a solution containing metal ions is called electrode half-cell represented symbolically as M^{n+}/M.

Definition

Electrode potential is a potential difference that is set up between a metal and its solution containing metal ions.

Factors affecting the magnitude of the potential difference

1. **Concentration of metal ions already in solution**. Since the ionization equation **(1)** is a reversible reaction, the higher the concentration of metal ions in solution, the further to the left will be the state of equilibrium and hence the smaller the electrode potential.
2. **Temperature.** Increasing temperature increases the ionization of metal atoms and thus increases the electrode potential.

3. **Pressure: applicable to gas systems**, the higher the pressure the higher the electrode potential because increased pressure increases the gas concentration at gas –liquid junction.
4. **Position of metal in electrochemical series.**

   Metals above hydrogen in electrochemical series, have ionization reactions that lie more to the right than left, thus, the metal tends to be negatively charged with respect to their solutions. Thus have negative electrode potentials.

   Metals below hydrogen in electrochemical series, their ionization reaction lie more to the left and their electrode potentials are positive.

Standard electrode potential (SEP)

This is the electrode potential of a metal dipped in a solution containing one mole of metal ions in a dm^3/litre of solution at 298K and 1 atmosphere. It is denoted by E^0.

Factors affecting standard electrode potential

Electrode potential involves formation of hydrated ions. It is a sum of atomization energy (which is endothermic) + ionization energy (which is endothermic) + ionic hydration energy (which is exothermic).

When atomization and/or ionization energy is high, the standard electrode potential becomes more positive.

On the other hand, when the hydration energy is higher than the sum of ionization and atomization energy, standard electrode potential is negative.

Short-hand Notation for an electrode half cells

A metal rod dipped in a solution of metal ions constitutes a half cell. The accepted short form of writing an electrode is to write is to write 'oxidized form/reduced form' of metal. For example, the zinc half-cell is written as Zn^{2+}/Zn and copper electrode as Cu^{2+}/Cu.

Standard Hydrogen electrode (fig. 4.2)

It consists of hydrogen gas at 298K and pressure of 1 atmospheres bubbling over a strip of platinized foil (i.e. platinum coated) in a solution which is 1M with respect to H^+ ions
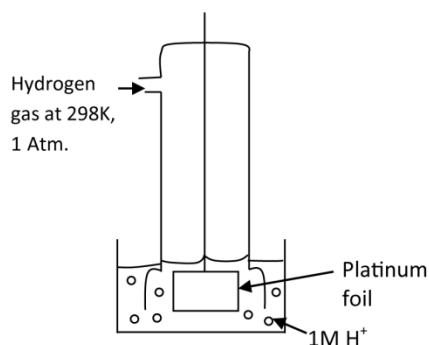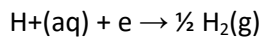

Fig. 4.2

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The short hand notation for a hydrogen electrode is

H^+, M/ ½ H_2, 1 atm. Or H^+/ ½ H_2.

And electrode reaction is

H+(aq) + e → ½ H_2(g)

A potential develops on the surface of the platinum; by convention, it is assigned an arbitrary value of zero volts.

Hydrogen electrode is use as a reference electrode and the electrode potential of all other electrodes are measured relative to this.

Measurement of electrode potential of metal (fig. 3)

A standard metal electrode is combined with a standard hydrogen electrode as shown in Fig.4.3 below
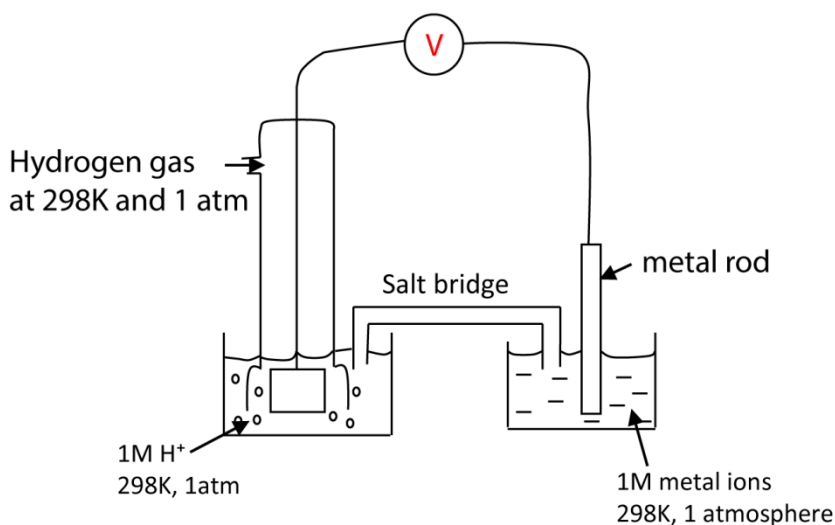

Fig. 4.3

The two compartments in the figure are connected by a **salt bridge**. This contains an electrolyte such as potassium chloride, which conducts electricity but does not allow mixing of two solutions in half cells. The measurement on the high resistance voltmeter is the standard electrode of the metal since that of hydrogen half-cell is zero.

Definition

Standard electrode potential is the electrode potential value of an electrode measure with respect to a standard hydrogen electrode of 0 volts. When an electrode is immersed or dipped into a solution of 1M concentration of its ions at a standard temperature of 298K and pressure of1atmospheres.

Some electrode and their standard electrode potentials are given below:

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Electrode	Electrode reaction	E^0/volts
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$	-0.76
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	+0.34
Fe^{2+}/Fe	$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	-0.44
Ag^{+}/Ag	$Ag^{+}(aq) + e \rightarrow Ag(s)$	+0.80

Galvanic or Voltaic cells or electrochemical cells

This is a type of cell in which a chemical reaction results in production of an electric current.

By combining two suitable electrodes (half cells) a cell of a particular emf may be obtained. One electrode acts as electron supplier and the other as electron acceptor.

The Daniel cell (fig. 4.4)

It consists of the zinc electrode dipped into 1M zinc sulphate solution and copper electrode dipped into 1M copper sulphate solution, the two solution separated by a porous partition. The cell develops an electromotive force (emf) of 1.10V.
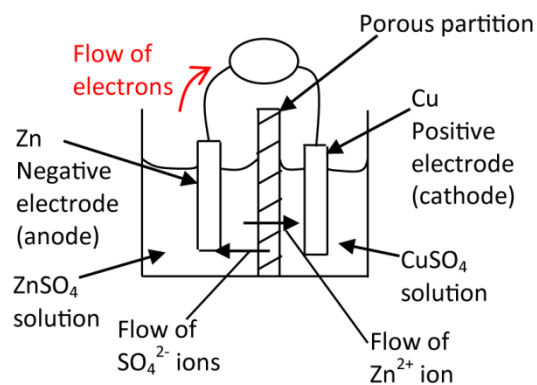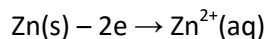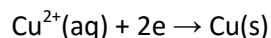

Fig.4.4

Half call reaction

At zinc electrode (anode)

Oxidation occurs and the electrode dissolves.

$Zn(s) – 2e \rightarrow Zn^{2+}(aq)$

At the copper electrode

Reduction occurs (cathode)

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

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Overall equation

$Zn(s) + Cu^{2+} (aq) \rightarrow Zn^{2+} (aq) + Cu(s)$
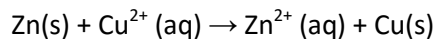
Cell notation

The cell in fig. 4 can be represented as

$Zn(s)/ZnSO_4 (aq)//CuSO_4 (aq)/Cu(s)$

Or simply

$Zn(s)/Zn^{2+} (aq)//Cu^{2+} (aq)/Cu(s)$
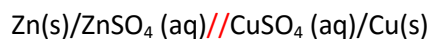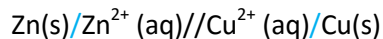
The single vertical line (/) indicates a phase boundary and double vertical lines (//) indicate a porous partition between the solutions.

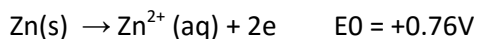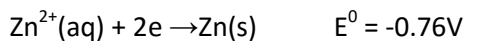**Emf of a cell**
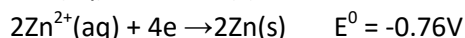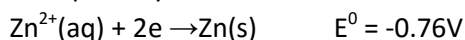
The emf of the above cell is given by

$E = E_{Cu} – E_{zn}$

Rules regarding electrode potentials

1. If the direction of an electrode reaction is reversed, the sign of its electrode potential must also be reversed.
    $Zn^{2+}(aq) + 2e \rightarrow Zn(s)$ $E^0 = -0.76V$
    $Zn(s) \rightarrow Zn^{2+} (aq) + 2e$ $E0 = +0.76V$

2. If an electrode reaction equation is multiplied by a positive factor. The electrode potential must **not** be multiplied by that factor. It remains unchanged.
    $Zn^{2+}(aq) + 2e \rightarrow Zn(s)$ $E^0 = -0.76V$
    $2Zn^{2+}(aq) + 4e \rightarrow 2Zn(s)$ $E^0 = -0.76V$
    Not 1.52V

Generally the emf of a cell is defined as follow

$E^0{}_{cell} = E^0{}_{R.H.E} – E^0{}_{L.H.E}$

NB. For a positive cell emf, R.H.E is for the half cell with most positive electrode potential.

Example 1

Calculate the standard emf of $Zn/Zn^{2+}//Cu^{2+}/Cu$ from the data given below. Write down the half cell reactions and cell reaction.

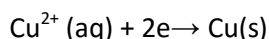Electrode E^0/V

Zn^{2+}/Zn -0.76

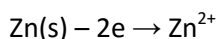Cu^{2+}/Cu +0.34

Answer

E^0_{cell} = $E^0_{R.H.E} - E^0_{L.H.E}$

          =   0.34 –(-0.76)   =   +1.10V

Electrode reactions

At R.H.E (cathode)

Cu^{2+} (aq) + 2e→ Cu(s)

L.H.E (anode)

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

Cell reaction

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
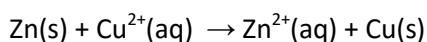
Implication of the emf of a cell

For electrode; since, standard electrode potentials are reduction potentials, a negative value for E^0 implies that the reduction reaction is non spontaneous while a positive value implies that the reduction reaction is spontaneous.

For a cell a negative value of E^0_{Cell} indicates that the cell reaction as written is non spontaneous and instead is spontaneous in the reverse direction.

Therefore, the value of standard electrode potential may be used to predict the direction of spontaneous chemical reaction. Then when writing down or constructing a cell given two electrodes together with their standard electrode potentials, the electrode with the less negative E^0 (if both are negative or electrode with more positive value if both are positive) must be the right hand electrode of the cell and the other the left hand electrode.

Example 2
   (a)   Construct a cell using Li^+/Li and Mg^{2+}/Mg electrodes, given that $E^0_{Li^+/Li}$ = -3.04V and $E^0_{Mg^{2+}/Mg}$ = -2.37V.
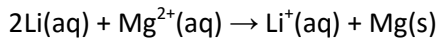   (b)   Calculate the E^0cell.
   (c)   Give the cell reaction

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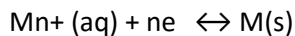 **Or call: 0753 80 2709, 0778 633 682**

Solution

(a) $Li(s)/Li^+//Mg^{2+}(aq)/Mg(s)$

(b) E^0_{cell} = $E^0_{R.H.E} - E^0_{L.H.E}$
     = $-2.37 - (-3.04)$
     = $+0.67V$

(c) Cell reaction

$2Li(aq) + Mg^{2+}(aq) \rightarrow Li^+(aq) + Mg(s)$

Standard electrode potential and standard free energy change

There is a relationship between electrochemistry and thermochemistry. In the electrode reaction

$Mn+ (aq) + ne \leftrightarrow M(s)$

If the standard free energy change, ΔG^0 then the value of the standard electrode potential, E^o, at the same temperature is given by

$\Delta G^0 = -nFE^0$

Where: n is the number of moles electrons transferred in the cell reactions

F is the Faraday constant =96500 C/mole of electrons

E^0 = cell potential in Volts or J/C.

Example 3

Calculate the standard emf and Gibbs free energy of $Zn/Zn^{2+}//Cu^{2+}/Cu$ from the data given below. Write down the half cell reactions and cell reaction.

Electrode E^0/V
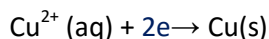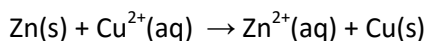
Zn^{2+}/Zn -0.76

Cu^{2+}/Cu +0.34

Answer

E^0_{cell} = $E^0_{R.H.E} - E^0_{L.H.E}$

         = $0.34 - (-0.76)$ = $+1.10V$

Electrode reactions

At R.H.E (cathode)

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

L.H.E (anode)

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

Cell reaction

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

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$\Delta G^0 = -nFE^0$

$= -(2 \text{mols of electrons}) \left(\frac{96,500 C}{\text{moles of electrons}} \right) \left(\frac{1.10 J}{C} \right)$

$= 212,300 J = 212.3 kJ$

Example 4

Calculate the standard emf and Gibbs free energy for the following cell reaction $2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$. Given

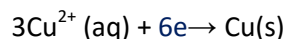| Electrode	E^0/V
Al^{3+}/Al	-1.66
Cu^{2+}/Cu	+0.34

Answer

$E^0_{cell} = E^0_{R.H.E} - E^0_{L.H.E}$

$= 0.34 - (-1.66) = +2V$

Electrode reactions

At R.H.E (cathode)

$3Cu^{2+}(aq) + 6e \rightarrow Cu(s)$

L.H.E (anode)

$2Al(s) - 6e \rightarrow Al^{3+}$

$\Delta G^0 = -nFE^0$

$= -(6 \text{mols of electrons}) \left(\frac{96,500 C}{\text{moles of electrons}} \right) \left(\frac{1.10 J}{C} \right)$

$= -1, 157, 820 J = 1157.82 kJ$

Implication of Gibbs free energy
Spontaneous reaction: ΔG^0 is negative, E^0 is positive
Non-spontaneous reaction: ΔG^0 is positive, E^0 is negative
Equilibrium: ΔG^0 is zero, E^0 is zero

Liquid junction potential
Is a potential difference set up across a phase boundary between two solutions in a cell. It tends to oppose the cell potential i.e. it reduces it and hence the observed cell emf is less than the actual emf of the cell

$E^0 cell = E^0 cell - E^0 j$
Observed   actual   the liquid junction
                                potential

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Causes of liquid junction potential

It is caused by the differential diffusion of charges across the porous partition between the two solutions of the cell. For example, in the Daniel cell, the Zn^{2+} ions diffuse into the $CuSO_4$ solution and Cu^{2+} diffuse into the $ZnSO_4$ solution.
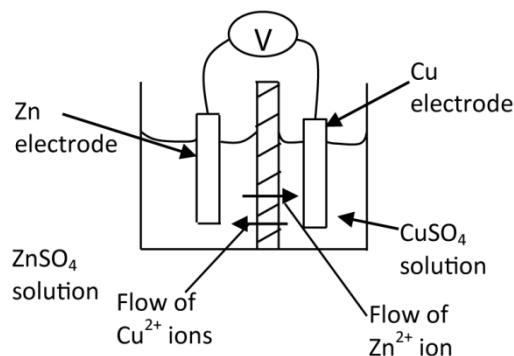
The speed of migration of Zn^{2+} and Cu^{2+} cations across the phase boundary is different due to a number of factors. Some of which are either the ionic size and/or the extent to which they are hydrated. Due to this, a p.d. is set up across the boundary called Liquid Junction Potential.

This liquid junction potential may be eliminated by connecting the solutions in the two half cells by means of a salt bridge which is a glass tube containing a saturated solution of either KCl or NH_4NO_3.

NB. In the cell diagram/notation, the double lines either represent a porous partition or a salt bridge.
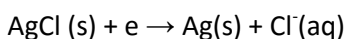
Types of electrodes

1. The metal/metalloid e.g. Zn^{2+}/Zn
2. The gas electrode e.g. Pt, H+/ ½ H_2
3. The metal/insoluble electrode: this type of a metal coated with one of its insoluble salt surrounded by a solution containing the anion of the salt e.g.
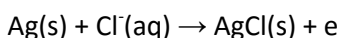   (i) Ag/AgCl(s), Cl⁻
      Possible electrode reactions
      As R.H.E (reduction)
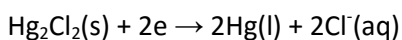 $AgCl (s) + e \rightarrow Ag(s) + Cl^-(aq)$
      As L.H.E (oxidation)
      $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e$
   (ii) Hg/Hg_2Cl_2, KCl(aq) or Hg/Hg_2Cl_2, Cl⁻ This electrode is commonly known as a calomel electrode.
      Possible electrode reactions
      As R.H.E (reduction)
      $Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$
      As L.H.E (oxidation)
      $Hg (s) + 2Cl^- (aq) - 2e \rightarrow Hg_2Cl_2(s)$
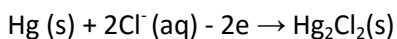
The two electrodes Ag/AgCl(s), Cl⁻ and Hg/Hg$_2$Cl$_2$, KCl(aq) have stable potential and are not easily affected by oxidants or reducing agents, and because of their high stability, they are sometimes used as reference electrodes since hydrogen electrode in practice is easily poisoned
by oxidants and reducing agents.

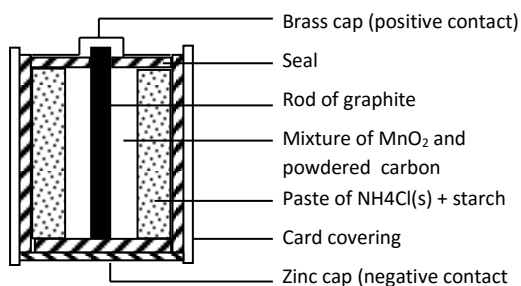4. Oxidation—reducing (redox) electrodes
   This type comprises of a reduced species and oxidized species in the same solution, e.g. Pt/Fe^{3+}, Fe^{2+} or Pt/Cr^{3+},Cr^{2+}.

Differences between electrolytic and e.m.f cells

| Electrolytic cell	E.m.f. cells
Uses single electrolyte	Uses two electrolytes
Changes electrical energy into chemical energy	Changes chemical energy into electrical energy
Cathode is negative electrode	Cathode is positive electrode
Anode is positive electrode	Anode is negative electrode

Dry cells

These were invented to overcome the difficulty of electrolytic solution leaking out of cell such as Daniel cell. In dry cell, the electrolyte is made into a paste. An example is shown below
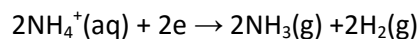

Brass cap (positive contact)
Seal
Rod of graphite
Mixture of MnO$_2$ and powdered carbon
Paste of NH4Cl(s) + starch
Card covering
Zinc cap (negative contact

This type of cell is used in radio, flash light and clocks as it is portable.
The initial electrode processes are
Anode:
Zn(s) → Zn^{2+}(aq) + 2e
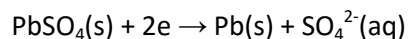Cathode:
2NH$_4^+$(aq) + 2e → 2NH$_3$(g) +2H$_2$(g)
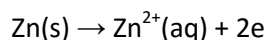
The lead-acid accumulator

The cell stores or accumulates electric charge. It consists of two lead plates dipping into a 30% solution of sulphuric acid. Both plate become covered with insoluble film of lead II sulphate
First the cell must be charged. A direct current is passed through the cell. The processes which take place are:
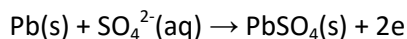Charge
Positive plate
PbSO$_4$(s) + 2e → Pb(s) + SO$_4^{2-}$(aq)
Negative plate

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The plates are now different and therefore have different potentials, so that, when they are connected, an electric current will flow between them. When the cell supplies an electric current, i.e. discharge the process which take place are:

Negative plate
$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e$
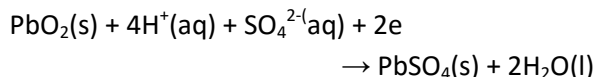
Positive plates
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e$
$$\rightarrow PbSO_4(s) + 2H_2O(l)$$
NB: the plate which is positive during the charge becomes negative during the discharge.

Explain why distilled water is preferred to dilute sulphuric acid when changing an accumulator cell.

During recharging, there can be some production of hydrogen and oxygen caused by splitting of the water part of the acid. This needs to be replaced with distilled water. The sulphuric acid level remains the same, but since water is being lost, the concentration goes up, so adding water restores it to how it was when the battery was new.
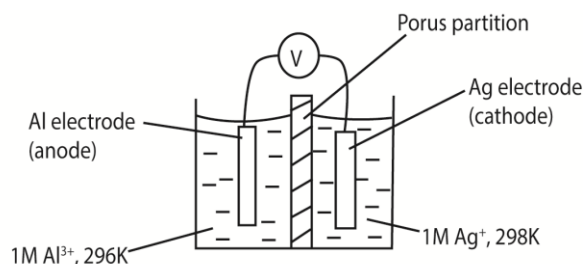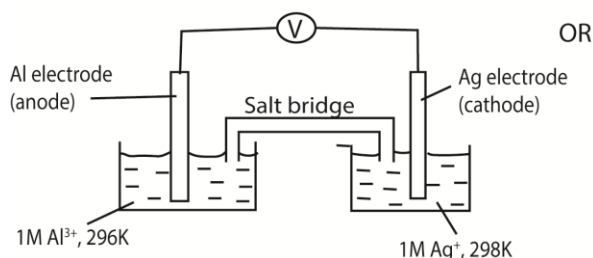
Exercise

1(a.) what is meant by the term voltaic cell?   2 marks

   A voltaic cell is an electrochemical cell that uses a chemical reaction to produce electrical energy.
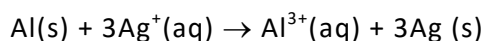
   b.(i) With aid of labeled diagram describe briefly how the standard electrode
        potential of a Voltaic cell made up of silver electrode and aluminium electrode can
        be determined.   8 marks

   (ii) Write the overall equation for the cell reaction.   1 ½ marks

      $Al(s) + 3Ag^+(aq) \rightarrow Al^{3+}(aq) + 3Ag (s)$

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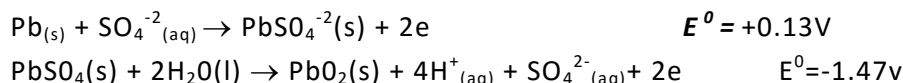**(iii)** If the cell liberated 708.9 kJ of heat, determine the e.m.f of the cell.
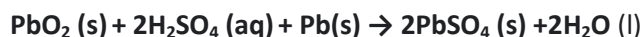
3 ½ marks

$\Delta G = -nFE^0$

$708.9 \times 1000 = 3 \times 96500 \times E^0$

$E^0 = 2.45V$

(c) Some electrode potentials of the electrode reactions of an accumulator cell are shown below;

$Pb_{(s)} + SO_4^{-2}{}_{(aq)} \rightarrow PbSO_4^{-2}(s) + 2e$ **E^0 = +0.13V**

$PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e$ $E^0 = -1.47v$

(i) Write the overall cell reaction and hence determine the e.m.f of the cell. 2 ½ marks

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

(ii) Explain why distilled water is preferred to dilute sulphuric acid when changing an accumulator cell.   2½ marks

During recharging, there can be some production of hydrogen and oxygen caused by splitting of the water part of the acid. This needs to be replaced with distilled water. The sulphuric acid level remains the same, but since water is being lost, the concentration goes up, so adding water restores it to how it was when the battery was new.

Trial 1

The diagram below shows an electrochemical cell
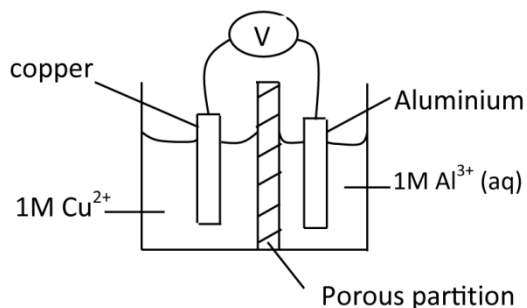
(i) State the purpose of porous partition (1mark)

   (ii) Give the ionic equation for the reaction taking place at each electrode (2marks)

(a) (i) the standard electrode potentials (E^0) at 25^0C are +0.34Volts for copper electrode and -1.66V for aluminium electrode. Calculate the e.m.f of the cell.

(ii) What does the value of the e.m.f calculated in (b)(i) signify?

Trial 2

(a) Explain what is meant by the terms

   (i) Standard electrode potential   (2mks)

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(ii) First ionization energy   (2marks)

(b) The first ionization energies (I.E/kJ) and standard electrode potentials (E^0/V) of group I elements of the Periodic Table are given in the table below

	Li	Na	K	Rb	Cs
1st I.E/ kJmol^{-1}	518.8	497.9	422.6	401.7	380.7
E^0/V		-3.03	-2.71	-2.93	-2.99	-3.02

(i)   Why is the standard electrode potential of lithium is anomalously high? (3mks)

(ii) What would you expect to be the trend in ionic radii of univalent cations formed by group I elements? Explain your answer.   (3mks)

Trail 3

(a) Draw a fully labeled diagram to show the arrangement of apparatus you would use to measure the emf of a cell consisting of copper and silver electrode. Indicate the direction of electron flow   (5mks)

(b) Write

(i)   The notation for the cell you have drawn in (a) and state the convention used   (3mks)

(ii) The equation taking place at each electrode   (2mks)

(iii) The overall cell reaction   (1mk)

(c) If the standard electrode potential for copper ions/copper and silver ions/silver are +0.34V and 0.81V respectively, calculate the e.m.f of the cell consisting of copper and silver electrodes.

(d) Describe briefly how the standard electrode potential of copper can be determined and write the cell notation   (7mks)

Trial 4.4

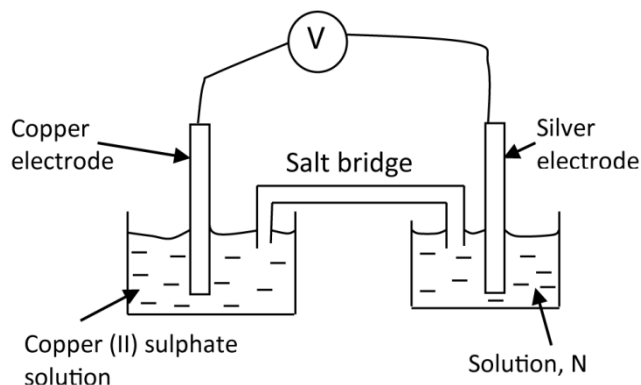The standard electrode potentials E^0 for four half-cell reactions are given below

	E^0/V
$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.52
$SO_4^{2-}(aq) + 2H^+(aq) + 2e \rightarrow SO_3^{2-}(aq) + H_2O(l)$	+ 0.20
$Br_2(aq) + 2e \rightarrow 2Br^-(aq)$	+1.06
$Cl_2(aq) + 2e \rightarrow 2Cl^-(aq)$	+1.36

(a) (i) write an equation between sulphate ions and acidified solution of potassium manganate (VII)

(ii) Calculate the E^0 for the reaction in (I)

(b) Explain why hydrochloric acid is not used to acidify titrants in volumetric analysis involving manganate (VII)

(c) Write the cell convention for the reaction between bromine water and acidified potassium manganate(VII)

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Trial 4.5

A cell consisting of copper and silver electrode is shown in the diagram below

(a) What is solution, N?   (1mark)

(b) Write

   (i) The notation for the cell   (2mks)

   (ii) Overall equation for the cell   (2mks)

(c) (i) Write a substance that can be used in the salt bridge   (1mk)

   (ii) State the purpose of the salt bridge   (1mk)

(d) Calculate the overall electrode potential, E, of the cell   (2mk)

Trial 4.6

A cell was constructed as shown below

$Pt/Cr^{2+}(aq), Cr^{3+}(aq)//MnO_4^-(aq), Mn^{2+}(aq), H^+(aq)/Pt$
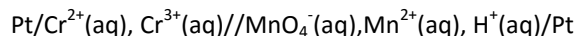
(a) Write equation for the reaction that occur at each electrode   (2½mks)

(b) Write the equation for overall reaction

(c) The electrode potential for system Cr^{3+}/Cr^{2+} and MnO_4^-/Mn^{2+} are -0.402 and +1.52volts respectively.
     Calculate the cell voltage   (1mk)

## Trial 4.7

Equation and electrode potentials for some reaction are given below

$$E^0/V$$

$2H^+(aq) + O_2(g) +2e \rightarrow H_2O_2(aq)$ +0.68

$Ag^+(aq) + e \rightarrow Ag(s)$ +0.80

$H_2O_2(aq) + 2H^+(aq) + 2e \rightarrow 2H_2O(l)$ +1.77
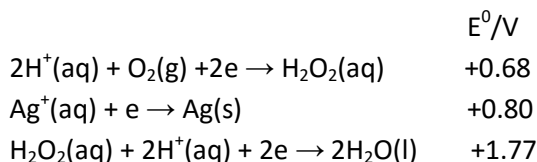
(a) (i) write equation for the reaction between silver nitrate and hydrogen peroxide (2mk)

   (ii) Calculate E^0 cell for the reaction (i)

(b) State the property shown by hydrogen peroxide in the reaction in (a)(i)   (1mk)

Trial 4.8

The equation for some half-cell reaction are given below

$Cd^{2+}(aq) + 2e \rightarrow Cd(s)$ E^0 = -0.440V

$H_2O_2(aq) + 2H^+(aq) +2e \rightarrow 2H_2O(l)$ E^0 = +1.77V
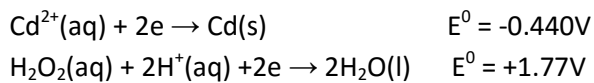
(a) Write

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(i) The cell notation

(ii) The equation for overall cell reaction.

(b) The electrodes were connected externally by a conductor. State the direction of flow of electrons.

Trial 4.9

Some half reactions and their corresponding reduction potentials are given below:

$$E^0/V$$

$MnO_4^-(aq) + 8H^+(aq) + 5e$
$\rightarrow Mn^{2+}(aq) +4H_2O(l)$ +1.52

$MnO_2(s) + 4H^+(aq) + 2e$
$\rightarrow Mn^{2+}(aq) +2H_2O(l)$ +1.23

$Sn^{2+}(aq) + 2e \rightarrow Sn(s)$ -0.136

$Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq)$ +0.15V

(a)   (i) state what would be observed when excess tin powder is added to acidified solution of potassium manganate (VII). Explain your answer

(ii) Write equation for the reaction that takes place.

(b)   Solid manganese (IV) oxide was added to acidified solution of tin (II) ions

(i) State what was observed and explain your answer   (3mks)

(ii) Write equation for the reaction (1½mks)

Trial 4.10

Given the following electrode potentials

$$E^0/V$$

$Na^+(aq) + e \rightarrow Na(s)$ -2.71

$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ +0.337

$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$ -0.763

$Ag^+(aq) + e \rightarrow Ag(s)$ +0.799

(a) Arrange the electrodes in order of reducing power starting with the least reducing (1mk)

(b) (i) Which two electrodes will form a cell of maximum emf?   (½mk)

(ii) Write the cell notation for the cell you gave in (i) above   (1½mks)

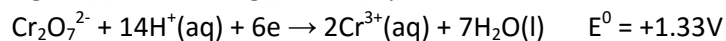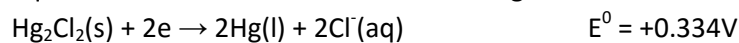(iii) Write the overall cell reaction for the cell in (i).   (1½mks)

Trial 4.11

The diagram below shows emf cell for the reaction between iron (III) chloride and potassium iodide solution
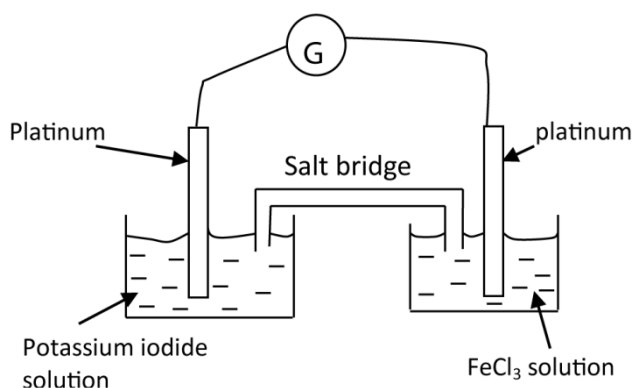
(a) Indicate on the diagram the direction of flow of current   (½mk)

(b) State what is observed at the

     (i)   Anode

     (ii)   cathode

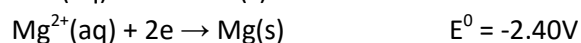(c) Write equation for the cell reaction

Trial 4.12

Equations for some half cell reactions are given below

$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$ $E^0 = +0.334V$

$Cr_2O_7^{2-} + 14H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E^0 = +1.33V$

(a) Write the convention for the cell   (1mk)

(b) Write equation for the overall reaction (1½)

(c) Calculate the cell voltage

Trial 4.13

The electrode potentials, E^0, of lead and magnesium are shown below

$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$ $E^0 = -0.13V$

$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$ $E^0 = -2.40V$

(a) Write the cell convention for the cell that can be formed

(b) Writ the equation for the

     (i)   Reaction taking place at each electrode

     (ii)   Overall reaction

(c) Calculate the emf of the cell

Trial 4.14

The standard electrode potentials for some system are given below:

                 E^0/V

$Mn^{3+}(aq)/Mn^{2+}(aq)$ +1.5

$V^{3+}(aq)/V^{2+}(aq)$ -0.26
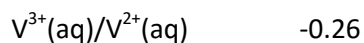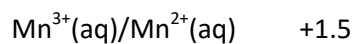
(i) Write the convention for the cell formed by combining two systems   (1mk)
(ii) Write the overall equation for the cell reaction   (1½mk)
(iii) Calculate the emf of the cell. State whether the reaction is feasible or not and give a reason for your answer   (2½mk)

Trial 4.15
(a)(i) Define 'standard electrode potential'
   (ii) Why is it not possible to measure standard electrode potential absolutely?
   (iii) Discus the factors which affect the value of standard electrode potential
(b)   Describe a standard hydrogen half cell
(c)   How would you measure standard electrode potential of a metal in a solution of its ions.
(d)   Given that
       $Ca^{2+}(aq) + 2e \rightarrow Ca(s)$ E0 = -2.87V
       $Mg^{2+}(aq) + 2e \rightarrow Mg(s)$ E0 = -2.37
       A cell was set up as below:
       $Mg(s)/Mg^{2+}(aq)//Ca^{2+}(aq)/Ca(s)$
   (i)   Calculate the emf of the cell
   (ii)   What conclusion can you draw from your emf value in (d)(i) above?

Trial 4.16 (2003/2/2, 2005/1/1)
(c) Explain is meant by the term 'standard electrode potential'   (2mks)
(d) Same half cells and their emf are given below:
   Half cell   emf/volts
   $I_2(aq)/2I^-(aq)$ 0.54
   $Fe^{3+}(aq)/Fe^{2+}(aq)$ 0.76
   (i)   Write the cell convention for the cell made up of the half cells   (01mk)
   (ii) Write equation for the cell reaction
   (iii) Determine emf of the cell
   (iv) Calculate the standard free energy for the reaction and indicate its units
   (v)   State whether the reaction (ii) is possible or not give reason for your answer (2mks)

Trial 4.17 (2004/2/4e)
Equations for some half cell reaction are shown below
$Sn^{4+}(aq) + 2e \leftrightarrow Sn^{2+}(aq)$ $E^0 = 0.15V$
$PbO_2(s) + 4H^+(aq) + 2e \leftrightarrow Pb^{2+}(aq) + 2H_2O(l)$ E0 = +1.46V
(i) Write the overall equation for the spontaneously feasible reaction
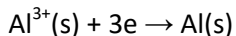(ii) Calculate the emf of the cell in (e)(i)
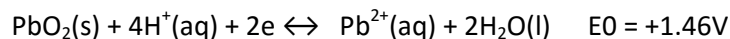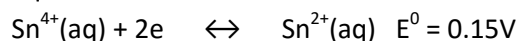
Solutions to the trials

Trial 1

(a)(i) the porous partition prevents mixing of solution while allowing exchange of charges.

(a)(ii) At copper electrode

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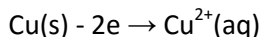
At aluminium electrode

$Al^{3+}(s) + 3e \rightarrow Al(s)$

(b) E^0_{cell} = $E^0_{R.H.E} - E^0_{L.H.E}$

= -1.66-0.34

= -2.00V

(i)   A negative emf indicates that the cell as set up is non spontaneous.

Trial 4.2

(a)(i) Standard electrode potential is a reduction potential between a metal and a solution containing 1mole of metal ions, at 298K and 1 atmosphere.

(a)(ii) First ionization energy is the minimum energy required to remove an electron in its ground state completely from a gaseous atom

(b)(i) The small Li^+ ion has a high charge density leading to high negative hydration energy that offsets its high positive ionization and its high atomization energies. Other elements group have ionization, atomization energies and hydration energies.

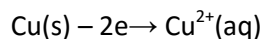(ii) ionic radii increase from Li to Cs because

-   There an additional filled electron shells from one element to another one element to the next.
-   The a reduction in the nuclear charge and an increase in the screening effect down the group
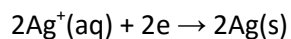
Trial 4.3

(a)

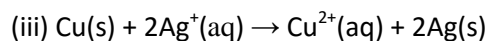(b) (i)$Cu(s)/Cu^{2+}(aq)//Ag^+(aq)/Ag(s)$
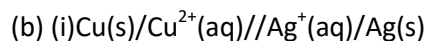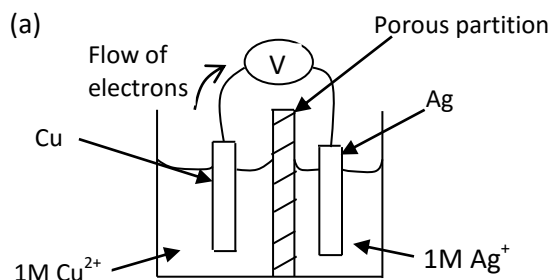
(Convention used?)

(ii) At copper electrode (anode)

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

At silver electrode (cathode)

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$2Ag^+(aq) + 2e \rightarrow 2Ag(s)$

Overall cell reaction

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

(c) 0.47V

(d) Arrange the apparatus as in fig.5 below; since the standard electrode potential of hydrogen gas is zero, the reading on the voltmeter is the standard electrode potential of copper electrode.
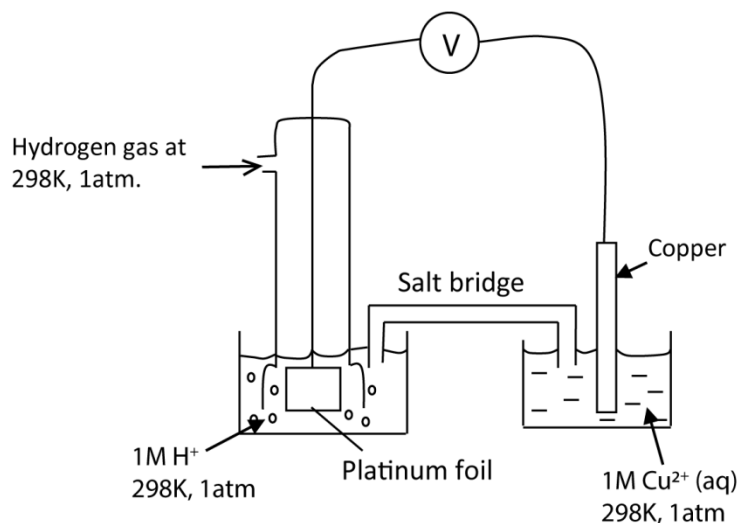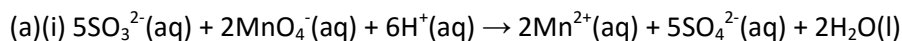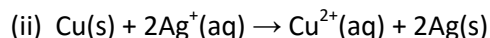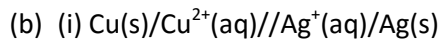

Fig. 5

Cell notation

$1H_2(g)/H^+(aq),Pt//Cu^{2+}(aq)/Cu(s)$

Trial 4.4

(a)(i) $5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 2H_2O(l)$

(a)(ii) E^0_{cell} = $E^0_{Reduction} - E^0_{oxidation}$

= 1.52-0.20

= 1.32V

(b) Because chloride ions are strong oxidizing agents and will be oxidized by manganate (VII) in the reaction.

(c) $Br-(aq)/\frac{1}{2} Br_2(aq)//MnO_4^-, H^+(aq)/Mn^{2+}(aq)$

Trial 4.5

(a) 1M Silver nitrate solution (or any soluble silver salt)

(b) (i) $Cu(s)/Cu^{2+}(aq)//Ag^+(aq)/Ag(s)$

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

(c) (i) KCl or NH_4NO_3

(d)   0.46V

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Trial 4.6

(a) L.H.E

$Cr^{2+}(aq) - e \; Cr^{3+}(aq)$

R.H.E

$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

(b) $5Cr^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Cr^{3+}aq) + 4H_2O(l)$

(c) 1.922V

Trial 4.7

$H_2O_2(aq) + 2Ag^+(aq) \rightarrow 2Ag(s) + 2H^+(aq) + O_2(g)$
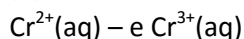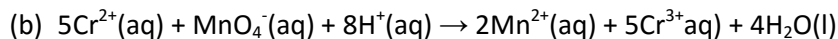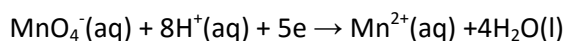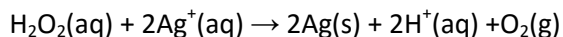
(a)(ii) +0.12V

(b) it is a reducing agent

Trial 4.8

(a)(i) $Cd(s)/Cd^{2+}(aq)//H_2O_2(aq)/H_2O(l), Pt$

(ii) $Cd(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow Cd^{2+}(aq) + H_2O(l)$
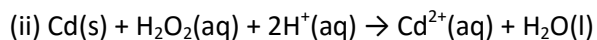
(b) from Cd (anode) to H_2O_2, Pt

Trial 4.9

(a)(i) The purple color of acidified potassium manganate (VII) decolorize; because manganate (VII) is reduced to colorless Mn^{2+} ions

(a)(ii) Note that in excess tin powder, tin is oxidized to tin II rather Tin (IV)
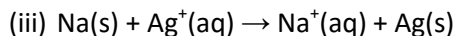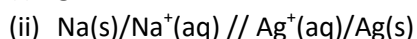
$5Sn(s) + 2MnO_4^-(aq) + 8H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Sn^{2+}aq) + 4H_2O(l)$
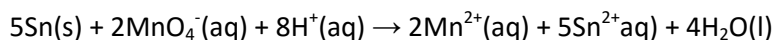
(b) (i) Solid manganese (IV) oxide dissolved forming colorless solution because it is reduced to soluble colorless Mn^{2+} ions.

   (ii) $MnO_2(s) + 4H^+(aq) + Sn^{2+}(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Sn^{4+}(aq)$
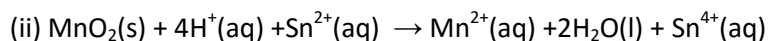
Trial 4.10

(a) Ag, Cu, Zn, Na (i.e. the more negative the E^0, the more reducing or the less oxidizing the electrode is)

(b) (i) Ag and Na

   (ii) $Na(s)/Na^+(aq) // Ag^+(aq)/Ag(s)$

   (iii) $Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$
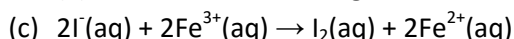
Trial 4.11

   (a) From a platinum electrode dipped into iron (III) chloride to platinum dipped in KI. Note current and electron flow are in opposite direction)
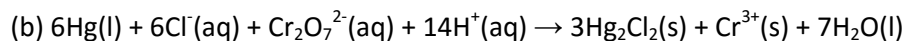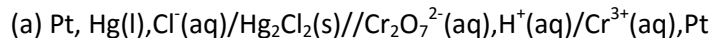
   (b) (i) brown solution
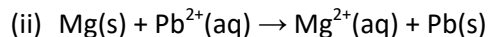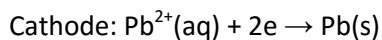
      (ii) Brown solution turns green

   (c) $2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$
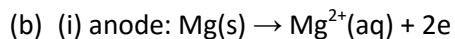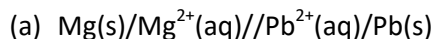
The best secondary school that teaches Sciences is The Science Foundation College,
 Or call: 0753 80 2709, 0778 633 682

Trial 4.12

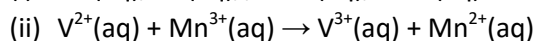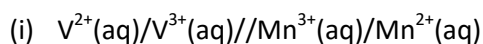(a) Pt, Hg(l),Cl^-(aq)/Hg_2Cl_2(s)//$Cr_2O_7^{2-}$(aq),H^+(aq)/Cr^{3+}(aq),Pt

(b) $6Hg(l) + 6Cl^-(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Hg_2Cl_2(s) + Cr^{3+}(s) + 7H_2O(l)$

(d) +0.996V

Trial 4.13

(a) Mg(s)/Mg^{2+}(aq)//Pb^{2+}(aq)/Pb(s)
(b) (i) anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e$
  Cathode: $Pb^{2+}(aq) + 2e \rightarrow Pb(s)$
  (ii) $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$
(c) -0.13—2.40 = +2.27V

Trial 4.14

(i) V^{2+}(aq)/V^{3+}(aq)//Mn^{3+}(aq)/Mn^{2+}(aq)
(ii) $V^{2+}(aq) + Mn^{3+}(aq) \rightarrow V^{3+}(aq) + Mn^{2+}(aq)$
(iii) 1.5 – (-0.27) = +1.77V

Trial 4.15

(a)(i) is the electrode potential value of an electrode measure with respect to a standard hydrogen electrode of 0 volts. When an electrode is immersed or dipped into a solution of 1M concentration of its ions at a standard temperature of 298K and pressure of 1 atmospheres.

(a)(ii) it requires a second electrode to be introduced since it's a difference in potential

However, the second electrode also produces its own electrode potential making such a difference relative rather than absolute

(a)(iii) Electrode potential = sublimation energy
  + ionization energy
  + Hydration energy

- Sublimation energy: the higher the sublimation energy the more positive the electrode potential. This is because it becomes difficult to convert a solid into gaseous atoms (i.e. sublimation is endothermic)
- Ionization energy: if ionization energy is high; electrode potential becomes more positive because ionization energy is endothermic.
- Hydration energy: a high hydration energy give a more negative electrode potential since hydration is exothermic reaction.

(b) It consists of a molar solution of H+ ions having platinized titanium or platinum coated with finely divided titanium, around which pure hydrogen gas at 1 atmosphere and 298K (25^0) is bubbled.
(c) The metal is placed in one molar solution of its ions and connected to the standard hydrogen electrode by a salt bridge

A voltmeter connected in parallel will show the emf of the cell

The standard electrode potential of the metal is equal to the emf shown by the voltmeter, measured relative to the electrode potential of hydrogen electrode considered to be zero

(d) (i) E^0_{cell} = $E^0_{Reduction} - E^0_{oxidation}$

   =   -2.87-(-2.37)

   =   -0.5V

(ii) The cell as set up is non spontaneous because emf is negative. It is spontaneous in the opposite direction.

Trial 4.16

(d)(i) $2I^-(aq)/I_2(aq)//Fe^{3+}(aq)/Fe^{2+}(aq)$

  (ii) $I^-(aq) + Fe^{3+}(aq) \rightarrow ½ I_2(aq) + Fe^{2+}(aq)$
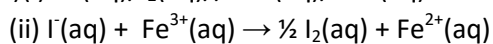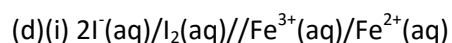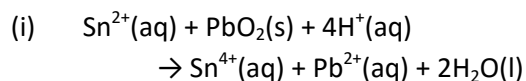
  (iii)   0.22V

  (iv) $\Delta G^0 = -1 \times 96500 \times (-0.22)$

            $= 42.46kJmol^{-1}$

  (v)   The reaction is feasible because emf is positive.

Trial 4.17

(i) $Sn^{2+}(aq) + PbO_2(s) + 4H^+(aq)$

            $\rightarrow Sn^{4+}(aq) + Pb^{2+}(aq) + 2H_2O(l)$

(ii)   1.31V

Thanx