CAMBRIDGE UNIVERSITY EXAMINATIONS

General Certificate of Education Advanced Subsidiary Level
and Advanced Level (As Level and A Level)
Notes(As Level)

CHEMISTRY
A - LEVEL

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ELECTROCHEMISTRY (Notes)

24 Electrochemistry

24.1 Electrolysis

Learning outcomes

Candidates should be able to:

1 predict the identities of substances liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration

2 state and apply the relationship $F = Le$ between the Faraday constant, F, the Avogadro constant, L, and the charge on the electron, e

3 calculate:

    (a) the quantity of charge passed during electrolysis, using $Q = It$

    (b) the mass and/or volume of substance liberated during electrolysis

4 describe the determination of a value of the Avogadro constant by an electrolytic method

24.2 Standard electrode potentials $E^{\ominus}$; standard cell potentials $E^{\ominus}_{cell}$ and the Nernst equation

Learning outcomes

Candidates should be able to:

1 define the terms:

    (a) standard electrode (reduction) potential

    (b) standard cell potential

2 describe the standard hydrogen electrode

3 describe methods used to measure the standard electrode potentials of:

    (a) metals or non-metals in contact with their ions in aqueous solution

    (b) ions of the same element in different oxidation states

4 calculate a standard cell potential by combining two standard electrode potentials

5 use standard cell potentials to:

    (a) deduce the polarity of each electrode and hence explain/deduce the direction of electron flow in the external circuit of a simple cell

    (b) predict the feasibility of a reaction

6 deduce from $E^{\ominus}$ values the relative reactivity of elements, compounds and ions as oxidising agents or as reducing agents

    onstruct redox equations using the relevant half-equations

24.2 Standard electrode potentials $E^{\ominus}$; standard cell potentials $E^{\ominus}_{cell}$ and the Nernst equation (continued)

Learning outcomes

Candidates should be able to:

8   predict qualitatively how the value of an electrode potential, E, varies with the concentrations of the aqueous ions

9   use the Nernst equation, e.g. $E = E^{\ominus} + (0.059/z) \log \dfrac{[\text{oxidised species}]}{[\text{reduced species}]}$

to predict quantitatively how the value of an electrode potential varies with the concentrations of the aqueous ions; examples include $Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$, $Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$

10 understand and use the equation $\Delta G^{\ominus} = -nE^{\ominus}_{cell}F$

Electrolysis

1 predict the identities of substances liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration

Electrolysis is the decomposition of an ionic compound into its elements by an electric current

Electrolyte solution or melt	negative cathode product	negative electrode cathode half-equation	positive anode product	positive electrode anode half-equation	comments
molten aluminium oxide $Al_2O_3(l)$	molten aluminium	$Al^{3+}_{(l)} + 3e^- \rightarrow Al_{(l)}$	oxygen gas	$2O^{2-}_{(l)} - 4e^- \rightarrow O_{2(g)}$ or $2O^{2-}_{(l)} \rightarrow O_{2(g)} + 4e^-$	The industrial method for the extraction of aluminium its ore
aqueous copper(II) sulfate $CuSO_4(aq)$	copper deposit	any conducting electrode e.g. carbon rod, any metal including copper itself $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	oxygen gas	inert electrode like carbon (graphite rod) or platinum (i) $4OH^-_{(aq)} - 4e^- \rightarrow 2H_2O_{(l)} + O_{2(g)}$ or $4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$ (ii) $2H_2O_{(l)} - 4e^- \rightarrow 4H^+_{(aq)} + O_{2(g)}$ or $2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$	The blue colour of the copper ion will fade as the copper ions are converted to the copper deposit on the cathode
aqueous copper (II) sulphate $CuSO_4(aq)$	copper deposit	any conducting electrode e.g. carbon rod, any metal including copper itself $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	copper(II) ions – the copper anode dissolves	copper anode $Cu_{(s)} - 2e^- \rightarrow Cu^{2+}_{(aq)}$ or $Cu_{(s)} \rightarrow Cu^{2+}_{(s)} + 2e^-$	Used for electroplating any conducting solid with a layer of copper. When using both copper cathode and anode, the blue colour of the copper ion does not decrease because copper deposited at the (-) cathode = the copper dissolving at the (+) anode.
molten sodium chloride $NaCl(l)$	molten sodium	$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$	chlorine gas	$2Cl^-_{(l)} - 2e^- \rightarrow Cl_{2(g)}$ or $2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^-$	This a method used to manufacture sodium and chlorine.
aqueous sodium chloride solution (brine) $NaCl(aq)$	hydrogen	$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ or $2H_3O^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2H_2O_{(l)}$ or $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$	chlorine gas	$2Cl^-_{(aq)} - 2e^- \rightarrow Cl_{2(g)}$ or $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$	This is the process by which hydrogen, chlorine and sodium hydroxide are manufactured
hydrochloric acid $HCl(aq)$	hydrogen gas	$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ or $2H_3O^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2H_2O_{(l)}$	chlorine gas	$2Cl^-_{(aq)} - 2e^- \rightarrow Cl_{2(g)}$ or $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$	All acids give hydrogen at the cathode. Theoretically the gas volume ratio is $H_2:Cl_2$ is 1:1, BUT, chlorine is slightly so there seems less chlorine formed than actually was.
sulphuric acid sulfuric acid $H_2SO_4(aq)$	hydrogen gas	$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ or $2H_3O^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2H_2O_{(l)}$	oxygen gas	(i) $4OH^-_{(aq)} - 4e^- \rightarrow 2H_2O_{(l)} + O_{2(g)}$ or $4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$ (ii) (+) $2H_2O_{(l)} - 4e^- \rightarrow 4H^+_{(aq)} + O_{2(g)}$ or $2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$	All acids give hydrogen at the cathode. Whereas hydrochloric acid gives chlorine at the anode, the sulfate ion does nothing and instead oxygen is formed. Theoretically the gas volume ratio is $H_2:O_2$ is 2:1 which you see with the Hofmann Voltameter
molten lead(II) bromide $PbBr_2(l)$	molten lead	$Pb^{2+}_{(l)} + 2e^- \rightarrow Pb_{(l)}$	bromine vapour	$2Br^-_{(l)} - 2e^- \rightarrow Br_{2(g)}$ or $2Br^-_{(l)} \rightarrow Br_{2(g)} + 2e^-$	A good demonstration in the school laboratory – brown vapour and silvery lump provide good evidence of what's happened
Silver nitrate $AgNO_3(aq)$	solid silver	$Ag^+_{(aq)} + 2e^- \rightarrow Ag_{(s)}$	oxygen gas	$4OH^-_{(aq)} - 4e^- \rightarrow 2H_2O_{(l)} + O_{2(g)}$	electroplating experiment

Resource author: machemb

2 state and apply the relationship $F = Le$ between the Faraday constant, F, the Avogadro constant, L, and the charge on the electron, e

$F = Le$,

where F is the Faraday constant, L is the Avogadro constant and e is the charge on an electron.

Charge on one electron = 1.60×10^{-19}
Avogadro constant = 6.02×10^{23}
Faraday constant = 96500 coulombs per mole of electron(aprox)
Note :- One coulomb is defined as when one ampere current is passed for one second

Faraday is the quantity of electric charge carried by 1 mole of electrons

3 calculate:

(a) the quantity of charge passed during electrolysis, using $Q = It$

(b) the mass and/or volume of substance liberated during electrolysis

The mass of a substance (or volume of a gas) produced at an electrode during electrolysis is proportional to:

- the time over which a constant electric current passes
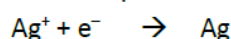- the strength of the electric current.

$$Q = I \ \times \ t$$

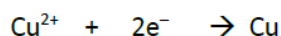**Where** I = current in amperes

Q = charge in coulombs

t = time in seconds

During the electrolysis of silver nitrate solution, silver is deposited at the cathode:

$$Ag^+ + e^- \ \rightarrow \ Ag$$

1 Faraday of electricity (96 500 C) is required to deposit 1 mole of silver.

During the electrolysis of copper(II) sulfate solution, copper is deposited at the cathode:

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

The equation shows that 2 moles of electrons are needed to produce 1 mole of copper from Cu2+ ions. So it requires 2 Faradays of electricity (2 × 96 500 C) to deposit 1 mole of copper.

Q1:- Calculate the mass of lead deposited at the cathode during electrolysis when a current of 1.50 A flows through molten lead(II) bromide for 20.0 min. (Ar value: [Pb] = 207; F = 96 500 C mol–1) ans 1.93 g Pb

Q2:- Calculate the volume of oxygen produced at r.t.p. when a concentrated aqueous solution of sulfuric acid, H_2SO_4, is electrolysed for 30.0 min using a current of 0.50 A. (F = 96 500 C mol–1; 1 mole of gas occupies 24.0 dm^3 at r.t.p.) and 0.0560 dm^3 O_2 at r.t.p.

Q3:- Calculate the mass of silver deposited at the cathode during the electrolysis of silver nitrate solution if you use a current of 0.10 amps for 10 minutes. And 0.067 g

Q4:- How long would it take to deposit 0.635 g of copper at the cathode during the electrolysis of copper(II) sulphate solution if you use a current of 0.200 amp. F = 9.65 x 10^4 C mol^{-1} (or 96500 C mol^{-1}). A$_r$ of Cu = 63.5.

4 describe the determination of a value of the Avogadro constant by an electrolytic method

Avogadro constant, L ,

To determine the Avogadro's constant, we will discuss the electrolysis as shown in fig.

Use this formula to determine the value of Avogadro's constant

$$L = \frac{\text{charge on 1 mole of electrons}}{\text{charge on 1 electron}}$$
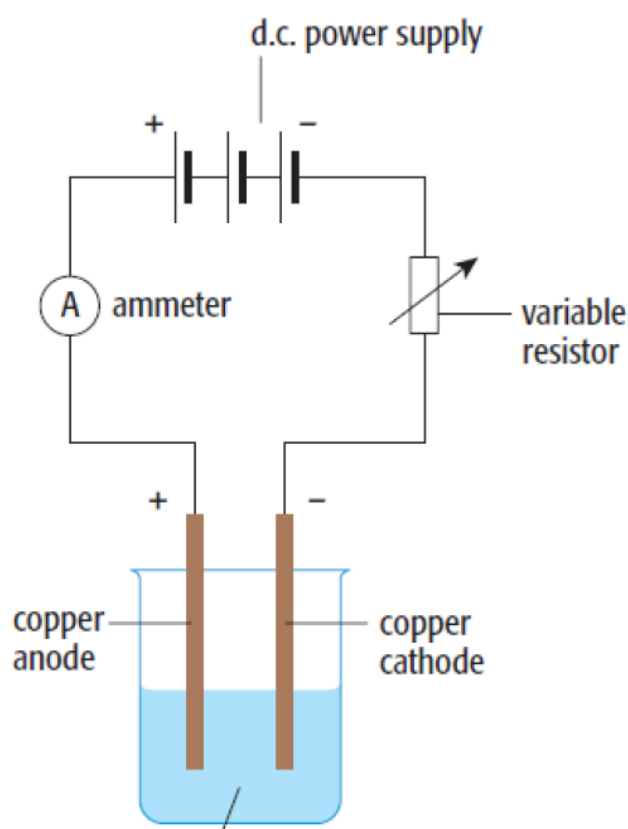
Where L is Avogadro constant and

- The charge of an electron is 1.6 x 10 $^{-19}$ coulombs per electron.
- To find the Charge on 1 mole of electrons we have to perform two steps

Step 1. Determine the charge (number of coulombs) used in the experiment by using the relationship:

$$Q = I \times t$$

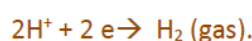Find the total charge used and the mass of anode decreased

[An ammeter is used in the experiment to measure the amperage and a clock or stopwatch is used to measure the time in seconds. The mass of copper that reacts can be determined by measuring the mass of the anode before and after the electrolysis.

In the drawing of the electrolytic cell both electrodes are copper and the electrolyte is 0.5 mol dm^{-3} H$_2$SO$_4$. In the course of the electrolysis, the copper electrode (the anode) connected to the positive pin of the power supply loses mass as the copper atoms are converted to copper ions. This loss of mass is visible to the eye after a while as pitting of the surface of the metal electrode. Also the copper ions, Cu^{2+}, produced, immediately pass into the water solution and impart a blue tint to the water.

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

At the same time at the other electrode, the cathode, hydrogen gas, H$_2$, is liberated at the surface through the **reduction** of hydrogen ions, H$^+$, in the aqueous sulfuric acid solution.

The reaction is

$$2H^+ + 2e \rightarrow H_2 \text{ (gas)}.$$

It is also possible to collect the hydrogen gas produced and use it to calculate Avogadro's number. However, in this experiment we will base calculation of Avogadro's number on loss of mass of the copper anode.]

Step 2. Find the total charge on one mole of electrons
By using the total charge consumed and the mass of anode decreased, we are able to find the charge on one mole of electrons
Finally use this formula to find Avogadro constant

$$L = \frac{\text{charge on 1 mole of electrons}}{\text{charge on 1 electron}}$$

Question:- In an electrolysis process, copper electrode and anode are used, a current of 0.20 A for 34 min is passed. The initial and final mass of anode given. Find Avogadro constant by using the given data. Ar of Cu is 63.5.

    mass of anode at start of the experiment = 56.53 g
    mass of anode at end of experiment = 56.40 g

Standard electrode potentials $E^{\ominus}$; standard cell potentials $E^{\ominus}_{cell}$ and the Nernst equation

1 define the terms:

(a) standard electrode (reduction) potential

(b) standard cell potential

When a metal is put into a solution of its ions, like when zinc is placed in a solution containing zinc ions, then two types of reactions are taking place.

Single electrode cell (half-cell)

- a tiny number of zinc atoms on the surface of the metal are converted to zinc ions, which go into solution.

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e-$$
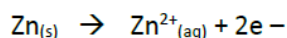
This leaves an excess of electrons on the surface of the zinc

- Now zinc metal has excess of electrons and the solution around the metal now has excess Zn^{2+} ions. So some of zinc ion can regain electrons and reduction takes place and deposit on metal rod

$$Zn^{2+}_{(aq)} + 2e- \rightarrow Zn_{(s)}$$
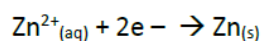
- The redox equilibrium is established

$$Zn^{2+}_{(aq)} + 2e- \rightleftharpoons Zn_{(s)}$$
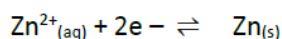
- This equilibrium establish an electric potential (voltage difference , or EMF) between the metal and the metal ions in solution. We cannot measure this potential directly.

A **potential** difference develops between the **electrode** and the electrolyte which is called **electrode potential** as given above.

Electrode potential is the tendency of an electrode to get reduced or to get oxidized

Definition: - standard electrode potential

The EMF of a cell made up of the test electrode and a standard hydrogen electrode. This EMF is measured under standard conditions of T, P and concentration

Definition: - standard Cell potential

A standard cell potential is the EMF (voltage) produced when two half-cells are connected under standard conditions
2 describe the standard hydrogen electrode

Individual half-cell electrode potentials cannot be measured in isolation, and so they are measured relative to a standard. The standard that is chosen is the standard hydrogen electrode

In the standard hydrogen electrode, hydrogen gas at 100 kPa (1 atmosphere) pressure is bubbled around a platinum electrode of very high surface area in a solution of H^+ ions of concentration 1 mol dm^{-3}. Platinum is chosen because it

is an inert metal, has very little tendency to be oxidised and does not react with acids. The reaction occurring in this half-cell is:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$
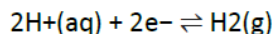
And electrode potential (E) for standard hydrogen electrode is 0.00 V.

Standard electrode potential, values for all half-cells are measured relative to this electrode. When connected to another half-cell, the value read on the voltmeter gives the standard electrode potential for that half-cell.

298K

$H_2(g)$
100 kPa pressure

platinum electrode

bubbles of hydrogen gas   1 M H^+(aq)
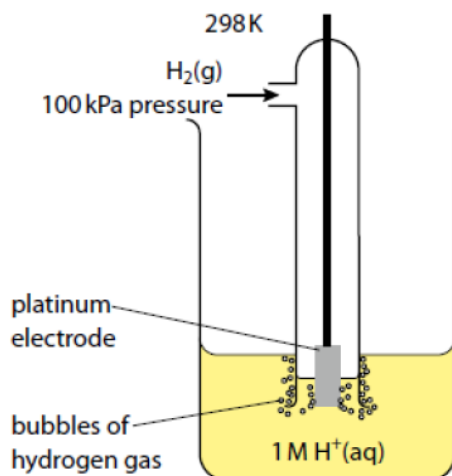
The standard hydrogen electrode.
Note: 1 M = 1 mol dm^{-3}.

3 describe methods used to measure the standard electrode potentials of:
(a) metals or non-metals in contact with their ions in aqueous solution
(b) ions of the same element in different oxidation states

Measuring standard electrode potentials
   (i)   Metal electrode

(a) The standard electrode potential (E) of copper could be measured by connecting a standard copper half-cell (1 mol dm^{-3} $Cu^{2+}_{(aq)}/Cu_{(s)}$) to the standard hydrogen electrode as shown in fig.

Salt Bridge

A **salt bridge** is a connection containing a weak electrolyte between the oxidation and reduction half-cells.

A salt bridge usually contains a concentrated solution of an ionic salt such as KCl, or KNO$_3$.

The salt bridge provides an electrical connection between the two half-cells to complete the circuit. It allows ions to flow into or out of the half-cells to balance out the charges in the half-cells.

0.34V

salt bridge

298 K

$H_2(g)$
100 kPa pressure

Cu

platinum electrode

bubbles of hydrogen gas   1 M H^+(aq)   1M Cu^{2+}(aq)
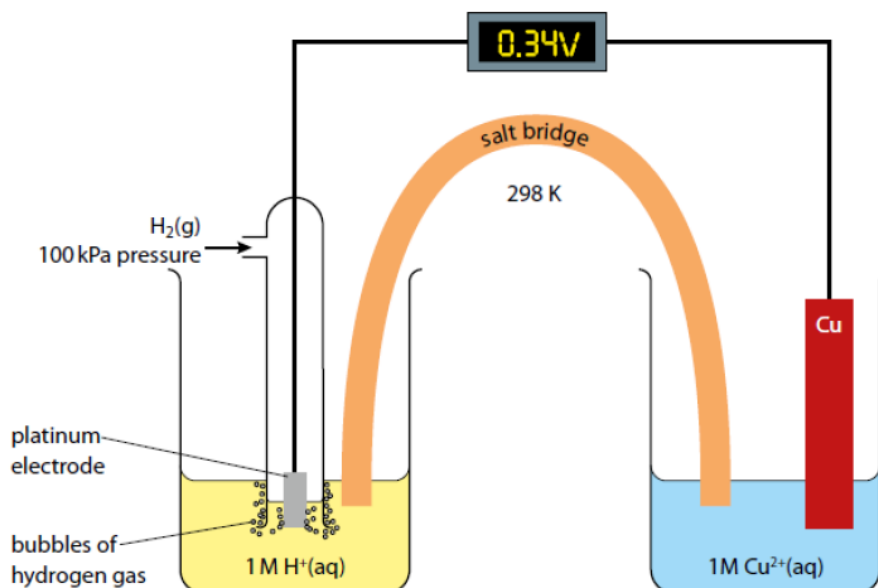
Measuring the standard electrode potential of the Cu^{2+}/Cu half-cell. Note: 1 M = 1 mol dm^{-3}.

The reactions that occur in the half-cells are:

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
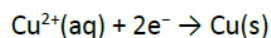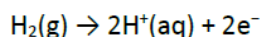
The hydrogen is oxidised and the copper(II) ions are reduced.

Explanation

standard electrode potentials are

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E = +0.34 \text{ V}$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E = 0 \text{ V}$$
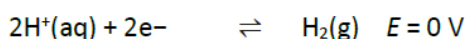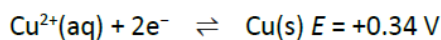
- By convention, the electrode potential refers to the reduction reaction. So the electrons appear on the left-hand side of the half-equation as given in above equations.

- The more positive (or less negative) the electrode potential, the easier it is to reduce the ions on the left hand side. So forward reaction will take place and positive ion will be reduced
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

- The more negative (or less positive) the electrode potential, the more difficult it is to reduce the ions on the left. So the element on the right is relatively reactive and will be oxidized.
$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$
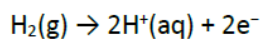
NOTE:- A voltmeter with very high resistance is used so that the current is as low as possible. If current flows, the concentrations of the species in the half-cells will change and the system will no longer be under standard conditions.

(b) Measuring the standard electrode potential of the Zn^{2+}/Zn half-cell. Note: 1 M = 1 mol dm^{-3}.

Figure shows a cell in which a standard zinc half-cell is connected to a standard hydrogen electrode. The reactions are:

The standard cell potential for Zn^{2+}/Zn half-cell is - 0.76 V.

This value will be shown on voltmeter.

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad E^{\ominus} = 0.00 \text{ V}$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76 \text{ V}$$

(i) The E^O values show us that Zn^{2+} ions are more difficult to reduce than H+ ions (they have a more negative E^O value).

(ii) Zn^{2+} ions are less likely to gain electrons than H+ ions.

(iii) So Zn will lose electrons to the H^+/H_2 half-cell and H+ ions will gain electrons from the Zn^{2+}/Zn half-cell.

So following reactions will be taking place

$$2H+(aq) + 2e- \rightarrow H2(g) \qquad\qquad Zn(s) \rightarrow Zn2+(aq) + 2e-$$
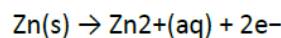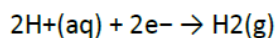
Activity:- Write half-equations for the reactions taking place in the half-cells shown below
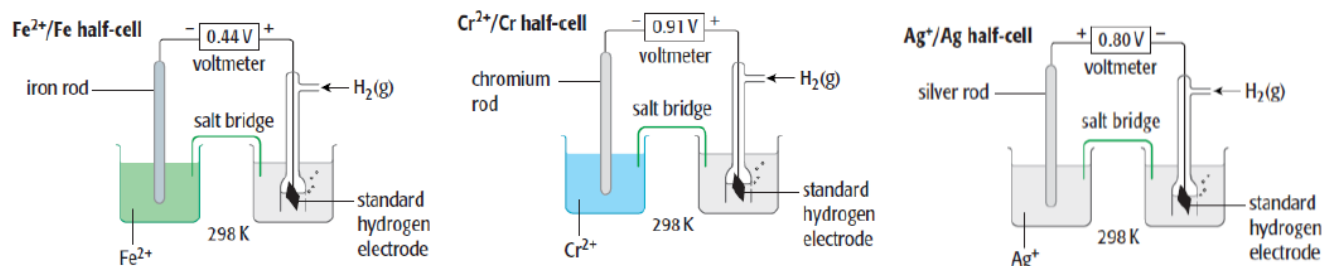
Reaction Taking palce

Measuring standard electrode potentials

(ii)   NON - Metal electrode

Measuring the standard electrode potential of a Cl_2/Cl^- half-cell.
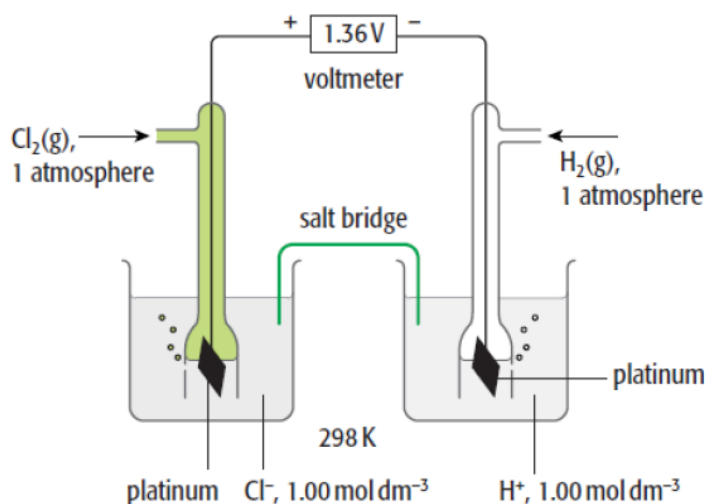
To measure the standard electrode potential of Chlorine, we use the same type of apparatus as used in Standard hydrogen electrode as shown in figure.

Platinum electrode is used, and chlorine gas at standard conditions is passed through this electrode and 1 mol dm^{-3} solution of chloride is taken.

Following values are given in data booklet

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq) \qquad\qquad E^\ominus = +1.36\,V$$
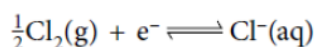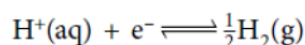
$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad\qquad E^\ominus = 0.00\,V$$

E° shows that Cl2 molecules are easy to reduce than H+ ion, So Ch2 will be reduced and H2 will be oxidized.

Measuring E° of Half-cells containing ions of the same element in different oxidation states
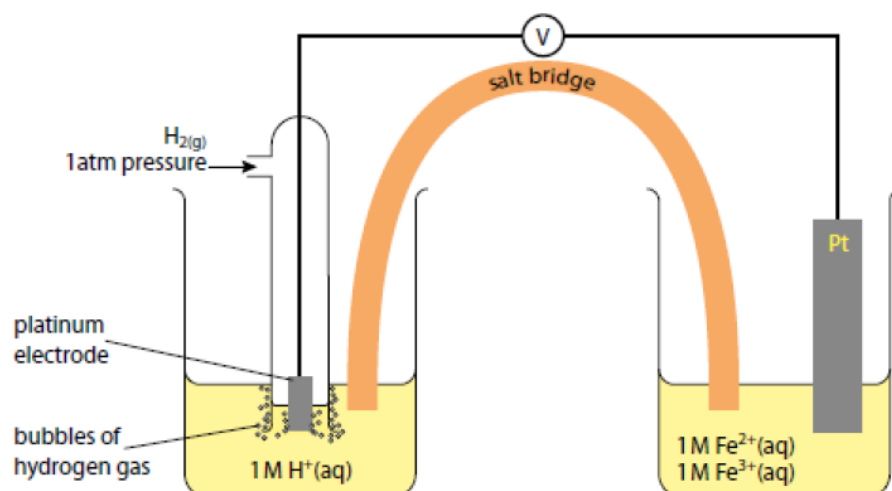
To measure, electrode potential of an element in different oxidation states, we use the apparatus as shown in fig.

Platinum electrode is used and 1 mole dm^{-3} solutions of two ions like Fe^{2+} and F^{3+} are used as electrolyte.

$Fe^{3+}(aq) + e- \rightleftharpoons Fe^{2+}(aq)$ $E°= +0.77$ V
This shows that iron(III) ion will be reduced .

4 calculate a standard cell potential by combining two standard electrode potentials

We can calculate the voltage of an electrochemical cell made up of two different half-cells as shown in figure.
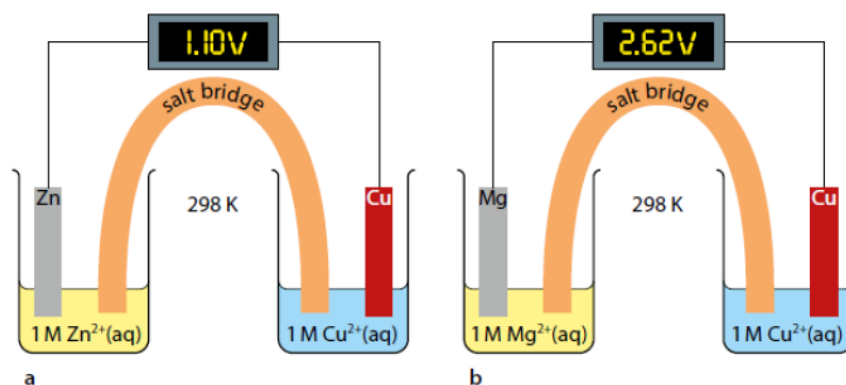
The voltage measured is the difference between the E^O values of the two half-cells. we call this value the standard cell potential.

NOTE :-

The bigger the difference in reactivity between the metal electrodes, the higher the voltage of the cell.

Zn|Zn^{2+}||Cu^{2+}|Cu cell voltage.

Figure a shows Zn|Zn^{2+}||Cu^{2+}|Cu cell.

The Standard electrode potential values in databooklet are as

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad\qquad E^\ominus = -0.76\,V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad\qquad E^\ominus = +0.34\,V$$

Cell Voltage = E°(More positive/ reduction) – E°(Less positive/ oxidation)

= +0.34 – (– 0 .76)

= 1.10 v

Figure b shows Mg|Mg²⁺||Cu²⁺|Cu cell.
To calculate its cell voltage, we need electrode potential values of Mg²⁺/Mg and Cu²⁺/Cu

$Cu^{2+} + 2e^-$	$\rightleftharpoons$	Cu	+0.34
$Mg^{2+} + 2e^-$	$\rightleftharpoons$	Mg	−2.38
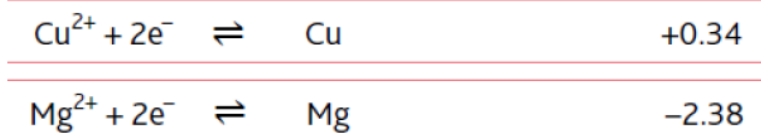
So Standard Cell Potential will be as

Cell Voltage = E°(More positive/ reduction) − E°(Less positive/ oxidation)

= +.34 - (-2.38)

= 2.72

Methods 2 . Cell Potential

We can use standard electrode potentials to work out the cell potential of the Zn|Zn²⁺||Ni²⁺|Ni cell

The standard electrode potentials are:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^\ominus = -0.76\,V$
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\ominus = -0.23\,V$

However, both of these are written as reduction reactions and in any cell there must be a reduction reaction *and* an oxidation reaction. One of the reactions must occur in the reverse direction.
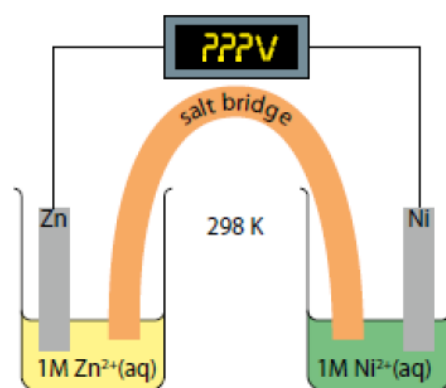
Because the value of the standard electrode potential is more negative for the Zn²⁺/Zn reaction, this means that the oxidation reaction is more favourable for zinc than for nickel. We therefore reverse the zinc half-equation:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^\ominus = +0.76\,V$ **oxidation**
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E^\ominus = -0.23\,V$ **reduction**
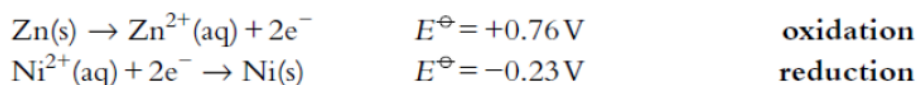
The cell potential is just the sum of these electrode potentials:

$E^\ominus_{cell} = 0.76 - 0.23 = +0.53\,V$

The overall reaction can be written by adding these two equation
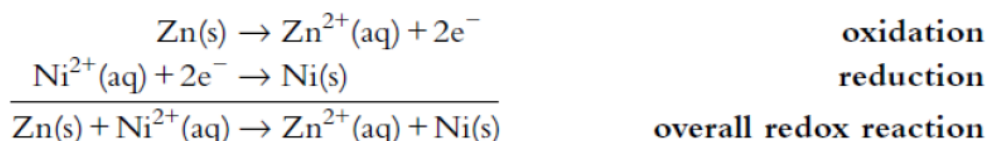
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ **oxidation**
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ **reduction**
$\overline{Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)}$ **overall redox reaction**

5 use standard cell potentials to:
(a) deduce the polarity of each electrode and hence explain/deduce the direction of electron flow in the external circuit of a simple cell

Charge flow and the nature of the electrodes

Negative charge always flows in the same continuous direction around a complete circuit – in this case the electrons are travelling clockwise around the circuit
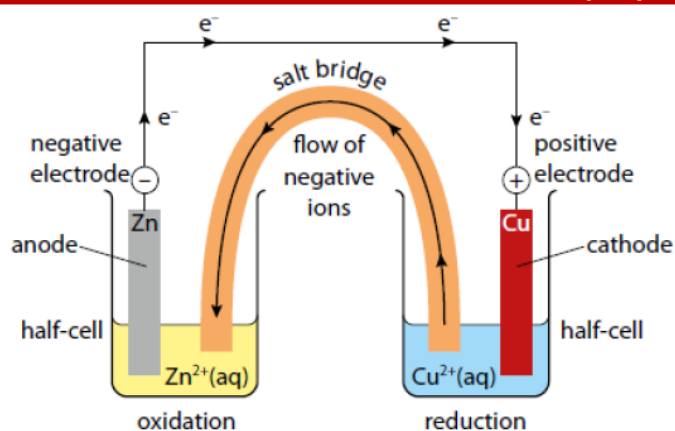
12

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad\qquad E^{\ominus} = -0.76\,V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad\qquad E^{\ominus} = +0.34\,V$$

As shown from E° values In the zinc half-cell, an oxidation reaction of Zn occurs:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$$
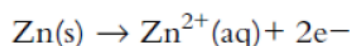
So the zinc electrode is the anode in this cell. Because electrons are released at the zinc electrode, this is the negative electrode.

In the copper half-cell, a reduction reaction occurs:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
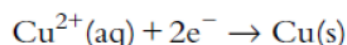
So the copper electrode is the cathode in this cell. Because electrons flow through the external circuit towards this electrode, and are used up there, this is the positive electrode.

In a voltaic cell, the cathode is the positive electrode and reduction takes place at cathode

In a voltaic cell, the anode is the negative electrode and oxidation takes place at anode.

(b) predict the feasibility of a reaction

Standard electrode potentials are widely used to predict the feasibility of redox processes. In general if the standard cell potential for the reaction is positive, it is regarded as being feasible and if E°_{cell} is negative, then reaction is not feasible.

A redox reaction is feasible only if the species which has higher potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidized i.e., loses electrons.

Example

If Zn Metal is immersed in CuSO4 as shown in fig, then predict either Zn will react with copper sulfate solution and replaces Copper ion or not.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
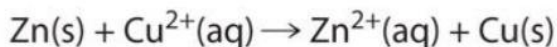
Or you can say, either the above reaction takes place or not.

METHOD 1

Step 1

Write the Standard Electrode Potential Values from data booklet

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.34\,V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = -0.76\,V$$

Step 2

These values shows that E° of Cu2+/Cu half cell is positive so Cu2+ ion will be reduced

And similarly E° of Zn2+/Zn half cell is negative so backward reaction takes place and Zn metal will be oxidized.

Step 3

Hence reaction is feasible

METHOD 2

Step 1

According to given question, Zn is oxidized into Zn2+ and Cu2+ is reduced as shown in equation

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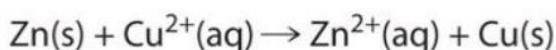
Step 2

Calculate the Standard cell Potential of the given reaction by using Standard electrode potentials.

$$E^o_{cell} = E^o_{reduction} - E^o_{oxidation}$$
$$= 0.34 - (-0.76)$$
$$= +1.10$$

As cell potential is positive ,so reaction is feasible.

So you can say Zn can react with CuSO4, but Cu cannot react with ZnSO4.

NOTE:-

Reduction reaction as shown from standard electrode potential is drawn on right-hand side of the cell (and in cell notation)and oxidation reaction as shown from standard electrode potential on the left-hand side of the cell (and cell notation.)

Cell notation Zn|Zn²⁺||Ni²⁺|Ni

$$Mg|Mg^{2+}||Zn^{2+}|Zn$$

electron flow in external circuit

anode   cathode

Cell notation is written so that the negative electrode is on the left.

WORKED EXAMPLES

3   Will chlorine oxidise Fe^{2+} ions to Fe^{3+} ions?

◻   Write down the two half-equations with the more positive $E^{\ominus}$ value first.

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq) \qquad E^{\ominus} = +1.36\,V$$

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V$$

◻   Identify the stronger oxidising agent and the stronger reducing agent.

Cl_2 is the better oxidising agent. This is because the more positive value of $E^{\ominus}$ indicates that Cl_2 molecules are more likely to accept electrons than are Fe^{3+} ions.

Fe^{2+} is the better reducing agent. This is because the more negative value of $E^{\ominus}$ indicates that Fe^{2+} ions are more likely to release electrons than are Cl^- ions.

◻   The stronger oxidising agent reacts with the stronger reducing agent, meaning that the reaction is feasible.

◻   The top reaction goes in the forward direction and the bottom reaction goes in the reverse direction:

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$$

$$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$$

◻   Combine the two half-equations:

$$\tfrac{1}{2}Cl_2(g) + Fe^{2+}(aq) \longrightarrow Cl^-(aq) + Fe^{3+}(aq)$$

WORKED EXAMPLES (CONTINUED)

This reaction is feasible. The prediction made using $E^{\ominus}$ values is correct, this reaction takes place in a suitable electrochemical cell, or when Cl_2 gas is bubbled into a $1.00\,mol\,dm^{-3}$ solution of Fe^{2+} ions.

This means that this reaction

$$Cl^-(aq) + Fe^{3+}(aq) \longrightarrow \tfrac{1}{2}Cl_2(g) + Fe^{2+}(aq)$$

is not feasible. If a $1.00\,mol\,dm^{-3}$ solution of Fe^{3+} ions is added to a $1.00\,mol\,dm^{-3}$ solution of Cl^- ions, no reaction takes place. This prediction has been made using $E^{\ominus}$ values, and it is correct.

$E^{\ominus}$ values are a very powerful tool for predicting which redox reactions are feasible, and which ones are not feasible.

4   Will iodine, I_2, oxidise Fe^{2+} ions to Fe^{3+} ions?
  - Give the two half-equations, with most positive $E^{\ominus}$ value first.

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V$$

$$\tfrac{1}{2}I_2(aq) + e^- \rightleftharpoons I^-(aq) \qquad E^{\ominus} = +0.54\,V$$
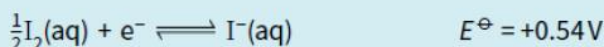
  - Identify the stronger oxidising agent and the stronger reducing agent.
    Fe^{3+} is the better oxidising agent. It is more likely to accept electrons than I_2 molecules.

    I^- is the better reducing agent. It is more likely to release electrons than Fe^{2+} ions.
  - I_2 is a relatively weaker oxidising agent and Fe^{2+} is a relatively weaker reducing agent. So the reaction is NOT feasible. (The reaction that is feasible is the reaction between Fe^{3+} ions and I^- ions.)

5   Will hydrogen peroxide, H_2O_2, reduce acidified manganate(VII) ions, MnO_4^-, to Mn^{2+} ions?
  - Write down the two half-equations with the more positive $E^{\ominus}$ value first.

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$
$$E^{\ominus} = +1.52\,V$$

$$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq) \quad E^{\ominus} = +0.68\,V$$
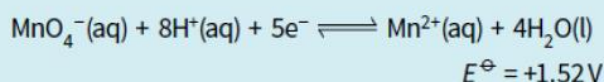
  - Identify the stronger oxidising agent and the stronger reducing agent.

    The system $MnO_4^- + H^+$ is the better oxidising agent. It is more likely to accept electrons than the system $O_2 + 2H^+$.

    H_2O_2 is the better reducing agent. It is more likely to release electrons than Mn^{2+} ions.

WORKED EXAMPLES (CONTINUED)

- The stronger oxidising agent reacts with the stronger reducing agent, so the reaction is feasible.
- The top reaction goes in the forward direction and the bottom reaction goes in the reverse direction:

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

$$H_2O_2(aq) \rightleftharpoons O_2(g) + 2H^+(aq) + 2e^-$$

- Balance the electrons, so that ten electrons are involved in each half-equation:

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightleftharpoons 2Mn^{2+}(aq) + 8H_2O(l)$$

$$5H_2O_2(aq) \rightleftharpoons 5O_2(g) + 10H^+(aq) + 10e^-$$

- Combine the two half-equations:

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

Note that 10 H$^+$ ions have been cancelled from each side.

6 deduce from $E^\ominus$ values the relative reactivity of elements, compounds and ions as oxidising agents or as reducing agents

strongest oxidising agent   weakest reducing agent

increasing oxidising power of ions/molecules on the left (increasing tendency to gain electrons)

$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	$E^\ominus = +1.36$ V
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	$E^\ominus = +0.80$ V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	$E^\ominus = +0.34$ V
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$	$E^\ominus = +0.00$ V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	$E^\ominus = -0.76$ V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	$E^\ominus = -2.38$ V

increasing reducing power of element on the right (increasing tendency to lose electrons)

weakest oxidising agent   strongest reducing agent

Standard electrode potential values are very helpful in finding the relative reactivities, oxidizing and reducing powers of ions, elements and compounds. As we read above that

- The more positive the value of $E^\ominus$, the easier it is to reduce the species on the left of the half-equation. So the substance present on the left side will be more good oxidizing agent

- The less positive the value of $E^{\ominus}$, the easier it is to oxidise the species on the right of the half-equation. Therefore the substance present on the right side will be more good reducing agent

The relative reactivity can also be predicted from standard electrode potential

- The negative sign of the E° value shows that it releases electrons more readily than if E° is positive

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad\qquad E^{\ominus} = +0.34\,V$$
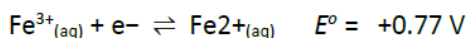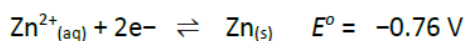
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad\qquad E^{\ominus} = -0.76\,V$$

For example, second (Zn) half cell has negative E°, and first (Cu) has positive E°, it means that Zn metal will oxidized rather than Cu metal, which means Zn will lose electrons and Cu can't lose electrons so we can say that Zn is more reactive than Cu.
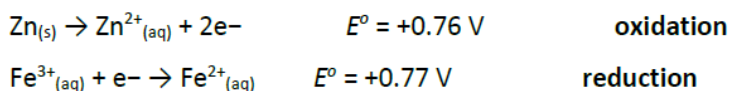
7 construct redox equations using the relevant half-equations

Lets consider the two half cells (Fe $^{3+}$/Fe^{2+} half-cell and a Zn^{2+}/Zn half-cell) connected with each other
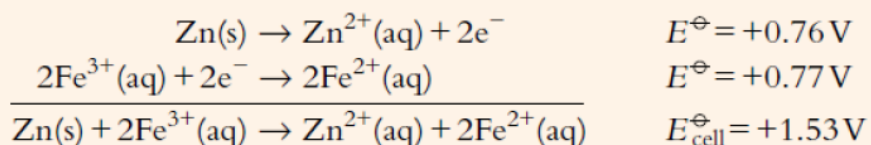
The two half-equations are:

$$Zn^{2+}{}_{(aq)} + 2e- \rightleftharpoons Zn_{(s)} \quad E^o = -0.76\,V$$

$$Fe^{3+}{}_{(aq)} + e- \rightleftharpoons Fe2+{}_{(aq)} \quad E^o = +0.77\,V$$

The more negative value is −0.76 V, and this half-equation is reversed and its E° *will become +0.76*

$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e- \qquad E^o = +0.76\,V \qquad\qquad \text{oxidation}$$

$$Fe^{3+}{}_{(aq)} + e- \rightarrow Fe^{2+}{}_{(aq)} \qquad E^o = +0.77\,V \qquad\qquad \text{reduction}$$

In order to combine the two half-equations to produce the overall redox equation, the Fe3+/Fe2+ half-equation must be multiplied by two so that the number of electrons is the same in the two half-equations. So the overall eq is

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E^{\ominus} = +0.76\,V$$
$$\underline{2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V}$$
$$Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq) \qquad E^{\ominus}_{cell} = +1.53\,V$$

8 predict qualitatively how the value of an electrode potential, *E*, varies with the concentrations of the aqueous ions

if we change the concentration of aqueous ions, then the value of electrode potential also changes. We can explain this by Le Chatelier's principle to redox equilibria.

If we increase the concentration of the species on the left of the equation, the position of equilibrium will shift to the right. So the value of *E* becomes more positive / less negative (i.e. value of E moves on right side on number line)

Similarly if we decrease the concentration of the species on the left of the equation, the position of equilibrium will shift to the left. So the value of *E* becomes less positive / more negative (i.e. value of E moves on left side on number line)

Example

$$Zn^{2+}(aq) + e^- \rightleftharpoons Zn(s) \qquad\qquad E^{\ominus} = -0.76\,V$$

Standard electrode potential value is − 0.76 V which means that the concentration of Zn^{2+} ion is 1moldm^{-3}
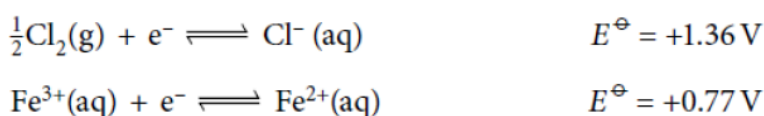
- If concetration of Zn^{2+} is greater than 1.00 mol dm^{-3}, the value of E becomes less negative / more positive. i.e. according to Le Chatelier's principle , equilibrium moves towards right side and value of E also more on right side on number line, so it becomes less negative .(for example −0.70 V).
- If concentration of Zn^{2+} is less than 1.00 mol dm^{-3}, the value of E becomes more negative / less positive (for example −0.90 V).

Question: - How can we predict whether or not a given reactionwill occur under non-standard conditions?

if the E° values of the two half-reactions involved differ by more than 0.30 V, then the reaction predicted by the E° values is highly likely to occur. But if the E° values of the two half-reactions involved differ by less than 0.30 V then we can not predict about the feasibility of the reaction.

Example:-

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^- (aq) \qquad\qquad E^{\ominus} = +1.36\,V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad\qquad E^{\ominus} = +0.77\,V$$

Under standard conditions, E° values shows that chlorine can oxidise Fe^{2+} ions into Fe^{3+} ion.

Now if we change the concentration of ions give in above equations, oxidation of Fe2+ is most likely because the difference in their E° values is 0.59 V, which is considerably greater than 0.30 V.

9 use the Nernst equation, e.g. $E = E^{\ominus} + (0.059/z) \log \dfrac{[\text{oxidised species}]}{[\text{reduced species}]}$

to predict quantitatively how the value of an electrode potential varies with the concentrations of the aqueous ions; examples include $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$, $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

The Nernst equation

$$E = E^{\ominus} + \frac{0.059}{Z} \log_{10} \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

$$E = E^{\ominus} + \frac{0.059}{Z} \log_{10} [\text{oxidised form}]$$

Calculate the value of the electrode potential at 298 K of a Cu(s)/Cu2+(aq) electrode that has a concentration of Cu2+(aq) ions of 0.001 mol dm^{-3}. E°= +0.34 V

(c) (i) The $E^{\ominus}$ of Ni²⁺(aq)/Ni(s) is –0.25 V.

State and explain how the electrode potential changes if the concentration of Ni²⁺(aq) is decreased.

....

....

.... [1]

(ii) The $E^{\ominus}$ of $Cr^{3+}(aq)/Cr^{2+}(aq)$ is –0.41 V.

Calculate the electrode potential when $[Cr^{3+}(aq)]$ is 0.60 mol dm^{-3} and $[Cr^{2+}(aq)]$ is 0.15 mol dm^{-3}. Use the Nernst equation.

$$E = E^{\ominus} + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

The concentration of $Cu^{2+}(aq)$ remaining in the solution is 1.00 mol dm^{-3}.
The concentration of $Cu^{+}(aq)$ in a saturated solution of CuI is 1.3×10^{-6} mol dm^{-3}.

(iii) Use the Nernst equation to calculate the electrode potential, E, for the Cu^{2+}/Cu^{+} half cell in this experiment.

(a) (i) Define the term *standard cell potential*, $E^{\ominus}_{cell}$.

....

....

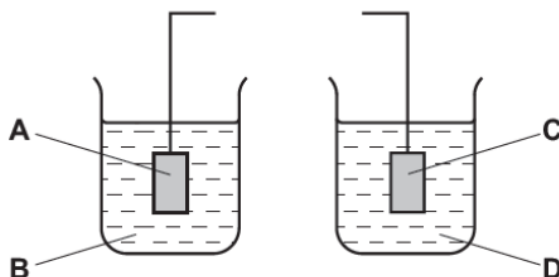... [1]

The following incomplete diagram shows the apparatus that can be used to measure the $E^{\ominus}_{cell}$ for a cell composed of the Fe^{3+}/Fe^{2+} and Ag^{+}/Ag half-cells.

(ii) Complete the diagram, labelling the components you add. [1]

(iii) Identify the components **A-D**.

A ....

B ....

C ....

D ....

[3]

(b) (i) Use $E^{\ominus}$ values to write an equation for the cell reaction that takes place if the two electrodes in **(a)** are connected by a wire and the circuit is completed.

....

.... [1]

(ii) Another electrochemical cell was set up using $0.31\,mol\,dm^{-3}$ $Ag^{+}(aq)$ instead of the standard Ag solution.

Use the Nernst equation, $E = E^{\ominus} + 0.059\log[Ag^{+}(aq)]$, and the relevant $E^{\ominus}$ values to calculate the new E_{cell} in this experiment.

E_{cell} = ... V [2]