Electrochemistry

A. REDOX REACTION

- Redox is an abbreviated term from words reduction and oxidation that means a reaction in which oxidation and reduction take place at the same time

- Oxidation is the loss of electrons from an atom, ion or molecule

- Reduction is the gain of electrons by an atom, ion or molecule

- To determine whether or not a substance has been oxidised or reduced, we can see the changes of oxidation number or electron transfer

- **Redox and Electron Transfer**
  For example, sodium reacts with chlorine to form table salt, NaCl

  $2Na_{(s)} + Cl_{2\,(g)} \longrightarrow 2NaCl_{(s)}$

  We can divide this equation to show which atom is oxidised and reduced

  $Na \longrightarrow Na^+ + e^-$
  $Cl_2 + 2e^- \longrightarrow 2Cl^-$

  The half-equation show that sodium loss one electron and it is oxidised while each chloride gain one electron and it is reduced

- **Oxidation Number**
  Oxidation number is a number showing a degree of oxidation of an atom or ion. This number have positive or negative value

  Oxidation Number Rules
  1. Any single element or diatomic element has zero value of oxidation number
     Example:
     S_8, Cl_2 and Zn has zero value of oxidation number
  2. Group 1 elements have +1
  3. Group 2 elements have +2
  4. Fluorine has –1
  5. Hydrogen has +1 but, there are a special case where hydrogen has –1 in metal hydrides
  6. Oxygen is –2 except in peroxides (–1) and in F_2O (+2)
  7. Monoatomic ion has the same oxidation number as its charge for example Al^{+3} has oxidation number of +3
  8. The total oxidation number in a compound is zero
  9. The total oxidation number in an ionic compound has the same value as its charge
  10. The more electronegative of an element either in a compound or ion will give more negative oxidation number

- **Redox and Oxidation Number**
  We can furtherly define reduction as an increase in oxidation number and oxidation as a decrease in oxidation number

  $Sn + 4HNO_3 \longrightarrow SnO_2 + 4NO_2 + 2H_2O$
  0   +5   +4   +4

  From this reaction, we can see that Sn is oxidised because its oxidation number has increased from 0 to +4 and N is reduced because its oxidation number has decreased from +5 to +4

- **Oxidizing and Reducing Agent**
  Oxidising agent or oxidant is a substance that brings oxidation by removing electrons from another atom or ion. The oxidation number of oxidation agent will decrease as it increases the oxidation number of another atom or ion

  Reducing agent or reductant is a substance that brings about reduction by donating electrons to another atom or ion. The oxidation number of reducing agent will increase as it decreases the oxidation number of another atom or ion

  From the reaction that given above, oxidation number of N is decreased from +5 to +4 and oxidation number of Sn is increased from 0 to +4. We can say that HNO_3 is the oxidising agent because it increases the oxidation state of Sn while Sn is the reducing agent because it decreases the oxidation state of N in HNO_3

- **Balancing Chemical Equations Using Ox. Number**
  We can use oxidation number to balancing chemical equation that involves redox reaction
  1. Write the unbalanced equation and identify the atoms which change in ox. number
  2. Deduce the ox. number changes
  3. Balance the ox. number changes
  4. Balance the atoms

Disproportionation

There are special cases where an atom can be reduced or oxidised by itself simultaneously. This is called disproportionation

For example, let's say we add chlorine to cold aqueous sodium hydroxide with the following disproportionation reaction below

$$Cl_{2\,(Aq)} + 2NaOH_{\,(Aq)} \longrightarrow NaCl_{\,(Aq)} + NaClO_{\,(Aq)} + H_2O_{\,(l)}$$

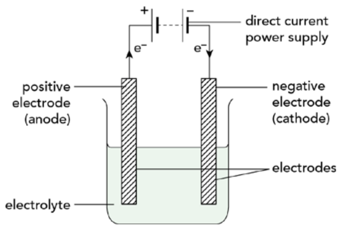
If we calculate oxidation number change respectively, we get

$$\underset{0}{Cl_{2\,(Aq)}} + \underset{2(+1\,-2\,+1)}{2NaOH_{\,(Aq)}} \longrightarrow \underset{+1\,-1}{NaCl_{\,(Aq)}} + \underset{+1\,+1\,-2}{NaClO_{\,(Aq)}} + \underset{2(+1)\,-2}{H_2O_{\,(l)}}$$

We can see that the chlorine atom is both has an increased and decreased oxidation number at NaCl with change from 0 to –1 and NaClO with change from 0 to +1

B. ELECTROLYSIS

Electrolysis is the decomposition of a molecule to its element by using electric current and it is carried out in an electrolysis cell



In this cell, there are

a. Electrolyte, the decomposed compound in the form of molten ionic compound or a concentrated aqueous solution of ions
b. Electrodes, rods that conduct electricity to and from electrolyte. There are two types of electrodes
    1) Positive Electrode/Anode
    2) Negative Electrode/Cathode

This method must have a direct current power supply because it deposits anions in the anode and cations in the cathode. Otherwise, the current would keep changing directions and would lead to an uneven distribution of ions in the electrodes

Electrolysis is used to

a. Purify metals
b. Produce non-metals such as fluorine
c. Extract metals from their metal ores when it is not possible to extract by heating it with carbon

Redox Reactions in Electrolysis

When electrolysis occurred, the positive ions move to the cathode and gain electrons from it

For example

$Cu^{2+} + 2e^- \longrightarrow Cu$

$2H^+ + 2e^- \longrightarrow H_2$

From reaction above, we already know that reduction is the gain of electrons so, we can also say that reduction always occurs at the cathode

On the other side, the negative ions move to the anode and lose electrons to it

For example

$2Cl^- \longrightarrow Cl_2 + 2e^-$

$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

From reaction above, we already know that oxidation is the loss of electrons so, we can also say that oxidation always occurs at the anode

C. QUANTITATIVE ELECTROLYSIS

Faraday's Law

The amount of substance that is formed at and electrode during electrolysis is proportional to the time and amount of electricity

$$Q = I \times t$$

The amount of electricity is also expressed by the faraday (F) unit where one faraday is the quantity of electric charge carried by one mole of electrons or 1 mole of singly charged ions with the value of 96500 C mol^{-1}

The relationship between Faraday and Avogadro constant is

$$F = L \times e$$

Where e is the charge on an electron

For example, during the electrolysis of copper (II) sulfate solution, copper is deposited at the cathode

$$\underset{1\text{ mol}}{Cu^{2+}_{\,(Aq)}} + \underset{2\text{ mol}}{2e^-} \longrightarrow \underset{1\text{ mol}}{Cu_{\,(s)}}$$

From the reaction given above, we can see that it needs two electrons to produce one mole of copper from Cu^{2+} ions and we can also say it requires two faradays of electricity to deposit one mol of copper (remember that 1 faraday 96500 C so 2 faraday is equal to 2 x 96500 C)

- **Calculating Amount of Substance Produced during Electrolysis**
  We can use value of F to calculate the mass of substance deposited and the volume of gas produced at an electrode

  a. Amount of Substance
     1. Write the half equation for the reaction
     2. Find the number of coulombs required to deposit 1 mole of product at the electrode
     3. Calculate the charged transferred during the electrolysis
     4. Calculate the mass by simple proportion using the relative atom mass

  b. Volume of Gas
     1. Write the half equation for the reaction
     2. Find the number of coulombs required to produce 1 mole of gas
     3. Calculate the charge transferred during the electrolysis
     4. Calculate the mass by simple proportion using the relationship 1 mole of gas occupies 24.0 dm^3 at R.T.P

- **Finding Avogadro Constant Experimentally**
  We can find Avogadro constant by calculating the charge associated with 1 mole of electrons

$$L = \frac{charge\ on\ 1\ mole\ of\ e^-}{charge\ on\ 1\ e^-}$$

In experiment, one charge on the electron is approximately 1.60 x 10^{-19} C

D. ELECTRODE POTENTIALS

- Electrode potential is the voltage measured for a half-cell compared with another half-cell

- The value of electrode potential can be used to determine how easy it is to reduce a substance

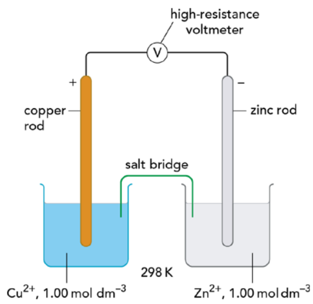
- This means that the electrode potential refers to the reduction reaction so the electrons appear on the left side of the half-equation

- The electrode potential with more positive value is easier to reduce the ions on the left and the right is relatively unreactive or poor reducing agent and vice versa with more negative value or less positive

E. COMBINING HALF-CELLS

- Half-cell is one half of an electrochemical cell which either donates electrons to or receives electrons from an external circuit when connected to another half-cell

- Half-cells are connected together using
  a. Wires connecting the metal rods in each half-cell to a high-resistance voltmeter
  b. Salt bridge that allows the movement of ions between two half-cells and does not allow the movement of electrons. It can be made from a strip of filter paper soaked in saturated solution of potassium nitrate



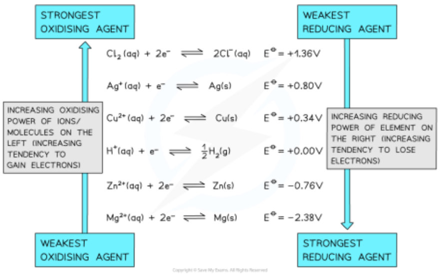
F. THE USE OF $E^{\ominus}$ VALUES

- **Predicting Cell Voltages**
  $E^{\ominus}$ values is used to calculate voltage between two half-cells by measuring the difference between both $E^{\ominus}$ values of half-cells. This is also called standard cell potential

- **Determine Direction of Electron Flow**
  The electron will flow from the negative pole to positive pole and in other word, it will flow from half-cell with more negative $E^{\ominus}$ values to more positive $E^{\ominus}$ values

- **Predict if a Reaction will Occur**
  The more positive the value, the half-cell will most likely proceed in forward direction and easier to reduce the species on the left of the half equation

The less positive the value, the half-cell will most likely proceed in reverse direction and easier to oxidise the species one the right of the half equation



The Nernst Equation

The effect of changes in temperature and ion concentration on the E_{cell} can be deduced using the Nernst equation

$$E = E^\ominus + \frac{RT}{zF}\ln\frac{[oxidised\ species]}{[reduced\ species]}$$
$$= E^\ominus + \frac{0.059}{z}\log_{10}\frac{[oxidised\ species]}{[reduced\ species]}$$

Note that this equation only works with aqueous ion and it is simplified in such a way because R, T and F are constant at standard temperature, ln x can be modify to $2.303\log_{10}x$ and z is number of electrons transferred in the reaction

C. MORE ABOUT ELECTROLYSIS

Electrolysis of Molten Electrolytes

Cation moves to the negatively charged cathode then gaining electron while anion moves to the positively charged anode then loses electron

Electrolysis of Aqueous Solution

Aqueous solutions have more than one cation and anion in solution due to the presence of water. The actual ions that are discharged during electrolysis will depend on the relative electrode potential and concentration of ions

Relative Electrode Potential of Ions

The positively charged cation with the most positive $E^\ominus$ will be discharged at the cathode because cation is easily reduced and the negatively charged anion with the most negative $E^\ominus$ will be discharged at the anode, because anion is easily oxidised

Concentration of Ions

Ions that are present in higher concentrations are more likely to be discharged

H. EXERCISE

1. [9701_S19_qp_13_01]
Manganese and nitrogen can show a range of different oxidation states. Calculate the sum of the oxidation states of Mn and N in each row of the table. In which row is this sum the smallest?

	manganese-containing species	nitrogen-containing species
A	$MnCl_4$	N_2
B	$MnCO_3$	NO_2^-
C	K_2MnO_4	NH_4^+
D	$Mn(OH)_3$	NH_2OH

Solution
From the question given above, it is instructed us to find each oxidation number from both manganese and nitrogen containing species then sum both oxidation number and find the smallest sum

$MnCl_4$	N_2	4 + 0 = 4
+4 -4	0	
$MnCO_3$	NO_2^-	2 + 3 = 5
+2 +4 -6	+3 -4	
K_2MnO_4	NH_4^+	6 – 3 = 3
+2 +6 -8	-3 +4	
$Mn(OH)_3$	NH_2OH	3 – 1 = 2
+3 -6 +3	-1 +2 -2 +1	

From calculation, the smallest sum of both Mn and N oxidation number value is the last one with total of 2 and thus, the answer is **(D)**

2. [9701_S19_qp_12_033]
In which reactions are nitrogen atoms reduced?

1 $2NO_2 \rightarrow N_2 + 2O_2$

2 $4NO_2 \rightarrow 2N_2O + 3O_2$

3 $4NO_2 + 6H_2O \rightarrow 4NH_3 + 7O_2$

Solution
To determine which reactions are nitrogen atoms reduced, we can define reduce of an atom as decreased oxidation number

$$\underset{+8\ -8}{2NO_2} \longrightarrow \underset{0}{N_2} + 2O_2$$

$$\underset{+16\ -16}{4NO_2} \longrightarrow \underset{+4\ -4}{2N_2O} + 3O_2$$

$$\underset{+16\ -16}{4NO_2} + 6H_2O \longrightarrow \underset{-12\ +12}{4NH_3} + 7O_2$$

By calculating the oxidation number, only reaction 2 and 3 where oxidation number of N is reduced and thus the answer is **2 and 3**

3. [9701_W19_qp_43_01]
This is a sectional question, not the full question

An electrochemical cell is constructed using two half-cells
- an Sn^{4+}/Sn^{2+} half-cell
- an Al^{3+}/Al half-cell

The cell is operated at 298 K
The Al^{3+}/Al half-cell has standard concentrations
The Sn^{4+}/Sn^{2+} half-cell has $[Sn^{4+}] = 0.300\ mol\ dm^{-3}$ and $[Sn^{2+}] = 0.150\ mol\ dm^{-3}$

(i) Use the Nernst equation to calculate electrode potential, E, of Sn^{4+}/Sn^{2+} half-cell under these conditions
(ii) Calculate the E_{cell} under these conditions
(iii) Write an equation for the overall cell reaction that occurs

Solution
(i) Remember that the formula of Nernst equation is

$$E = E^{\theta} + \frac{0.059}{z}\log_{10}\frac{[oxidised\ species]}{[reduced\ species]}$$
$$E = 0.15 + \frac{0.059}{2}\log_{10}\frac{0.300}{0.150}$$
$$E = +0.159\ or\ 0.160$$

(ii) $E_{cell} = 0.160 - (-1.66) = +1.82\ V$
(iii) The overall reaction is
$2Al + 3Sn^{4+} \longrightarrow 2Al^{3+} + 3Sn^{2+}$

4. [9701_W21_qp_41_01]
When dilute sulfuric acid is electrolysed, water is split into hydrogen and oxygen

$$2H_2O_{(l)} \longrightarrow 2H_{2\,(l)} + O_{2\,(g)}$$

A current of **x**A is passed through the solution for 14.0 minutes. 462 cm^3 of hydrogen are produced at the cathode, measured under room conditions

a. Calculate the number of hydrogen molecules produced during the electrolysis
b. Calculate the total number of electrons transferred to produce this number of hydrogen molecules
c. Calculate the quantity of charge, in coulombs, of the total number of electrons calculated in **(b)**
d. Calculate the current, **x**, passed during this experiment

Solution

a. Calculate the mole of hydrogen then multiply it by Avogadro constant

$$nH_2 = \frac{462}{24000} = 0.01925$$
$$= n \; x \; L$$
$$= 0.01925 \times 6.02 \times 10^{23}$$
$$= 1.16 \times 10^{22} \text{ molecules}$$

b. $2 \times 1.16 \times 10^{22} = 2.32 \times 10^{22}$ electrons

c. $Q = 2.32 \times 10^{22} \times 1.6 \times 10^{-19}$
$= 3.71 \times 10^{3}$ C

d. $I = \frac{Q}{t} = \; 3.71 \times \frac{10^{3}}{14 \times 60}$
$= 4.4 \; A$