PART SIX
ELECTROCHEMISTRY

Is the study of chemical changes produced by electrical current and the production of electricity by chemical reactions. It is the scientific study of the chemical species and reactions that take place at the interface between an electron conductor and an ion conductor (electrolyte) in which an electron transfer occurs between the electrode and the electrolyte in solution.

Chapter 20
REDOX REACTIONS

INTRODUCTION

Redox reactions occur every day and are vital to some of the basic functions of life. Some examples include photosynthesis, respiration, combustion and rusting. In these redox reactions electrons are transferred between two species. The transfer of electrons leads to a change in oxidation number of the species involved in the redox reactions.

The modern definition of redox reaction is based on this concept of electron transfer or electron flow. In this perspective, redox reactions can simply be defined as *chemical reactions which involve transfer of electrons.*

Oxidation and reduction

We have seen that, in the redox reactions there is a transfer of electrons. The transfer of electrons means that one specie is losing electrons while another specie is gaining electrons simultaneously. The action of losing electrons is known as **oxidation** while that of gaining electrons is known as **reduction**. Actually even the term **redox** itself originated from these two terms, **red**uction and **ox**idation.

In the order of their discovery (according to development of study of chemistry) starting with the oldest one to the latest one, **oxidation** can be defined in the following ways:

Oxidation can be defined as *the loss of electrons(s) by an atom, ion or a molecule* whereas **reduction** *is the gain of electrons by an atom, ion or a molecule.*

When electrons are removed from an atom or ion, the **oxidation state** of the atom or ion **increases.** So oxidation may also be defined as *an increase of oxidation state of an atom, ion or a molecule.*
On another hand when electrons are added to an atom or ion, the **oxidation state** of the atom **decreases.** So reduction may also be defined as *the decrease of oxidation state of an atom, ion or a molecule.*
Therefore, in redox reactions, *oxidation number of a molecule, atom or ion changes by gaining or losing electron(s).*

Oxidising agent and reducing agent

An **oxidising agent (**or **oxidant)** *is the specie which gains electrons from the electron donating specie during redox reaction.*

- Oxidising agents are **reduced** during redox reaction and their **oxidation states decrease** during the reaction.

On another hand, reducing agent (or **reductant**) *is the specie which donates electrons to the electron deficient specie during redox reaction.*

- Reducing agents are **oxidised** during redox reactions and their **oxidation states increase** during the reaction

It should be noted that:

Number of electrons lost by reductant = Number of electrons gained by oxidant

So it can be concluded that **the reaction will be redox if and only if it involves the change in oxidation state of species involved in the reaction. Otherwise the reaction is not redox.**
So the ability to determine oxidation states of species involved in the reaction is very important to determine whether the reaction is redox or not. Rules of determining oxidation states are going to be discussed in the next section.

Oxidation state

Oxidation state (also termed as **oxidation number**) *is the number of electrons gained or lost by an atom in combining with another atom by assumption that the bond formed between the atoms is ionic.*

- Oxidation number (**O.N**) gives the relative electron electronegativity of the two combining atoms; whereby the more electronegative atom has negative oxidation number while the more electropositive (less electronegative) has positive oxidation number.

Rules of assigning oxidation numbers

- The oxidation number of neutral element is zero.
- The total oxidation number of atoms in a neutral compound is zero.
- The oxidation number of an ion (charged atom) is equal to the charge of the ion.
- The total oxidation number of atoms in a charged radical is equal to the amount of the charge of the radical.
- Some atoms of elements have fixed oxidation number in their compounds. For example:
- Atoms of all group I elements have oxidation number $+1$ in their compounds.
- Atoms of all group II elements have oxidation number of +2 in their compounds.
- Fluorine atom has oxidation number of -1 in its compounds.
- Oxidation number oxygen atom is -2 except in:
- Peroxides (e.g. H_2O_2, Na_2O_2) where its oxidation number is -1.
- F_2O where its oxidation number is +2
- Superoxides like KO_2 where is $-1/2$.
- Oxidation number of hydrogen atom is +1 except in ionic hydrides (e.g. NaH) where its oxidation number is -1.

Example 1

In the following reactions determine whether the reaction is redox or not and state the oxidising and reducing agent for redox ones.

(i) $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$
(ii) $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
(iii) $2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$
(iv) $Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

Solution

(i) Assigning oxidation numbers of each atom involved in the reaction.

$$\overset{+2}{Ba}\overset{-1}{Cl_2} + \overset{+1}{Na_2}\overset{+6}{S}\overset{-2}{O_4} \rightarrow \overset{+2}{Ba}\overset{+6}{S}\overset{-2}{O_4} + 2\overset{+1}{Na}\overset{-1}{Cl}$$

Hence the reaction is not redox because oxidation states of all species involved in the reaction have remained the same

(ii) Assigning oxidation numbers of each atom or ion involved in the reaction.

$$\overset{+7}{M}\overset{-2}{nO_4^-} + \overset{+2}{Fe^{2+}} + 8\overset{+1}{H^+} \rightarrow \overset{+2}{Mn^{2+}} + 5\overset{+3}{Fe^{3+}} + 4\overset{+1}{H_2}\overset{-2}{O}$$

The reaction is redox because:

- The oxidation number of manganese decreased from +7 to +2
- The oxidation number of iron increased from +2 to +3

Hence:

- The oxidising agent is MnO_4^-
- The reducing agent is Fe^{2+}

(On your own follow the same procedures to attempt solving (iii) and (iv))

Disproportionation reactions

Disproportionation reaction *is the redox reaction whereby both reduction and oxidation occurs in the* ***same element*** *contained in a particular molecule or compound.* It is also known as **dismutation reaction.**

- Examples of disproportionation reaction are:

1) Chlorine gas disproportionate in cold and dilute sodium hydroxide (NaOH) yielding hypochlorite and chloride and its **yellowish colouration disappears.**

$$\mathrm{Cl_2} \quad + \quad \mathrm{2NaOH(diluted)} \quad \underset{\mathrm{Cold}}{\longrightarrow} \quad \underset{\textbf{Sodium hypochlorite}}{\mathrm{NaOCl}} \quad + \quad \underset{\textbf{Sodium chloride}}{\mathrm{NaCl}} \quad + \quad \mathrm{H_2O}$$

Where: Oxidation number of Cl atom in $\mathrm{Cl_2}$ is 0

Oxidation number of Cl atom in NaOCl is +1

Oxidation number of Cl atom in NaCl is -1

From above example, it is clearly understood that chlorine atom has been oxidised to hypochlorite in which its oxidation number increases from 0 to +1 while another chlorine atom from the same chlorine element has been reduced to chloride in which its oxidation number has been decreased from 0 to -1.

2) Chlorine gas disproportionate in hot concentrated NaOH yielding chlorate and chloride and its yellowish colouration disappear.

$$\mathrm{3Cl_2 + 6NaOH\ (concentrated)} \quad \underset{\mathrm{Hot}}{\longrightarrow} \underset{\textbf{Sodium chlorate}}{\mathrm{NaClO_3}} + \underset{\textbf{Sodium chloride}}{\mathrm{5NaCl}} + \mathrm{3H_2O}$$

Where: Oxidation number of Cl atom in $\mathrm{Cl_2}$ is 0

Oxidation number of Cl atom in $\mathrm{NaClO_3}$ is +5

Oxidation number of Cl atom in NaCl is -1

Again, it is clearly understood that chlorine atom has been oxidised to chlorate in which its oxidation number increases from 0 to +5 while another chlorine atom from the same chlorine element has been reduced to chloride in which its oxidation number has been decreased from 0 to -1.

3) Decomposition of hydrogen peroxide, disproportionates the peroxide into water and oxygen gas which is observed as effervescence of colourless gas which relight glowing splint.

$$\mathrm{H_2O_2} \rightarrow \mathrm{H_2O} \quad + \mathrm{O_2}$$

Where:
Oxidation number of oxygen in $\mathrm{O_2}$ is 0
Oxidation number of oxygen in $\mathrm{H_2O_2}$ is -1 (Decreases from 0 hence reduction)
Oxidation number of oxygen in $\mathrm{H_2O}$ is $+1$ (Increases from 0 hence oxidation)

4) Heating of NaOCl, disproportionates the hypochlorite into chlorate and chloride.

$$\mathrm{3NaOCl} \underset{\Delta}{\rightarrow} \mathrm{NaClO_3 + 2NaCl}$$

The reader should understand that:
In some cases, the opposite of disproportionation may happen whereby two reactants containing the same element in different oxidation states react to give a product in which the element's oxidation state is different to either of the original oxidation state. Reactions of this kind are known as **comproportionation** or **synproportionation reactions**.
A good example of this is the reaction between hydrogen sulphide and sulphur dioxide whereby the two compounds comproportionate to elemental sulphur.

$$\mathrm{2H_2S + SO_2 \longrightarrow 3S + 2H_2O}$$

Where:
Oxidation number of sulphur in $\mathrm{H_2S}$ increases from -2 to 0 in S (oxidation).
Oxidation number of sulphur in $\mathrm{SO_2}$ decreases from $+4$ to 0 in S (reduction).

By definition, **comproportionation reaction** *is the redox reaction in which two reactants containing the same element in different oxidation states react to give a product containing the element in an intermediate oxidation state.*

BALANCING REDOX REACTIONS IN ACIDIC AND BASIC MEDIUM

Like **acid – base reactions**, redox reactions are matched set, that is, there cannot be an oxidation reaction without a reduction reaction happening simultaneously. The oxidation alone and the reduction alone are each called a **half – reaction**, because two half – reactions always occur together to form a whole reaction. When writing half – reaction the gained or lost electrons are typically included explicitly in order that the half – reaction be balanced with respect to electric charge.

Balancing in acidic medium

Redox reactions are balanced by using the following procedures:

1. Balancing material

This involves balancing all other atoms present leaving oxygen and hydrogen atoms. This is done by trial and error method.

2. Balancing oxygen atoms

This is done by adding suitable number of water molecules to the side of fewer oxygen atoms

3. Balancing hydrogen atoms

This is done by adding suitable number of hydrogen protons (H^+) to the side of fewer hydrogen atoms.

4. Balancing charges

This is done by adding suitable number of electrons to the side of higher charge.

It should be noted that:

The above four procedures are done after splitting the overall reaction equation into **two half reactions** (hence the name '**half reaction method'** of balancing redox reactions). The two half reactions are **oxidation half reaction** and **reduction half reaction**

5. Conservation of electrons (Balancing of electrons)

This is done in writing overall reaction equation by making sure that number of electrons lost in oxidation half reaction is equal to the number of electrons gained in reduction half reaction. This may require multiplication of number(s) to all terms of half reaction(s)

Example 2

By using half reaction method, balance the following redox reaction:

$$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$$

Solution

Oxidation half reaction: $Fe^{2+} \rightarrow Fe^{3+}$ (Not balanced)

Balancing charges: $Fe^{2+} \rightarrow Fe^{3+} + e$ ……………………………………………(i)
(The equation (i) above is the balanced oxidation half reaction equation)

Reduction half reaction: $MnO_4^- \rightarrow Mn^{2+}$

Balancing oxygen atoms: $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
Balancing hydrogen atoms: $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4\,H_2O$
Balancing charges: $MnO_4^- + 8\,H^+ + 5e \rightarrow Mn^{2+} + 4\,H_2O$……..(ii)
(The equation (ii) above is the balanced reduction half reaction equation)
Overall reaction equation: Taking (i) × 5 + (ii) gives;
$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ + \cancel{5e} \rightarrow 5Fe^{3+} + Mn^{2+} + 4\,H_2O + \cancel{5e}$

Hence the overall balanced reaction equation is:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

It should be noted that:

Presence of H^+ at the left hand side confirms that the reaction took place under acidic medium **(The medium should be present at the start of the chemical reaction i.e. it must appear at left hand side of the reaction equation).**

Example 3

By using half reaction method, balance the following redox reaction under acidic medium.

$$Cr_2O_7^{2-} + C_2O_4^{2-} \rightarrow Cr^{3+} + CO_2 + H_2O$$

Solution

Oxidation half reaction

Balancing material: $C_2O_4^{2-} \rightarrow 2CO_2$
Balancing charge: $C_2O_4^{2-} \rightarrow 2CO_2 + 2e$
Reduction half reaction

Balancing material: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
Balancing oxygen atoms: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
Balancing hydrogen atoms: $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
Balancing charges: $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$
Overall reaction equation
Taking (i) ×3 + (ii) gives;

$$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ + \cancel{6e} \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O + \cancel{6e}$$

Hence the overall reaction equation is:

$$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$$

Example 4

By using half reaction method, balance the following redox reactions:

$Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + SO_2 + H_2O$
$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$
Solution

Oxidation half reaction: $Al + H_2SO_4 \rightarrow Al_2(SO_4)_3$

Balancing material: $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3$
Balancing hydrogen atoms: $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H^+$
Balancing charges: $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H^+ + 6e$---------(i)
Reduction half reaction: $H_2SO_4 \rightarrow SO_2$

Balancing oxygen atoms: $H_2SO_4 \rightarrow SO_2 + 2H_2O$
Balancing hydrogen atoms: $H_2SO_4 + 2H^+ \rightarrow SO_2 + 2H_2O$
Balancing charges: $H_2SO_4 + 2H^+ + 2e \rightarrow SO_2 + 2H_2O$---------------(ii)
Writing overall reaction equation by taking (i) + 3× (ii):

$2Al + 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$-----------------(ii)

Oxidation half reaction

Following the same procedures as in (i), it gives the following oxidation half reaction equation:

$Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2H^+ + 2e$---(i)

Reduction half reaction

In this case the equation is: $HNO_3 + 3H^+ + 3e \rightarrow NO + 2H_2O$------------------------(ii)

Writing overall reaction equation by taking (i) × 3 + (ii) × 2

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Balancing in basic medium

Balancing the redox reaction equation under basic medium is simply done by eliminating H^+ from the overall balanced equation by adding suitable number of OH^- to obtain OH^- on one side and H_2O on the other side.

However **it should be noted that**, H_2O and OH^- may be on one side if:

- The reaction is between amphoteric metal with NaOH(aq) or
- The reaction is a disproportionation one.

Example 5

Balance the following redox reactions in basic medium

(i) $MnO_4^- + C_2O_4^{2-} \rightarrow MnO_2 + CO_3^{2-} + H_2O$
(ii) $Al + H_2O \rightarrow Al(OH)_4^- + H_2$

Solution

Reduction half reaction: $MnO_4^- \rightarrow MnO_2$
Balancing oxygen atoms: $MnO_4^- \rightarrow MnO_2 + 2H_2O$
Balancing hydrogen atoms: $MnO_4^- + 4H^+ \rightarrow MnO_2 + 2H_2O$
Balancing charges: $MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O$………...(i)
Oxidation half reaction: $C_2O_4^{2-} \rightarrow CO_3^{2-}$

Balancing material: $C_2O_4^{2-} \rightarrow 2CO_3^{2-}$
Balancing oxygen atoms: $C_2O_4^{2-} + 2H_2O \rightarrow 2CO_3^{2-}$
Balancing hydrogen atoms: $C_2O_4^{2-} + 2H_2O \rightarrow 2CO_3^{2-} + 4H^+$
Balancing charges: $C_2O_4^{2-} + 2H_2O \rightarrow 2CO_3^{2-} + 4H^+ + 2e$…………(ii)
Taking (i) × 2 + (ii) × 3 gives

$2MnO_4^- + 3C_2O_4^{2-} + 2H_2O \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+$ **(Appearing of H^+ at right hand side of the equation suggests that the reaction takes place under basic medium)**

Adding $4OH^-$ both sides gives

$2MnO_4^- + 3C_2O_4^{2-} + 2H_2O + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+ + 4OH^-$

Or $2MnO_4^- + 3C_2O_4^{2-} + 2H_2O + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H_2O$

Hence the balanced overall reaction equation is:

$2MnO_4^- + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + 2H_2O$

Oxidation half reaction
$Al \rightarrow Al(OH)_4^-$
Balancing oxygen atoms: $Al + 4H_2O \rightarrow Al(OH)_4^-$
Balancing hydrogen atoms: $Al + 4H_2O \rightarrow Al(OH)_4^- + 4H^+$
Balancing charges: $Al + 4H_2O \rightarrow Al(OH)_4^- + 4H^+ + 3e$……………(i)
Reduction half reaction: $H_2O \rightarrow H_2$

Balancing oxygen atoms: $H_2O \rightarrow H_2 + H_2O$
Balancing hydrogen atoms: $H_2O + 2H^+ \rightarrow H_2 + H_2O$
Balancing charges: $2H^+ + 2e \rightarrow H_2$…………………………………….(ii)
Taking (i) × 2 + (ii) × 3 gives:

$2Al + 8H_2O + 6H^+ \rightarrow 2Al(OH)_4^- + 3H_2 + 8H^+$

Or $2Al + 8H_2O \rightarrow 2Al(OH)_4^- + 3H_2 + 2H^+$

Adding $2OH^-$ both sides gives overall reaction equation as follows:

$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2$$

ACTION OF HYDROGEN PEROXIDE

In redox reactions, hydrogen peroxide can undergo oxidation, reduction or disproportionation depending on reacting conditions.

Oxidation: It can be oxidised to oxygen gas thus acting as reducing agent. This happen when the peroxide reacts with strong oxidising agent.

e.g. $2Fe^{3+} + H_2O_2 + 2OH^- \rightarrow 2Fe^{2+} + O_2 + 2H_2O$

Reduction: It can be reduced to water thus acting as oxidising agent. This happen when the peroxide reacts with strong reducing agent. e.g. $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$

Disproportionation: It can disproportionate to water and hydrogen gas. This occurs in its decomposition according to the following equation:

Oxidation

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Reduction

Note: *The volume in cm³ of oxygen gas produced when 1cm³ of H_2O_2 (hydrogen peroxide) is decomposed at given conditions of temperature and pressure (normally at s.t.p) is known as* **volume strength** or **volume rating.** It answers the question: ***the volume of oxygen gas produced (on decomposition of the peroxide) is how many times the volume of hydrogen peroxide?***

COMMON REDUCTION AND OXIDATION HALF REACTIONS

To make the work of dealing with problems which involve knowledge of redox reactions easier, a student should be able to memorise the following common reduction and oxidation half reactions.

Common reduction half reactions (oxidising agents are on left hand side)

(i) $\underset{\text{Purple}}{MnO_4^-} + 8H^+ + 5e \rightarrow \underset{\text{Colourless}}{Mn^{2+}} + 4H_2O$

(ii) $\underset{\text{Orange}}{Cr_2O_7^{2-}} + 14H^+ + 6e \rightarrow \underset{\text{Green}}{2Cr^{3+}} + 7H_2O$

(iii) $2IO_3^- + 12H^+ + 10e \rightarrow \underset{\text{Dark brown}}{I_2} + 6H_2O$

(iv) $2Cu^{2+} + 2I^- + 2e \rightarrow Cu_2I_2$

(v) $H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$

(vi) $\underset{\text{Dark brown}}{I_2} + 2e \rightarrow \underset{\text{Colourless}}{2I^-}$

(vii) $\underset{\text{Reddish brown (rusty)}}{Fe^{3+}} + e \rightarrow \underset{\text{Green}}{Fe^{2+}}$

The reader should not confuse the formation of colourless solution in (i) above after reduction of MnO_4^- to Mn^{2+} and the pink colouration which is obtained at the end point of redox titration which employ $KMnO_4$ as an oxidising agent. The pink colouration is explained by presence of excess (very small unreacted amount) $KMnO_4$ just after the equivalence point.

Common oxidation half reaction (reducing agents are on left hand side)

(i) $Fe^{2+} \rightarrow Fe^{3+} + e$
(ii) $\underset{\text{Yellow}}{S^{2-}} \rightarrow S + 2e$

(iii) $2I^- \rightarrow I_2 + 2e$
(iv) $H_2O_2 \rightarrow O_2 + 2H^+ + 2e$
(v) $C_2O_4^{2-} \rightarrow 2CO_2 + 2e$
(vi) $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$

Example 6

With help of balance chemical equation state what will you observe when solution of Iron (II) sulphate is added into a beaker containing acidified solution of $K_2Cr_2O_7$.

Solution

A colour mixture of reddish brown and green colouration is observed

i.e. $\underset{\text{Orange}}{Cr_2O_7^{2-}} + \underset{\text{Green}}{6Fe^{2+}} + 14H^+ \rightarrow \underset{\text{Green}}{2Cr^{3+}} + \underset{\text{Reddish brown}}{6Fe^{3+}} + 7H_2O$

Example 7

What happen when hydrogen sulphide is added into a beaker containing acidified solution of potassium permanganate?

Solution

$KMnO_4$ is reduced to Mn^{2+} while H_2S is oxidised to sulphur which is recognised by its yellow colouration precipitate. i.e. $2MnO_4^- + 5S^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O$

Example 8

Explain what happens when a solution of sodium thiosulphate is added into a beaker containing iodine solution.

Solution

Sodium thiosulphate being a reducing agent, reduces I_2 which is an oxidising agent to I^- and itself become oxidised to $S_4O_6^{2-}$ and dark brown colouration of I_2 disappears.

i.e. $I_2 + 2S_2O_3^{2-} \rightarrow SO_4O_6^{2-} + 2I^-$

ACTION OF $KMnO_4$ IN DIFFERENT MEDIUM

Most of common redox reactions take place under acidic medium. In most cases, basic medium lowers actions (power) of oxidising agent while acidic medium increases the power of oxidising agents to oxidize reducing agents. Some oxidising agents like **$K_2Cr_2O_7$ and KIO_3 needs acidic medium to show their oxidising power, they cannot show oxidation characters in basic or neutral medium.** However $KMnO_4$ being strongest oxidising agent can show oxidising properties in all three conditions (acidic, basic and neutral medium).

Under strongly alkaline medium, $KMnO_4$ has the following reduction half reaction:

$$\underset{\text{Permanganate ion}}{MnO_4^-} + e \rightarrow \underset{\text{Manganate ion (green in colour)}}{MnO_4^{2-}}$$

Whereby permanganate gains 1 electron only and its O.N decreases by 1 from +7 (in MnO_4^-) to +6 (in MnO_4^{2-}). Apart from the medium being strong alkali like KOH, the reaction is more predominant when the permanganate is in excess.

Under neutral medium, $KMnO_4$ has the following reduction half reaction

$$MnO_4^- + 2H_2O + 3e \rightarrow \underset{\text{Manganese(IV) oxide (black or brown precipitate)}}{MnO_2} + 4OH^-$$

Whereby the permanganate gains 3 electrons and its oxidation number decreases by 3 from +7 to +4 (in MnO_2) and hence it is stronger oxidising agent under neutral medium than in alkaline (basic) medium. However, the reaction can also occur in basic medium if the base is not very strong.

Under acidic medium, $KMnO_4$ has the following reduction half reaction:

$$MnO_4^- + 8H^+ + 5e \rightarrow \underset{\text{Manganous ion (colourless)}}{Mn^{2+}} + 4H_2O$$

Whereby the permanganate gains 5 electrons and its oxidation number decreases by 5 from +7 to +2 and hence of the three media, the permanganate is strongest oxidising agent in acidic medium.

ACTION OF POTASSIUM DICHROMATE (VI)

Potassium dichromate (VI), $K_2Cr_2O_7$ is very strong reducing agent. However, it is not strong oxidising agent as potassium permanganate, $KMnO_4$.

- It acts as an oxidising agent in acidic medium only.
- The neutral aqueous solution of dichromate ($K_2Cr_2O_7$) is equilibrium mixture which contains equal amount of dichromate and chromate(K_2CrO_4) as result of hydrolysis of dichromate according to the following equation:

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \text{ ----------(i)}$$

- Whereby chromate is weak oxidising agent and hence the oxidising strength of dichromate is decreased in the neutral solution. ***What is the effect of adding acid like dilute H_2SO_4 to the above equilibrium?***
- Addition of acidic solution like sulphuric acid which ionises completely to give H^+ thus increasing concentration of H^+ to above equilibrium, shifts position of equilibrium to the left hand side by forming more dichromate which is strong oxidising agent. Hence the dichromate is stronger oxidising agent in acidic solution. We have seen the effect of acidic medium. Then ***what is the effect of adding strong alkaline solution like NaOH (aq) to the above equilibrium?***
- Addition of basic solution like sodium hydroxide which ionises completely to give OH^-, eliminate H^+ from the above equilibrium thus decreasing its concentration, ***how?*** This is because the hydroxyl ions (OH^-) combine with hydrogen proton (H^+) to form water (H_2O). This shifts the position of equilibrium to the right hand side by forming more chromate which is weak oxidising agent according to the following equation of the reaction which is irreversible:

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \rightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O\text{-----------(ii)}$$

(The equation is simply derived from the above equilibrium by adding $2OH^-$ to both sides of the equation (i) above).

Hence dichromate is very weak oxidising agent under basic medium.

It should be noted that: $KMnO_4$ Being stronger oxidising agent than $K_2Cr_2O_7$ and KIO_3, has the following disadvantage: It cannot be used in redox titration which involve Cl^- because the permanganate is capable of oxidising Cl^- to Cl_2 unlike other oxidising agents which are not strong oxidising agents enough to oxidize the chloride ions.

Example 9

Complete and balance the following redox reactions:

(i) $IO_3^- + I^- \rightarrow$
(ii) $MnO_4^- + H_2O_2 \rightarrow$

Solution

(i) $IO_3^- + I^- \rightarrow$ No reaction

Under neutral medium (no medium is shown in the reaction equation), IO_3^- is incapable of showing oxidising character; it need acidic medium to exhibit oxidising characters.

(ii) $3H_2O_2 + 2MnO_4^- \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

Under neutral medium; MnO_4^- is reduced to MnO_2.

Thus **reduction half reaction** can be written as follows: $MnO_4^- \rightarrow MnO_2$;

Balancing oxygen atoms: $MnO_4^- \rightarrow MnO_2 + 2H_2O$;

Balancing hydrogen atoms: $MnO_4^- + 4H^+ \rightarrow MnO_2 + 2H_2O$;

Balancing charges: $MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O$;

Adding $4OH^-$ both sides: $MnO_4^- + 4H^+ + 3e + 4OH^- \rightarrow MnO_2 + 2H_2O + 4OH^-$;

Simplifying the equation: $MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4OH^-$;

Thus: the balanced reduction half reaction: $MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4OH^-$-----(i)

The balanced oxidation half reaction equation: $H_2O_2 \rightarrow 2H^+ + O_2 + 2e$ ------------------(ii)

Taking (i)×2+(ii) × 3 : $2MnO_4^- + 4H_2O + 3H_2O_2 \rightarrow 2MnO_2 + 8OH^- + 6H^+ + 3O_2$;

Simplifying the equation gives: $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 2OH^- + 3O_2 + 2H_2O$

Example 10

Dark brown colouration is observed when dilute hydrochloric acid is added to a beaker containing solution mixture of potassium iodate and potassium iodide. Explain.

Solution

Hydrochloric acid acts as an acidic medium to allow redox reaction between $KIO_3$and KI so as to liberate iodine which appears in dark brown colouration

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Example 11

Explain why acidified $KMnO_4$ cannot be used in redox titration of the permanganate against iron (II) chloride.

Solution

$KMnO_4$ being very strong oxidising agent, oxidizes both Fe^{2+} and Cl^- (from $FeCl_2$) to Fe^{3+} and Cl_2 respectively thus interfering measurement of correct volume of $KMnO_4$ solution which is exactly used to oxidize Fe^{2+} and Fe^{3+}.

i.e. $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

And $2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

Example 12

Hydrochloric acid can be used as an acidic medium in redox titration of potassium dichromate (VI) against potassium iodide while the same acid cannot be applied as an acidic medium in redox titration of potassium manganate (VII) against potassium iodide. Explain

Solution

$K_2Cr_2O_7$ being weaker oxidising agent (than $KMnO_4$) is unable to oxidize Cl^- (from HCl) to Cl_2 while $KMnO_4$being stronger oxidising agent, oxidizes Cl^- (From HCl (aq)) to Cl_2 thus interfering measurement of correct volume of $KMnO_4$ which is exactly used to oxidize Cl^- to Cl_2.

i.e. $Cr_2O_7^{2-} + Cl^- + H^+ \rightarrow$ No reaction

While $2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

To close the discussion about oxidising characters of oxidising agents in different media……….!

- Concentrated sulphuric acid has oxidising properties, so it should not be used as an acidic medium for redox titration in its concentrated form.
- Sulphuric acid is always used as an acidic medium in its diluted form.
- The oxidising character of nitric acid (HNO_3) also explains why the acid should not be used as an acidic medium for redox titration in its either dilute or concentrated form.

Example 13

Concentrated sulphuric acid should not be used in redox titration of potassium permanganate against $FeSO_4$. Explain

Solution

Concentrated H_2SO_4 is good oxidising agent so it tends to oxidize Fe^{2+} (from $FeSO_4$) to Fe^{3+} as $KMnO_4$ does thus interfering measurement of correct volume of $KMnO_4$ which is exactly used to oxidize Fe^{2+} to Fe^{3+}.

EQUIVALENT WEIGHT AND NORMALITY IN REDOX REACTION

Equivalent weight

Generally; **Equivalent weight** can be defined as *the mass of a compound required to give (or react with) one mole (Avogadro's number) of fundamental entity in a reaction we might consider.*

In redox reaction, the fundamental entity is **electron.**

Thus, **for an oxidising agent:** equivalent weight *is the mass of the oxidising agent required to gain one mole of electrons from reducing agent in the redox reaction.*

$$\text{Equivalent weight} = \frac{\text{Molar mass of the oxidising agent}}{\text{Number of moles eletrons gained gained by one mole of the oxidising agent}}$$

But **Number of mole of electrons gained by one of the compound = Number of electrons gained by one molecule of the compound**

So, $\text{Equivalent weight} = \frac{\text{Molar mass of the oxidising agent}}{\text{Number of electrons gained by one molecule of the oxidising agent}}$

And **for a reducing agent:** equivalent weight *is the mass of the reducing agent required to donate one mole of electrons to oxidising agent during redox reaction.*

$$\text{Equivalent weight} = \frac{\text{Molar mass of the reducing agent}}{\text{Number of moles eletrons gained gained by one mole of the oxidising agent}}$$

Or $\text{Equivalent weight} = \frac{\text{Molar mass of the reducing agent}}{\text{Number of electrons gained by one molecule of the reducing agent}}$

Whence the two results for reducing and oxidising agent may be combined to get the following result:

For redox reaction:

$$\textbf{Equivalent weight} = \frac{\textbf{Molar mass}}{\textbf{Number of electrons transferred by one molecule of the reactant}}$$

Examples:

1) Acidified $KMnO_4$ has the following reduction half reaction:

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

Whereby one molecule of the permanganate gains five electrons (or five moles of the permanganate gains five moles of electrons) and hence:

$$\text{Equivalent weight of } KMnO_4 \text{ in acidic medium} = \frac{\text{Molar mass of } KMnO_4}{5}$$

2) Sodium thiosulphate ($Na_2S_2O_3$) has the following oxidation half reaction:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e \quad \text{Or} \quad S_2O_3^{2-} \rightarrow \tfrac{1}{2}S_4O_6^{2-} + e$$

(Dividing by two throughout the first equation so as to get **one molecule** of the reactant)

Whereby one molecule of the thiosulphate donates one electron and hence:

$$\text{Equivalent weight of } Na_2S_2O_3 = \frac{\text{Molar mass of } Na_2S_2O_3}{1}$$

Normality

Generally; **Normality** *is the number of equivalents of solute dissolved in one litre of the solution*

Thus: $\text{Normality} = \frac{\text{number of euivalents of solute}}{\text{volume of solution in litres (or dm}^3)}$

Its unit is N

But number of equivalents of solute = $\frac{\text{mass of solute}}{\text{Equivalent weight of solute}}$

Then: $\text{Normality} = \frac{\text{mass of solute}}{\text{volume of solution in dm}^3 \times \text{equivalent weight of solute}}$

But $\frac{\text{mass of solute}}{\text{volume of solution in dm}^3} = \text{mass concentration of solute in g/dm}^3$

Thus: $\text{Normality} = \frac{\text{mass concentration in g/dm}^3}{\text{equivalent weight of solute}}$

For redox reactions:

$\text{Equivalent weight} = \frac{\text{molar mass}}{\text{number of electrons transferred by one molecule of the reactant}}$

Then from $\text{Normality} = \frac{\text{mass concentration in g/dm}^3}{\text{equivalent weight of solute}}$;

It becomes; Normality =

$$\frac{\text{mass concentration in g/dm}^3 \times \text{number of electrons transfered by one molecule of the reactant}}{\text{Molar mass of solute}}$$

But $\frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute}} = \text{Molarity}$

Hence **for redox reactions:**

Normality

= Molarity × Number of electrons transferred by one molecule of oxidising or reducing agent

The term **'A normal solution'** is used to express the solution of 1N

Note: Normality of oxidising and reducing agent are connected by the following equation:

$$\mathbf{N_oV_o = N_rV_r}$$

Where $\mathbf{N_o}$ and $\mathbf{N_r}$ is the normality of oxidising and reducing agent respectively

$\mathbf{V_o}$ and $\mathbf{V_r}$ is the volume of oxidising and reducing agent respectively.

Proof:

Recall: $\text{Normality} = \frac{\text{number of euivalents of solute}}{\text{volume of solution in litres (or dm}^3)}$

From which; $\text{Number of equivalents} = \text{Normality} \times \text{Volume} = \text{NV}$

But at equivalence point;

$\textbf{Number of equivalents of oxidizing agent} = \textbf{Number of equivalents of reducing agent}$

Where $\text{Number of equivalents of oxidising agent} = N_oV_o$

And $\text{Number of equivalents of reducing agent} = N_rV_r$

Hence $\mathbf{N_oV_o = N_rV_r}$

REDOX TITRATION

Redox titration involves titration of an oxidant with reductant or vice-versa. There must be a sufficiently large difference between oxidising and reducing capabilities of these agents for the reaction to undergo completion with sharp end point.

Types of redox indicators

There are three common types of redox indicator, namely:

- Self-indicators
- Internal indicators
- External indicators

Self-indicators

When the titrant itself is **strongly coloured** that after equivalence point, a single drop of the titrant (of negligible volume) produces an intense colour in the reaction mixture thus acting as an indicator; such indicators are known as self-indicators. A good example of self-indicator is potassium permanganate ($KMnO_4$) which is deep purple coloured and it is reduced by reductant to form Mn^{2+} which is colourless. After complete reduction of the analyte, the solution mixture is colourless at the equivalence point; and since the permanganate is strongly coloured, its single drop of negligible volume can change the colour of solution into pink thus detecting end point. ***However, although $K_2Cr_2O_7$ solution is strongly coloured and its single drop change the colour of colourless solution into yellow, it is not used as self-indicator like $KMnO_4$, why?***

This is because its reduction product, Cr^{3+}, it is green in colour and not colourless like Mn^{2+} which is reduction product of acidified $KMnO_4$. This hinders visual detection of the end point by observing the dichromate colour. Hence indicator must be used in titrations of dichromate solutions.

Internal indictors

Such indicators are added to the reaction mixture and they show their action through redox reaction. The indicators are always weaker reducing agent than the analyte so that they react with titrant only when whole of the analyte has consumed, producing a readily detectable colour change. A good example of internal indicator is diphenylamine which is used in titrations of potassium dichromate (VI).

External indicators

In case a suitable redox indicator is not available for given system; an indicator may be employed which will indicate the completion of reaction by physically or chemically reacting with analyte **(not through redox reaction).** Such indicators are called external indicators. A good example of external indicator is **starch indicator** which is commonly used in titrations which involve iodine. With iodine, starch gives blue colouration which disappears after complete reduction of the iodine i.e. when the iodine is absent. Thus iodine is used to detect presence of iodine. ***However, when iodine is an analyte, the starch must be added just close to the end point, why?***

This is because in large amount of iodine (at the beginning of titration), starch form a complex with the iodine. The iodine in the complex resists reduction of reducing agents like sodium thiosulphate and therefore blue colouration cannot disappear and hence end point can never be reached.

Iodometry and iodimetry titration

Iodometry and **iodimetry** are similar in a manner that both are redox titrations which involve iodine as an oxidising agent. The titration of iodine may be done directly or indirectly.

Iodimetry *is the redox titration whereby an analyte which is reducing agent is titrated directly with standard iodine solution.*
Iodometry *is the redox titration whereby an analyte which is an oxidising agent is added to excess iodide solution to liberate iodine whose amount is determined by titration with sodium thiosulphate*

Calculations on redox titrations

Example 14

52.3cm^3 of sodium nitrite solution, added from a burette were needed to discharge the colour of 25cm^3 of an acidified 0.02M KMnO_4 solution.

(a) What was the concentration of the nitrite solution in grams of anhydrous salt per dm^3?
(b) Why was nitrite in the burette?

$$2\text{MnO}_4^- + 5\text{NO}_2^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\,\text{H}_2\text{O}$$

Solution

(a) Number of moles KMnO_4 in 25cm^3 of its solution

$$= \frac{25}{1000} \times 0.02\text{mol} = 5 \times 10^{-4}\text{mol} = \text{Number of moles of MnO}_4^-$$

MnO_4^- reacts with NO_2^- (from NaNO_2) according to the following equation:

$$2\text{MnO}_4^- + 5\text{NO}_2^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\,\text{H}_2\text{O}$$

From which mole ratio of MnO_4^- to NO_2^- is $2:5$

Thus number of moles of NO_2^- in 52.3cm^3 of its solution

$$= \frac{5}{2} \times 5 \times 10^{-4}\text{mol} = 1.25 \times 10^{-3}\text{mol} = \text{Number of moles of NaNO}_2$$

Mass concentration of $\text{NaNO}_2 = [\text{NaNO}_2]\text{M}_{\text{NaNO}_2}$

But $[\text{NaNO}_2] = \frac{1.25 \times 10^{-3}}{0.0523}\text{M}$ and $\text{M}_{\text{NaNO}_2} = 69\text{gmol}^{-1}$

Thus mass concentration of NaNO_2 in $\text{gdm}^{-3} = \frac{1.25 \times 10^{-3} \times 69}{0.0523}\text{gdm}^{-3}$

Hence mass concentration of sodium nitrite is 1.649gdm^{-3}

(b) If a solution of a nitrite is titrated in the ordinary way with potassium permanganate by putting the permanganate in the burette, poor results are obtained, because the nitrite solution has first to be acidified with dilute sulphuric acid which reacts with the nitrite to give nitrous acid. The liberated nitrous acid being volatile and unstable is partially lost.

Example 15

1.6g of ethanedioic acid crystals, $H_2C_2O_4.2H_2O$, was made up to $250cm^3$ of aqueous solution and $25cm^3$ of this solution heated to temperature of about $70°C$, needed $26.2cm^3$ of a manganate (VII) for oxidation in titration.

(a) Calculate the molarity of the manganate (VII).
(b) Concentration of the manganate solution in gdm^{-3}
(c) Why in that particular experiment, ethanedioic must be heated?

Solution

(a) Molar mass of $H_2C_2O_4.2H_2O$ is $126gmol^{-1}$

Using; $[\quad] = \frac{m}{M_rV}$,

Then $[H_2C_2O_4.2H_2O] = \frac{1.6}{126 \times 0.25}M = 0.05M$

Number of moles of $H_2C_2O_4.2H_2O$ in $25cm^3$ of its solution

$= \frac{25}{1000} \times 0.05mol = 1.25 \times 10^{-3}mol$ = number of moles of $C_2O_4^{2-}$

$C_2O_4^{2-}$ reacts with MnO_4^- according to the following equation:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

From which mole ratio of MnO_4^- to $C_2O_4^{2-}$ is $2:5$

Thus number of moles of manganate (VII) solution

$$= \frac{2}{5} \times 1.25 \times 10^{-3}mol = 5 \times 10^{-4}mol$$

Then $[MnO_4^-] = \frac{5\times10^{-4}\times10^3}{26.2}M = 0.019M$

Hence Molarity manganate (VII) solution is 0.019M

(b) Molar mass of $KMnO_4$ is $158gmol^{-1}$

Using mass concentration in $gdm^{-3} = [\quad]Mr$

Mass concentration of $KMnO_4 = 0.019 \times 158gdm^{-3} = 3.002gdm^{-3}$

Hence mass concentration of manganate (VII) solution is $3.002gdm^{-3}$

(c) The reaction at room reaction is slow because of the equilibrium nature of the reaction. furthermore:

- CO_2 is soluble in water, thus heating removes all dissolved CO_2 out of the solution, driving the reaction in forward direction.
- Also at low temperature, the reduction of MnO_4^- may not be complete producing Mn (III) instead of Mn (II).

Example 16

Calculate X in the formula $FeSO_4.XH_2O$ from the following data: 24.400g of iron (II) sulphate crystals were made up to $1dm^3$ of aqueous solution acidified with sulphuric acid. $25cm^3$ of this solution required $20cm^3$ of 0.022M $KMnO_4$.

Solution

Number of moles of $KMnO_4 = \frac{20}{1000} \times 0.022mol = 4.4 \times 10^{-4}mol$

$KMnO_4$ reacts with $FeSO_4.XH_2O$ according to the following equation:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

From which mole ratio of MnO_4^- to Fe^{2+} is 1:5

Then number of moles of Fe^{2+} (from $FeSO_4.XH_2O$)

$= 5 \times 4.4 \times 10^{-4}mol = 2.2 \times 10^{-3}mol$ in $25cm^3$ of its solution

Number of moles of $FeSO_4.XH_2O$ in $1dm^3$ ($1000cm^3$) of its solution

$$= \frac{2.2 \times 10^{-3} \times 1000}{25} mol = 0.088mol$$

Using $M_r = \frac{m}{n}$;

Molar mass of $FeSO_4.XH_2O = \frac{24.4}{0.088} gmol^{-1} = 277.3gmol^{-1}$

It follows that; $56 + 32 + 64 + 18x = 277.3$; $x = 7$

The value of x is 7

Example 17

Calculate the percentage of iron in a sample of iron wire from the following data: 1.400g of the wire dissolved in excess of dilute sulphuric acid and the solution made up to $250cm^3$. $25cm^3$ of this solution needed $25.37cm^3$ of $0.0196MKMnO_4$ for oxidation.

Solution

With dilute sulphuric acid, Fe gives Fe^{2+} which will further be oxidised by $KMnO_4$ to Fe^{3+}.

Fe^{2+} reacts with MnO_4^- (from $KMnO_4$) according to the following equation:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Number of moles of $KMnO_4$ in $25.37cm^3$ of its solution

$$= \frac{25.37}{1000} \times 0.0196mol = 4.97252 \times 10^{-4}mol$$

Number of moles Fe^{2+} (from $FeSO_4$) $= 5 \times 4.97252 \times 10^{-4}mol$

$= 2.48626 \times 10^{-3}mol$ in $25cm^3$ of its solution

Number of moles of Fe^{2+} in $250cm^3$ of its solution

$$= \frac{2.48626 \times 10^{-3} \times 250}{25} mol = 2.48626 \times 10^{-2}mol$$

Fe reacts with dilute H_2SO_4 to give Fe^{2+} [from $FeSO_4$] according to the following ionic equation: $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$

From which mole ratio of Fe to Fe^{2+} is 1:1

Thus number of moles of Fe in 1.4g of iron wire was also $2.48626 \times 10^{-2}mol$

Using $m = nM_r$;

Mass of iron was $2.48626 \times 10^{-2} \times 56g = 1.3923056g$

Then % Fe $= \frac{1.3923056}{1.4} \times 100\% = 99.4504\%$

Hence the percentage of iron was 99.4504%.

Example 18

$25cm^3$ of a solution containing ethanedioc acid and sodium ethanedioate required $14.75cm^3$ of 0.1M sodium hydroxide solution for neutralisation, and $30.5cm^3$of 0.0205M potassium manganate (VII) solution for oxidation in acidic condition at about 70°C. Calculate the number of grams of each (anhydrous) constituent per dm^3 of the solution.

Solution

Number of moles of NaOH (aq) reacted with $H_2C_2O_4$ (ethanedioc acid)

$$= \frac{14.75}{1000} \times 0.1\text{mol} = 1.475 \times 10^{-3}\text{mol}$$

NaOH reacts with $H_2C_2O_4$ according to the following equation:

$$2NaOH + H_2C_2O_4 \rightarrow Na_2C_2O_4 + 2\,H_2O$$

From which mole ratio of NaOH to $H_2C_2O_4$ is $2:1$

Then number of moles of $H_2C_2O_4$ in $25cm^3$ of the solution

$$= {}^{1}\!/_{2} \times 1.475 \times 10^{-3}\text{mol} = 7.375 \times 10^{-4}\text{mol}$$

Using $m = nM_r$;

Mass of $H_2C_2O_4$ in $25cm^3$ of the solution $= 7.375 \times 10^{-4} \times 90g = 0.066375g$

Thus mass of ethanedioic acid in $1000cm^3$ of the solution

$$= \frac{0.066375 \times 1000}{25}g = 2.655g$$

Number of moles of $KMnO_4$ (Potassium manganate (VII))

$$= \frac{30.5}{1000} \times 0.0205\text{mol} = 6.2525 \times 10^{-4}\text{mol}$$

$C_2O_4^{2-}$ (from $H_2C_2O_4$ and $Na_2C_2O_4$) reacts with MnO_4^- (From $KMnO_4$) according to the following equation: $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8\,H_2O$

From which mole ratio of MnO_4^- to $C_2O_4^{2-}$ is $2:5$

Thus total number of moles of $C_2O_4^{2-}$ in $25cm^3$ of the solution

$$= \frac{5}{2} \times 6.2525 \times 10^{-4}\text{mol} = 1.563125 \times 10^{-3}\text{mol}$$

But the number of moles of $C_2O_4^{2-}$ from $H_2C_2O_4$ in $25cm^3 = 7.375 \times 10^{-4}$mol

Thus number of moles of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in $25cm^3$

$$= (1.563125 \times 10^{-3} - 7.375 \times 10^{-4})\text{mol} = 8.25625 \times 10^{-4}\text{mol}$$

= Number of moles of $Na_2C_2O_4$ in $25cm^3$ of the solution

Mass of $Na_2C_2O_4$ in $25cm^3 = 8.25625 \times 10^{-4} \times 134g$

Mass of $Na_2C_2O_4$ in $1000cm^3 = \frac{8.25625 \times 10^{-4} \times 134 \times 1000}{25}g = 4.42535g$

Hence: Mass of ethanedioic acid in $1000cm^3$ is 2.655g

Mass of sodium ethanedioate in $1000cm^3$ is 4.42535g.

Example 19

$25cm^3$ of a solution containing iron (II) and iron (III) sulphates required $18.50cm^3$ of 0.02M potassium manganate (VII) solution for oxidation in acidic condition. After complete reduction by zinc amalgam, $25cm^3$ of the solution required $32.6cm^3$ of the same manganate (VII) solution. Calculate the number of grams of each anhydrous sulphate per dm^3 of the solution.

Solution

First titration:

In this titration, $KMnO_4$ will oxidize Fe^{2+} from $FeSO_4$. Fe^{3+} does not undergo oxidation.

Number of moles of $KMnO_4$ in $18.5cm^3$ of its solution

$$= \frac{18.5}{1000} \times 0.02\text{mol} = 3.7 \times 10^{-4}\text{ mol} = \text{number of moles of } MnO_4^-$$

Fe^{2+} reacts with MnO_4^- according to the following equation:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

From which, mole ratio of Fe^{2+} to MnO_4^- is $5:1$

Thus number of moles of Fe^{2+} in $25cm^3$ of the solution

$= 5 \times 3.7 \times 10^{-4} = 1.85 \times 10^{-3}mol =$ Number of moles of Iron (II) sulphate in $25cm^3$ the mixture of iron (II) sulphate and iron (III) sulphate

Then mass of iron (II) sulphate in $25cm^3$ of the solution$= 1.85 \times 10^{-3} \times 152g = 0.2812g$

Whence mass of iron (II) sulphate in $1dm^3$ $(1000cm^3)$ of the solution

$$= \frac{0.2812 \times 1000}{25}g = 11.248g$$

Second titration:

After complete reduction, the iron (II) ions derived from the original iron (III) are also oxidised by the manganate (VII) solution. Thus the increase in volume of $KMnO_4$ solution used in second titration is what used to oxidizes these iron (II) ions

i.e. $(32.6 - 18.5)cm^3$ or $14.1cm^3$ of 0.02M $KMnO_4$ solution was used.

Number of moles of $KMnO_4$ used to oxidize the reduced ions

$$= \frac{14.1}{1000} \times 0.02mol = 2.82 \times 10^{-4}mol$$

From the mole ratio;

Number of moles of Fe^{2+} from reduction of Fe^{3+}

$$= 5 \times 2.82 \times 10^{-4}mol = 1.41 \times 10^{-3}mol$$

Equation of reduction of Fe^{3+} by Zn

$$2Fe^{3+} + Zn \rightarrow 2Fe^{2+} + Zn^{2+}$$

From which mole ratio of Fe^{3+} to Fe^{2+} is $1:1$

Thus number of moles of Fe^{3+} was also $1.41 \times 10^{-3}mol$

But one mole of iron (III) sulphate $(Fe_2(SO_4)_3)$ produces 2moles of Fe^{3+} according to equation: $Fe_2(SO_4)_3 \rightarrow 2Fe^{3+} + 3SO_4^{2-}$

It follows that, number of moles of $Fe_2(SO_4)_3 = \frac{1.41 \times 10^{-3}}{2}mol = 7.05 \times 10^{-4}mol$

Then mass of $Fe_2(SO_4)_3$ in $25cm^3$ of the solution $= 7.05 \times 10^{-4} \times 400g = 0.0282g$

Whence mass of iron (III) sulphate in $1dm^3$ $(1000cm^3)$ of the solution

$$= \frac{0.282 \times 1000}{25}g = 11.28g$$

Hence: Mass of iron (II) sulphate in $1dm^3$ is 11.25g

Mass of iron (III) sulphate in $1dm^3$ is 11.28g

Example 20

$12.5cm^3$ of a given solution of hydrogen peroxide were diluted to $500cm^3$ with distilled water. $25cm^3$of this diluted solution then required $22.5cm^3$ of 0.02M potassium manganate (VII) solution for titration in acidic conditions. Calculate:

(a) The concentration of the original hydrogen peroxide solution.
(b) The volume strength of the hydrogen peroxide solution, assuming s.t.p conditions.

Solution

(a) Number of moles of $KMnO_4$ in $22.5cm^3$ of its solution

$$= \frac{22.5}{1000} \times 0.02mol = 4.5 \times 10^{-4}mol = \text{number of moles of } MnO_4^-$$

MnO_4^- reacts with H_2O_2 according to the following equation:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

From which mole ratio of MnO_4^- to H_2O_2 is $2:5$

Number of moles of H_2O_2 in $25cm^3$ of diluted solution

$$= \frac{5}{2} \times 4.5 \times 10^{-4}mol = 1.125 \times 10^{-3}mol$$

Molarity of diluted solution of $H_2O_2 = \frac{1.125 \times 10^{-3} \times 10^3}{25}M = 0.045M$

Using dilution principle: $M_cV_c = M_dV_d$

Where:

M_c is the molarity of concentrated H_2O_2 solution

M_d is the molarity of diluted H_2O_2 solution = 0.045M

V_c is the volume of concentrated H_2O_2 solution = $12.5cm^3$

V_d is the volume of diluted H_2O_2 solution = $500cm^3$

Then $M_c = \frac{M_dV_d}{V_c} = \frac{0.045 \times 500}{12.5}M = 1.8M$

Mass concentration of the original H_2O_2 solution= $1.8 \times 34gdm^{-3} = 61.2gdm^{-3}$

Hence the concentration of original hydrogen peroxide is $61.2gdm^{-3}$

(b) Hydrogen peroxide decomposes to give oxygen gas according to the following equation:

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

From which mole ratio of H_2O_2 to O_2 is $2:1$

Number of moles of H_2O_2 in $12.5cm^3$ of its solution

$$= \frac{12.5}{1000} \times 1.8mol = 0.0225mol$$

Thus 0.0225mol of H_2O_2 produces $\frac{0.0225}{2}$mol or 0.01125mol of oxygen

But 0.0225mol of H_2O_2 is contained in $12.5cm^3$ of its volume

And 1mol of O_2 is contained in $22.4dm^3$ or $22400cm^3$ of its volume

It follows that: $12.5cm^3$ of H_2O_2 produces $0.01125 \times 22400cm^3$ or $252cm^3$ of O_2

Whence $1cm^3$ of H_2O_2 produces $\frac{252}{12.5}cm^3$ or $20.16cm^3$ of O_2

Hence the volume strength of H_2O_2 solution is 20.16 (The hydrogen peroxide solution produces 20.16 times its own volume of oxygen gas when heated)

Example 21

Calculate the percentage of calcium in calspar from the following data: 1.25g of calspar was dissolved in dilute hydrochloric acid and calcium ethanedioate was precipitated from neutralised solution by ammonium ethanedioate. Then washed precipitate was dissolved by addition of hot dilute sulphuric acid and made up to $250cm^3$. $25cm^3$ of this solution needed $24cm^3$ of $0.0208MKMnO_4$ for oxidation.

Solution

Number of moles of $KMnO_4$ in $24cm^3$ of its solution $= \frac{24}{1000} \times 0.0208mol = 4.992 \times 10^{-4}mol$

MnO_4^- (from $KMnO_4$) reacts with $C_2O_4^{2-}$ (from CaC_2O_4) according to the following equation

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

From which mole ratio of MnO_4^- to $C_2O_4^{2-}$ is $2:5$

Thus number of moles of $C_2O_4^{2-}$ was $\frac{5}{2} \times 4.992 \times 10^{-4}mol$

$= 1.248 \times 10^{-3}mol$ in $25cm^3$ of the solution.

Then number of moles of $C_2O_4^{2-}$ in $250cm^3$ of its solution $= \frac{1.248 \times 10^{-3} \times 250}{25}mol = 0.01248mol =$ number of moles of Ca in CaC_2O_4 **(In one mole of CaC_2O_4, there is one mole of Ca and whence their mole ratio is 1:1)**

Mass of calcium in $CaC_2O_4 = 0.01248 \times 40g = 0.4992g$ = mass of calcium (Ca) in 1.25g of calspar

Whence % Ca = $\frac{0.4992}{1.25} \times 100\% = 39.936\%$

Hence the percentage of calcium in calspar is 39.936%

Example 22

A solution of ethanedioic acid was made up and it was calculated that $22.5cm^3$ of certain potassium manganate (VII) solution would oxidize $25cm^3$ of the ethanedioic acid solution. In practice it was found that only $16.1cm^3$ of the manganate (VII) solution were needed. The error lay in fact that the calculation was based on formula of anhydrous acid where the crystalline acid was actually weighed out. What is the value of X in the formula: $H_2C_2O_4.XH_2O$.

Solution

MnO_4^- reacts with $C_2O_4^-$ according to the following equation:

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Let mass of ethanedioic acid in $25cm^3$ of its solution be m in grams

First case: If the acid is considered to be anhydrous

Number of moles of anhydrous $H_2C_2O_4 = \frac{m}{90}$

But number of moles of $KMnO_4 = \frac{22.5}{1000}M_O$

Where M_O is the Molarity of oxidising agent ($KMnO_4$)

Then from above equation, mole ratio of $C_2O_4^{2-}$ (from $H_2C_2O_4$) to MnO_4 is $5:2$;

Thus $\frac{5 \times 22.5}{2 \times 1000}M_o = \frac{m}{90}$ or $5.0625M_o = m$ -------------------------------- (i)

Second case: If the acid is considered to be crystalline

Number of moles of $H_2C_2O_4.XH_2O = \frac{m}{90 + 18x}$

And number of moles of $KMnO_4 = \frac{16.1}{1000} M_o$

Then $\frac{5\times16.1}{2\times1000}M_o = \frac{m}{90+18x}$

Or $0.04025M_o = \frac{m}{90+18x}$ ---(ii)

$\frac{(i)}{(ii)}$ gives $\frac{5.0625}{0.04025} = 90 + 18x$ or $1.44 = 0.7245x$ or $x = 2$

Hence the value of x in the given formula is 2

Example 23

3g of a sample of haematite (Fe_2O_3) were dissolved in concentrated hydrochloric acid and the solution diluted to $250cm^3$.$25cm^3$ of this solution, after reduction with tin (II) chloride, required $26.6cm^3$ of 0.02M potassium dichromate for oxidation. Calculate the percentage of iron (III) oxide in the ore.

Solution

Potassium dichromate (VI), $K_2Cr_2O_7$ reacts with Fe^{2+} according to the following ionic equation: $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ + \rightarrow 2Cr^{3+} + 6Fe^{3+}\ 7H_2O$

Number of moles $K_2Cr_2O_7$ in $26.6cm^3$ of its solution

$$= \frac{26.6}{1000} \times 0.02mol = 5.32 \times 10^{-4}mol\ of\ Cr_2O_7^{2-}$$

From the above equation; 1 mol of $Cr_2O_7^{2-}$ reacts with 6 mol of Fe^{2+}

Thus number of moles of Fe^{2+} in $25cm^3$ of its solution

$$= 6 \times 5.32 \times 10^{-4}mol = 3.192 \times 10^{-3}mol$$

Then number of moles of Fe^{2+} in $250cm^3$of its solution

$$= \frac{3.192\times10^{-3}\times250}{25}mol = 3.192\times10^{-2}mol$$

But 1 mol of Fe_2O_3 produce 2moles of Fe^{3+} which in turn produce 2 moles of Fe^{2+} after reduction.

Thus number of moles of Fe_2O_3 was $\frac{3.192\times10^{-2}}{2}mol = 1.596 \times 10^{-2}mol$

Then using $m = nM_r$;

Mass of Fe_2O_3 is $1.596 \times 10^{-2} \times 160g$ or $2.5536g$

But total mass of the ore (haematite) is 3g

It follows that, $\%Fe_2O_3$ in the ore $= \frac{2.5536}{3} \times 100\% = 85.12\%$

Hence the percentage of iron (III) oxide in the ore is 85.12%

Example 24

$25cm^3$of a copper (II) sulphate solution were added to $20cm^3$of potassium iodide solution, i.e. excess potassium iodide. The iodine liberated was titrated by $22.5cm^3$of 0.1080M sodium thiosulphate solution. Calculate the concentration of the solution in grams of the pentahydrate, $CuSO_4.5H_2O$ per dm^3 of the solution.

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$$
$$2\,S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Solution

Equations for reactions:

$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$ ……………………………….(i)

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$…………………………….….(ii)

(i)+(ii) gives the overall reaction equation which is:

$2Cu^{2+} + 2S_2O_3^{2-} + 2I^- \rightarrow Cu_2I_2 + S_4O_6^{2-}$

From which mole ratio of Cu^{2+} to $S_2O_3^{2-}$ is $2:2$ or $1:1$

Number of moles of $Na_2S_2O_3$ in $22.5cm^3$ of its solution

$$= \frac{22.5}{1000} \times 0.1080mol = 2.43 \times 10^{-3} mol \text{ of } S_2O_3^{2-}$$

Thus number of moles of Cu^{2+} = Number of moles of $CuSO_4.5\,H_2O$ was also 2.43×10^{-3}mol in $25cm^3$ of its solution.

$$[CuSO_4.5H_2O] = \frac{2.43 \times 10^{-3} \times 10^3}{25} M = 0.0972M$$

But molar mass of $CuSO_4.5\,H_2O$ is $250gmol^{-1}$

Thus mass concentration of the solution $= 0.0972 \times 250gdm^{-3} = 24.3gdm^{-3}$

Hence concentration of solution of $CuSO_4.5H_2O$ is $24.3gdm^{-3}$

Example 25

A standard solution is prepared by dissolving 1.185g of potassium dichromate (VI), $K_2Cr_2O_7$ making up to $250cm^3$of solution. The solution is used to find the concentration of sodium thiosulphate ($Na_2S_2O_3$) solution. A $25cm^3$portion of the potassium dichromate (VI) solution was acidified and added to an excess of potassium iodide (KI) to liberate iodine according to the following equation:

$$Cr_2O_7^{2-} + 6\,I^- + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7\,H_2O$$

The liberated iodine may be estimated by using sodium thiosulphate solution which is oxidised as follows.

$$I_2 + 2\,S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

When the solution was titrated against sodium thiosulphate, $17.5cm^3$ of sodium thiosulphate were required. Calculate:

(i) The concentration mole per litre of potassium dichromate solution.
(ii) The concentration in mole per litre of sodium thiosulphate solution.
(iii) The number of electrons which were accepted by potassium dichromate (VI) during the reaction.
(iv) Normality of potassium dichromate (VI) solution.
(v) Normality of sodium thiosulphate solution.

Solution

(i) Using [ ] = $\frac{m}{M_rV}$

$$[K_2Cr_2O_7] = \frac{1.185 \times 1000}{294 \times 250} M = 0.0161M$$

(ii) Given that:

$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ --------- (i)
$I_2 + 2\,S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$ ---------------------------------- (ii)

Eliminating I_2 in the two equations (i) and (ii) by taking (i) + 3× (ii) so as to write overall reaction equation as follows:

$$Cr_2O_7^{2-} + 6I^- + 14H^+ + 3I_2 + 6S_2O_3^{2-} \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O + 3S_4O_6^{2-} + 6I^-$$

Cancelling like terms which appears in both sides of the equation gives overall reaction equation which is:

$$Cr_2O_7 + 6S_2O_3^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O$$

Number of moles of $K_2Cr_2O_7$ in $25cm^3$ of its solution

$$= \frac{25}{1000} \times 0.0161mol = 4.025 \times 10^{-4} mol \text{ of } Cr_2O_7^{2-}$$

From above overall reaction equation: Mole ratio of $Cr_2O_7^{2-}$ to $S_2O_3^{2-}$ is $1:6$.

Thus number of moles of $S_2O_3^{2-}$

$= 6 \times 4.025 \times 10^{-4}$mol $= 2.415 \times 10^{-3}$ of $Na_2S_2O_3$ in 17.5cm^3

$$[Na_2S_2O_3] = \frac{2.415 \times 10^{-3} \times 10^3}{17.5} = 0.138M$$

(iii) $K_2Cr_2O_7$ gains electrons according to the following equation (reduction half reaction):

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$$

From which, one mole of $Cr_2O_7^{2-}$(or$K_2Cr_2O_7$) gains 6 moles of electrons;

But number of moles of $K_2Cr_2O_7$reacted was 4.025×10^{-4}mol

Thus number of moles of electrons gained was $6 \times 4.025 \times 10^{-4}$mol

$= 2.415 \times 10^{-3}$mol of electrons

Using N = nN_A, number of electrons gained $= 2.415 \times 10^{-3} \times 6.02 \times 10^{23}$

$=1.45383 \times 10^{21}$electrons

Hence number of electrons gained in the reaction was 1.45383×10^{21}electrons

(iv) Normality of $K_2Cr_2O_7$= $[K_2Cr_2O_7]$ × number of electrons gained by its one molecule.

But form (iii) above;

Number of electrons gained by one molecules of $K_2Cr_2O_7$ is six electrons

Thus Normality of $K_2Cr_2O_7 = 0.0161 \times 6N = 0.0966N$

Hence normality of potassium dichromate (VI) solution is 0.0966N

(v) $Na_2S_2O_3$ donates electrons according to the following equation (oxidation half reaction):

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$$

Dividing by 2 throughout the above equation so as to get one molecule of $Na_2S_2O_3$ (or $S_4O_6^{2-}$)

$$S_2O_3^{2-} \rightarrow \frac{1}{2} S_4O_6^{2-} + e$$

From which one molecule of $S_2O_3^{2-}$ donates 1 electron

And normality $Na_2S_2O_3 = [Na_2S_2O_3] \times$ number of electrons donated by 1 molecule

$= 0.138 \times 1N = 0.138N$

Hence normality of $Na_2S_2O_3$ is 0.138N

Alternative solution

Using $N_rV_r = N_oV_o$;

Where $N_o = 0.0966N, V_o = 25cm^3, V_r = 17.5cm^3$

Then $N_r = \frac{N_oV_o}{V_r} = \frac{0.0966 \times 25}{17.5}N = 0.138N$

Hence normality of sodium thiosulphate solution is 0.138N.

Example 26

56dm^3 of air containing a trace of chlorine were passed slowly through an excess of potassium iodide solution at 10°C and 100000 Nm^{-2} (750mmHg). The solution was made up to 250cm^3 with water and 25cm^3 of it then required 20.6cm^{3}of 0.1M sodium thiosulphate solution to react with the iodine. What is the percentage by volume of chlorine in the air?

Solution

Equations for reactions:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

From air

Then $2\,S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$(ii)

Taking (i) + (ii) gives overall reaction equation which is:

$$2\,S_2O_3^{2-} + Cl_2 \rightarrow S_4O_6^{2-} + 2Cl^-$$

From which mole ratio of $S_2O_3^{2-}$ to Cl_2 is $2:1$

Number of moles of $Na_2S_2O_3$ in 20.6cm^3 of its solution

$$= \frac{20.6}{1000} \times 0.1\text{mol} = 2.06 \times 10^{-3}\text{mol of } S_2O_3^{2-}$$

Then number of moles of Cl_2 in 25cm^3 of solution $= \frac{2.06 \times 10^{-3}}{2}\text{mol} = 1.03 \times 10^{-3}\text{mol}$

And number of moles of Cl_2 in 250cm^3 of solution

$= 10 \times 1.03 \times 10^{-3}\text{mol} = 1.03 \times 10^{-2}\text{mol}$

From ideal gas equation: $PV = nRT$ or $V = \frac{nRT}{P}$

Substituting $V = \frac{1.03 \times 10^{-2} \times 0.082 \times 283 \times 760\text{dm}^3}{750} = 0.2422\text{dm}^{-3}$

$\%Cl_2 = \frac{V_{Cl_2}}{V_{air}} \times 100\% = \frac{0.2422}{56} \times 100\% = 0.4325\%$

Hence the percentage of chlorine in the air is 0.4325%.

DIGGING EXERCISE 20

EXERCISE 20A: BINDER QUESTIONS

Question 1

Would you use an oxidising agent or reducing agent in order for the following reactions to occur?

$ClO_3^- \longrightarrow ClO_2^-$ (b) $SO_4^{2-} \longrightarrow S^{2-}$ (c) $Mn^{2+} \longrightarrow MnO_2$ (d) $Zn \longrightarrow ZnCl_2$

Question 2

Chlorate(I) ions are capable of undergoing disproportionation.

(a) What is meant by the term disproportionation?
(b) Write an ionic equation for the disproportionation of sodium chlorate(I). Indicate the oxidation numbers of chlorine in each species in which it occurs.
(c) Write two ionic half equations for this process which illustrate your definition of disproportionation.

Question 3

Given the experimental evidence that $Au^{3+}(aq)$ will react with $Sn(s)$, and that $Ag^+(aq)$ will react with $Sn(s)$ but not with $Au(s)$, arrange ions $Ag^+(aq)$, $Au^{3+}(aq)$ and $Sn^{2+}(aq)$ in increasing order of their tendency to gain electrons.

Question 4

Write a balanced ionic equation and identify the oxidants and reductants in each of the following chemical reactions:

(i) Iron (II) sulphate reacts with an acidified potassium dichromate solution.
(ii) Potassium iodide reacts with an acidified potassium iodate solution.
(iii) Copper (II) sulphate solution and potassium iodide solution react together.
(iv) Chlorine gas and hot concentrated potassium hydroxide react together.

Question 5

(a) State the oxidation number of iodine in KIO_3 and KIO_4.
(b) In the reaction

$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(s) + 3H_2O(l)$,
iodine is simultaneously oxidised and reduced. Explain why this is **not** a disproportionation reaction and hence give the appropriate name for the reaction.

(c) Describe a chemical test you could carry out to show that iodine was produced in (b) above.
(d) Suggest, by reference to the ionic equation in (b), the ionic equation for the reduction of KIO_4 to iodine in the presence of excess acid and excess potassium iodide.

EXERCISE 20B: REAL QUESTIONS

Question 6

Potassium manganate (VII) is not used as a primary reagent in volumetric analysis as potassium dichromate (VI) does. Explain.

Question 7

Hydrochloric acid cannot be used as acidic medium during redox titration of potassium permanganate against iron (II) sulphate. Explain.

Question 8

When acidified potassium dichromate reacts with sodium chloride, green colouration is observed. Explain.

Question 9

Why the temperature in the experiment involving reaction between oxalic acid and acidified potassium permanganate, must be above 60°C?

Question 10

In an experiment done by **Mr. Akilikubwa** in a school's chemistry laboratory: 50cm^3 of solution of hydrogen peroxide were diluted to 1dm^3 with water. 25cm^3 of this solution, when acidified with dilute sulphuric acid, needed 20.25cm^3 of 0.02MKMnO_4 on the titration.

(i) What is the concentration of the original hydrogen peroxide in moldm^{-3}?
(ii) Why NaMnO_4 should not be used as an oxidant in this experiment? What would be the effect on the value of the obtained titre volume if NaMnO_4 would be used instead of KMnO_4?
(iii) Why concentrated sulphuric acid should not be used as an acidic medium in this experiment? What would be effect on the obtained titre volume if concentrated sulphuric acid would be used instead of dilute sulphuric acid?

EXERCISE 20C: HOT QUESTIONS

Question 11

50.0cm^3 of solution of hydrogen peroxide were diluted to 1.00dm^3 with water. 25.0cm^3 of this solution, when acidified with dilute sulphuric acid, reacted with 20.25cm^3 of 0.0200moldm^{-3} $KMnO_4$.What is the concentration of the original hydrogen peroxide solution in mol dm^{-3}?

Question 12

Given the following two half–reactions:

(i) $S_4O_6^{2-}(aq) + 2e \longrightarrow 2S_2O_3^{2-}(aq)$
(ii) $I_2(aq) + 2e \longrightarrow 2I^-(aq)$

(a) Construct the full ionic redox equation for the reaction of the thiosulphate ion, $2S_2O_3^{2-}$, and iodine.
(b) What mass of iodine reacts with 23.5cm^3 of 0.0120moldm^{-3} sodium thiosulphate solution?
(c) 25.0 cm^3 of a solution of iodine in potassium iodide solution required 26.5 cm^3 of 0.0950 mol dm^{-3} sodium thiosulphate solution to titrate the iodine. What is the molarity of the iodine solution and the mass of iodine per dm^3? (Atomic masses: I = 126.9, S = 32, O = 16).

Question 13

25.0cm^3 of the potassium iodate solution were added to about 15cm^3 of a 15% solution of potassium iodide (ensures excess iodide ion). On acidification, the liberated iodine needed 24.1cm^3 of 0.0500moldm^{-3} sodium thiosulphate solution to titrate it.

(i) Calculate the concentration of potassium iodate(V) in gdm^{-3}
(ii) What indicator is used for this titration and what is the colour change at the end–point?

Question 14

Calculate the molarities of iron(II) and iron(III) ions in a mixed solution from the following data:

25.0cm^3 of the original mixture was acidified with dilute sulphuric acid and required 22.5cm^3 of 0.0200moldm^{-3} $KMnO_4$ for complete oxidation.

A further 25.0cm^3 of the original iron(II)/iron(III) mixture was reduced with zinc and acid and it then required 37.6cm^3 of the $KMnO_4$ for complete oxidation.

Question 15

2.83g of a sample of haematite iron ore (iron(III) oxide, Fe_2O_3) were dissolved in concentrated hydrochloric acid and the solution diluted to 250cm^3.

25.0cm^3 of this solution was reduced with tin(II) chloride (which is oxidised to Sn^{4+} in the process) to form a solution of iron(II) ions. This solution required 26.4cm^3 of 0.0200moldm^{-3} potassium dichromate(VI) for oxidation.

(a) Calculate the percentage of iron(III) oxide in the ore.
(b) Why is not potassium manganate(VII) used for this titration?

Question 16

13.2g of iron(III) alum were dissolved in water and reduced to an iron(II) ion solution by zinc and dilute sulphuric acid. The mixture was filtered and the filtrate and washings made up to $500cm^3$ in a standard volumetric flask.

If $20.0cm^3$ of this solution required $26.5cm^3$ of $0.0100moldm^{-3}$ $KMnO_4$ for oxidation. Calculate the percentage by mass of iron in iron alum.

Question 17

1.01g of an impure sample of potassium dichromate(VI), $K_2Cr_2O_7$, was dissolved in dil. sulphuric acid and made up to $250cm^3$ in a calibrated volumetric flask. A $25.0cm^3$ aliquot of this solution pipetted into a conical flask and excess potassium iodide solution and starch indicator were added. The liberated iodine was titrated with $0.100moldm^{-3}$ sodium thiosulphate and the starch turned colourless after $20.0cm^3$ was added.

(a) Calculate the moles of sodium thiosulphate used in the titration and hence the number of moles of iodine titrated.
(b) Calculate the moles of dichromate(VI) ion that reacted to give the iodine titrated in the titration.
(c) Calculate mass of potassium dichromate(VI) in the $25.0cm^3$ aliquot titrated.
(d) Calculate the total mass of potassium dichromate(VI) in the original sample and hence its % purity.

Chapter 21

ELECTRODE POTENTIAL

INTRODUCTION

When an electrode is immersed in the solution containing its ions, e.g. M(s) in $M^{n+}(aq)$, two things occur:

Firstly, the electrode starts to dissolve in the solution giving its ions according to the following equation:

$\mathbf{M(s) \rightarrow M^{n+}(aq) + ne}$**…………………………Oxidation**

Electrostatic force of attraction between positively charged cations and electrons (released by the electrode in the ionisation process) which are negative, prevent cations from going far away from the electrode. So cations are attracted very close to the electrode.

Secondly, the cations attracted to the electrode gain electrons from the electrode surface to form neutral atoms according to the following equation:

$\mathbf{M^{n+}(aq) + ne \longrightarrow M(s)}$**……………………………Reduction**

The tendency of a metal in contact with its salt solution to attract metal ions from the solution and convert them into metal atoms by losing electrons is called **deposition pressure**.

Combining oxidation and reduction reaction equations shown above, gives the following reversible reaction equation:

$$\mathbf{M^{n+}(aq) + ne \rightleftharpoons M(s)}$$

Eventually the equilibrium is established and the electric double layer of oppositely charged ions (positive and negative charges) is formed as shown in the figure below:

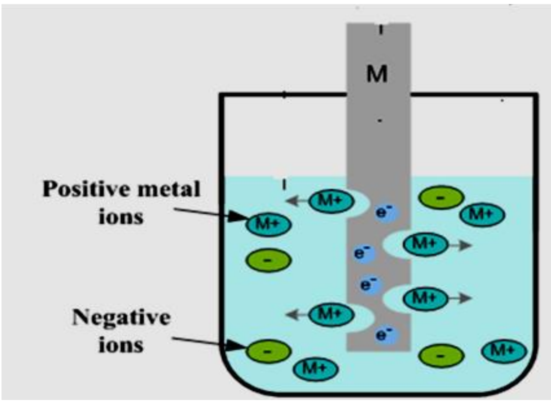


Figure 21.1 Electric double layers in electrode potential formation

The formation of the electric double layers leads to formation of a potential difference between the electrode and its solution and the potential difference formed under this situation is what we call **electrode potential** denoted by a letter **'E'**.

Definition of electrode potential

Quantitatively; electrode potential can be defined as *the potential difference between the electric double layers which is formed when an electrode is in contact with solution containing its ions.*

Qualitatively; electrode potential can be defined as *the tendency of a metal when placed in contact with solution of its ions to become positively or negatively charged with respect to the solution.* It can be **reduction** or **oxidation potential**.

Reduction potential *is the tendency of a metal in contact with solution of its ions to become positively charged with respect to the solution.*

$$M^{n+}(aq) + ne \rightarrow M(s)$$

Oxidation potential *is the tendency of a metal in contact with a solution of its ions to become negatively charged with respect to the solution.*

$$M(s) \rightarrow M^{n+}(aq) + ne$$

Thus in the equilibrium: $M^{n+}(aq) + ne \rightleftharpoons M(s)$

If the position of the equilibrium of one reaction lies more to the right hand side than another, then:

- The reduction potential of the reaction is more positive (or less negative).
- The oxidation potential of the reaction is more negative (or less positive).
- The electrode is more positive with respect to the solution containing its ions (when the electrode and the solution are in contact to each other).
- The metal, M, is weaker reducing agent (it undergo reduction more readily).

If the position of the equilibrium of one reaction lies more to the left hand side than another, then:

- The reduction potential of the reaction is more negative (or less positive).
- The oxidation potential of the reaction is more positive (or less negative).
- The electrode is more negative with respect to the solution containing its ions.
- The metal, M, is stronger reducing agent (it undergoes oxidation more readily).

It should be noted that:

Oxidation potential is equal in magnitude and opposite in sign to the reduction potential.

$$\mathbf{E_{oxid} = -E_{red}}$$

According to IUPAC convention, the term electrode potential means the reduction potential. **Thus electrode potentials are always given as reduction potentials and hence whenever we talk about just electrode potential we always imply reduction potential.**

FACTORS AFFECTING ELECTRODE POTENTIAL

Electrode potential depends upon the following factors:

- Nature of the electrode
- Concentration of metal ions in the solution
- Temperature
- Pressure

Nature of the electrode

No two electrodes have the same standard electrode potential, why? This is because no two electrodes have exactly the same structure and the tendency to gain or lose electrons is also different.

Generally, a solid electrode dissolves to form its ions in aqueous solution according to the following steps:

1. Sublimation (Atomisation)
2. Ionisation
3. Hydration

1. Atomisation (sublimation)

This involves converting solid electrode to its corresponding gaseous atoms**. The process is endothermic.** $M(s) \rightarrow M(g)$ $\Delta H = +ve$

2. Ionisation

This involves converting gaseous atoms to its corresponding gaseous ions. **The process is also endothermic.** $M(s) \rightarrow M^{n+}(g) + ne$ $\Delta H = +ve$

3. Hydration

This involves dissolving gaseous ions in water to form aqueous the ions in the solution. **The process is exothermic.** $M^{n+}(g) + N(aq) \rightarrow M^{n+}(aq)$ $\Delta H = -ve$

The summation of **atomisation energy, ionisation energy** and **hydration energy** determine the ability (easiest) of the solid electrode to dissolve in aqueous solution as per forward reaction of the following reaction equation: $M(s) \rightleftharpoons M^{n+}(aq) + ne$

If the summation for one electrode is smaller (more negative or less positive) than another electrode, then:

- The oxidation potential of the electrode will be large (more positive or less negative) and hence forward reaction is more favoured.
- The reduction potential (electrode potential) will be smaller (more negative or less positive) and hence reverse reaction is less favoured.

If the summation of one electrode is larger (more positive or less negative) than another electrode, then:

- The oxidation potential of the electrode will be smaller (more negative or less positive) and hence forward reaction is less favoured.
- The reduction potential (electrode potential) will be larger (more positive or less negative) and hence reverse reaction is more favoured.

Concentration (activity) of metal ions in the solution

Consider the following equilibrium: $M^{n+}(aq) + ne \rightleftharpoons M(s)$

From the above equilibrium it is clearly understood that:

- Increasing **activity (effective concentration)** of $M^{n+}(aq)$ shifts the position of chemical equilibrium to the right hand side thus:
  - Increasing electrode potential (reduction potential)
  - Decreasing oxidation potential
- Decreasing **effective concentration (activity)** of $M^{n+}(aq)$ shifts the position of chemical equilibrium to the left hand side thus:
  - Decreasing electrode (reduction) potential
  - Increasing oxidation potential

So generally we can conclude that, **the electrode potential increases with an increase in concentration of the electrolyte.**

It should s be noted that: The electrode potential does not depend upon the surface area of the electrode because the concentration of the solid metal is taken to be unity (one).

Temperature

The electrode potential decreases with rise in temperature. The variation of electrode potential with change in temperature is given by **Nernst equation** (this will be discussed in detail later).

Pressure

Pressure has effect on electrode potential of gaseous electrode only.

STANDARD ELECTRODE POTENTIAL

Standard electrode potential *is the electrode potential which is measured when an electrode is in contact with 1M solution of its ions at 25^oC and 1atm (standard conditions).* **It is denoted as E^θ.**

Measurement of standard electrode potential

The absolute value of a single electrode cannot be measured experimentally, why?

This is because a half-cell reaction cannot take place independently. To measure the potential difference between an electrode and its solution, the electrical connection between two half cells which contain different electrodes must be made. Thus one can measure only the difference between the electrode potential of any two half-cell reaction**. *So how the electrode potential is measured?***

The only way out is to use arbitrarily a second electrode which acts as a reference electrode. The common standard reference electrode is standard hydrogen electrode (SHE). Its standard electrode potential is arbitrarily (by convention) taken to be zero at all temperatures so that electrode potentials of all other electrodes are measured against it. ***What does standard hydrogen electrode consist of?***

A standard hydrogen electrode consists of a platinum foil coated with platinum black and is dipped in an acid solution with 1M hydrogen ions (H^+) concentration. The platinum foil is in contact with hydrogen gas at 1atm pressure at 25^oC.

The reader should not confuse (as many do) the use of two terms: **Normal hydrogen electrode (NHE)** and **standard hydrogen electrode (SHE);** the former applies when the hydrogen electrode is immersed in **a normal solution (a solution of normality of 1N)** and it is no longer in use; its use has been replaced by the later (SHE) which applies when the hydrogen electrode is immersed to **a molar solution** (**a solution of molarity of 1M**) at standard conditions (25^oC and 1atm).

Construction of electrochemical cell for electrode potential measurement

In order to obtain a cell reaction, one must know the oxidised (reductant) and reduced (oxidant) species to determine the cathode and anode of the cell. In the **electrochemical (galvanic or voltaic) cell**:

- **Anode is negative electrode**, i.e. the oxidised specie (reducing agent) becomes the anode.
- **Cathode is positive electrode**, i.e. the reduced specie (oxidising agent) becomes the cathode.

Conventionally it has been agreed that, **anode (oxidation half-cell) must be kept at the left hand side while cathode (reduction half-cell) must be kept at right hand side.**

- The two half cells are connected by salt bridge and **voltmeter of very high resistance (**so that it does not allow passage of current through it) reads the electrode potential of the electrode.

Measurement of standard electrode potential of a metal which is stronger reducing agent than hydrogen

In this case the electrode (like zinc) is anode while standard hydrogen electrode is cathode.

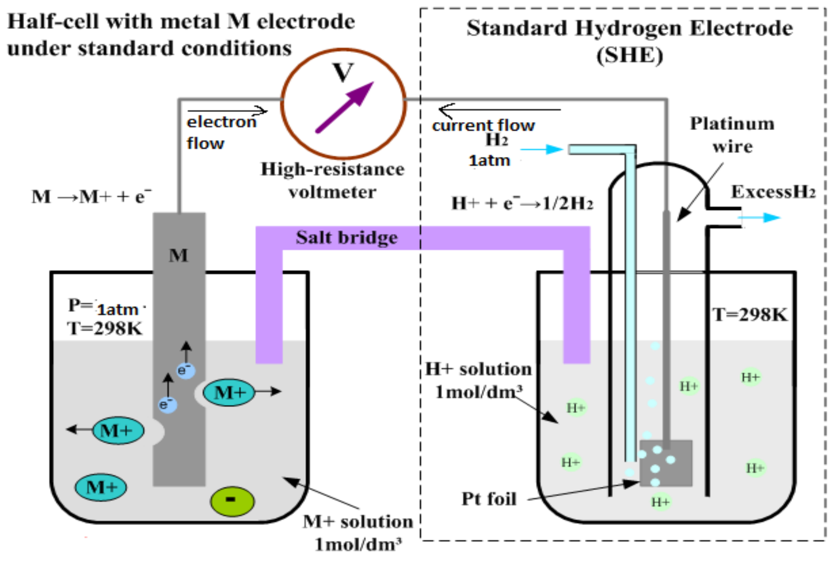


Figure 21.2 Electrochemical cell for standard electrode potential measurement

From zinc electrode, the standard electrode potential is found to be -0.76 V. A negative value means that when Zn/Zn^{2+} half cell is combined with standard hydrogen electrode (SHE); zinc is negative electrode (anode) and the electrons move from the zinc plate to the platinum electrode of SHE though the external circuit. Oxidation takes place at zinc electrode and reduction at the platinum electrode.

At Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$
At cathode: $2H^{+}(aq) + 2e \rightarrow H_2(g)$

Measurement of standard electrode potential of a metal which is weaker reducing agent than hydrogen

In this case, the electrode like copper become cathode while standard hydrogen electrode is anode.

For copper electrode, the standard electrode potential is found to be +0.34V. The positive value means that when Cu^{2+}/Cu half cell is combined with SHE, copper is positive electrode (cathode) and electrons move from the platinum electrode of SHE to the copper plate through the external circuit. Reduction takes place at copper electrode and oxidation at platinum electrode of SHE.

At anode: $H_2(g) \rightarrow 2H^{+}(aq) + 2e$

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

Composition of salt bridge

A salt bridge is inverted U – tube containing an inert paste of a strong electrolyte (potassium chloride or sodium sulphate is commonly used) and agar – gel.

Significance of salt bridge

The salt bridge:

- Allows the ions to migrate from cathode half-cell into the anode half-cell so as to complete the circuit
- Prevents the diffusion of the electrolytes from one half – cell to the other thus maintaining the charge balance in the two half cells.

Functions of platinised platinum in the standard hydrogen electrode

The platinised platinum is useful in the following ways:

- It adsorbs hydrogen gas
- It acts as inert electrode by allowing electrons to flow from hydrogen gas (H_2) to platinum (Pt) and from it (Pt) to H^+.

Electrodes

Electrodes help in the conduction of electrons into and out of the cell as well as provide the surface for electrode reaction.

- They are made up of electric conductors like metals or graphite.
- They may be in the form of rods or as surface coating on the rods of other material or as a coating on the inside surface of the cell.

By definition:
Electrode is *a solid electric conductor through which an electric current enters or leaves an electrolytic cell or other medium.*
Electrodes may be divided into two types depending on how they are involved in the electrochemical (or electrolytic) process. These are:

- Inert electrodes and
- Active electrodes

Inert electrodes *are electrodes which do not enter into the electrolytic chemical reaction.*

- The electrodes made up of noble metals like platinum are used as inert electrodes.

Active electrodes *are electrodes which take part in the electrolytic reaction.*

- These are either dissolved into the electrolyte or a substance is deposited on them.

Electrodes can also be divided into:

- Anode and
- Cathode

Anode is *the electrode at which oxidation occurs.*
Cathode *is the electrode at which reduction occurs.*
Don't confuse: Most of students have misconception that 'anode is positive electrode' and 'cathode is negative electrode'. That is not correct because polarity of the electrode depends on the kind of cell; while for electrochemical cell, anode is negative and cathode is positive, for electrolytic cell, anode is positive and cathode is negative. However, in both cells, oxidation occurs at anode and reduction occurs at cathode, the simple fact which provides the basis above definitions.

Electrolyte

The electrolyte *is the substances that give free ions either in molten state or in the aqueous solution.* They can be **anolyte** or **catholyte**.

Anolyte *is an electrolyte at anode half-cell in which the anode is dipped.*
Catholyte *is an electrolyte at cathode half-cell in which cathode is dipped.*

APPLICATIONS OF ELECTRODE POTENTIAL

Electrode potential is useful in:

- Construction of electrochemical cells
- Construction of electrochemical series

Construction of electrochemical cells

What is electrochemical cell?

Electrochemical cell *is a device which uses spontaneous chemical reactions to generate electricity which consists of two half cells connected with a salt bridge.* Electrochemical cells are also known as **galvanic cell** or **voltaic cell.**

In constructing electrochemical cell from given standard electrode potentials:

The electrode with more negative (or less positive) electrode potential must be anode i.e. must appear in the left handed half-cell.

Reasons for the choice: Oxidation half reaction of cell reaction occurs at anode half-cell. So the anode electrode (negative electrode) must be stronger reducing agent, i.e. it must undergo reduction by difficulty and this is justified by its smaller value (more negative or less positive) of electrode potential which is reduction potential.

The electrode with more positive (or less negative) electrode potential must be cathode, i.e. it must appear at right handed half-cell.

Reason for the choice: Reduction half reaction of cell reaction occurs at cathode half-cell. So the cathode electrode (positive electrode) must be weaker reducing agent i.e. it must undergo reduction more readily and this is justified by its large value (more positive or less negative) of the electrode potential which is reduction potential.

It should be understood that: Since the anode is better electron donor than cathode, electrons flow from the anode to cathode and the conventional current, flow from the cathode to anode (in opposite direction of electron flow).

Example 1

Draw a voltaic cell diagram which consists of copper and zinc electrodes, given that:

$$E^{\theta}_{Zn^{2+}/Zn} = -0.76V; \; E^{\theta}_{Cu^{2+}/Cu} = +0.34V$$

Solution

Zinc having more negative electrode potential, its electrode is negative electrode (anode) and it must kept at left handed half cell as shows in the diagram below:

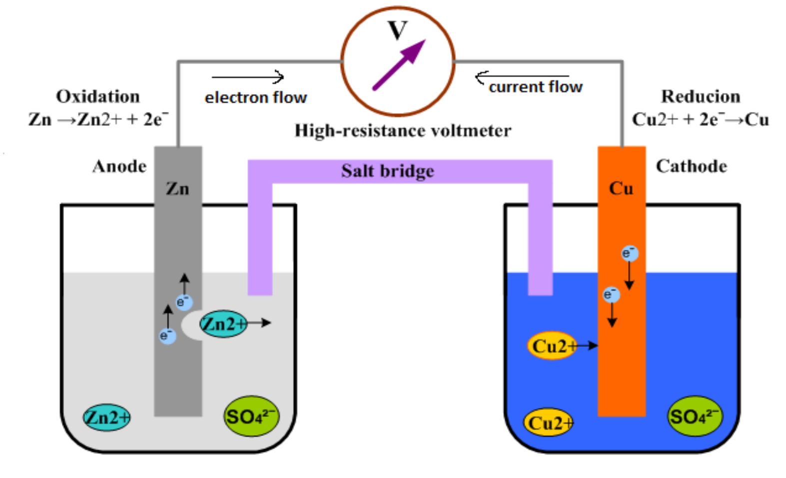


Figure 22.3 Electrochemical cell for example 1

It should be noted that: The galvanic (electrochemical) cell which consists of zinc and copper electrodes immersed in $ZnSO_4$ and $CuSO_4$ solutions at anode and cathode respectively is known as **Daniel cell**.

Cell notation

Cell notation express cell reaction of given cell. It also used in writing cell diagram instead of using drawing. For example, cell notation for Daniel cell is;

$Zn(s)\,|\,Zn^{2+}(M)||Cu^{2+}(M)\,|\,Cu(s)$ whereby:

- The anode reaction (negative electrode) must be written on the left hand side and the cathode reaction (positive electrode) on the right hand side.
- A vertical line indicates a contact between two phases. As an example $Zn\,|\,Zn^{2+}$ indicates that zinc electrode is in contact with a solution containing zn^{2+} ions or $Cu^{2+}\,|\,Cu$ indicates that copper electrode is in contact with a solution containing Cu^{2+}
- In anode reaction, neutral atom is written before its corresponding cation indicating that there is oxidation at the anode while in cathode reaction, the cation is written before its corresponding neutral atom indicating that there is a reduction at the cathode.
- A double line indicates that the solutions in the half cells are separated by a porous barrier or salt bridge
- The molar concentration of the solution is written in brackets after the formula of the ion e.g. $Zn\,|\,Zn^{2+}(0.1M)$ indicates that the zinc plate is in contact with $0.1MZn^{2+}$ solution.

Also from above cell notation:

$$\text{At anode: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e$$

$$\text{At cathode: } Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$

Combining anode reaction and cathode reaction, the overall cell reaction is obtained which is

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

Hence cell diagram can be used to deduce cell reaction. The converse of this is also true, i.e. the cell reactions can be used to deduce the cell diagram.

Example 2

Write cell diagram from the following cell reactions:

(i) $Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$
(ii) $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s) \quad E^{\theta}$
(iii) $M(s) + 2H^{+}(aq) \rightarrow M^{2+}(aq) + H_2(g) \quad E^{\theta}$
(iv) $H_2(g) + M^{2+}(aq) \rightarrow 2H^{+}(aq) + M(s) \quad E^{\theta}$

Solution

(i) $Zn(s)\,|\,Zn^{2+}(aq)||Pb^{2+}(aq)\,|\,Pb(s)$
(ii) $Mg(s)\,|\,Mg^{2+}(1M)||Cu^{2+}(1M)\,|\,Cu(s)$ **(With standard electrode potential, E^{θ}, at the end of the equation means concentration of ions is 1M)**
(iii) $M(s)\,|\,M^{2+}(1M)||H^{+}(1M)||H_2(1atm)$, Pt **(With standard electrode potential, E^{θ}, at the end of the equation means concentration of ions is 1M and partial pressure of the hydrogen gas is 1atm)**
(iv) $Pt, H_2(1atm)\,|\,H^{+}(1M)||M^{2+}(1M)\,|\,M(s)$

Note: In writing cell diagram, it is not necessary to include stoichiometric coefficients of species appearing in the cell reaction because multiplying a fixed number to a half-cell reaction does not alter the value of electrode potential.

Calculating standard cell potential (e.m.f)

The **cell potential** of electrochemical cell *is the difference in electrode (reduction) potential of the cathode half reaction and that of the anode half reaction.*

Cell potential, $\mathbf{E_{cell} = E_{red(cathode)} - E_{red\,(anode)}}$

Since the cathode always appears at **r**ight hand side and anode at **l**eft hand side, then we can donate:

$E_{red(cathode)}$ as E_R

And $E_{red\,(anode)}$ as E_L

Then, $\mathbf{E_{cell} = E_R - E_L}$

The cell potential of a cell, measured at 25°C and 1atm pressure (standard conditions) when concentration of the electrolytes in both half cells is 1M, is known as **standard cell potential**, $\mathbf{E^{\theta}_{cell}}$.

Thus $\mathbf{E^{\theta}_{cell} = E^{\theta}_R - E^{\theta}_L}$

The cell potential of a cell when the circuit draws no current (in zero current flow) is known as **electromotive fore (e.m.f).**

In order to construct a cell with maximum e.m.f. one must choose the electrode with most negative electrode potential to be anode and that of most positive electrode potential to be the cathode.
It should be noted that: In applying above formulas in calculation of cell potential (or e.m.f), make sure that reduction potentials are used and not otherwise. If the oxidation electrode potential is given instead of reduction electrode potential don't forget to convert it to the reduction potential by using the following relationship: $\mathbf{E_{red} = -E_{oxid}}$

Example 3

What is the cell potential for the following cell?

$$Zn(s)\,|\,Zn^{2+}(1M)||Pb^{2+}(1M)\,|\,Pb(s)$$

$$E^{\theta}_{Pb^{2+}/Pb} = -0.12V;\ E^{\theta}_{Zn^{2+}/Zn} = -0.76V$$

Solution

According to the convention, the right hand side electrode is cathode.

So using $E^{\theta}_{cell} = E^{\theta}_{R} - E^{\theta}_{L} = -0.12V - (-0.76V) = +0.64V$

Hence the cell potential for the cell is +0.64V

Example 4

The e.m.f of the following cell is:

$Ag\,|\,Ag^{+}(1M)||Cu^{2+}(1M)\,|\,Cu$ $\quad E^{\theta} = 0.46V$

$Zn\,|\,Zn^{2+}(1M)||Cu^{2+}(1M)\,|\,Cu$ $\quad E^{\theta} = 1.1V$

Calculate e.m.f of the cell:

$Zn\,|\,Zn^{2+}(1M)||Ag^{+}(1M)\,|\,Ag$

Solution

Using $E_{cell} = E_{R} - E_{L}$

Then:

$0.46V = E_{Cu^{2+}/Cu} - E_{Ag^{+}/Ag}$ ……………………………(i)

And $1.1V = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$ ……………………………(ii)

(ii) − (i) give;

$0.64V = E_{Ag^{+}/Ag} - E_{Zn^{2+}/Zn}$ = e.m.f of the given cell

Hence e.m.f the cell is +0.64V

Example 5

A cell is set up between copper and silver $Cu(s)\,|\,Cu^{2+}(aq)||Ag^{+}(aq)\,|\,Ag(s)$

If two half cells work under standard conditions, calculate e.m.f of the cell

$$E^{\theta}_{Cu/Cu^{2+}} = -0.34V, E^{\theta}_{Ag^{+}/Ag} = 0.8V$$

Solution

In this problem it is given oxidation electrode potential of copper instead of its reduction electrode potential.

Using $E^{\theta}_{red} = -E^{\theta}_{oxid}$

$$E^{\theta}_{Cu^{2+}/Cu} = -\ E^{\theta}_{Cu/Cu^{2+}} = -(-0.34V) = 0.34V$$

Then $E^{\theta}_{cell} = E^{\theta}_{R} - E^{\theta}_{L} = 0.8V - 0.34V = 0.46V$

Hence the e.m.f of the cell is +0.46V

Example 6

An electrochemical cell is made up of iron rod dipped in 1M solution of Fe^{2+} ions in a beaker and nickel rod dipped in 1M solution of Ni^{2+} in another beaker. A salt bridge is used to connect two half cells;

(a) In which cell does reduction occur?
(b) Write half reactions involved
(c) Which metal is anode
(d) In which direction are the electrons passing through voltmeter?
(e) What would be the effect on the voltmeter reading if Fe^{2+}concentration were increased?
(f) What was the cell potential at the time the cell operation starts?

$$E_{Fe^{2+}/Fe} = -0.44V;\ E_{Ni^{2+}/Ni} = -0.25V$$

Solution

The electrode potential of iron is more negative than nickel so it is negative electrode (anode)

Thus the cell diagram of the cell is $\mathrm{Fe(s)}\,|\,\mathrm{Fe^{2+}(1M)||Ni^{2+}(1M)}\,|\,\mathrm{Ni(s)}$

(a) Reduction occurs at nickel electrode half cell
(b) Half reactions involved are:

At anode: $\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2e}$ …………………….Oxidation
At cathode: $\mathrm{Ni^{2+}(aq) + 2e \rightarrow Ni(s)}$ ……………...…Reduction

(c) The anode is iron.
(d) Electrons flow from iron electrode to nickel electrode.
(e) The potential difference will decrease and hence the voltmeter reading will be decreased too.
(f) At the time cell potential starts, e.m.f = cell potential;

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

Overpotential

In gaseous electrode, the measured e.m.f is greater than the standard (calculated) e.m.f. This is because the accumulation of gaseous molecules on the electrode increases the potential of the ion approaching the electrode hence forming **overpotential.**

Definition of overpotential

This is the potential difference in excess of the potential required to discharge an ion.

Standard e.m.f of galvanic cell and feasibility of reactions

There is important relationship between standard e.m.f and feasibility of the reaction. For the cell reaction of occur the e.m.f must be positive. If the e.m.f is negative, then the reaction occurs in reverse direction. Furthermore:

- The more positive e.m.f the more readily the reaction occurs and vice-versa.
- If there is a factor which increases the easiest for the cell reaction to take place, then the factor is said to increase the e.m.f of the cell in the direction of the reaction.
- If there is a factor which makes more difficulty for the reaction to take place, then the factor is said to decrease the e.m.f of the cell.

Example 7

Given the Daniel cell: $\mathrm{Zn}\,|\,\mathrm{Zn^{2+}(1M)||Cu^{2+}(1M)}\,|\,\mathrm{Cu(s)}$

(a) Calculate the e.m.f of the cell at standard condition
(b) Explain how the e.m.f of the cell would be affected by
  (i) Increasing concentration of Cu^{2+}
  (ii) Increasing concentration of Zn^{2+}

$\left(E_{Zn^{2+}/Zn} = -0.76V;\ E_{Cu^{2+}/Cu} = +0.34V\right)$

Solution

(a) $E^\theta_{cell} = E^\theta_R - E^\theta_L = 0.34V - (-0.76V) = 1.1\ V$

Hence the e.m.f of the cell at standard conditions is 1.1V

(b) From the cell diagram; overall cell reaction is:

$\mathrm{Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)}$ $\qquad E^\theta = 1.1V$

(i) Increasing concentration of Cu^{2+} shifts the position of equilibrium to the right hand side and hence e.m.f of the cell is increased.
(ii) Increasing concentration Zn^{2+} shifts the position of equilibrium to the left hand side and hence e.m.f of the cell is decreased.

Example 8

Predict which of the following reactions are favoured and which are not favoured:

(i) $Fe^{3+} + Cr^{2+} \rightarrow Fe^{2+} + Cr^{3+}$
(ii) $Zn^{2+} + 2Cr^{2+} \rightarrow Zn(s) + 2Cr^{3+}$
(iii) $Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}$
(iv) $2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2H_2O + 2Fe^{3+}$
(v) $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$
(vi) $I_2 + 2F^- \rightarrow 2I^- + F_2$

Given that:

$Cr^{3+} + e \rightarrow Cr^{2+}$ …………………………………………… $E^\theta = -0.408V$

$Zn^{2+} + 2e \rightarrow Zn$ ……………………………………………….. E^θ = -0.76V

$Fe^{3+} + e \rightarrow Fe^{2+}$ …………………………………………….. $E^\theta = 0.771V$

$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ ……………………………………… $E^\theta = 1.776V$

$Sn^{4+} + 2e \rightarrow Sn^{2+}$ ……………………………………………… $E^\theta = 0.150V$

$I_2 + 2e \rightarrow 2I^-$ …………………………………………………. $E^\theta = 0.540V$

$Cl_2 + 2e \rightarrow 2Cl^-$ ……………………………………………… $E^\theta = 1.360V$

$F_2 + 2e \rightarrow 2F^-$ ………………………………………………….. $E^\theta = 2.850V$

$Br_2 + 2e \rightarrow 2Br^-$ ……………………………………………….. $E^\theta = 1.070V$

Solution

(i) Cell diagram according to given cell reaction

$Cr^{2+} | Cr^{3+} || Fe^{3+} | Fe^{2+}$
Then $E^\theta_{cell} = E^\theta_R - E^\theta_L = 0.771V - (-0.408V) = +1.179V$

Since standard e.m.f of the cell is positive, the reaction is spontaneous and hence the reaction is favoured

(ii) Cell diagram according to the given cell reaction is:

$Cr^{2+} | Cr^{3+} || Zn^{2+} | Zn$
Then $E^\theta_{cell} = E^\theta_R - E^\theta_L = -0.760V - (-0.408V) = -0.352V$

Since standard e.m.f. of the cell is negative, the reaction is not spontaneous and hence the reaction is not favoured.

(iii) Cell diagram according to the given cell reaction is;

$Sn^{2+} | Sn^{4+} || Fe^{3+} | Fe^{2+}$
Then $E^\theta_{cell} = E^\theta_R - E^\theta_L = 0.771V - 0.150V = +0.621V$

Since the standard e.m.f of the cell is positive, the reaction is favoured

(iv) Cell diagram according to the given cell reaction is;

$Fe^{2+} | Fe^{3+} || H_2O_2 | H_2O$
Then $E^\theta_{cell} = E^\theta_R - E^\theta_L = 1.776V - 0.771V = +1.005V$

Since the standard e.m.f of the cell is positive, the reaction is favoured

(v) Cell diagram according to the given cell reaction is;

$Br^- | Br_2 || Cl_2 | Cl^-$

Then $E^{\theta}_{cell} = E^{\theta}_{R} - E^{\theta}_{L} = 1.36V - 1.07V = +0.29V$

Since the standard e.m.f of the cell is positive, the reaction is favoured

(vi) Cell diagram according to the given cell reaction is;

$F^{-} \mid F_2 \| I_2 \mid I^{-}$

Then $E^{\theta}_{cell} = E^{\theta}_{R} - E^{\theta}_{L} = 0.54V - 2.85V = -2.31V$

Since the standard e.m.f of the cell is negative, the reaction is not favoured.

Variation of electrode potential with concentration

Increasing concentration of an electrolyte, increases electrode potential of an electrode immersed in the electrolyte; the effect of concentration of electrolyte on the electrode potential is well explained by **Nernst equation.**

The **Nernst equation** is used to find out the electrode potential of an electrode in which the concentration of metal ions in solution is not 1M (and of course if temperature is not 25°C).

If the electrode reaction (reduction in forward reaction) is: $M^{n+}(aq) + ne \rightleftharpoons M(s)$

The reaction quotient for the reaction, Q_c, is given by: $Q_c = \frac{1}{[M^{n+}]}$

Then by Nernst equation: $\mathbf{E = E^{\theta} - \frac{RT}{nF}lnQ_c}$

But lnR_Q = 2.303logQ_c

If follows that: $E = E^{\theta} - \frac{2.303RT}{nF}logQ_c$

Substituting $Q_c = \frac{1}{[M^{n+}]}$, to the Nernst equation gives: $E = E^{\theta} - \frac{2.303RT}{nF}log\frac{1}{[M^{n+}]}$

Where:

E is the electrode potential of an electrode at any temperature dipped in the solution containing its ions at any concentration.

E^{θ} is the standard electrode potential of the electrode

$[M^{n+}]$ is the molar concentration of the ions

R is the gas constant = 8.3143$JK^{-}mol^{-}$

T is the absolute temperature in Kelvin, K

F is the Faraday's constant = 96500 Coulombs

n is the number of electrons involved in the balanced equation of the half reaction

If the standard temperature (25°C or 298K) is maintained, the Nernst equation becomes:

$$E = E^{\theta} - \frac{2.303 \times 8.3143 \times 298}{n \times 96500}log\frac{1}{[M^{n+}]}$$

$$= E^{\theta} - \frac{0.0591}{n}log\frac{1}{[M^{n+}]}$$

Hence if only concentration of ions is altered, the simplified form of Nernst equation become:

$$\mathbf{E = E^{\theta} - \frac{0.0591}{n}log\frac{1}{[M^{n+}]} \text{ or } E = E^{\theta} + \frac{0.0591}{n}log[M^{n+}]}$$

From which it is clearly understood that, when concentration of ions, $[M^{n+}]$ is increased, the electrode potential also increases as explained earlier.

It should be noted that, in writing reaction quotient, Q_c:

- Concentration of solid metal (electrode) does not appear in Q_c expression. Only liquid (aqueous solution) and gases (if any) species should appear in Q_c expression. This is because effective concentration (activity) of the solid metal is taken to be 1(unity)
- Effective molar concentration (activity) of a gas is taken as its partial pressure in atmosphere.

Example 9

What is the half-cell potential for Fe^{3+}/Fe electrode in which concentration of Fe^{3+}ion is 0.1M at 25°C?

$$E^{\theta}_{Fe^{3+}/Fe} = +0.771V$$

Solution

Half-cell reaction: $Fe^{3+}(aq) + 3e \rightarrow Fe(s)$

From which: n = 3 and $Q_c = \frac{1}{[Fe^{3+}]} = \frac{1}{0.1} = 10$

From Nernst equation: $E = E^{\theta} - \frac{0.0591}{n}\log Q_c$

Substituting $E = 0.771 - \frac{0.0591}{3}\log 10 = 0.7513V$

Hence the cell potential of the half-cell is 0.7513V

Example 10

What is the electrode potential of Mg^{2+}/Mg electrode at which concentration of Mg^{2+} is 0.1M at 25°C? $E^{\theta}{}_{Mg^{2+}/Mg} = -2.36V$

Solution

Half-cell reaction: $Mg^{2+}(aq) + 2e \rightarrow Mg(s)$

From which: n = 2 and $Q_c = \frac{1}{[Mg^{2+}]} = \frac{1}{0.1} = 10$

From Nernst equation: $E = E^{\theta} - \frac{0.591}{n}\log Q_c$

Substituting $E = -2.36V - \frac{0.0591}{2}\log 10 = -2.38955V$

Hence the electrode potential is -2.38955V

Example 11

What is the cell potential of the following half-cell at 25°C?

$$Pt,Cl_2(2atm)/\,Cl^-\ (0.1M)$$

Given that: $E^{\theta}_{Cl_2/Cl^-} = 1.36V$

Solution

Half-cell reaction: $Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$

From which: $n = 2$ and $Q_c = \frac{[Cl^-]^2}{P_{Cl_2}} = \frac{(0.1)^2}{2} = 5 \times 10^{-3}$

From Nernst equation; $E = E^{\theta} - \frac{0.0591}{n}\log Q_c$

Substituting $E = 1.36 - \frac{0.0591}{2}\log(5 \times 10^{-3}) = 1.428V$

Hence the cell potential of the half-cell is 1.428V

Example 12

The standard electrode potential of Au^{3+}/Au electrode is +1.42V. At what concentration of Au^{3+} the electrode potential is zero at 25°C?

Solution

Half-cell reaction: $Au^{3+}(aq) + 3e \rightarrow Au(s)$

From which $n = 3$ and $Q_c = \frac{1}{[Au^{3+}]}$

Then from Nernst equation; $E = E^{\theta} - \frac{0.0591}{n}\log Q_c$

Substituting $0 = 1.42 - \frac{0.0591}{3}\log\frac{1}{[Au^{3+}]}$ or $0.0197\log[Au^{3+}] = -1.42$

Or $[Au^{3+}] = \log^{-1}\left(\frac{-1.42}{0.0197}\right) = 8.29 \times 10^{-73}M$

Hence at 25°C, the electrode potential is zero when concentration of Au^{3+} is

$8.29 \times 10^{-73}M$.

Variation of cell potential with concentration

Increasing concentration of anolyte of the electrochemical cell, decreases cell potential of the cell, while increasing concentration of catholyte increases the cell potential.

The cell potential of a cell constructed from non – standard electrodes is given by the following modified form of Nernst equation: $\mathbf{E_{cell} = E^{\theta}_{cell} - \frac{0.0591}{n}\log Q_c \text{ at } 25^{o}C}$

Where:

E_{cell} is the cell potential of the cell

E^{θ}_{cell} is the standard cell potential of the cell = $E^{\theta}_{R} - E^{\theta}_{L}$

n is the number of electrons involved in the balanced equation of the **overall cell reaction**

Q_c is the reaction quotient which is derived from the equation of the **overall cell reaction**

Example 13

A galvanic cell consists of metallic zinc plate immersed in $0.1MZn(NO_3)_2$ solution and metallic plate of lead in $0.02MPb(NO_3)_2$ solution. Calculate the e.m.f cell at 25˚C

$$E^{\theta}_{Zn^{2+}/Zn} = -0.76V;\ E^{\theta}_{Pb^{2+}/Pb} = -0.13V$$

Solution

Cell diagram of given cell: $Zn\,|\,Zn^{2+}(0.1M)||Pb^{2+}(0.02M)\,|\,Pb$

Oxidation half-cell reaction (at anode):

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e$ ……………..……………………(i)

Reduction half-cell reaction (at cathode):

$Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$ ………………………………..…(ii)

Writing overall cell reaction by taking (i) + (ii):

Cell reaction: $Zn(s) + Pb^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Pb(s)$

From which $n = 2$ and $Q_c = \frac{[Zn^{2+}]}{[Pb^{2+}]} = \frac{0.1}{0.02} = 5$

And $E^{\theta}_{cell} = E^{\theta}_{cathode} - E^{\theta}_{anode} = -0.13V - (-0.76V) = 0.63V$

From Nernst equation: $E_{cell} = E^{\theta}_{cell} - \frac{0.0591}{n}\log Q_c$

Substituting $E_{cell} = 0.63 - \frac{0.0591}{2}\log 5 = 0.6093V$

Hence the e.m.f of the cell is 0.6093V

Example 14

What is potential for the cell at 25˚C:

$$Cr\,|\,Cr^{3+}(0.1M)||Fe^{2+}(0.01M)\,|\,Fe$$

Given that: $E^{\theta}_{Cr^{3+}/Cr} = -0.74V$; $E^{\theta}_{Fe^{2+}/Fe} = -0.44V$

Solution

Oxidation half-cell reaction (at anode):

$$Cr(s) \rightleftharpoons Cr^{3+}(aq) + 3e \text{ ……………………………………(i)}$$

Reduction half-cell reaction (at cathode)

$$Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s) \text{ ………………………………..…(ii)}$$

Writing overall cell reaction by taking (i) × 2 + (ii) × 3 to give

$$2Cr(s) + 3Fe^{2+}(aq) + \cancel{6e} \rightleftharpoons 2Cr^{3+}(aq) + 3Fe(s) + \cancel{6e}$$

Where n = 6

Simplifying the above equation by cancelling like terms to give the following cell reaction:

$$2Cr(s) + 3Fe^{2+}(aq) \rightleftharpoons 2Cr^{3+}(aq) + 3Fe(s)$$

From which $Q_c = \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} = \frac{(0.1)^2}{(0.01)^3} = 10000$

And $E^{\theta}_{cell} = E^{\theta}_{cathode} - E^{\theta}_{anode} = -0.44V - (-0.74V) = 0.3V$

From Nernst equation; $E_{cell} = E^{\theta}_{cell} - \frac{0.0591}{n}\log Q_c$

Substituting $E_{cell} = 0.3 - \frac{0.0591}{6}\log 10000 = 0.2606V$

Hence the cell potential is 0.2606V

Example 15

What is the potential for the cell at 25˚C:

$$Ag\,|\,Ag^{+}(0.01M)||Cl^{-}(0.2M)\,|\,Cl_2(0.5atm), Pt$$

Given that: $E^{\theta}_{Ag^{+}/Ag} = 0.8V$; $E^{\theta}_{Cl_2/Cl^{-}} = 1.36V$

Solution

Oxidation half-cell reaction (at anode): $Ag(s) \rightleftharpoons Ag^{+}(aq) + e$ ………………………(i)

Reduction half-cell reaction (at cathode): $Cl_2(g) + 2e \rightleftharpoons 2Cl^{-}$ ………..…………………(ii)

Writing overall cell reaction by taking (i) × 2 + (ii)

Cell reaction: $2Ag(s) + Cl_2(g) \rightleftharpoons 2\,Ag^{+}(aq) + 2Cl^{-}(aq)$

Where $n = 2$ and $Q_c = \frac{[Ag^{+}]^2\,[Cl^{-}]^2}{P_{Cl_2}} = \frac{(0.01)^2 \times (0.2)^2}{0.5} = 8 \times 10^{-6}$

And $E^{\theta}_{cell} = E^{\theta}_{cathode} - E^{\theta}_{anode} = 1.36V - 0.8V = 0.56V$

From Nernst equation: $E_{cell} = E^{\theta}_{cell} - \frac{0.0591}{n}\log Q_c$

Substituting $E_{cell} = 0.56 - \frac{0.0591}{2}\log(8 \times 10^{-6}) = 0.7106V$

Hence the potential for the cell is 0.7106V

Concentration cells

If two plates of the same metal are dipped separately into two solutions of the same electrolyte at different concentration and the solutions are connected with a salt bridge, the whole arrangement is found to act as galvanic (electrochemical) cell, why? This is because at different concentration of the electrolyte, the two half cells have different electrode potential.

The plate in more dilute solution has lower electrode potential and hence it acts as anode (negative electrode) while the plate in more concentrated solution has greater electrode potential thus acting as cathode.

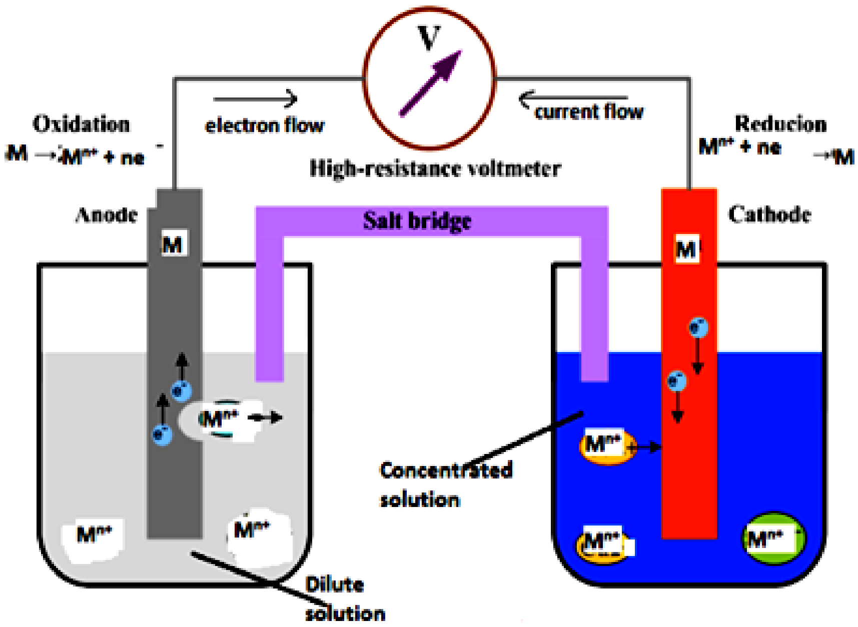


Figure 21.4 Concentration cell

Anode reaction: $M(s) \rightleftharpoons M^{n+}(Dilute) + ne$ **(The solid electrode dissolves in solution at anode half-cell)**

Cathode reaction: M^{n+} (concetrated) $+ ne \rightleftharpoons M(s)$ **(The solid deposits at cathode half-cell)**

Definition of concentration cell

This *is the electrochemical cell which consists of the same electrodes and the same electrolytes at different concentration which are connected by a salt bridge.*

Calculations of cell potential (e.m.f) of concentration cells

By using Nernst equation:

$$E = E^{\theta} - \frac{0.0591}{n}\log Q_c$$

If M_d respesents $[M^{n+}$ (dilute)$]$

M_c respesents $[M^{n+}$ (concentrated)]

Then $E_{anode} = E_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{M_d}$

And $E_{cathode} = E_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{M_c}$

Using $E_{cell} = E_{cathode} - E_{anode}$

Then $E_{cell} = (E_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{M_c}) - (E_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{M_d})$

Thus $E_{cell} = \frac{0.0591}{n}\log\frac{1}{M_d} - \frac{0.0591}{n}\log\frac{1}{M_c}$

Or $E_{cell} = \frac{0.0591}{n}\left(\log\frac{1}{M_d} - \log\frac{1}{M_c}\right)$

$= \frac{0.0591}{n}\log\left(\frac{1}{M_d} \div \frac{1}{M_c}\right) = \frac{0.0591}{n}\log\frac{M_c}{M_d}$

Hence e.m.f of concentration cell is given by: $\mathbf{E_{cell} = \frac{0.0591}{n}\log\left(\frac{M_c}{M_d}\right)}$

Where **n is the number of electrons involved in the cell reaction = oxidation state of the metal ion.**

Example 16

What is the cell potential of the cell at 25˚C: $Ni\,|\,Ni^{2+}(0.01M)||Ni^{2+}(0.1M)\,|\,Ni$

Given that: $E^{\theta}_{Ni^{2+}/Ni} = -0.25V$

Solution

$$E_{cell} = \frac{0.0591}{n}\log\left(\frac{M_c}{M_d}\right)$$

Where: n = 2, $M_c = 0.1M$ and $M_d = 0.01M$

Then $E_{cell} = \frac{0.0591}{n}\log\left(\frac{0.1}{0.01}\right) = 0.02955V$

Hence the cell potential is 0.02955V

Example 17

A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of $10^{-6}M$ hydrogen ions. The e.m.f of the cell is a 0.118V. Calculate the concentration of hydrogen ions at the positive electrode

Solution

The positive electrode is the electrode dipped in more concentrated solution. So it is asked to find concentration more concentrated electrolytic solution, M_c

Using $E_{cell} = \frac{0.0591}{n}\log\left(\frac{M_c}{M_d}\right)$

But oxidation state of H^+ is 1, i.e. n = 1

Substituting $0.118 = \frac{0.0591}{1}\log\left(\frac{M_c}{10^{-6}}\right)$

$\frac{M_c}{10^{-6}} = \log^{-1}\left(\frac{0.118}{0.0591}\right) = \log^{-1}(2) = 100$

Or $M_c = 10^{-6} \times 100 = 10^{-4}M$

Hence concentration of hydrogen ions at positive electrode is $1 \times 10^{-4}moldm^{-3}$

Determination of pH of solution by using electrochemical cells

pH of hydrogen ions (H^+) solution can be determined without using pH meter if the electrochemical cell (concentration electrochemical cell) with the following features is constructed:

- One of the half-cell consists of standard electrode (electrode dipped in 1M solution of its ions at 25˚C).
- Another half-cell which is the hydrogen electrode (adsorbed in platinum at pressures of 1atm) dipped in unknown concentration of its ions, (H^+) whose pH is to be determined.
- The cathode half-cell is the standard electrode if the electrode has positive electrode potential i.e. if the standard electrode has positive $E^{\theta}$the cell diagram is $Pt, H_2(1atm) \mid H^+(aq) \| M^{n+}(1M) \mid M(s)$ where M is the standard electrode
- The anode half-cell is the standard electrode if the electrode has negative electrode potential and the cell diagram become $M(s) \mid M^{n+}(1M) \| H^+(aq) \mid H_2(1atm), Pt$.
- After determination of cell potential of the cell (through voltmeter reading), pH of unknown concentration of H^+ (hydrogen ions) can be calculated.

Example 18

The measured voltage of the cell: $Pt(s), H_2(g, 1atm) \mid H^+(aq) \| Ag^+(aq, 1M) \mid Ag(s)$

is 0.900V at 25°C. Given $E^{\theta}_{Ag^+/Ag} = 0.8V$; Calculate the pH of the solution

Solution

Oxidation half-cell reaction (at anode):

$$H_2(g) \rightleftharpoons 2\,H^+(aq) + 2e \text{ ……………………………………… (i)}$$

Reduction half-cell reaction (at cathode):

$$Ag^+(aq) + e \rightleftharpoons Ag(s) \text{ ………………………………………. (ii)}$$

Writing overall cell reaction by taking (i) + 2(ii);

Cell reaction: $H_2(g) + 2Ag^+(aq) \rightleftharpoons 2H^+(aq) + 2Ag(s)$

From which $n = 2$ and $Q_c = \frac{[H^+]^2}{(P_{H_2})\,[Ag^+]^2} = \frac{[H^+]^2}{1 \times 1^2} = [H^+]^2$

And $E^{\theta}_{cell} = E^{\theta}_{cathode} - E^{\theta}_{anode} = 0.8V - 0V = 0.8V$

By Nernst equation; $E_{cell} = E^{\theta}_{Cell} - \frac{0.0591}{n}\log Q_c$

Substituting $0.9 = 0.8 - \frac{0.0591}{2}\log[H^+]^2$; $0.1 = -0.0591\log[H^+]$

$$-\log[H^+] = \frac{0.1}{0.0591} = 1.69\text{; but } -\log[H^+] = pH$$

Hence pH of the solution is 1.69

Equilibrium constant of a cell

An electrochemical (voltaic) cell generates electricity only when the cell potential is positive. The use of the electrochemical cell increases the concentration of the electrolyte in the anodic compartment and decreases the concentration the concentration of the electrolyte in the cathodic compartment as the following general cell reaction suggests:

$$P(s) + \underbrace{Q^{n+}(aq)}_{\text{Electrolyte at Cathode (catholyte)}} \rightleftharpoons \underbrace{P^{n+}}_{\text{Electrolyte at anode (anolyte)}} + Q(s) \text{ … … … … …. } E_{cell}$$

From the above reversible cell reaction, it is clearly understood that: at the start of cell operation, forward reaction is highly favoured thus making the cell potential to be at maximum. As the cell operation proceeds, $[P^{n+}]$ increases and $[Q^{n+}]$ decreases and the backward reaction starts to take place. ***What is the effect of this in the cell potential?***

This results in a gradual decrease in the cell potential and ultimately an equilibrium reaches where the cell potential is zero and the cell stops producing electricity. When this happens, the cell reaction is said to be in equilibrium.

From the simplified Nernst equation: $E_{cell} = E^{\theta}_{Cell} - \frac{0.0591}{n}\log Q_c$

When the cell does not generate e.m.f, its cell potential is zero and the reaction quotient become equal to the equilibrium constant of the cell, K_c.

That is at equilibrium: $E_{cell} = 0$ and $Q_c = K_c$

Then 0 = $E^{\theta}_{cell} - \frac{0.0591}{n}\log K_c$

Hence $\mathbf{E^{\theta}_{cell} - \frac{0.0591}{n}\log K_c}$

From the above equation, K_c can be easily understood that: If the K_c value of a cell is very large then the cell lasts long (continue operating for long time)

Example 19

Calculate the equilibrium constant for the reaction at 25˚C,

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

The standard cell potential for the reaction at 25˚C is 0.46V

Solution

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

Cathode reaction: $\left(Ag^{+}(aq) + e \rightleftharpoons Ag(s)\right) \times 2$

Cell reaction: $Cu(s) + 2\,Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2\,Ag(s)$

Thus $n = 2$

Substituting $0.46 = \frac{0.0591}{2}\log K_c$; $\log K_c = 15.567$

$K_c = \log^{-1}(15.567) = 3.69 \times 10^{15}$

Hence the equilibrium constant for the cell is 3.69×10^{15}

(The very large value of K_c implies that the operating time of the cell is large .i.e. the cell lasts long as the cell reaction is far forward)

CONSTRUCTION OF ELECTROCHEMICAL SERIES

This is the another application of electrode potential.

What is the electrochemical series?

This is the arrangement of elements (metal and non – metal) in order of increasing reduction electrode potential.

Electrochemical series is useful determination of:

- Reactivity of metal
- Reactivity of non-metals
- Displacement of hydrogen from acids by metal
- Efficiency of zinc and tin as protective against rusting of iron

Reactivity of metals

Metals react by losing electrons. Thus metals are reducing agents and themselves are oxidised in the reaction by losing electrons. So reactivity of metals increases in the same order of their reducing strengths.

- Metals with more negative (or less positive) electrode potential are stronger reducing agents. Thus metals which are found at the top side electrochemical series are stronger reducing agents.
- Being stronger reducing agents, these metals are stronger electropositive and more reactive so that they displace weaker electropositive metals which are found below the electrochemical series from their salt solution.

For example zinc being above copper in the electrochemical series, it is stronger reducing agent and more reactive so that it displaces Cu^{2+} from salt of copper like $CuSO_4$.

i.e. $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

Or ionically $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ and hence the **coating** of copper metal on the zinc metal is observed.

While $Cu(s) + Zn^{2+}(aq) \rightarrow$ No reaction

Example 20

Below is the part of electrochemical series:

$$Mg^{2+}/Mg \rightarrow -2.38V$$
$$Zn^{2+}/Zn \rightarrow -0.76V$$
$$Pb^{2+}/Pb \rightarrow -0.13$$
$$Cu^{2+}/Cu \rightarrow +0.34V$$

What happen when:

Zinc metal is dipped into Pb^{2+}?
Copper metal is dipped into Mg^{2+}?
Solution

Having more negative electrode potential, zinc metal displaces Pb^{2+} from the solution (reduces Pb^{2+} to Pb) and the coating of lead metal on the zinc metal is observed.

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

Nothing happen because copper has greater electrode potential than magnesium (Cu is below Mg electrochemical series) so it cannot displace Mg^{2+} from the solution.

$$Cu(s) + Mg^{2+}(aq) \rightarrow \text{No reaction}$$

Reactivity of non – metal

In most cases, non-metal reacts by gaining electrons. Gaining of electrons is reduction. So in other words we can say that non - metal are oxidising agents and hence their reactivity increases in the same order to their oxidising strengths. Being oxidising agents, non-metals have positive electrode potential and are found at the bottom side of electrochemical series.

- Non – metals with more positive electrode potential are stronger oxidising agents. Thus non – metals which are found in more bottom side of electrochemical series are stronger oxidising agents.
- Being stronger oxidising agents, these non – metals are more reactive so that they displace weaker electronegative non – metals which are found above them in electrochemical series from their salt solution.

For example chlorine being below iodine in electrochemical series, it is stronger oxidising agent and more reactive so that it displaces I^- from salt of iodine like KI.

$Cl_2 + 2KI \rightarrow 2KCl + I_2$

Or ionically $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$

While $I_2 + 2Cl^- \rightarrow$ No reaction

Displacement of hydrogen from acid by metals

Metals which are found above hydrogen in electrochemical series have negative electrode potential. So these metals are stronger reducing agents so that they can displace hydrogen from dilute acids by reducing H^+ of the acids to H_2 and themselves become oxidised. For example, zinc being above hydrogen in electrochemical series, has negative electrode potential and greater reducing strength so that it and can displace hydrogen from dilute sulphuric according to the following equation:

$$Zn(s) + H_2SO_4\,(dil) \rightarrow ZnSO_4 + H_2$$

Or ionically $Zn(s) + 2\,H^+(aq) \rightarrow Zn^{2+}\,(aq) + H_2(g)$

On another hand metals which are found below hydrogen in electrochemical series have positive electrode potential. So these metals are weaker reducing agent so that they cannot displace (reduce) hydrogen from dilute acids. For example, copper being below hydrogen in electro chemical series cannot displace hydrogen from dilute sulphuric acid.

$$Cu(s) + H_2SO_4(dil) \rightarrow \text{No reaction}$$

However:

- Concentrated sulphuric acid being good oxidising agent, can oxidize Cu to $Cu^{2+}$and itself become reduced to SO_2 thus reacting with copper according to the following equation:

$$Cu(s) + 2H_2SO_4(conc) \rightarrow CuSO_4(aq) + SO_2(g) + 2H_2O(l)$$

- In ionic hydride (a compound which consist of strong electropositive metal and hydrogen only like KH), hydrogen acts as non – metal so that it can be displaced from the salt by any non – metal with positive electrode potential which are stronger oxidising agent than hydrogen.

For example: $2KH + Cl_2 \rightarrow 2KCl + H_2$

Efficiency of zinc and tin as protective against rusting of iron

Before comparing the efficiency of zinc and tin in preventing iron rusting, it is important to answer the following two questions firstly:

1. What is rusting of iron?
2. How rusting process occurs?

Rust is the hydrated iron (III) oxide, $Fe_2O_3\,.XH_2O$. Thus rusting of iron is the formation of hydrated iron (III) oxide, $Fe_2O_3\,.XH_2O$ by iron.

Rusting of iron occurs in the following procedures:

Step 1: Oxidation of Fe into Fe^{2+}

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

Step 2: Formation of $Fe(OH)_2(s)$

$Fe^{2+}(aq)$ combines with OH^- from water (H_2O) i.e. $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

Then $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$

Step 3: Formation of $Fe(OH)_3(s)$

$$4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$$

Step 4: Decomposition of $Fe(OH)_3(s)$

$$2Fe(OH)_3(s) \rightarrow Fe_2O_3(s) + 3H_2O$$

Step 5: Formation of hydrated $Fe_2O_3(s)$ (rust)

$$Fe_2O_3 + XH_2O \rightarrow \underbrace{Fe_2O_3.XH_2O}_{\textbf{Rust}}$$

Rust is easily recognised by its reddish brown colouration

Comparison:

Electrode potentials for Fe, Sn and Zn are given below:

$$E^{\theta}_{Zn^{2+}/Zn} = -0.76V$$

$$E^{\theta}_{Fe^{2+}/Fe} = -0.44V$$

$$E^{\theta}_{Sn^{2+}/Sn} = -0.14V$$

First case: If zinc is used as a protective

Zinc having more negative electrode (reduction) potential, it undergoes oxidation more readily than iron.

- Thus the reaction Zn(s) → $Zn^{2+}(aq) + 2e$ occurs in preference to Fe(s) → $Fe^{2+} + 2e$.

This makes electrons to move from zinc surface to iron surface and eventually the zinc surface become the anode and the iron surface become the cathode.
In pressure of water(H_2O); OH^- and H^+ from self ionisation of water migrate towards anode and cathode respectively.

At anode (zinc surface): $Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2$

At cathode (iron surface): $2H^+(aq) + 2e \rightarrow H_2(g)$

Hence zinc is a good protective. Any scratch which exposes the iron surface to the atmosphere does not result into oxidation of the iron.

Second case: If tin is used as a protective

Iron having more negative electrode potential, it undergoes oxidation more readily than tin.

- Thus the reaction Fe(s) → $Fe^{2+}(aq) + 2e$ occurs in the preference to Sn(s) → $Sn^{2+}(aq) + 2e$.

This makes electron to move from iron surface to tin surface and eventually the iron surface become the anode and the tin surface become the cathode.
Thus $OH^-$and H^+ from self ionisation of water migrates towards anode and cathode respectively.

At anode (iron surface): $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2$

At cathode (tin surface): $2H^+(aq) + 2e \rightarrow H_2(g)$

Formation of $Fe(OH)_2$ (**step 2** of the rusting process) at anodic area allows the rusting to continue. So any scratch which expose iron surface to the atmosphere, results into rusting of iron and hence tin is not good protective.

DIGGING DEEPER EXERCISE 21

EXERCISE 21A: BINDER QUESTIONS

Question 1

A cell is formed by dipping Zn rod in 0.01 M Zn^{2+}solution and Ni rod in 0.5M Ni^{2+} solution. The standard elect rode potential of Zn and Ni are -0.76 V and -0.25Vrespectively.

(a) Write the cell representation
(b) Write cell reaction
(c) Calculate the e.m.f of the cell.

Question 2

(a) Use the data below to explain why copper(I) ions disproportionate in aqueous solution, but silver(I) ions do not.

	E^{θ}/V
$Ag^{2+}(aq) + e \longrightarrow Ag^{+}(aq)$	+1.98
$Ag^{+}(aq) + e \longrightarrow Ag(s)$	+0.80
$Cu^{2+}(aq) + e \longrightarrow Cu^{+}(aq)$	+0.34
$Cu^{+}(aq) + e \longrightarrow Cu(s)$	+0.52

(b) In the light of the information in (a), suggest what you might observe when copper (I) oxide is added to excess dilute sulphuric acid. Write an equation for the reaction.

Question 3

The standard reduction potential of Cu^{2+}/Cu and Ag^{+}/Ag electrodes are 0.337V and 0.799V respectively. Construct a galvanic cell using these electrodes so that its E^{θ}_{cell} is positive. For what $[Ag^{+}]$ will the e.m.f of cell be zero if $[Cu^{2+}]$ is 0.01M?

Question 4

Calculate e.m.f of the following cell: $Zn(s) \mid Zn^{2+}(0.1M) \parallel Sn^{2+}(0.001M \mid Sn(s)$

Given that: $E^{\theta}_{(Zn^{2+}/Zn)} = -0.76V$; $E^{\theta}_{(Sn^{2+}/Sn)} = -0.14V$

Question 5

Calculate the e.m.f of the cell: $Zn(s) \mid Zn^{2+}$ (0.024 M) $\parallel$ Zn^{2+} (2.4 M) $\mid Zn(s)$

EXERCISE 21B: REAL QUESTIONS

Question 6

Predictions from E^{θ} values concerning the feasibility of a reaction are not always realised in real life. Suggest reasons for this.

Question 7

Use the data below to explain concisely why zinc is used in preference to tin for coating steel which is used to manufacture cars.

	E^{θ}/V
$Sn^{2+}(aq) + 2e \longrightarrow Sn(s)$	-0.14
$Fe^{2+}(aq) + 2e \longrightarrow Fe(s)$	-0.44
$Zn^{2+}(s) + 2e \longrightarrow Zn(s)$	-0.76

Question 8

The position of some metals in the electrochemical series in the decreasing order of electropositive characters is given:

$$Mg > Al > Zn > Cu > Ag$$

Can copper spoon be used to stir a solution of aluminium? Explain.

Question 9

Study the following electrode potentials then answer question which follows:

$E^{\theta}_{Cu^{2+}/Cu} = +0.34V$

$E^{\theta}_{Ni^{2+}/Ni} = -0.25V$

$E^{\theta}_{Fe^{2+}/Fe} = -0.44V$

(i) What would happen if a nickel spatula were used to stir a solution of copper (II) sulphate?

(ii) Can 1M ferrous sulphate solution be stored in a nickel container? Explain your answer.

Question 10

Kipute read the following statement in the chemistry textbook; *"A salt bridge is inverted U – tube containing an inert paste of potassium chloride and agar – gel."* Unfortunately, she was unable to understand the use of potassium chloride and agar-gel. If **Kipute** came to you and asked for your help, what would be your explanation?

EXERCISE 21C: HOT QUESTIONS

Question 11

$$\mathbf{Sr(s) + Mg^{2+}(aq) \longrightarrow Sr^{2+}(aq) + Mg(s)}$$

Consider the reaction represented above that occurs at 25°C. All reactants and products are in their standard states. The value of the equilibrium constant, K_c, for the reaction is 4.2×10^{17} at 25°C.

(a) Predict the sign of the standard cell potential, E^{θ}, for a cell based on the reaction. Explain your prediction.
(b) Identify the oxidising agent for the spontaneous reaction.
(c) If the reaction were carried out at 60°C instead of 25°C, how would the cell potential change? Justify your answer.
(d) How would the cell potential change if the reaction were carried out at 25°C with a 1.0 M solution of $Mg(NO_3)_2$ and a 0.10 M solution of $Sr(NO_3)_2$? Explain.
(e) When the cell reaction in part (d) reaches equilibrium, what is the cell potential?

Question 12

Consider the electrochemical cell below:

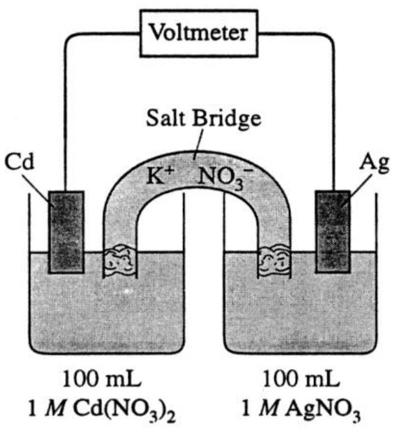


Figure 21.5 Electrochemical cell for question 8

(a) Write the balanced net-ionic equation for the spontaneous reaction that occurs as the cell operates, and determine the cell voltage.
(b) In which direction do anions flow in the salt bridge as the cell operates? Justify your answer.
(c) If 10.0 mL of 3.0-molar $AgNO_3$ solution is added to the half-cell on the right, what will happen to the cell voltage? Explain.
(d) If 1.0 grams of solid NaCl is added to each half-cell, what will happen to the cell voltage? Explain.
(e) If 20.0 mL of distilled water is added to both half-cells, the cell voltage decreases. Explain.

Given that:

$$Cd^{2+}(aq) + 2e \longrightarrow Cd(s);\ E^{\theta} = -0.4V$$

$$Ag^{+}(aq) + e \longrightarrow Ag(s);\ E^{\theta} = +0.8V$$

Question 13

Calculate the equilibrium constant for the Daniel cell at 25°C, if standard oxidation potential for Zn electrode is +0.765V and for copper electrode is −0.337 V.

Question 14

Calculate equilibrium constant for the reaction of the following cell at 25°C

$$Zn(s) \mid Zn^{2+}(0.01M) \parallel Fe^{3+}(0.001M) \mid Fe^{2+}(aq)$$

Given that standard e.m.f of the cell is 1.71V

Question 15

The standard cell potential, E^{θ}, for the reaction: $Zn^{2+} + Fe \rightleftharpoons Zn + Fe^{2+}$is $-0.353V$. If a piece of iron is placed in a 1M Zn^{2+} solution, what is the equilibrium concentration of Fe^{2+}?

Question 16

The standard reduction potentials, E^{θ}, for some electrodes are listed below. This data should be used, where appropriate, to help answer the questions that follow.

	E^{θ}/V
$Mg^{2+}(aq) + 2e \longrightarrow Mg(s)$	-2.38
$Fe^{2+}(aq) + 2e \longrightarrow Fe(s)$	-0.44
$I_2(aq) + 2e \longrightarrow 2I^-(aq)$	$+0.54$
$Fe^{3+}(aq) + e \longrightarrow Fe^{2+}(aq)$	$+0.77$
$Br_2(l) + 2e \longrightarrow 2Br^-(aq)$	$+1.07$
$Cl_2(g) + 2e \longrightarrow 2Cl^-(aq)$	$+1.36$

(a) Give the formula of the species given in the data which, under standard conditions, is:
   (i) The most powerful reducing agent;
   (ii) The most powerful oxidising agent.

(b) Which of the halogens listed would oxidise $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ under standard conditions?

(c)
   (i) Write an equation to show the reaction that occurs when chlorine is bubbled into a solution containing bromide ions. Give a reason why you would expect the reaction you suggest.
   (ii) Give an industrial application of this reaction.

Chapter 22

ELECTROLYSIS AND ELECTROLYTIC CONDUCTION

ELECTROLYSIS

The term **electrolysis** comes from two words: **electro** from **electricity** and **lysis** which means dissociation. Electrolysis involves dissociation by using electric current. In this process, electromotive force is used to carry out a non – spontaneous redox chemical reaction. The setup used to serve this purpose is known as **electrolytic cell**.

Electrolytic cell uses electromotive force to produce non – spontaneous redox reaction in contrast to electrochemical cell which use spontaneous redox reaction to produce electromotive force.

By definition; **electrolysis** *is the decomposition of an electrolyte or formation of free elements from the electrolytic solution by passage of an electric current through it (the electrolyte).*

- Electrolysis takes place inside a device which is known as **electrolytic cell** or **voltameter**.

Definition of electrolytic cell

This is a device (vessel) in which electric current is used to produce chemical reaction.

What electrolytic cells consist of?

An electrolytic cell is a container made of glass, a metal or any other material and contains a substance (compound) called electrolyte either is solution or molten state. Two metallic plates called electrodes (carbon rods can also be used) are dipped in the liquid (solution or molten). One electrode is connected to the positive terminal and the other to the negative terminal of a battery by metallic wire.

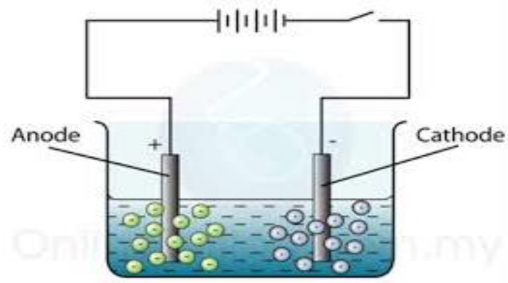


Figure 22.1 Electrolytic cell

Table 22.1 Differences between electrolytic and electrochemical cells

ELECTROCHEMICAL CELL		ELECTROLYTIC CELL	
	Definition		Definition
	Uses chemical reactions to produce electric current.		Uses electric current to produce chemical reactions.
	Anode is negative electrode while cathode is positive electrode.		Anode is positive electrode while cathode is negative electrode.
	Electrons flow from the negative terminal to the positive terminal.		Electrons flow from the negative battery terminal to the negative cathode.
	Chemical reaction is spontaneous.		Chemical reaction is forced by applying a voltage - it is not spontaneous.

Faraday's laws of electrolysis

Faraday's first law of electrolysis

It states that: *The mass of substance liberated by electrolysis is directly proportional to the quantity of electricity which is passed.*

The quantity of electricity, Q, is measured in coulombs (C) such that: $Q = It$

Where: I is current in amperes (A), t is time in seconds (s)

Thus from the law: $m \propto Q$ or $m \propto It$

Introducing the constant for proportionality, the equation become: $m = ZIt$ or $m = ZQ$

Where Z, is the proportionality constant which is known as **electrochemical equivalent of an element (E.C.E)** whose value depends on the nature of a substance

Definition of electrochemical equivalent of an element

This is the mass of the element liberated by the passage of one coulomb of electricity i.e. one ampere for one second.

Thus $Z = \frac{m}{Q}$ or $Z = \frac{m}{It}$

Faraday's second law of electrolysis

It states that: *When the same quantity of electricity is passed through different electrolytes, the masses of the different substances liberated are directly proportional to their equivalent weights.*

Where equivalent weight is given by the following formula:

$$\text{Equivalent weight, E} = \frac{\text{Atomic mass}}{\text{Magnitude of ionic charge}}$$

Warning! The above formula does not give general definition of equivalent weight. Refer to the **chapter 5** of this book to get the general definition.

Relationship between equivalent weight (E) and electrochemical equivalent of an element

Assuming the same amount of electricity Q is passed through two different electrolytes such that:

m_1 is the mass of substance liberated in the first electrolytic cell,

m_2 is the mass of substance liberated in the second electrolytic cell.

Then **from the Faraday's first law of electrolysis:** $m \propto Q$ or $m = ZQ$

Then $m_1 = Z_1Q$ and $m_2 = Z_2Q$

Then $\frac{\mathbf{m_1}}{\mathbf{m_2}} = \frac{\mathbf{Z_1}}{\mathbf{Z_2}}$

(Is the form of the Faraday's first law if there is passage of the same quantity of electricity in the two electrolytes).

But **from the Faraday's second law of electrolysis:**

$m \propto E$ or $m = kE$ where k is the proportionality constant

Then $m_1 = kE_1$ and $m_2 = kE_2$

It follows that: $\frac{\mathbf{m_1}}{\mathbf{m_2}} = \frac{\mathbf{E_1}}{\mathbf{E_2}}$ (Is another form of the Faraday's second law)

Combining Faraday's first and second law by substituting;

$$\frac{E_1}{E_2} \text{ for } \frac{m_1}{m_2} \text{ in } \frac{m_1}{m_2} = \frac{Z_1}{Z_2} \text{ gives } \frac{\mathbf{E_1}}{\mathbf{E_2}} = \frac{\mathbf{Z_1}}{\mathbf{Z_2}}$$

Alternatively the above relationship can be re-written as; $\frac{E_1}{Z_1} = \frac{E_2}{Z_2} = \text{constant}$

That is $\frac{E}{Z}$ is constant and the constant is known as **Faraday's constant, F**

Hence $\mathbf{F} = \frac{\mathbf{E}}{\mathbf{Z}}$

But $Z = \frac{m}{Q}$

Then substituting $\frac{m}{Q}$ for Z in $F = \frac{E}{Z}$ gives $\mathbf{F} = \frac{\mathbf{EQ}}{\mathbf{m}}$

The last equation is the summation of Faraday's first law and Faraday's second law of electrolysis.

Definition of Faradays constant

Faraday constant *is the quantity of electricity that passes when one mole of univalent element (or half a mole of a divalent element, etc.) is discharged or dissolved in electrolysis.* Its value is 96500C i.e. **1F = 96500C.**

Calculations involving Faraday's laws of electrolysis

Example 1

The electrochemical equivalent of silver is 0.00112gC^{-1}. What mass of silver is deposited by the passage of a steady current of 0.5ampere for 1hour in a silver plating bath.

Solution

Using $m = ZIt = 0.00112 \times 0.5 \times 60 \times 60\text{g} = 2.016\text{g}$

Hence mass of silver deposited is 2.016g

Example 2

0.198g of copper is deposited on a cathode in 40 minutes by passing a steady current of 0.25ampere through copper (II) sulphate solution. Calculate the electrochemical equivalent of copper.

Solution

Using $Z = \frac{m}{Q} = \frac{m}{It}$

Where m = 0.198g, I = 0.25A and t = 40min = 40 × 60s

Substituting $Z = \frac{0.198}{0.25 \times 40 \times 60}\text{gC}^{-1} = 3.3 \times 10^{-4}\text{gC}^{-1}$

Hence the electrochemical equivalent of copper is $3.3 \times 10^{-4}\text{gC}^{-1}$

Example 3

A steady current of 0.27A passed for half an hour in a water voltameter liberated 56cm^3 of hydrogen at s.t.p.

(a) Calculate the electrochemical equivalent of hydrogen
(b) What are the electrochemical equivalents of:
  (i) Oxygen
  (ii) Aluminium

Solution

(a) **At s.t.p:**

Mass of hydrogen gas in 22400cm^3 (22.4dm^3) is 2g

Thus mass of hydrogen gas in $56\text{cm}^3 = \frac{56}{22400} \times 2\text{g} = 5 \times 10^{-3}\text{g}$

Whence mass of hydrogen liberated in electrolysis is $5 \times 10^{-3}\text{g}$

Using $Z = \frac{m}{Q} = \frac{m}{It} = \frac{5\times10^{-3}}{0.27\times0.5\times3600}gC^{-1} = 1.0288 \times 10^{-5}gC^{-1}$

Hence electrochemical equivalent of hydrogen is $1.0288 \times 10^{-5}gC^{-1}$.

(a) Atomic mass of hydrogen = 1

Magnitude of charge of H^+ = 1

Then equivalent weight of hydrogen, $E_1 = \frac{1}{1} = 1$

Atomic mass of oxygen = 16

Magnitude of charge of O^{2-} = 2

Then equivalent weight of oxygen, $E_2 = \frac{16}{2} = 8$

Atomic mass of aluminium = 27

Magnitude of charge of $Al^{3+} = 3$

Then equivalent weight of aluminium $E_3 = \frac{27}{3} = 9$

But electrochemical equivalent of hydrogen, $Z_1 = 1.0288 \times 10^{-5}gC^{-1}$

And $\frac{E}{Z} = \text{constant}$

Then: (i) $\frac{E_1}{Z_1} = \frac{E_2}{Z_2}$; $\frac{1}{1.0288\times10^{-5}} = \frac{8}{Z_2}$; $Z_2 = 8.2304 \times 10^{-5}gC^{-1}$

Hence electrochemical equivalent of oxygen is $8.2304 \times 10^{-5}gC^{-1}$

(ii) $\frac{E_1}{Z_1} = \frac{E_3}{Z_3}$; $\frac{1}{1.0288\times10^{-5}} = \frac{9}{Z_3}$; $Z_3 = 9.2592 \times 10^{-5}gC^{-1}$

Hence electrochemical equivalent of aluminium is $9.2592 \times 10^{-5}gC^{-1}$

Example 4

What volume of hydrogen at 15°C and $100700Nm^{-2}$ (755mmHg) would be liberated in a water voltameter by the passing one ampere for 30minutes?

Solution

Hydrogen is liberated at cathode according to the following equation: $2H^+(aq) + 2e \rightarrow H_2(g)$

From which 2F = 2 × 96500C or 193000C liberates 2g of H_2

Then 1 × 30 × 60C or 1800C liberates $\frac{1800}{193000} \times 2g = 0.01865g$ of H_2

From ideal gas equation; $PV = \frac{m}{M_r}RT$

Or $V = \frac{mRT}{PM_r} = \frac{0.01865\times0.082\times288\times760}{755\times2}dm^3 = 0.22168dm^3$ or $221.68cm^3$

Hence volume of hydrogen gas liberated is $221.68cm^3$

Applications of electrolysis

Electrolysis has various applications including:

- Electroplating of metals
- Electro – refining metals
- Extraction of metals
- Production of some non-metal elements and compounds

Electroplating of metals

Electroplating *is a process whereby a thin coating of desired material is applied on a required material*. This is mostly done on stainless steel to prevent rusting, or on some decorative items, so that they look attractive. On stainless steel, generally nickel-chromium plating is done. On decorative items, such as spoons, plates, jewellery items, silver, gold or other plating is done. Electroplating is cheap and cost effective. It enhances the life of the object and makes it look better in appearance.

The following method is adapted:

- First the item to be electroplated is smoothened and cleaned thoroughly. It should not have any oily or dirt marks on it.
- An electrolyte is selected whose ions are required to be deposited on the item.
- Direct current is preferred to alternating current, as alternating current may result in non-smooth deposit.
- The item to be electroplated forms the anode or cathode of the electrolytic cell. **This is the drawback of the electroplating process. The item has to be electrically conducting, or has to be made electrically conducting.**
- For a smooth coating, the electrolytic process has to be optimized for time, temperature and current in the cell.

Electro-refining of metals

Similar to the process of electro-deposition, electrolysis can be used to **purifying metals** that are obtained from the ores. The process is known as electro-refining of metals. The metals that are generally refined by this process are Zn, Ag, Ni, Cu, Pb, Al, etc.

Extraction of metals

Extraction of metals by the process of electrolysis is known as **electro-metallurgy.** This process is used in case highly reactive metals such as sodium. An ore containing sodium is used in a molten form. This forms the electrolyte. Anode and cathodes are generally carbon rods or steel. The Na atoms get attracted to the cathode of the cell and then the entire cathode with its coating is stored for further use.

Production of some non-metals and compounds

- Non-metals like hydrogen, fluorine and chlorine are produced by electrolysis.
- Compounds like $NaOH$, KOH, Na_2CO_3, $KClO_3$ and D_2O (heavy water) are produced by electrolysis (**electro-synthesis method**).

ELECTRLYTIC CONDUCTION

Substances may be identified as strong, weak, or non-electrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with electrolytic conductivity increasing as ion concentration increases. So there are two conditions which are necessary to electrolytic conduction to take place which are:

- Presence of enough concentration of ions.
- The ions must be free to move.

Substances which satisfy the two conditions either in molten state or in aqueous solution are said to have high ability of doing electrolytic conduction and vice-versa.

Important definitions and concepts

Conductance, G

This *is the reciprocal of resistance.*

That is $G = \frac{1}{R}$ where R is the resistance.

Its unit is Ω^{-1}(ohm^{-1}) or Siemen (S)

Also from $R = \frac{\rho l}{A}$

Where: ρ (pronounced rho) is the resistivity of the electrolyte

l is the distance between the two electrodes in half cells (electrolytes)

A is the cross section area of the electrodes.

But for the given cell, l and A are constant and hence $\frac{l}{A}$ is known as **cell constant.**

That is $\frac{l}{A}$ = **cell constant** and **R = ρ × cell constant**

Whence **Conductance**, $\mathbf{G = \frac{1}{R} = \frac{1}{\rho \times cell\ constant}}$

Conductivity, κ

This *is the conductance of an electrolyte placed between electrodes 1metre (1m) apart and having a cross - sectional area of $1m^2$*

- It is denoted by Greek letter 'kappa', **κ** and its unit is $\Omega^{-1}m^{-1}$ or Sm^{-1}
- It is reciprocal of the resistivity. It is also known as **electrolytic conductivity**, **normal conductivity**, or **specific conductance**.

From $R = \frac{\rho l}{A}$; $\rho = \frac{AR}{l}$; From which $\kappa = \frac{1}{\rho} = \frac{l}{RA}$

But $\frac{l}{A}$ = cell constant and $\frac{1}{R}$ = conductance

Hence **conductivity = conductance × cell constant**

Molar conductivity, Λ or Λ_m

Electrolytic conductivity is found to increase with dilution of electrolytic solution i.e. it increases as the concentration of the electrolyte decreases. So the electrolytic conductivity is concentration dependent. ***Why electrolytic conductivity increases as the concentration of the electrolyte decreases?***

According to Ostwald dilution law of weak electrolyte; degree of dissociation of the electrolyte increases as the concentration of the electrolyte decreases (or as the dilution of the electrolyte increases). **Increasing degree of dissociation of the electrolyte results to an increase of concentration of free ions in the solution and hence the electrolytic conductivity is found to increase.** If the electrolyte is diluted to infinity where its concentration is very close to zero, its ionisation is complete and therefore its degree of dissociation become maximum (100%) and hence the electrolytic conductivity becomes maximum too at infinite dilution.

Thus if: $\boldsymbol{\Lambda_m}$($\boldsymbol{\Lambda}$ is Greek capital letter 'lambda') is the electrolytic conductivity of the electrolyte at certain concentration where its degree of dissociation is α

And $\boldsymbol{\Lambda_\infty}$ is the electrolytic conductivity of the electrolyte at infinite dilution where its degree of dissociation is 1 (or 100%)

And as the electrolytic conductivity at certain concentration of the electrolyte varies direct proportional to the degree of dissociation of the electrolyte at that concentration,

It follows that: $\Lambda_m = k\alpha$

And $\Lambda_\infty = k \times 1$ where k is the constant for proportionality

Then $\frac{\Lambda_m}{\Lambda_\infty} = \frac{k\alpha}{k} = \alpha$

Hence $\boldsymbol{\frac{\Lambda_m}{\Lambda_\infty} = \alpha}$

The conductivity at infinity dilution is known as **limiting conductivity**.

And, $\frac{\Lambda_m}{\Lambda_\infty}$ is also known as **conductance ratio.**

Definition of conductance ratio:

Is the ratio of conductivity (molar conductivity or equivalent conductivity) at given concentration to that at infinite dilution.

The formula which consider the effect of concentration in the electrolytic conductivity is **molar conductivity** (usually is denoted as $\boldsymbol{\Lambda}$ or $\boldsymbol{\Lambda_m}$)

That is molar conductivity, $\Lambda_m = \frac{\text{Conductivity}}{\text{Molar concentration}} = \frac{\kappa}{[\ \ ]}$

But $\frac{1}{[\ \ ]}$ = Volume of solution containing 1mole of the electrolyte, V

Hence $\boldsymbol{\Lambda_m = \kappa V}$

Thus the **molar conductivity** can be defined as; *the conductance of that volume of solution containing one mole of an electrolyte.*

The unit of V in the formula $\Lambda_m = \kappa V$ may be m^3/mol or cm^3/mol depending on unit of conductivity, κ;

- If the unit of κ is $\Omega^{-1}m^{-1}$ (or Sm^{-1}), then the unit V must be m^3mol^{-1} and hence the unit of Λ_m will be $\Omega^{-1}m^2mol^{-1}$ (or Sm^2mol^{-1})
- If the unit of κ is $\Omega^{-1}cm^{-1}$ (or Scm^{-1}), then the unit of V must be cm^3mol^{-1} and hence the unit of Λ_m will be $\Omega^{-1}cm^2mol^{-1}$ (or Scm^2mol^{-1})

When the solution is diluted to infinite, the molar conductivity becomes maximum. *The molar conductivity at infinity dilution* is known as **limiting molar conductivity**.

Equivalent conductivity, Λ_e or Λ_{eq}

If the conductance is divided by normality instead of concentration (molar concentration), the result is known as equivalent conductivity (Λ_{eq}).

That is; **equivalent conductivity** $\boldsymbol{(\Lambda_{eq}) = \frac{\text{conductivity}}{\text{normality}}}$

But from normality = $\frac{\text{number of equivalents}}{\text{volume of solution}}$

$\frac{1}{\text{normality}} = \frac{\text{volume of solution}}{\text{number of equivalent}}$ = volume of solution containing one equivalent of the electrolyte.

So substituting volume of solution containing one equivalent of the electrolyte to $\frac{1}{\text{normality}}$ in the formula, equivalent conductivity = $\frac{\text{conductivity}}{\text{normality}}$ gives;

$$\boldsymbol{\Lambda_{eq} = \kappa V}$$

Where Λ_{eq} represents equivalent conductivity

κ represents conductivity of the solution

V represents volume of the solution containing 1 equivalent of the electrolyte.

Hence equivalent conductivity can be defined as *the conductance of that volume of solution containing one equivalent of an electrolyte*. Its unit is $\Omega^{-1}m^2eq^{-1}$ (or Sm^2eq^{-1}) or $\Omega^{-1}cm^2eq^{-1}$ (or Scm^2eq^{-1}) depending on the unit of κ.

Like in molar conductivity, when the solution is diluted to infinite, the equivalent conductivity becomes maximum. *The equivalent conductivity at infinity dilution* is known as **limiting equivalent conductivity**.

Relation between molar conductivity and equivalent conductivity

From equivalent conductivity = $\frac{\text{conductivity}}{\text{normality}}$

Normality = molar concentration × equivalent factor

Then it becomes:

Equivalent conductivity $= \frac{\text{conductivity}}{\text{molar concentration} \times \text{equivalent factor}}$

But $\frac{\text{conductivity}}{\text{molar concentration}}$ = molar conductivity

It follows that:

Equivalent conductivity = $\frac{\text{molar conductivity}}{\text{equivalent factor}}$

Or Molar conductivity = Equivalent conductivity × equivalent factor of the electrolyte
Hence:

$$\boldsymbol{\Lambda_m = \Lambda_{eq} \times \text{equivalent factor of the electrolyte}}$$

Factors affecting the conductivity of electrolyte solution

Important factors to consider here are:

- Temperature
- Nature of electrolyte
- Mobility
- Nature of solvent and its viscosity
- Concentration

Temperature

The conductance of an electrolyte solution increases with increase in temperature due to increase in the extent of ionisation.

Nature of electrolyte

The strong electrolyte undergoes complete ionisation and hence show higher conductivities since they give more number of ions whereas weak electrolyte undergoes partial ionisation and hence show comparatively low conductivities in their solution.

Mobility

The electrolyte with ions of greater mobility has higher conductance. The mobility of ions depends on whether electrolyte is in the molten state or aqueous solution.

- In the molten state, ionic mobility **decreases** with **increase** in its size and hence conductivity also decreases.
- In aqueous solution, ionic mobility **decreases** with **decrease** in its size (smaller ions are more hydrated in the solution and whence they become heavier) and hence conductivity also decreases.

As an example, in molten state, the conductivities of lithium salts are greater than those of potassium salts since the size of Li^+ ion is smaller than that of K^+ ion. However in aqueous solution, lithium salts show lower conductivities compared to those of potassium salts because Li^+ ion being smaller in size is more hydrated than K^+ ion.

Nature of solvent and its viscosity

The ionic mobility is reduced in more viscous solvent and hence conductivity decreases.

Concentration

The specific conductance increases with increase in concentration solution as the number of ions per unit volume increases whereas, both the equivalent conductivity and molar conductivity increase with decrease in concentration (i.e. upon dilution) since the extent of ionisation increases.

Kohlrausch's law

Kohlrausch's law of independent migration of ions is used to determine molar conductivity at infinite dilution for the weak electrolytes. It states that:

"The molar conductivity of an electrolyte at infinite dilution is the sum of molar conductivities of individual constituent ions present in the solution".

That is Λ_∞(compound) = $x\Lambda_\infty$(cation) + $y\Lambda_\infty$(anion); where x and y are stoichiometric number of cations and anions in the chemical equation showing ionisation of the salt.

E.g. Λ_∞ of NaCl = Λ_∞ of Na^+ + Λ_∞ of Cl^-

It should be noted that:

Molar conductivities of two different solutions at infinite dilution are always different although both solutions ionise by 100% at the infinite dilution, why?

This is simply because transport numbers of different ions in solution are also different. ***What is transport number***?

Transport number *is the fraction of the total current carried by ions.*

Calculations involving electrolytic conduction

Example 5

The resistivity of $0.02\text{M}KCl$ solution is 361Ωcm and a conductivity of a cell containing such a solution had a resistance of 550Ω.

(a) What is the cell constant?
(b) The same cell filled with $0.1\text{M}ZnSO_4$ solution had a resistance of 72Ω. What is the conductivity of $0.1\text{M}ZnSO_4$ solution?

Solution

(a) Using $\text{R} = \rho \times \text{cell constant}$

From which cell constant $= \frac{\text{R}}{\rho} = \frac{550\Omega}{361\Omega\text{cm}} = 1.5235\text{cm}^{-1}$

Hence the cell constant is 1.5235cm^{-1}

(b) Using cell constant $= \frac{R}{\rho}$; But $\frac{1}{\rho}$ = conductivity, κ

Thus cell constant = R × conductivity

Or conductivity $= \frac{\text{cell constant}}{R} = \frac{1.5235\Omega^{-1}\text{cm}^{-1}}{72} = 0.02116\Omega^{-1}\text{cm}^{-1}$

Hence the conductivity of 0.1M$ZnSO_4$ is $0.02116\Omega^{-1}\text{cm}^{-1}$

Example 6

In a particular cell, 0.01M solution of KCl gave a resistance of 15Ω while 0.01M solution of HCl gave a resistance of 51.4Ω at the same temperature. If the specific conductance of 0.01MKCl is 0.1409Sm^{-1}, calculate:

(i) Cell constant.
(ii) Specific conductance of HCl solution.
(iii) Equivalent conductivity of HCl solution.

Solution

(i) Conductivity (specific conductance) = conductance × cell constant

But, conductance $= \frac{1}{\text{resistance}}$.
Thus specific conductance $= \frac{\text{cell constant}}{\text{resistance}}$
Or cell constant = specific conductance × resistance
Substituting given data for KCl;

Cell constant = $0.14009\Omega^{-1}\text{m}^{-1} \times 15\Omega = 2.1135\text{m}^{-1}$
Hence cell constant is 2.1135m^{-1}

(ii) Substituting given data for HCl;

Specific conductance $= \frac{2.1135\text{m}^{-1}}{51.4\Omega} = 0.04112\Omega^{-1}\text{m}^{-1}$
Hence specific conductance of HCl solution is 0.04112Sm^{-1}

(iii) Equivalent conductivity $= \frac{\text{specific conductance}}{\text{normality}}$

Since HCl is monobasic (has basicity of 1);
Normality of HCl = Molarity of HCl = 0.01N = 0.01eq/dm^3 = 10eq/m^3
Thus equivalent conductivity $= \frac{0.04112\text{Sm}^{-1}}{10\text{eqm}^{-3}} = 0.004112\text{Sm}^2\text{eq}^{-1}$
Hence the equivalent conductivity for HCl is $0.004112\text{Sm}^2\text{eq}^{-1}$ or $41.12\ \text{Scm}^2\text{eq}^{-1}$

Example 7

A solution of 0.1MHCOOH has conductivity of $0.166\Omega^{-1}\text{m}^{-1}$ at 25°C. The molar conductivity at infinite dilution is $4.04 \times 10^{-2}\Omega^{-1}\text{m}^2\text{mol}^{-1}$, calculate:

(i) The degree of dissociation
(ii) The dissociation constant of HCOOH

Solution

(i) Using $\alpha = \frac{\Lambda_m}{\Lambda_\infty}$ where $\Lambda_m = \kappa V$

Then $\alpha = \frac{\kappa V}{\Lambda_\infty}$; Where $\kappa = 0.166\Omega^{-1}\text{m}^{-1}, \Lambda_\infty = 4.04 \times 10^{-2}\Omega^{-1}\text{m}^2\text{mol}^{-1}$

And $V = \frac{1}{0.1\text{moldm}^{-3}} = 10\text{dm}^3\text{mol}^{-1} = 10 \times 10^{-3}\text{m}^3\text{mol}^{-1} = 10^{-2}\text{m}^3\text{mol}^{-1}$

Substituting $\alpha = \frac{0.166\times10^{-2}}{4.04\times10^{-2}} = 0.041$ or 4.1%

Hence degree of dissociation of 0.1MHCOOH is 0.041 or 4.1%

(ii) Since degree of dissociation of the acid (HCOOH) is very small, Ostwald dilution law is applicable (Ostwald's dilution law cannot be applied when $\alpha > 0.1$. For Ostwald's dilution law to be applied the degree of dissociation must be negligible compared to 1)

From Ostwald dilution law, $\alpha = \sqrt{\frac{K_a}{C}}$

From which $K_a = \alpha^2 C = (0.041)^2 \times 0.1\text{moldm}^{-3} = 1.681 \times 10^{-4}\text{M}$

Hence the dissociation constant of HCOOH is $1.681 \times 10^{-4}\text{M}$

Example 8

A solution of dichloroethonoic acid of concentration $1.25 \times 10^{-4}\text{M}$ has conductivity at infinite dilution of $3.85 \times 10^{-2}\Omega^{-1}\text{m}^2\text{mol}^{-1}$. Given the conductivity of dichloroethonoic acid is $2.5 \times 10^{-3}\Omega^{-1}\text{m}^{-1}$. Calculate the degree of dissociation and hence dissociation constant.

Solution

$$V = \frac{1}{\text{concentration}} = \frac{1}{1.25 \times 10^{-4}\text{moldm}^{-3}} = 8000\text{dm}^3\text{mol}^{-1} = 8\text{m}^3\text{mol}^{-1}$$

Using: $\alpha = \frac{\Lambda_m}{\Lambda_\infty} = \frac{\kappa V}{\Lambda_\infty} = \frac{2.5\times10^{-3}\times8}{3.85\times10^{-2}} = 0.5195$ or 51.95%

Hence the degree of dissociation of the acid is 0.5195 or 51.95%

Here the degree of dissociation is large whose amount cannot be neglected compared to 1 and hence Ostwald dilution law cannot be applied i.e. the equation $\boldsymbol{\alpha = \sqrt{\frac{K_a}{C}}}$ does not hold.

Dichloroethanoic acid ($CHCl_2COOH$) ionises according to the following equation:

$$CHCl_2COOH(aq) \rightleftharpoons CHCl_2COO^-(aq) + H^+(aq)$$

At equilibrium $\quad \boldsymbol{(1-\alpha)C} \quad \boldsymbol{\alpha C} \quad \boldsymbol{\alpha C}$

$$K_a = \frac{[CHCl_2COO^-][H^+]}{[CHCl_2COOH]} = \frac{\alpha C\times\alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{(1-\alpha)}$$

Substituting $K_a = \frac{(0.5195)^2\times1.25\times10^4}{(1-0.5195)} = 7.02 \times 10^{-5}\text{M}$

Hence the dissociation constant for the acid is $7.02 \times 10^{-5}\text{M}$

Example 9

The following and Λ_∞values at 25°C in $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$;

Electrolytes	$\boldsymbol{\Lambda_\infty}$
CH_3COONa	91
HNO_3	421
$NaNO_3$	122
KNO_3	145

Calculate:

(a) Λ_∞ of CH_3COOK
(b) Λ_∞ of CH_3COOH
(c) If the value of Λ for 0.016M CH_3COOH is $13\Omega^{-1}cm^2mol^{-1}$at 25ºC. What is the K_a value and pH of CH_3COOH?

Solution

Given that:

$\Lambda_1 = \Lambda_\infty(CH_3COONa) = \Lambda_\infty(CH_3COO^-) + \Lambda_\infty(Na^+) = 91$

$\Lambda_2 = \Lambda_\infty(HNO_3) = \Lambda_\infty(NO_3^-) + \Lambda_\infty(H^+) = 421$

$\Lambda_3 = \Lambda_\infty(NaNO_3) = \Lambda_\infty(NO_3^-) + \Lambda_\infty(Na^+) = 122$

$\Lambda_4 = \Lambda_\infty(KNO_3) = \Lambda_\infty(NO_3^-) + \Lambda_\infty(K^+) = 145$

(a) $\Lambda_\infty(CH_3COOK) = \Lambda_\infty(CH_3COO^-) + \Lambda_\infty(K^+)$

$$= \Lambda_1 + \Lambda_4 - \Lambda_3 = 91 + 145 - 122 = 114\Omega^{-1}cm^2mol^{-1}$$

Thus Λ_∞ of CH_3COOK is $114\Omega^{-1}cm^2mol^{-1}$

(b) $\Lambda_\infty(CH_3COOH) = \Lambda_\infty(CH_3COO^-) + \Lambda_\infty(H^+)$

$$= \Lambda_1 + \Lambda_2 - \Lambda_3 = 91 + 421 - 122 = 390\Omega^{-1}cm^2mol^{-1}$$

Thus Λ_∞ of CH_3COOH is $390\Omega^{-1}cm^2mol^{-1}$

(c) Using $\alpha = \frac{\Lambda_m}{\Lambda_\infty}$;

Where $\Lambda_m = 31\Omega^{-1}cm^2mol^{-1}$ and $\Lambda_\infty = 390\Omega^{-1}cm^2mol^{-1}$

Substituting $\alpha = \frac{13}{390} = \frac{1}{30}$

Since α is small, Ostwald's dilution law is applicable

From Ostwald dilution law $\boldsymbol{\alpha} = \sqrt{\frac{\mathbf{K_a}}{\mathbf{C}}}$

It follows that, $K_a = \alpha^2C = \left(\frac{1}{30}\right)^2 \times 0.016moldm^{-3} = 1.78 \times 10^{-5}M$

Using $[H^+] = \alpha C$

Then $pH = -\log[H^+] = -\log\alpha C = -\log\left(\frac{1}{30} \times 0.016\right) = 3.273$

Hence the pH of 0.016MCH_3COOH is 3.273

Example 10

At 13ºC, the specific conductivity of a saturated solution of AgCl in water was $2.4 \times 10^{-6}\ \Omega^{-1}cm^{-1}$ and that of water was $1.16 \times 10^{-6}\ \Omega^{-1}cm^{-1}$

Given that:

$\Lambda_\infty(NaCl) = 110.3\Omega^{-1}cm^2mol^{-1}$, $\Lambda_\infty(AgNO_3) = 116.5\Omega^{-1}cm^2mol^{-1}$,

$\Lambda_\infty(NaNO_3) = 105.2\Omega^{-1}cm^2mol^{-1}$.

Calculate the solubility, hence the solubility product of AgCl at this temperature.

Solution

From Kohlrausch's law; $\Lambda_\infty(\text{AgCl}) = \Lambda_\infty(\text{AgNO}_3) + \Lambda_\infty(\text{NaCl}) - \Lambda_\infty(\text{NaNO}_3)$

Substituting $\Lambda_\infty(\text{AgCl}) = 116.5 + 110.3 - 105.2 = 121.6\Omega^{-1}\text{cm}^2\text{mol}^{-1}$

Using $\kappa_{\text{solution}} = \kappa_{\text{AgCl}} + \kappa_{\text{H}_2\text{O}}$;

From which $\kappa_{\text{AgCl}} = \kappa_{\text{solution}} - \kappa_{\text{H}_2\text{O}}$

$$= 2.4 \times 10^{-6}\Omega^{-1}\text{cm}^{-1} - 1.16 \times 10^{-6}\Omega^{-1}\text{cm}^{-1} = 1.24 \times 10^{-6}\Omega^{-1}\text{cm}^{-1}$$

But for sparingly soluble substances like AgCl:

$\textbf{Molar conductivity at infinite dilution} = \textbf{Molar conductivity of saturated solution}$

$$= 121.6\Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

(This is because saturated solution of sparingly soluble substance is so dilute that it can be assumed to be the same as the solution at infinite dilution keeping in the mind that the solution contains very small amount of the solute).

Using $\Lambda_\text{m} = \kappa\text{V}$;

Then $\text{V} = \frac{\Lambda_\text{m}}{\kappa} = \frac{121.6}{1.24\times10^{-6}}\text{cm}^3\text{mol}^{-1} = \frac{121.6}{1000\times1.24\times10^{-6}}\text{dm}^3\text{mol}^{-1} \quad = 98064.516\text{dm}^3\text{mol}^{-1}$

Using $[\quad] = \frac{1}{\text{V}}$; where V is dilution

Then molar solubility of AgCl $= \frac{1}{98064.51}\text{moldm}^{-3} = 1.0197 \times 10^{-5}\text{moldm}^{-3}$

And its solubility (mass solubility)$= 1.0197 \times 10^{-5} \times 143.5\text{gdm}^{-3} = 1.4633 \times 10^{-3}\text{gdm}^{-3}$

And K_{sp} $[\text{Ag}^+][\text{Cl}^-] = (1.0197 \times 10^{-5})^2\text{mol}^2\text{dm}^{-6}$

$$= 1.0398 \times 10^{-10}\text{mol}^2\text{dm}^{-6}$$

Be aware of this: Example 9 and 10 summarises **applications of Kohlrausch's law** which are:

- Determination of molar electrolytic conductivity of weak electrolytes at infinite dilution.
- Determination of degree of dissociation (ionisation) of weak electrolytes.
- Determination of dissociation (ionisation) constant of weak electrolytes.
- Determination of solubility and hence solubility product of sparingly soluble salts.

DIGGING DEEPER EXERCISE 22

Use 1F = 96485.309 C

EXERCISE 22A: BINDER QUESTIONS

Question 1

Calculate the quantity of electricity (Coulombs) necessary to deposit 100g of copper from a $CuSO_4$ solution.

Question 2

How many minutes will take to plate out 40.00 g of Ni form a solution of $NiSO_4$ using a current of 3.4500A?

Question 3

What is the equivalent weight of a metal if a current of 0.2500A causes 0.5240 g of metal to plate out a solution undergoing electrolysis in 1 hour?

Question 4

How many hours will it take to plate out copper in 200.0mL of a 0.15M Cu^{2+} solution using a current of 0.200A?

Question 5

A constant electric current deposits 0.3650 g of silver metal in 12960 seconds from a solution of silver nitrate. What is the current?

Question 6

The specific conductance of a 0.02M solution of KCl at 25℃ is $0.002765\Omega^{-1}\text{cm}^{-1}$. If the resistance of cell containing this solution is 400 Ω, what is the cell constant?

Question 7

The resistance of a 0.01M solution of an electrolyte is 210 Ω at 25℃. Calculate the molar conductance of the solution at the same temperature. The cell constant is 0.88cm^{-1}.

Question 8

The resistance of 0.5M solution of an electrolyte in a cell was found to be 45 Ω. Calculate the molar conductance of the solution if the electrodes of the cell are 2.2cm apart and have an area of 3.8cm^2.

Question 9

0.5N solution of a salt placed between two platinum electrodes, 20cm apart and of area 4cm^2 has a resistance of 25 Ω. Calculate equivalent conductance of the solution.

Question 10

The resistance of decinormal solution of a salt occupying a volume between two platinum electrodes 1.80cm apart and 5.4cm^2 in area was found to be 32 Ω. Calculate equivalent conductance of the solution.

Question 11

The resistance of 0.1N solution is 2500 Ω. Calculate equivalent conductance of the solution. Cell constant = 1.15cm^{-1}.

EXERCISE 22B: REAL QUESTIONS

Question 12

Why solid table salt does not conduct electricity although it is known as strong electrolyte?

Question 13

Explain at least three challenges of applying Faraday's second law in real life.

Question 14

When two different solutions, one containing $0.1M\ CH_3COOH$ and another containing $0.1M\ HCl$ are diluted to 0.01M of each, the acetic acid solution shows greater increase in its molar conductivity than the hydrochloric acid. Explain.

Question 15

Your friend **Kipute** argued to you, *"I know you know that molar conductivity depends on the extent of ionisation. And I know you know that strong electrolytes ionises completely in the solution and for that reason, dilution does not affect their extent of ionisation."* She then concluded, *"Dilution does not affect molar conductivity of strong electrolytes."*

Do you agree to **Kipute's** conclusion? Explain.

Question 16

In a conductivity test, 5 different solutions were set up with light bulbs. The following observations were recorded:

Solution A glowed brightly.

Solution B glowed dimly.

Solution C glowed dimly.

Solution D did not glow.

Solution E glowed brightly.

(a) Which solution(s) could contain strong bases?
(b) Which solution(s) could contain weak acids?
(c) Which solution(s) could contain ions?
(d) Which solution(s) could contain pure water?
(e) Based solely on these observations, would it be possible to distinguish between acidic and basic solutions? Explain.

EXERCISE 22C: HOT QUESTIONS

Question 17

How many Faradays are required to oxidize the following?

(a) One mole of sodium thiosulphate solution
(b) Two moles of hydrogen peroxide solution
(c) $500cm^3$ of 1M oxalic acid

Question 18

In an electrolytic cell, Cu(s) is produced by the electrolysis of $CuSO_4(aq)$. Calculate the maximum mass of Cu(s) that can be deposited by a direct current of 100amperes passed through 5.00L of 2.00M $CuSO_4(aq)$ for a period of 1.00hour.

Question 19

In an electrolytic cell, a current of 0.250ampere is passed through a solution of a chloride of iron, producing Fe(s) and $Cl_2(g)$.

(a) Write the equation for the reaction that occurs at the anode.
(b) When the cell operates for 2.00hours, 0.521gram of iron is deposited at one electrode. Determine the formula of the chloride of iron in the original solution.
(c) Write the balanced equation for the overall reaction that occurs in the cell.

(d) How many litres of $Cl_2(g)$, measured at 25°C and 750mmHg, are produced when the cell operates as described in part (b)?

(e) Calculate the current that would produce chlorine gas at a rate of 3.00 grams per hour.

Question 20

A conductivity cell is filled with 0.05M KCl. Its specific conductance and observed resistance is $0.00667\Omega^{-1}cm^{-1}$ and 243 Ω, respectively. When the cell is filled with 0.01M NaOH, observed resistance is 681 Ω. Calculate specific and molar conductance of 0.01M NaOH.

Question 21

The specific conductance of water is $0.076Sm^{-1}$ and the specific conductance of 0.1M aqueous solution of KCl is $1.1639Sm^{-1}$. A cell has a resistance of 33.20Ω when filled with 0.1M KCl solution and 300Ω when filled with 0.1M CH_3COOH solution. Calculate the molar conductance of acetic acid.

Question 22

The conductivity of $0.001M\ CH_3COOH$ is $4.95\times10^{-5}Scm^{-1}$. Calculate its dissociation constant, given that $\Lambda_\infty(CH_3COOH) = 390.5Scm^2mol^{-1}$

Question 23

Molar conductivity at infinite dilution for NH_4Cl, $NaOH$ and $NaCl$ at 298K are respectively 129.8, 218.4 and $108.9Scm^2mol^{-1}$ and molar conductivity of $0.01MNH_4OH$ is $9.33Scm^2mol^{-1}$. Calculate the degree of dissociation of NH_4OH at 298K.

EXAMINATION QUESTIONS FOR PART SIX

Question 1

(a) Complete and balance the following redox reaction: $MnO_4^- + H_2S + H^+ \rightarrow$

(b) A standardization of potassium manganate (VII) solution yielded the following data: 0.16g of the potassium salt, $KHC_2O_4.H_2C_2O_4.2H_2O$ needed $24.5cm^3$ of the manganate (VII) solution. What is the molarity of the manganate (VII) solution?

Question 2

9.85g of pure ammonium iron (II) sulphate $(FeSO_4.(NH_4)_2SO_4.6H_2O)$ were made up to 250cm^3 of solution in cold, boiled – out, dilute sulphuric acid. $25cm^3$ of the solution reacted completely with $24.75cm^3$ of a potassium manganate (VII) solution.

Calculate:

(a) The molarity of the manganate (VII) solution
(b) The concentration of the manganate in gdm^{-3}
(c) The dilution needed to convert the remaining $1800cm^3$ of it $(KMnO_4)$ to exactly 0.02M concentration
(d) Why the simple iron (II) sulphate $(FeSO_4)$ should not be used in this titration experiment?

Question 3

(a) Explain how mobility of ions in the solution are affected by concentration of electrolyte?

(b) Calculate the percentage by mass of iron (III) in a salt from the following data: 25g of the salt were dissolved in water and reduced to an iron (II) solution by zinc and dilute sulphuric acid. The mixture was filtered and the filtrate and washings made up to $1dm^3$. $20cm^3$ of this solution required $20.7cm^3$ of $0.01M$ $KMnO_4$ for oxidation.

Question 4

(a) Although potassium dichromate (VI) is strongly coloured, it is not used as self-indicator in the redox titrations; why?

(b) 1.5g of a mixture of anhydrous sodium ethanedioate and ethanedioic acid crystals was made up to $100cm^3$ of aqueous solution. $20cm^3$ of this solution required $19.8cm^3$of $0.1MNaOH$ for neutralisation, phenolphthalein as indicator. How many $cm^3$of $0.01MKMnO_4$ will be necessary to oxidize $25cm^3$ of the original solution in the presence of excess dilute sulphuric acid?

Question 5

$100cm^3$of solution of hydrogen peroxide were diluted to $1dm^3$ with water. $25cm^3$of this solution, when acidified with dilute sulphuric acid, reacted with $47.8cm^3$ of $0.02MKMnO_4$

(a) What is the concentration of the original hydrogen peroxide solution in gdm^{-3}?
(b) What is the 'volume' rating of this solution (referred to s.t.p)?

Question 6

(a) Why an end point of redox titration involving potassium permanganate as self-indicator is pink in colour?

(b) Calculate the concentration in gdm^{-3} of a solution of potassium chlorite (V) from the following data: $50cm^3$ of a solution of ammonium iron (II) sulphate $(FeSO_4(NH_4)_2SO_4.6H_2O)$ (acidified) were boiled for ten minutes with $25cm^3$of potassium chlorate solution. After cooling the excess iron (II) salt was oxidised by $24.6cm^3$ of $0.02M$ $KMnO_4$ solution. $25cm^3$ of the same acidified ammonium iron (II) sulphate $(FeSO_4.(NH_2)_2SO_4.6H_2O)$ solution required $24.2cm^3$ of $0.02M$ $KMnO_4$.

$$6Fe^{2+} + 6H^+ + ClO_3^- \rightarrow Cl^- + 3H_2O + 6Fe^{3+}$$

Question 7

Sodium thiosulphate reacts with iodine according to the equation:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

(a) Explain whether the iodine molecules are being oxidised or reduced.
(b) What is the mass of iodine would be required to react with $30cm^3$ of 0.1M thiosulphate($Na_2S_2O_3$).
(c) Is the titration iodimetry or iodometry? Why?

Question 8

In a standardization of sodium thiosulphate solution, $25cm^3$ of 0.0204M potassium manganate (VII) solution were added to excess of acidified potassium iodide solution. The iodine liberated required $24.4cm^3$ of sodium thiosulphate solution for reduction.

(a) Write down the balanced ionic equation:
  (i) Taking place between potassium manganate (VII) and potassium iodide
  (ii) Taking place between sodium thiosulphate and iodine
(b) What is the overall reaction equation for above experiment?
(c) Calculate the molarity of the sodium thiosulphate solution
(d) If $1750cm^3$ of sodium thiosulphate remain, how may it made exactly decimolar?
(e) Is the titration iodo or iodimetry? Give a reason for your choice.

Question 9

(a) Which medium favours oxidation and which one favours reduction?
(b) 2.5g of a sample of bleaching powder were ground with successive amounts of water, transferred to a measuring flask and made up to $250cm^3$of mixture. $25cm^3$ of it, added to excess of potassium iodide solution and acidified, liberated iodine requiring $24.2cm^3$ of decimolar sodium thiosulphate solution. Calculate the percentage of available chlorine in the bleaching power.

Question 10

A weight 3.9g of an ore is composed of haematite and siderite. Haematite is Fe_2O_3 and siderite is $FeCO_3$. The ore is dissolved in acid and titrated against 0.1M cerium sulphate. The volume of cerium (IV) sulphate used was $100cm^3$. The reduction of Ce^{4+} is given by the equation: $Ce^{4+} + e \rightarrow Ce^{3+}$

(i) Calculate the % of each compound in the ore.
(ii) Suppose a similar weight of the ore is first reduced to +2 oxidation state by suitable reagents then titrated with 0.1M cerium (IV) sulphate solution. What volume of cerium (IV) sulphate would be required?
(iii) If instead of using cerium (IV) sulphate, 0.05M $KMnO_4$ solution was used in (ii), what volume of $KMnO_4$would be used?

Question 11

(a) The e.m.f of a cell corresponding to the reaction:
$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(0.1M) + H_2\ (g, 1\ atm)$ is 0.58V, at 25°C. Calculate the pH of the solution at hydrogen electrode $E^\theta_{Zn^{2+}/Zn} = 0.76V$
(b) Calculate the equilibrium constant for the reaction: $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$

$$\left(\text{Given: } E^\theta_{Ce^{4+}/Ce^{3+}} = +1.44,\ E^\theta_{Fe^{3+}/Fe^{2+}} = +0.68V\right)$$

Question 12

(a) What does the positive value for E^θ_{cell} in case of galvanic cell like $Zn\,|\,Zn^{2+}||Cu^{2+}\,|\,Cu$ indicate?
(b) The standard electrode potential for the half reaction:

$$Pb(s) \rightarrow Pb^{2+} + 2e \qquad \text{is} - 0.13V$$

What is the standard electrode potential for the half reaction: $2Pb(s) \rightarrow 2Pb^{2+}(aq) + 4e$

(c)
  (i) Arrange the following metals in the increasing order of the reactivity. The value in brackets are that of reduction electrode potentials

$$Mg\ (-2.37);\ Na\ (-2.71);\ Ag(+0.80);\ Cu\ (+0.34);\ Fe\ (-0.44);\ Zn(-0.76)$$

(ii) Which one is the stronger reducing agent?
(iii) Which one is the weakest reducing agent?
(iv) Construct a cell with greatest e.m.f (write a cell diagram of the cell).

Question 13

(a) What is meant by the following statements:
(i) "The reduction electrode potential of zinc is $-0.76V$"
(ii) "The reduction electrode potential of copper is $+0.34V$"
(b) When does a cell formulation represent a non – spontaneous activity of galvanic cell?

Question 14

(a) What are spontaneous reactions? Are spontaneous reactions exothermic or endothermic?
(b) Calculate the electrode potential of the half-cell, $Fe^{3+}(aq)/Fe^{2+}(aq)$ when Fe^{3+} concentration is 1M and Fe^{2+} concentration is 0.6M (Given: $E^{\theta}_{Fe^{3+}/Fe^{2+}} = 0.771V$)

Question 15

(a) What does each of the following terms represent?
(i) Standard electrode potential
(ii) Redox reaction
(b) Calculate e.m.f of a Daniel cell at 35˚C using a 2.0M zinc sulphate solution and 0.5M copper (II) sulphate solution. Electrode reduction potentials are given as:

$Ag^{+}(aq)/Ag(s)$ $E^{\theta}/V = +0.8V$

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

$Mg^{2+}(aq)/Mg(s)$ $E^{\theta}/V = -2.37V$

$Zn^{2+}(aq)/Zn(s)$ $E^{\theta}/V = -0.76V$

Question 16

(a) Explain the function of moisture in the rusting process.
(b) Zinc rod is dipped in $0.1MZnSO_4$. The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential. Given that: $E^{\theta}_{Zn^{2+}/Zn} = -0.76V$.

Question 17

(a) What is the meaning of each of the following terms?
(i) Corrosion
(ii) Disproportionation reaction
(b) Calculate equilibrium constant of the following redox reaction

$$2Fe^{2+}(aq) + Sn^{4+}(aq) \rightleftharpoons 2Fe^{3+}(aq) + Sn^{2+}(aq)$$

Given that:

$E^{\theta}_{Fe^{3+}/Fe^{2+}} = 0.771V$

$E_{Sn^{4+}/Sn^{2+}} = 0.150V$

Question 18

(a) Why is it necessary to use a salt bridge in a galvanic cell?
(b) Electrode potential value of the copper electrode, were determined by varying concentration of copper ions in solution at 298K. The following data were obtained:

Concentration of Cu^{2+} in $moldm^{-3}$	0.1	0.2	0.3	0.4	0.5
Electrode potential in volts	0.310	0.320	0.324	0.328	0.331

Use these data to construct a graph which you will then use to determine the standard electrode potential of copper electrode

Question 19

(a) A salt bridge is used to connect the two half-cells.
  (i) State what chemical is contained in the salt bridge.
  (ii) Give a possible reason why the salt bridge cannot be replaced by an unreactive metal wire.
(b) If the cost of electricity to produce magnesium is *x*Tsh per one kilogram of the metal, what is the cost of electricity for producing *y*kg of aluminium at the same rates?

Question 20

(a) Briefly explain how voltaic cell differ from electrolytic cells.
(b) A steady current of 0.65A is passed for 5.5hours through solutions of sulphuric acid and copper (II) sulphate in series at 13°C and 100000Nm^{-2} (750mmHg) pressure. Calculate:
  (i) The volume of hydrogen liberated from the acid.
  (ii) The volume oxygen liberated from the acid.
  (iii) The mass of copper precipitated.

Question 21

(a) Briefly explain any two methods for rusting prevention.
(b) After making allowance for conductivity of water, the conductivity of saturated solution of silver chloride at 25°C is $1.5 \times 10^{-4}\ \Omega^{-1}\text{m}^{-1}$. If molar conductivity at infinite dilution of Ag^+ is $6.2 \times 10^{-3}\Omega^{-1}\text{m}^2\text{mol}^{-1}$. and that of Cl^- is $7.6 \times 10^{-3}\Omega^{-1}\text{m}^2\text{mol}^{-1}$. Calculate molar solubility of silver chloride.

Question 22

Given the following reduction potentials:

Half reaction	$\mathbf{E^\theta(V)}$
$\text{Cl}_2(\text{g}) + 2\text{e} \rightarrow 2\text{Cl}^-$	$+1.36$
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$+1.33$
$\text{Cr}^{3+} + \text{e} \rightarrow \text{Cr}^{2+}$	-0.50
$\text{Cr}^{3+} + 3\text{e} \rightarrow \text{Cr}$	-0.73
$\text{S}_4\text{O}_6^{2-} + 2\text{e} \rightarrow 2\text{S}_2\text{O}_3^{2-}$	$+0.17$

(i) Determine the standard e.m.f of the following cell with the following cell reaction:

$$\text{Cr}^{3+}(1\text{M}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(1\text{M}) + \text{Cl}^-\ (1\text{M})$$

(ii) Sketch the galvanic cell based on the reaction in (i) above and show the direction of the electron flow
(iii) Calculate the equilibrium constant for the following reaction:

$$\text{S}_4\text{O}_6^{2-}(\text{aq}) + \text{Cr}^{2+}(\text{aq}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + \text{S}_2\text{O}_3^{2-}(\text{aq})$$

(iv) What conclusion can be made from the equilibrium constant obtained in (iii) above?

Question 23

(a) Differentiate between an electronic conductors and electrolytic conductors.
(b) A conductivity cell with electrodes 2 cm^3 in area and 1 cm apart has a resistance of 7.25Ω when filled with 5% potassium chloride solution;
  (i) Calculate the cell constant.
  (ii) Determine the conductivity of potassium chloride solution.
  (iii) If the cell was filled with 0.02M KCl, with resistivity of $361\Omega\text{cm}$, what would the cell resistance be?

Question 24

(a) What do the following mean?

(i) Cathode

(ii) Anode

(iii) Standard electrode potential

(iv) Concentration cell

(b) The standard electrode potential for Zn^{2+}/Zn is $-0.76V$ and for Cu^{2+}/Cu is $+0.34V$

(i) Draw a cell diagram of a cell that can be formed from Cu and Zn electrodes.

(ii) Write the cell reaction and calculate its e.m.f under standard conditions.

(iii) Calculate the equilibrium constant for the reaction.

Question 25

(a) Using the following half reactions:

$Au^{3+} + 3e \rightarrow Au \qquad E^{\theta} = 1.5V$

$NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O \quad E^{\theta} = 0.96V$

Predict whether $1MHNO_3$ will dissolve gold metal to form $1MAu^{3+}$ solution or not.

(b) Isolation of an acid from aqueous solution gave crystals **C** of molecular formula $C_2H_2O_4 \bullet xH_2O$. The acid can be oxidised quantitatively to carbon dioxide and water by acidified aqueous manganate (VII) above 60°C. This reaction can be represented by the equation:

$$2MnO_4^-(aq) + 5\,C_2H_2O_4 \bullet xH_2O(aq) + 6H^+ \rightarrow 2Mn^{2+}(aq) + (8 + 5x)H_2O(l) + 10CO_2(g)$$

Given that 0.126g of **C** required $20.00\ cm^3$ of aqueous manganate (VII) of concentration 0.02M for complete reaction, calculate the value of x in $C_2H_2O_4 \bullet xH_2O$.

ANSWERS TO DIGGING DEEPER EXERCISES

EXERCISE 20

1. (a) Reducing agent (b) Reducing agent (c) Oxidising agent (d) Oxidising agent

2. Hint: Chlorate(I) ion is ClO^-

3. $Sn^{2+}(aq) < Ag^+(aq) < Au^{3+}(aq)$

4. (i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Oxidant is potassium dichromate. Reductant is iron (II) sulphate.

(ii) $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

Oxidant is potassium iodate. Reductant is potassium iodide.

(iii) $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$

Oxidant is copper (II) sulphate. Reductant is potassium iodide.

(iv) $2Cl_2 + 6OH^- \rightarrow ClO_3^- + 5Cl^- + 3H_2O$

Oxidant is chlorine gas. Reductant is chlorine gas.

5. (a) +5 and +7 respectively (b) Does not involve only one iodine containing specie as the reactant. It involves two iodine species as reactants, giving only one iodine containing specie as product; this is opposite to disproportionation reaction and hence the reaction is **comproportionation reaction**. (c) On addition of starch, the solution turns blue (d) $IO_4^-(aq) + 7I^-(aq) + 8H^+(aq) \longrightarrow 4I_2(s) + 4H_2O(l)$

6. This is because, unlike $K_2Cr_2O_7$:

- $KmnO_4$ cannot be obtained pure enough.
- $KmnO_4$ readily reacts with traces of organic material or other reducing substances in water.
- $KmnO_4$ decomposes in sunlight.

7. Potassium permanganate ($KMnO_4$) is so strong oxidising agent that can oxidise Cl^- from HCl thus interfering the measurement of volume of $KMnO_4$ which was exactly used to oxidise Fe^{2+} in the titration.

$2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

8. This is due to oxidation of Cl^- (reducing agent) in NaCl to Cl_2 by potassium dichromate (VI), $K_2Cr_2O_7$ (oxidizing agent) while itself becomes reduced to Cr^{3+}which is detected by its green colouration.

$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$

9. This is because:

- It ensures that the reaction occurs at reasonable high rate.
- It enables complete reduction of MnO_4^- to Mn (II) and not to Mn (III) which would be formed at lower temperature.
- CO_2 is soluble in water, thus heating removes all dissolved CO_2 out of the solution, driving the reaction in forward direction.

10.

(i) Number of moles of $KMnO_4 = \frac{20.25}{1000} \times 0.02\text{mol} = 4.05 \times 10^{-4}\text{mol}$

$KMnO_4$ reacts with H_2O_2 according to the following equation:

$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

From which mole ratio of MnO_4^- to H_2O_2 reacted $= \frac{5}{2} \times 4.05 \times 10^{-4}$ mol

$= 1.0125 \times 10^{-3}$ mol in $25cm^3$ of its solution

Then $[H_2O_2] = \frac{n}{V} = \frac{1.0125\times10^{-3}}{25\times10^{-3}}M = 0.0405M$

Using dilution principle: $M_cV_c = M_dV_d$

Then substituting $M_c \times 50 = 0.0405 \times 1000$; $M_c = 0.81M$.

Hence original concentration of H_2O_2 was 0.81 $moldm^{-3}$

(ii) $NaMnO_4$ is hygroscopic.

The titre volume would be larger than the obtained one.

Concentrated H_2SO_4 is good oxidizing agent; so it would oxidize H_2O_2 as $KmnO_4$ does.
The titre volume would therefore be less than the obtained one.

11. 0.810moldm^{-3}

12.(a) $2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$ (b) 0.0358g (c) 0.0504 moldm^{-3}, 12.8gdm^{-3}

13. (i) 1.72gdm^{-3} (ii) **Starch indicator** is used for the titration, when the last of the iodine reacts with the thiosulphate, the blue colour from the starch–iodine mixture is discharged and the solution becomes colourless.

14. $0.090MFe^{2+}$, $0.060MFe^{3+}$

15. (a) 89.4% (b) Potassium manganate(VII) is not used for this titration because it is strong enough to oxidise chloride ions (from the hydrochloric acid) to form chlorine, thus interfering measurement of correct volume of the permanganate which is exactly used to oxidise Fe^{2+} in the titration.

16. 14%

17. (a) 0.002mol of $Na_2S_2O_3$, 0.001mol of iodine (b) 0.000333mol (c) 0.0980g (d) 0.98g, 97.0%

EXERCISE 21

1. 0.5603V

2. (a) **Equation for disproportionation of copper(I) ions**

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

The cell diagram corresponding to the above disproportionation reaction is $Cu^+(aq) \mid Cu^{2+} \parallel Cu^+(aq) \mid Cu(s)$

From which $E^\theta_{cell} = E^\theta_R - E^\theta_L = 0.52 - 0.34 = +0.18V$

Since e.m.f of a cell corresponding to the above reaction is positive, the reaction is spontaneous and hence Cu^+ ions disproportionate in aqueous solution.

Equation for disproportionation of silver(I) ions

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

The cell diagram corresponding to the above disproportionation reaction is $Ag^+(aq) \mid Ag^{2+}(aq \parallel Ag^+(aq) \mid Ag(s)$

From which $E^\theta_{cell} = E^\theta_R - E^\theta_L = 0.8 - 1.98 = -1.18V$

Since e.m.f of a cell corresponding to the above reaction is negative, the reaction is not spontaneous and hence Ag^+ ions do not disproportionate in aqueous solution.

(b) Blue solution of $CuSO_4$

$$Cu_2O(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + Cu(s) + H_2O(l)$$

Or ionically $Cu_2O(s) + 2H^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s) + H_2O(l)$

3. $1.47 \times 10^{-9}M$

4. 0.56V

5. 0.0591V

6. (i) Kinetic factors (ii) Non-standard conditions (iii) Very small difference in E^θvalues.

7. Zinc having more negative E^θ, undergoes oxidation in preference to iron to form Zn^{2+} while iron undergoes oxidation in preference to tin because it has more negative E^θ than tin. Hence zinc prevents the initiation of iron corrosion (rusting) by preventing the oxidation of iron, $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e$, which is necessary for the corrosion to occur.

8. Yes; can be used.

Explanation

Al having smaller value of reduction potential, is more reactive than copper. Therefore, Al cannot be reduced by Cu from the solution and hence the solution of aluminium can be safely stirred by using the copper spoon.

$$Al^{3+}(aq) + Cu(s) \longrightarrow \text{No reaction}$$

9. (i) Having lower reduction potential, nickel is stronger reducing agent and more reactive than copper and therefore it displaces the copper from copper sulphate solution (nickel spatula appears to dissolve in solution) and hence nickel spatula should not be used tom stir $CuSO_4(aq)$. $Ni(s) + Cu^{2+}(aq) \rightarrow Ni^{2+}(aq) + Cu(s)$

(ii) Having larger reduction electrode potential, nickel is weaker reducing agent and less reactive than iron thus making it incapable of displacing iron from the salt and hence ferrous sulphate can be stored in a nickel container.

$$Ni(s) + FeSO_4(aq) \rightarrow \text{No reaction}$$

10. The salt bridge connects the two half-cell solutions and thus completes the circuit of electrochemical cell. Therefore:

- Potassium chloride is used because it is strong electrolyte and hence it enables conduction of electricity in the two half-cells.
- Agar-gel is used to mix with potassium chloride so that they remain semi-solid and thus do not mix with the half-cell solutions, and also the semi-solid state prevents the diffusion of the electrolytes from one half – cell to the other, maintaining the charge balance in the two half cells.

11. (a) Positive **Reasons: (i)** K_c is large (greater than 1) (ii) The reaction occurs (It is spontaneous) (b) The oxidising agent is Mg^{2+} (c) Would increase Hint: To justify use Nernst equation (d) Would increase (Again you may use Nernst equation to explain by considering effect of change of value of Q_c on the cell potential) (e) 0V.

12. (a) $Cd(s) + 2Ag^+(aq) \longrightarrow Cd^{2+}(aq) + 2Ag(s)$; $E^\theta = +1.2V$ (b) Anions (NO_3^- ions) will flow from the Ag^+ solution to the Cd^{2+} solution to balance the positive charges of new produced Cd^{2+}. (c) **The cell voltage will increase**. Ag^+ is a reactant, so increasing $[Ag^+]$ will increase the driving force for the forward (spontaneous) reaction and hence the cell potential will increase (Alternatively, you may use Nernst equation by considering the change in value of Q_c). (d) **The cell voltage will decrease**. Adding NaCl will have no effect on the Cd half-cell, but will cause AgCl to precipitate in the Ag half-cell ($Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$). Thus $[Ag^+]$ decreases, and since Ag^+ is a reactant, decreasing $[Ag^+]$ causes a decrease in voltage. (e) **The cell voltage will decrease**. $R_Q = \frac{[Cd^{2+}]}{[Ag^{2+}]^2}$; so diluting solution in both half-cells by the same amount make the value of Q_c to increase and hence according to Nernst equation; $E_{cell} = E^{\theta}_{cell} - \frac{RT}{nF}\ln Q_c$, if Q_c increases, cell voltage decreases.

13. 1.96×10^{37} **14.** 9.247×10^{57} **15**. 1.2×10^{-12}M

16. (a) (i) Mg (ii) Cl_2 (b) Cl_2 and Br_2 (c) (i) $Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$; $\mathbf{E^{\theta} = +0.29V}$

Reason: The overall e.m.f is positive and hence the reaction is feasible (ii) Extraction of bromine from sea water.

EXERCISE 22

1. 3.0367×10^5 C **2.** 635.3 min

3. 56.18 g per equivalent weight

4. 8.04 hours **6.** $1.106 cm^{-1}$ **8.** $25.73\ \Omega^{-1}cm^2mol^{-1}$

5. 0.0252A **7.** $419.04\Omega^{-1}cm^2mol^{-1}$ **9.** $400\ \Omega^{-1}cm^2eq^{-1}$

10. $104.16\Omega^{-1}cm^2eq^{-1}$ **11.** $4.6\ \Omega^{-1}cm^2eq^{-1}$

12. Because in the solid form, ions are not free to move.

13.

1) **Non-ideality of conditions:** Faraday's second law assumes ideal conditions such as constant temperature, concentration of electrolyte, and absence of side reactions and impurities in the electrolyte. These ideal conditions are difficult to achieve in practice, and as such, the law may not hold in real life situations.
2) **Limited to single-electrode reactions:** Faraday's second law applies only to reactions that involve a single electrode, meaning that only one substance is being deposited or liberated. In more complex electrochemical systems, where multiple species may be involved, Faraday's law becomes less applicable.
3) **Does not account for overpotential:** Overpotential is the additional voltage required to drive a reaction at an electrode due to the activation energy barrier. Faraday's second law does not take into account the effect of overpotential, which can lead to deviations from the expected amount of substance deposited or liberated.
4) **Variation of current:** Faraday's second law assumes that the current passing through the electrolyte is constant, which is not always the case in practical systems. Variations in current can affect the deposition or liberation of substances and lead to deviations from Faraday's law.
5) **Concentrated solutions:** Faraday's second law of electrolysis is applicable only to dilute solutions of electrolytes. This is because, in concentrated solutions, the ions tend to interact with each other, which makes the electrolyte behave differently from the predictions of the law.

14. Hydrochloric acid being strong electrolyte, it is almost full ionised even at 0.1M concentration. So the dilution does not increase number of ions significantly, it only increases mobility of ions and hence the increase in the molar conductivity is small. This is different to acetic acid which is a weak electrolyte. For the weak electrolyte, the dilution increases both number of ions (due to an increase on degree of dissociation in accordance with Ostwald's dilution law) and their mobility, leading to greater increase in the molar conductivity.

15. Don't agree

Explanation

It is true that a strong electrolyte is completely dissociated in solution and thus, furnishes all ions for conductance. However, at higher concentrations, the dissociated ions are close to each other and thus, the inter-ionic attractions (ion-ion interactions) are greater. These forces reduce mobility of the ions and thus, conductivity is low. With a decrease in concentration (dilution), the ions move far away from each other thereby decreasing inter-ionic forces of attractions. This results to a slight increase in molar conductivity on dilution.

16. (a) solution A and solution E (b) solution B and solution C (c) solution A, solution B, solution C and solution E (all solutions except solution D) (d) solution D (e) not possible: the conductivity is determined by the ability of compounds to ionise in the solution (not by the solution pH which could be used to distinguish acid base). So both strong acid and base will give the same observation but different to those of weak acid and base which will also give the same observation on their side.

17. (a) 1F (b) 4F (c) 1F

18. 118g

19. (a) $2Cl^-(aq) \longrightarrow Cl_2(g)$+2e (b) $FeCl_2$ (You must deduce this from calculations of given data)

(c) $Fe^{2+}(aq) + 2Cl^-(aq) \longrightarrow Fe(s) + Cl_2(g)$ (d) 0.231L (e) 2.27A

20. $0.00238\Omega^{-1}cm^{-1}$, $238\Omega^{-1}cm^2mol^{-1}$

21. $0.528 \mathrm{Scm^2mol^{-1}}$

22. $1.84 \times 10^{-5} \mathrm{moldm^{-3}}$

23. 0.039

SOLUTIONS TO EXAMINATION QUESTIONS

Question 1

(a) $2MnO_4^- + 5H_2S + 6H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O$

The student should understand that: It is recommended to give the answer in the same form as that of the question unless it is instructed differently.

In this question, a student may consider H_2S as the producer of S^{2-} which is oxidised to S by MnO_4^- thus writing overall balanced redox reaction equation as follows;

$2MnO_4^- + 5S^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O$

But in the problem, it is given H_2S and not S^{2-} (which is not necessary to be from H_2S). So in the half oxidation reaction we must consider H_2S as appears in the question.

i.e. $H_2S \rightarrow S + 2H^+ + 2e$ and not $S^{2-} \rightarrow S + 2e$ so as to give correct overall reaction equation.

(b) Molar mass of potassium salt is $254gmol^-S$

Using n = $\frac{m}{M_r}$;

Number of moles of the potassium salt = $\frac{0.16g}{254gmol^{-1}} = 6.299 \times 10^{-4}mol$

From the molecular formula of the potassium salt, one mole of the salt produces 2 moles of the oxalate ions$(C_2O_4^{2-})$.

Thus number of moles of $C_2O_4^{2-}$ was $2 \times 6.299 \times 10^{-4}$mol or 1.2598×10^{-3}mol

$C_2O_4^{2-}$ reacts with MnO_4^- according to the following equation:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

From which mole ratio of $C_2O_4^{2-}$ to MnO_4^- is 5: 2

Thus number of moles of MnO_4^- reacted $= \frac{2}{5} \times 1.2598 \times 10^{-3}mol$

or 5.0392×10^{-4}mol in $24.5cm^3$ of its solution

Using [ ] = $\frac{n}{v}$;

Molarity of manganate (VII) solution= $\frac{5.0392\times10^{-4}\times10^3}{24.5}M = 0.02M$

Molarity of manganate (VII) solution is 0.02M.

Question 2

(a) The given sulphate produced Fe^{2+} which reacts with $KMnO_4$ according to the following equation:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Where the mole ratio of MnO_4^- to Fe^{2+} is 1: 5

But $[FeSO_4.(NH_4)_2SO_2.6H_2O] = \frac{9.85}{392\times0.25}M = 0.1M$

Number of moles of Fe^{2+} in $25cm^3$ of its solution $= \frac{25}{1000} \times 0.1mol = 2.5 \times 10^{-3}mol$

Then from the above mole ratio;

Number of moles of $MnO_4^- = \frac{1}{5} \times 2.5 \times 10^{-3}mol = 5 \times 10^{-4}$mol of $KMnO_4$ in $24.75cm^3$ of its solution.

Thus $[KMnO_4] = \frac{5\times10^{-4}\times10^3}{24.75}M = 0.0202M$

Hence Molarity of $KMnO_4$ is 0.0202M

(b) Then mass concentration in gdm^{-3} = Molarity × molar mass $= 0.0202 \times 158gdm^{-3} = 3.1916gdm^{-3}$

Thus mass concentration of $KMnO_4$ is $3.1916gdm^{-3}$

(c) Using dilution principle; $M_cV_c = M_dV_d$

Where:

M_c is the molarity of more concentrated $KMnO_4$ solution = 0.0202M

V_c is the volume of more concentrated $KMnO_4$ solution = $1800cm^3$

M_d is the molarity of more diluted $KMnO_4$ solution = 0.02M

V_d is the volume of more diluted $KMnO_4$ solution

Then $V_d = \frac{M_cV_c}{M_d} = \frac{0.0202\times1800}{0.02}cm^3 = 1818cm^3$

Thus volume of distilled water to be added $= (1818 - 1800)cm^3 = 18cm^3$

Hence $18cm^3$ of distilled water should be added

(d) The simple $FeSO_4$ is less preferred than $FeSO_4.(NH_4)_2SO_4.6H_2O$ due to the following reasons:

Fe^{2+} in $FeSO_4$ is unstable to oxidation. It oxidised easily by oxygen from the air thus interfering measurement of correct volume of $KMnO_4$ which is exactly used to oxidize Fe^{2+}into Fe^{3+}.
Having lower molar mass compared to $FeSO_4.(NH_4)_2SO_4.6\,H_2O$, the $FeSO_4$ does not allows weighing error during preparation of its solution. This makes difficulty to prepare its solution of exactly intended concentration.

Question 3

(a) High concentration decreases mobility of ions because in the more concentrated solution ions are close to each other, leading to strong ion-ion interactions (inter-ionic forces) and hence the ionic mobility is lowered.

(b) Number of moles of $KMnO_4$ in $20.7cm^3$ of its solution

$$= \frac{20.7}{1000} \times 0.01mol = 2.07 \times 10^{-4}mol = \text{Number of moles of } MnO_4^-$$

MnO_4^- reacts with Fe^{2+} according to the following equation

$$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \rightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

From which mole ratio of MnO_4^- to Fe^{2+} is 1: 5

Thus number of moles of Fe^{2+} in $20cm^3$ of its solution $= 5 \times 2.07 \times 10^{-4}mol$

Thus number of moles of Fe^{2+} in $1dm^3$ $(1000cm^3)$ of its solution

$$= \frac{5 \times 2.07 \times 10^{-4} \times 1000}{20}mol = 0.05175mol$$

Equation for reduction of Fe^{2+} by zinc: $2Fe^{3+} + Zn \rightarrow Zn^{2+} + 2Fe^{2+}$

From which mole ratio of Fe^{3+} to Fe^{2+} is 1:1

Thus number of moles of Fe^{3+} in $1000cm^3$ of the solution was also 0.05175mol

Mass of iron (III) in 25g of the salt $= 0.05175 \times 56g = 2.898g$

Then % $Fe^{3+} = \frac{2.898}{25} \times 100\% = 11.592\%$

Hence the percentage of iron (III) by mass is 11.592%

(In above calculation, mass of one mole of Fe^{3+} has taken as that of neutral atom of Fe because mass of an electron which removed in the ionisation process is very small and it is negligible compared to total mass of protons and neutrons which are unaltered in the ionisation process).

Question 4

(a) Because its **reduction product,** Cr^{3+}**, is not colourless**; it is green.

(b) Ethanedioic acid crystals $(H_2C_2O_4.2H_2O)$ react with NaOH (aq) according to the following equation:

$$H_2C_2O_4.2\,H_2O + 2NaOH \rightarrow Na_2C_2O_4 + 4\,H_2O$$

From which mole ratio of $H_2C_2O_4.2H_2O$ to NaOH is 1:2

Number of moles of NaOH in $19.8cm^3$of its solution

$$= \frac{19.8}{1000} \times 0.1mol = 1.98 \times 10^{-3}mol$$

Then number of moles of $H_2C_2O_4.2\,H_2O$ in $20cm^3$ of the solution

$$= \frac{1.98 \times 10^{-3}}{2}mol = 9.9 \times 10^{-4}mol$$

And number of moles of $H_2C_2O_4.2\,H_2O$ in $100cm^3$ of the solution

$$= \frac{9.9 \times 10^{-4} \times 100}{20}mol = 4.95 \times 10^{-3}mol$$

Using $m = nM_r$;

Mass of $H_2C_2O_4.2\,H_2O$ in $100cm^3$ of the solution $= 4.95 \times 10^{-3} \times 126g = 0.6237g$

And mass of $Na_2C_2O_4 = (1.5 - 0.6237)g = 0.8763g$

Then number of moles of $Na_2C_2O_4 = \frac{0.8763}{134gmol^{-1}} = 0.00654mol$

It follows that:

- Number of moles of $C_2O_4^{2-}$ from $H_2C_2O_4.2\,H_2O$ = number of moles of $H_2C_2O_4.2\,H_2O = 0.00495mol$
- Number of moles of $C_2O_4^{2-}$ from $Na_2C_2O_4$ = Number of moles of $Na_2C_2O_4 = 0.00654mol$

The total number of moles of $C_2O_4^{2-}$ in $100cm^3$ of the solution

$$= (0.00495 + 0.00654)mol = 0.01149mol$$

Thus total number of moles $C_2O_4^{2-}$ in $25cm^3$ of the solution

$$= \frac{0.01149 \times 25}{100}mol = 0.0028725mol$$

$C_2O_4^{2-}$ reacts with MnO_4^- according to the following equation:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8\,H_2O$$

From which mole ratio of MnO_4^- to $C_2O_4^{2-}$ is 2: 5

Thus number of moles of MnO_4^- required

$= \frac{2}{5} \times 0.0028725\text{mol} = 0.001149\text{mol}$= number of moles of $KMnO_4$

From $[\quad] = \frac{n}{v}$; $V = \frac{n}{[\quad]}$

Thus volume of $KMnO_4$ solution required = $\frac{0.001149}{0.01}\text{dm}^3 = 0.1149\text{dm}^3$ or 114.9cm^3

Hence 114.9cm^3 is required to for complete oxidation of the solution.

Question 5

(a) Number of moles of $KMnO_4$ in 47.8cm^3 of its solution

$$= \frac{47.8}{1000} \times 0.02\text{mol} = 9.56 \times 10^{-4}\text{mol of } MnO_4^-$$

MnO_4^- reacts with H_2O_2 according to the following equation:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

From which mole ratio of MnO_4^- to H_2O_2 is $2:5$

Then number of moles of H_2O_2 in $25\text{cm}^3$of its diluted solution

$$= \frac{5}{2} \times 9.56 \times 10^{-4}\text{mol} = 2.39 \times 10^{-3}\text{mol}$$

Thus molarity of diluted solution = $\frac{2.39 \times 10^{-3} \times 10^3}{25}\text{M} = 0.0956\text{M}$

Using dilution principle, $M_cV_c = M_dV_d$ or $M_c = \frac{M_dV_d}{V_c}$

Where $M_d = 0.0956\text{M}, V_d = 1000\text{cm}^3(1\text{dm}^3), V_c = 100\text{cm}^3$

Substituting $M_c = \frac{0.0956 \times 1000}{100} = 0.956\text{M}$

Using mass concentration in gdm^{-3} = $[\quad]M_r$= 0.956 × 34gdm^{-3} = 32.504gdm^{-3}

Hence mass concentration of original H_2O_2 is 32.504gdm^{-3}

(b)H_2O_2 undergo decomposition to produce O_2 according to the following equation;

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

From which mole ratio of H_2O_2 to O_2 is $2:1$

Number of moles of H_2O_2 in 100cm^3 of its solution = $\frac{100}{1000} \times 0.956\text{mol} = 0.0956\text{mol}$

Thus 0. 0956mol of H_2O_2 produces $\frac{0.0956}{2}$ or 0.0478mol of O_2

But 0.0956mol of H_2O_2 is contained in 100cm^3 its solution

And 1mol of O_2 contains 22.4dm^3 or 22400cm^3 of its volume

Thus 100cm^3 of H_2O_2 produces $0.0478 \times 22400\text{cm}^3$ or 1070.72cm^3 of O_2

Whence 1 cm^3 of H_2O_2 produces $\frac{1070.72}{100}\text{cm}^3$ or 10.7072cm^3 of O_2

Hence volume rating of H_2O_2 solution is 10.7072.

Question 6

(a) It is due to presence of very small amount of unreacted potassium permanganate after the equivalence point.

(b) **Titration by $KMnO_4$ only:**

Number of moles of $KMnO_4$ in 24.2cm^3 of its solution

$$=\frac{24.2}{1000} \times 0.02\text{mol} = 4.84 \times 10^{-4}\text{mol of } MnO_4^-$$

Fe^{2+} (from $FeSO_4(NH_4)_2SO_4.6H_2O$) reacts with MnO_4^- according to the equation:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

From which mole ratio of MnO_4^- to Fe^{2+} is $1:5$

Number of moles of Fe^{2+} $= 5 \times 4.48 \times 10^{-4}\text{mol} = 2.42 \times 10^{-3}\text{mol}$ in 25cm^3 of its solution

Then $[Fe^{2+}] = [FeSO_4.(NH_4)_2SO_4.6H_2O] = \frac{2.42 \times 10^{-3} \times 10^3}{25}\text{M} = 0.0968\text{M}$

Titration by $KClO_3$ followed by $KMnO_4$:

Number of moles $KMnO_4$ in 24.6cm^3 of its solution

$$= \frac{24.6}{1000} \times 0.02\text{mol} = 4.92 \times 10^{-4}\text{mol of } MnO_4^-$$

But 1 mol of MnO_4^- reacts with 5 mol of Fe^{2+} (from the mole ratio of equation of the reaction between Fe^{2+} and MnO_4^-)

Then number of moles of an excess $FeSO_4.(NH_4)_2SO_4.6H_2O$ which unreacted with $KClO_3$

$$= 5 \times 4.92 \times 10^{-4}\text{mol or } 2.46 \times 10^{-3}\text{mol}$$

But total number of moles of $FeSO_4.(NH_4)_2SO_4.6\,H_2O$ in $50cm^3$ of its solution

$$= \frac{50}{1000} \times 0.0968mol = 4.84 \times 10^{-3}mol$$

Thus number of moles of $FeSO_4.(NH_4)_2SO_4.6\,H_2O$ reacted with $KClO_3$

$$= (4.84 \times 10^{-3} - 2.46 \times 10^{-3})mol = 2.38 \times 10^{-3}mol \text{ of } Fe^{2+}$$

From the given equation; mole ratio of Fe^{2+} to ClO_3^- is 6: 1

It follows that:

Number of moles of ClO_3^- in $25cm^3$ of its solution $= \frac{1}{6} \times 2.38 \times 10^{-3}mol$

Then $[ClO_3^-] = [KClO_3] = \frac{2.38 \times 10^{-3} \times 10^3}{6 \times 25}M = \frac{2.38}{150}M$

Using mass concentration in $gdm^{-3} = [\quad]M_r$

Then mass concentration of potassium chlorate (V) $= \frac{2.38}{150} \times 122.5gdm^{-3} = 1.94gdm^{-3}$

Hence the concentration of potassium chlorate (V) solution is $1.94gdm^{-3}$.

Question 7

(a) Assigning oxidation numbers for iodine: $2\,Na_2S_2O_3 + \overset{0}{I_2} \rightarrow \overset{-1}{2NaI} + Na_2S_4O_6$

Thus iodine molecules are being reduced because their oxidation state has been decreased from 0 to -1 in the reaction.

(b) Number of moles of $Na_2S_2O_3$ in $30cm^3$ of its solution

$$= \frac{30}{1000} \times 0.1mol$$

From the given reaction equation, mole ratio of $Na_2S_2O_3$ to I_2 is 2: 1

Then number of moles of $I_2 = \frac{30 \times 0.1}{1000 \times 2}mol = 1.5 \times 10^{-3}mol$

Using $m = nM_r$;

Mass of iodine required $= 1.5 \times 10^{-3} \times 254g = 0.381g$

Hence mass of iodine required is 0.381g

(c) The titration is iodimetry

Reason:

Sodium thiosulphate which is reducing agent is titrated directly with iodine solution which was initially present at the start of the titration.

Question 8

(a)(i) Balanced ionic equation between $KMnO_4$ and KI

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

(ii) Balanced ionic equation between $Na_2S_2O_3$ and I_2

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

(b) From (a) above

$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$……………………..…(i)

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$…………………………………………………(ii)

The overall reaction equation is written by eliminating I_2 in the two equations.

Thus taking (i) + 5× (ii) gives:

$$2MnO_4^- + \cancel{10I^-} + 16H^+ + 10S_2O_3^{2-} + \cancel{5I_2} \rightarrow 2Mn^{2+} + 8\,H_2O + \cancel{5I_2} + 5S_4O_6^{2-} + \cancel{10I^-}$$

Hence the overall reaction equation is:

$$2MnO_4^- + 10S_2O_3^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 5S_4O_6^{2-} + 8\,H_2O$$

(c) Number of moles of $KMnO_4$ in $25cm^3$ of its solution

$$= \frac{25}{1000} \times 0.0204mol = 5.1 \times 10^{-4}mol \text{ of } MnO_4^-$$

But from the overall reaction equation, mole ratio of MnO_4^- to $S_2O_3^{2-}$ is 2: 10 or 1: 5

Thus number of moles of $S_2O_3^{2-}$ in $24.4cm^3$ of its solution

$$= 5 \times 5.1 \times 10^{-4}mol = 2.55 \times 10^{-3}mol \text{ of } Na_2S_2O_3$$

Then using $[\quad] = \frac{n}{v}$;

$$[Na_2S_2O_3] = \frac{2.55 \times 10^{-3} \times 10^3}{24.4}M = 0.1045M$$

Hence Molarity of sodium thiosulphate solution is 0.1045M

(d)By dilution principle; $M_cV_c = M_dV_d$

From which, $V_d = \frac{M_cV_c}{M_d}$

Where $M_d = 0.1$ M (Decimalor solution)

$M_c = 0.1045M, V_c = 1750cm^3$

Substituting $V_d = \frac{0.1045 \times 1750}{0.1} cm^3 = 1828.75cm^3$

Volume of distilled water added = $(1828.75 - 1750)cm^3 = 78.75cm^3$

Hence $78.75cm^3$ of distilled water must be added to $1750cm^3$ solution in order to convert into a decimolar solution.

(e) The titration is iodometry because iodine used in the titration was firstly produced from oxidation of potassium iodide which is reducing agent by potassium permanganate which is an oxidising agent i.e. there was indirect titration of iodine.

Question 9

(a) Oxidation: acidic medium; reduction: basic medium.

(b) Equations for reactions:

$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$ ………………………………..(i)

From bleaching power

Then $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ ………………………..(ii)

Taking (i) + (ii) gives overall reaction equation which is:

$$2S_2O_3^{2-} + Cl_2 \rightarrow S_4O_6^{2-} + 2Cl^-$$

From which, mole ratio of $S_2O_3^{2-}$ to Cl_2 is 2: 1

Number of moles of $Na_2S_2O_3$ in $24.2cm^3$ of its solution

$$= \frac{24.2}{1000} \times 0.1mol = 2.42 \times 10^{-3} mol \text{ of } S_2O_3^{2-}$$

Thus number of moles of Cl_2 in $25cm^3$ of the solution

$$= \frac{2.42 \times 10^{-3}}{2} mol = 1.21 \times 10^{-3} mol$$

Then number of moles of Cl_2 in $250cm^3$ of the solution

$$= \frac{1.21 \times 10^{-3} \times 250}{25} = 1.21 \times 10^{-2} mol$$

Using $m = nM_r$;

Mass of chlorine in 2.5g of bleaching powder $= 1.21 \times 10^{-2} \times 71g = 0.8591g$

Whence the percentage of chlorine $= \frac{0.8591}{2.5} \times 100\% = 34.364\%$

Therefore, the percentage of the chlorine is 34.364%.

Question 10

(i) Cerium sulphate oxidizes siderite only which is reducing agent as it contains Fe^{2+} (in $FeCO_3$) which can be oxidised according to the following equation of oxidation half reaction: $Fe^{2+} \rightarrow Fe^{3+} + e$

Combining the above equation and the given reduction half reaction equation gives the overall reaction equation which is:

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$$

From which, mole ratio of Fe^{2+} to Ce^{4+} is 1:1;

Number of moles of cerium (IV) sulphate in $100cm^3$ of its solution

$$\frac{100}{1000} \times 0.1mol = 0.01mol = \text{number of moles of } Ce^{4+}$$

Thus from the mole ratio, number of moles of Fe^{2+} is also 0.01mol = Number of moles of $FeCO_3$.

Using $m = nM_r$;

Mass of $FeCO_3$ (siderite) = 0.01 × 116g = 1.16g

Whence mass of haematite (Fe_2O_3) is $(3.9 - 1.16)g = 2.74g$

Then $\%Fe_2O_3 = \frac{2.74}{3.9} \times 100 = 70.3\%$

And $\%FeCO_3 = \frac{1.16}{3.9} \times 100 = 29.7\%$

Hence:

- The percentage of $FeCO_3$ (siderite) is 29.7%
- The percentage of Fe_2O_3 (haematite) is 70.3%

(ii) Using, $n = \frac{m}{M_r}$;

Number of moles of $Fe_2O_3 = \frac{2.74}{160} mol = 0.017125mol$

But 1 mole of Fe_2O_3 contains 2 moles of Fe^{3+} which in turn gives 2 moles of Fe^{2+} after reduction.

Hence number of moles of Fe^{2+} which are formed after reduction of the haematite = 0.017125 × 2 mole = 0.03425 mole

It follows that; Total number of moles of Fe^{2+} after the reduction = (0.03425 + 0.01) mole = 0.04425 mole

Where 0.01 mole of Fe^{2+} is from siderite (from (i) above)

From the mole ratio in (i); number of moles of cerium (IV) sulphate required to react with Fe^{2+} will be also 0.04425mol

Using $V = \frac{n}{[\ ]}$;

Substituting $V = \frac{0.04425}{0.1}dm^3 = 0.4425dm^3$ or $442.5cm^3$

Hence 442.5 cm^3 of cerium (IV) sulphate would be required

Fe^{2+} reacts with $KMnO_4$ according to the following ionic equation:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

From which mole ratio of MnO_4^- to Fe^{2+} is 1:5

Thus number of moles required to react with 0.04425 mol of $Fe^{2+} = \frac{0.04425}{5}mol = 8.85 \times 10^{-3}mol$

Using $V = \frac{n}{[\ ]}$; then volume of $KMnO_4 = \frac{8.85\times10^{-3}}{0.05}dm^3 = 0.177dm^3 = 177cm^3$

Hence $177cm^3$ of $KMnO_4$ would be used.

Question 11

(a) Cell diagram corresponding to given cell reactions is:

$$Zn(s)\,|\,Zn^{2+}(0.1M)||H^+(aq)\,|\,H_2(1atm)$$

$E^\theta_{cell} = E^\theta_{cathode} - E^\theta_{anode} = 0 - (0.76V) = 0.76V$

Also from given cell reaction: $R_Q = \frac{[Zn^{2+}]\,P_{H_2}}{[H^+]^2} = \frac{0.1\times1}{[H^+]^2}$ and n = 2

Then by Nernst equation; $E_{cell} = E^\theta_{cell} - \frac{0.0591}{n}logR_Q$

Substituting $0.58 = 0.76 - \frac{0.0591}{2}log\frac{0.1}{[H^+]^2}$; $0.02955\,log\,0.1\,[H^+]^{-2} = 0.18$

$$0.02955log0.1 + 0.02955log[H^+]^{-2} = 0.18$$

Or $-2 \times 0.02955log[H^+] = 0.20955; -log[H^+] = \frac{0.20955}{2\times0.02955} = 3.5$

Hence the pH solution at hydrogen electrode is 3.5

(b) Anode reaction : $Fe^{2+} \rightarrow Fe^{3+} + e$

Cathode reaction : $Ce^{4+} + e \rightarrow Ce^{3+}$

Where n = 1 and $E^\theta_{cell} = E^\theta_{cathode} - E^\theta_{anode} = (1.44 - 0.68)V = 0.76V$

Using $E^\theta_{cell} = \frac{0.0591}{n}logK_c$

Substituting 0.76 = 0.0591logK_c; From which $K_c = 7.237 \times 10^{12}$

Hence the equilibrium constant for the reaction is 7.237×10^{12}

Question 12

(a) The positive value of the cell potential indicates that the cell as formulated is spontaneous

(b) The electrode potential is (-0.13V) (Electrode potential remains the same even if the half-reaction is multiplied by any coefficient)

(c)

(i) Ag < Cu < Fe < Zn > Mg < Na
Least Reactive **Most Reactive**

(ii) Na

(iii) Ag

(iv) Greatest e.m.f is obtained by taking most positive electrode as cathode and most negative electrode as anode.

Cell diagram is: $Na(s)\,|\,Na^+(aq)||Ag^+(aq)\,|\,Ag(s)$

Question 13

(a)(i) This means that when Zn/Zn^{2+} half cell is connected to standard hydrogen electrode (SHE), the Zn/Zn^{2+} half cell acts as the anode half cell and SHE becomes the cathode half cell

(ii) This means that when Cu^{2+}/Cu half cell is connected to standard hydrogen electrode (SHE), Cu^{2+}/Cu half cell acts as the cathode and SHE becomes the anode half cell.

(b) When electrode formulated as cathode has lower reduction potential than electrode formulated as the anode and hence e.m.f of the cell becomes negative.

Question 14

(a) **Spontaneous reactions** *are chemical reactions which can occur without the input of work from an external source.*

Most of spontaneous reactions are exothermic.

(b) Half-cell reaction: $Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$

From which n = 1 and $Q_c = \frac{[Fe^{2+}]}{[Fe^{3+}]} = \frac{0.6}{1} = 0.6$

From Nernst equation; $E = E^{\theta} - \frac{0.0591}{n}\log Q_c$

Substituting $E = 0.771 - \frac{0.0591}{1}\log 0.6 = 0.784$

Hence electrode potential of the half-cell is 0.784V.

Question 15

(a) (i) Represents the electrode potential which is measured when an electrode is in contact with 1M solution of its ions at 25°C and 1atm (standard conditions).

(ii) Represents the chemical reaction which involves transfer of electrons.

(b) Assuming complete (100%) ionisation of salts; then:

$[Zn^{2+}] = [ZnSO_4] = 2M$ and $[Cu^{2+}] = [CuSO_4] = 0.5M$

And cell diagram of the Daniel cell is: $Zn(s)\,|\,Zn^{2+}(2M)||Cu^{2+}(0.5M)\,|\,Cu(s)$

From which $E^{\theta}_{cell} = E^{\theta}_{cathode} - E^{\theta}_{anode}$ = 0.34V – (-0.76V) = 1.1V

Cell reaction: $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

From which n = 2 and $Q_c = \frac{[zn^{2+}]}{[Cu^{2+}]} = \frac{2}{0.5} = 4$

From Nernst equation: $E_{cell} = E^{\theta}_{cell} - \frac{RT}{nF}\text{In}\, Q_c$

But $\text{In}Q_c$= 2.303$\log Q_c$; Then $E_{cell} = E^{\theta}_{cell} - \frac{2.303RT}{nF}\log Q_c$

Where $E^{\theta}_{cell} = 1.1V, R = 8.3143, T = 35°C = (35 + 273)K = 308K$, n = 2, F = 96500 and R_Q = 4

Substituting $E_{cell} = 1.1 - \frac{2.303\times8.3143\times308}{2\times96500}\log 4 = 1.0816$

Hence the e.m.f of the cell is 1.0816

Note: In the above question temperature is not standard (25°C) so we cannot use the simplified Nernst equation which assumes the temperature to be 25°C.

Question 16

(a) To enable formation of $\mathbf{Fe(OH)_2}$, then $\mathbf{Fe(OH)_3}$ and finally to hydrate $\mathbf{Fe_2O_3}$ to form the rust ($\mathbf{Fe_2O_3 \bullet xH_2O}$).

That is:

$H_2O \rightleftharpoons H^+ + OH^-$

Then $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

Then $Fe(OH)_2 + O_2 + H_2O \rightarrow Fe(OH)_3$

And finally $Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \bullet XH_2O$

(b) **Reduction half reaction:** $Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$

From which n = 2 and $Q_c = \frac{1}{[Zn^{2+}]}$

Since $ZnSO_4$ is 95% dissociated and its mole ratio to Zn^{2+} is 1:1;

It follows that; $[Zn^{2+}] = \frac{95}{100} \times 0.1M = 0.095M$; Whence $Q_c = \frac{1}{0.095} = 10.5263$

From Nernst equation: $E = E^{\theta} - \frac{0.0591}{n}\log Q_c$

Substituting $E = -0.76 - \frac{0.0591}{2}\log 10.5263 = -0.79V$

Hence the electrode potential is $-0.79V$

Question 17

(a) (i) Is the degradation of the metal caused by unwanted oxidation over its surface.

(ii) Is the redox reaction whereby both reduction and oxidation occurs in the same element contained in a particular molecule or compound.

(b) Cell diagram corresponding to given redox reaction is: $Fe^{2+}(aq)\,|\,Fe^{3+}(aq)||Sn^{4+}(aq)\,|\,Sn^{2+}(aq)$

Then; $E^{\theta}_{cell} = E^{\theta}_{cathode} - E^{\theta}_{anode} = (0.150 - 0.771)V = -0.621V$

Using $E^{\theta}_{cell} = \frac{0.0591}{n}\log K_c$; Where n = 2 (From cell reaction)

Then $-0.621 = \frac{0.0591}{2}\log K_c$; $\log K_c = -21$

$K_c = \log^{-1}(-21) = 1 \times 10^{-21}$

Hence the equilibrium constant of the reaction is 1×10^{-21}

(Very small value of K_c indicates that the position of chemical equilibrium is far backward i.e. reverse reaction is spontaneous while forward reaction is not spontaneous).

Question 18

(a) This is due to its significances which are:

1. It allows the ions to migrate from cathode half-cell into the anode half-cell so as to complete the circuit.
2. It prevents the diffusion of the electrolyte from one half-cell to the other thus maintaining the charge balance in the two half cells.

(b) From Nernst equation; $E = E^{\theta} - \frac{0.0591}{n}\log Q_c$

But reduction half-cell reaction for copper is: $Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$

From which $Q_c = \frac{1}{[Cu^{2+}]}$ and $n = 2$

Then $E = E^{\theta} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]}$ or $E = -0.02955\log[Cu^{2+}]^{-1} + E^{\theta}$

Or $\mathbf{E = 0.02955\log[Cu^{2+}] + E^{\theta}}$

Hence (by comparing the bolded equation with general equation of straight line, **y = mx + c**) if the graph of electrode potential, **E**, is constructed against logarithms of concentrations of copper (II) ions, $[\mathbf{Cu^{2+}}]$, will have the following features:

The graph will be straight line with positive slope amounted to 0.02955

The y – intercept = E^{θ} (standard electrode potential)

TABLE OF DATA ANALYSIS

Electrode potential, E in volts	0.310	0.320	0.324	0.328	0.331
$[Cu^{2+}]$ in $moldm^{-3}$	0.1	0.2	0.3	0.4	0.5
$\log[Cu^{2+}]$	-1.0	-0.7	-0.5	-0.4	-0.3

Then on your own plot the graph of E (on y – axis) against $\log[Cu^{2+}]$ (on x – axis); thereafter determine the y – intercept of the graph whose value is equal to standard electrode potential of copper.

Question 19

(a) (i) **Salt** which is **strong electrolyte** like potassium nitrate (KNO_3)

(ii) Salt bridge allows flow of ions while the wire allows flow of electrons and not the required flow of ions.

The cost of electricity will vary directly proportional to electrochemical equivalent of the metal.

So if:

C_1 and C_2 are electricity costs per kg for producing Mg and Al respectively,

Z_1 and Z_2 are electrochemical equivalent for Mg and Al respectively,

And E_1 and E_2 are equivalent weights for Mg and Al respectively.

Then from; $\frac{E_1}{Z_1} = \frac{E_2}{Z_2}$

It follows that; $\frac{E_1}{C_1} = \frac{E_2}{C_2}$

But $E_1 = \frac{\text{Atomic mass of Mg}}{\text{Magnitude of charge in } Mg^{2+}} = \frac{24}{2} = 12$

$$E_2 = \frac{\text{Atomic mass of Al}}{\text{Magnitude of charge in } Al^{3+}} = \frac{27}{3} = 9$$

And $C_1 = x$Tsh

Substituting $E_1 = \frac{12}{x} = \frac{9}{C_2}$; $C_2 = \frac{12}{9}x$ or $\frac{4}{3}x$Tsh per kg of Al

Then for y kg, the cost become $\left(\frac{4}{3}x\right)y = \frac{4}{3}xy$Tsh

Hence the cost for producing y kg of aluminium $\frac{4}{3}xy$Tsh

Question 20

(a) Voltaic cell is a device which uses spontaneous chemical reactions to generate electricity while electrolytic cell is a device which uses electric current to produce non-spontaneous chemical reaction.

(b) **For water electrolysis:**

(i) Hydrogen gas is liberated at cathode as per reaction equation: $2H^{+}(aq) + 2e \rightarrow H_2(g)$

From which 2F = 2 × 96500C or 193000C liberates 1 mol of H_2

Then by using $Q = It = 0.65 \times 5.5 \times 3600C$ or 12870C liberates $\frac{12870}{193000} = 0.06668$mol of H_2

From ideal gas equation; $V = \frac{nRT}{P}$

Substituting $V = \frac{0.06668\times0.082\times286\times760}{750}dm^3 = 1.585dm^3$

Hence volume of hydrogen gas liberated is $1.585dm^3$

(ii)Oxygen gas is liberated at anode according to the following equation:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e$$

From which 4F liberates one mole of O_2

Then 2F liberates 0.5mol of O_2

But according Avogadro's law; mole ratio = volume ratio (For gases)

Thus 0.5mol of O_2 ≡ A half of volume of hydrogen liberated by the same amount of electricity.

Hence volume of oxygen liberated = $\frac{1.585}{2}dm^3 = 0.7925dm^3$

(iii) **For $CuSO_4$ electrolysis:**

Copper is deposited at cathode according to the following equation:

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

From which $2F = 2 \times 96500C$ deposit 64g of copper

Then 12870C deposits $\frac{12870}{2\times96500} \times 64g = 4.268g$ of Cu

Hence mass of copper precipitated is 4.268g

Question 21

(a) The methods are:

1. Galvanization

In this method, iron is covered with another metal like zinc which form protective layer to prevent iron from rusting. The protective metal must be stronger reducing agent than iron for the method to be more efficient.

2. Cathodic protection

In this method iron is connected to more reactive metal like magnesium and zinc whereby the iron (weaker reductant) acts as cathode while the more reactive metal (stronger reductant) acts as anode of the galvanic cell. In this galvanic cell arrangement, iron behaving as cathode will not get oxidized and hence it is prevented from rusting.

(b) By Kohlrausch's law: $\Lambda_\infty(AgCl) = \Lambda_\infty(Ag^+) + \Lambda_\infty(Cl^-)$

$$= 6.2 \times 10^{-3} + 7.6 \times 10^{-3} = 1.38 \times 10^{-2}\Omega^{-1}m^2mol^{-1}$$

AgCl being sparingly soluble electrolyte;

$$\text{molar conductivity of its saturated solution} = \text{molar conductivity at infinite dilution}$$

Using $V = \frac{\Lambda_m}{\kappa} = \frac{1.38\times10^{-2}\Omega^{-1}m^2mol^{-1}}{1.5\times10^{-4}m^{-1}\Omega^{-1}} = 92m^3mol^{-1} = 92000dm^3mol^{-1}$

Then molar solubility of AgCl $= \frac{1}{89610}moldm^{-3} = 1.087 \times 10^{-5}moldm^{-3}$

Question 22

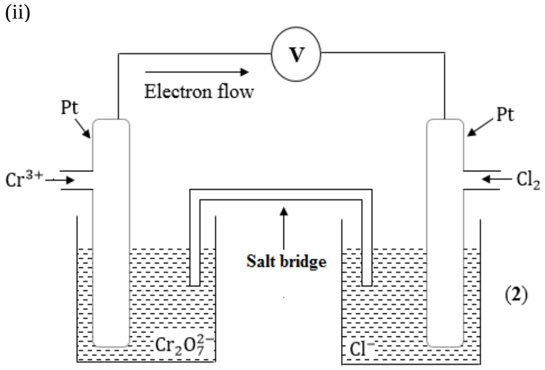
(i) The cell diagram corresponding to the given cell reaction is:

$Cr^{3+}(1M) \mid Cr_2O_7^{2-}(1M) \parallel Cl_2(g) \mid Cl^-(1M)$

Thus $E^\emptyset_{cell} = E^\emptyset_R - E^\emptyset_L = (1.36 - 1.33)V = 0.03V$

Hence the standard e.m.f is 0.03V

(ii)



(2)

(iii) Oxidation half reaction: (At anode)

$Cr^{2+} \rightarrow Cr^{3+} + e$ ………………. (i)

Reduction half reaction: (At cathode)

$S_4O_6^{2-} + 2e \rightarrow 2S_2O_3^{2-}$ ……….. (ii)

Taking 2(i) + (ii) to get overall reaction equation;

$2Cr^{2+} + S_4O_6^{2-} \rightarrow Cr^{3+} + 2S_2O_3^{2-}$

From which, number of electron transferred, $n = 2$

Also using $E^{\emptyset}_{cell} = E^{\emptyset}_{cathode} - E^{\emptyset}_{anode}$

The e.m.f corresponding to given reaction;

$E^{\emptyset}_{cell} = 0.17V - (-0.5V) = 067V$

Using $E_{cell} = E^{\emptyset}_{cell} - \frac{0.0591}{n}\log Q_c$

But at equilibrium; $E_{cell} = 0$ and $Q_c = K_c$

It follows that: $0 = E^{\emptyset}_{cell} - \frac{0.0591}{n}\log K_c$ or $E^{\emptyset}_{cell} = \frac{0.0591}{n}\log K_c$

Substituting $0.67 = \frac{0.0591}{n}\log K_c$

$K_c = 4.71 \times 10^{22}$

Hence the equilibrium constant is 4.71×10^{22}

(iv) The equilibrium constant is **very large** implying that the **operating time of the cell is large.**

Question 23

(a) The differences are:

1. Electronic conductors, conduct electricity by using moving electrons (delocalised valence electrons) while electrolytic conductors conduct electricity by using moving ions.
2. Electronic conductors, conduct electricity in solid state while electrolytic conductors, conduct electricity in liquid state.
3. Electronic conductors are elements while electrolytic conductors are compounds.

(b) Cell constant $= \frac{l}{A}$

Substituting: Cell constant $= \frac{1cm}{2cm^2} = 0.5\ cm^{-1}$

The cell constant is $\mathbf{0.5\ cm^{-1}}$

Conductivity $=$ Conductance $\times$ Cell constant

But Conductance $= \frac{1}{\text{Resistance}}$

The conductivity $= \frac{\text{Cell constant}}{\text{Resistance}} = \frac{0.5\ cm^{-1}}{7.25\ \Omega} = 0.069\ \Omega^{-1}cm^{-1}$

The conductivity is $\mathbf{0.069\ \Omega^{-1}cm^{-1}}$

Resistance, $R = \rho \times$ Cell constant

Where $\rho = 361\Omega cm$

And cell constant $= 0.5\ cm^{-1}$ (It is constant for given cell)

Then $\mathbf{R = 361\Omega cm \times 0.5\ cm^{-1} = 180.5\ \Omega}$

Question 24

(a)

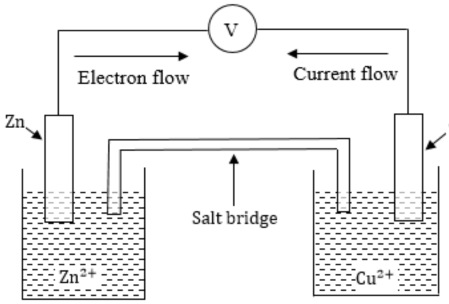
(i) Is the electrode at which **reduction** occurs.

(ii) Is the electrode at which **oxidation** occurs.

(iii) Is the potential difference between the electric double layers which is formed when an electrode is in contact with solution containing 1M of its ions measured at 25℃ and 1 atm (standard conditions).

(iv) Is the **electrochemical cell** which consists of the same electrodes and the same electrolyte at different concentration which are connected by salt bridge.

(b)(i)



(2)

(ii) Cell reaction:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

$E^{\emptyset}_{Cell} = E^{\emptyset}_{cathode} - E^{\emptyset}_{anode} = E^{\emptyset}_{Cu^{2+}/Cu} - E^{\emptyset}_{Zn^{2+}/Zn} = +0.34V - (-0.76V) = 1.1V$

The e.m.f is 1.1V

From the Nernst equation; $E_{cell} = E^{\emptyset}_{Cell} - \frac{0.0591}{n}\log Q_c$

But at equilibrium: $E_{cell} = 0$ and $Q_c = K_c$

Thus $0 = E^{\emptyset}_{Cell} - \frac{0.0591}{n}\log K_c$

An therefore $E^{\emptyset}_{Cell} = \frac{0.0591}{n}\log K_c$

Where $E^{\emptyset}_{Cell} = 1.1V$ and $n = 2$

Substituting $1.1 = \frac{0.0591}{n}\log K_c$

From which $K_c = 1.68 \times 10^{37}$

Hence the equilibrium constant is 1.68×10^{37}

Question 25

(a) For HNO_3 to dissolve Au, the following reaction must occur:

$NO_3^- + Au + 4H^+ \rightarrow Au^{3+} + NO + 2H_2O$

The cell diagram corresponding to the above reaction is as follows:

$Au \mid Au^{3+}(aq) \parallel NO_3^- \mid NO$

From which: $E^{\emptyset}_{Cell} = E^{\emptyset}_{R} - E^{\emptyset}_{L} = E^{\emptyset}_{NO_3^-/NO} - E^{\emptyset}_{Au^{3+}/Au} = (0.96 - 1.5)V = -0.54V$

Since $E^{\emptyset}_{Cell}$ is negative, the reaction is not spontaneous and hence the given nitric acid will not dissolve the gold.

(b) Using $n = MV$;

Number of moles of $KMnO_4$ used $= \frac{20}{1000} \times 0.02$ mol $= 4 \times 10^{-4}$ mol $=$ number of moles of MnO_4^-

But from the given balanced reaction equation; mole ratio of MnO_4^- to $C_2H_4O_4 \bullet xH_2O$ is 2: 5

Thus number of moles of $C_2H_4O_4 \bullet xH_2O$ is $\frac{5}{2} \times 4 \times 10^{-4}$ mol $= 1 \times 10^{-3}$ mol

Using $M_r = \frac{m}{n}\left(\text{From } n = \frac{m}{M_r}\right)$

Where $m = 0.126g$ (given)

$M_r(C_2H_4O_4 \bullet xH_2O) = \frac{0.126g}{1\times10^{-3}\ mol} = 126g/mol$

Thus: $(2 \times 12) + (4 \times 1) + (4 \times 16) + 18x = 126$

From which $x = 2$

Hence the value of x is 2