

CHAPTER 21: Electrode Potentials

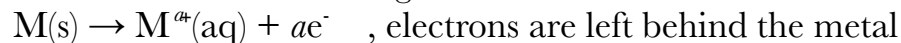
- 21.1 Standard Electrode Potential
- 21.2 Measuring Standard Electrode Potential
- 21.3 Using E° Values
- 21.4 Cells and Batteries
- 21.5 Quantitative Electrolysis

- (a) *define the terms:*
 - (i) *standard electrode (redox) potential.*
 - (ii) *standard cell potential.*
- (b) *describe the standard hydrogen electrode.*
- (c) *describe methods used to measure the standard electrode potentials of:*
 - (i) *metals or non-metals in contact with their ions in aqueous solution.*
 - (ii) *ions of the same element in different oxidation states.*
- (d) *calculate a standard cell potential by combining two standard electrode potentials.*
- (e) *use standard cell potentials to:*
 - (i) *explain/deduce the direction of electron flow from a simple cell.*
 - (ii) *predict the feasibility of a reaction.*
- (f) *construct redox equations using the relevant half-equations.*
- (g) *predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion.*
- (h) *state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage.*
- (i) *state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron.*
- (j) *predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration.*
- (k) *calculate:*
 - (i) *the quantity of charge passed during electrolysis.*
 - (ii) *the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of $H_2SO_4(aq)$, $Na_2SO_4(aq)$.*
- (l) *describe the determination of a value of the Avogadro constant by an electrolytic method.*

21.1 Standard Electrode Potential

Electrode potentials and half-cells

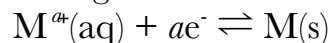
- 1) i. When a metal, M is immersed into water, there is a **tendency** that it will lose electrons and enter the water as metal ions, M^{aq} . Soon, the water becomes a solution of the metal ions. This leaves the electrons on the metal and the metal becomes more and more negative.



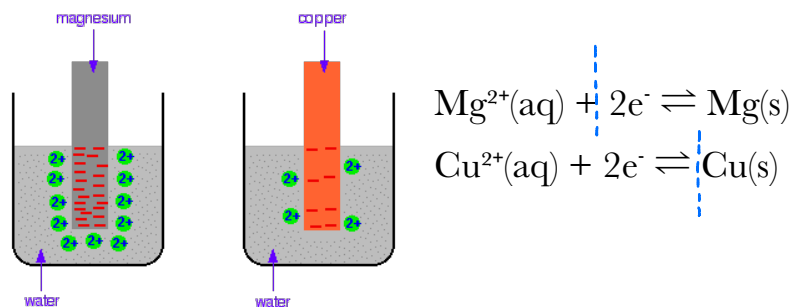
- ii. The positive metal ions in the solution will be attracted towards the negative metal. Eventually some will accept the electrons and re-form the metal.



- 2) When the rate of these two reactions becomes equal, an equilibrium is established. At this equilibrium, the metal goes into the solution at a rate exactly same as the ions depositing.

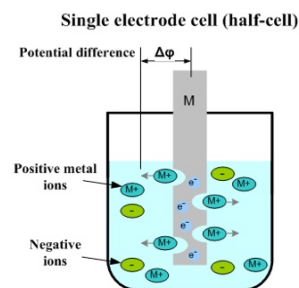


- 3) **Different metals will have different tendencies of doing so.** Some will lose electrons more readily than others. Reactive metals like magnesium prefer to stay as ions, therefore the position of equilibrium lies further to the left. Oppositely, unreactive metals like copper prefer to stay as metals, therefore the position of equilibrium lies further to the right.



- 4) This arrangement of a metal dipping into a solution of its ions is called a **half-cell**. The metal in a half-cell is called an electrode.

- 5) Since there is a **difference in charge** between the negative metal and the positive metal ion solution, a potential difference exists between them. This potential difference is called the **electrode potential, E**. Electrode potential is measured in volts, V.



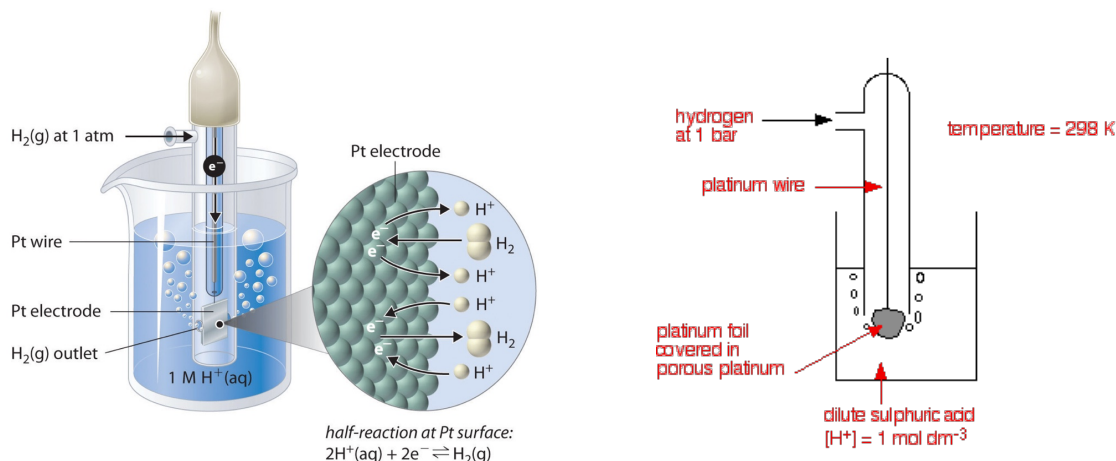
- Electrode potential is also a numerical method to express **the tendency of a metal to form ions**.
- The bigger the difference between the negativeness and positiveness, the greater the electrode potential. However, this electrode potential is **impossible to measure**.
- However, the difference of electrode potentials between two half-cells is measurable. This can be done by connecting a wire between the two electrodes with a voltmeter between them.
- Hence, to standardise, a standard half-cell must be chosen as the reference electrode so that all electrode potentials measured are relative to this.
- This standard half-cell is called the **standard hydrogen electrode, SHE**.

Standard hydrogen electrode, SHE

- A standard hydrogen electrode has hydrogen gas in equilibrium with hydrogen ions. The electrode potential of this half-cell is taken as **0 V**.

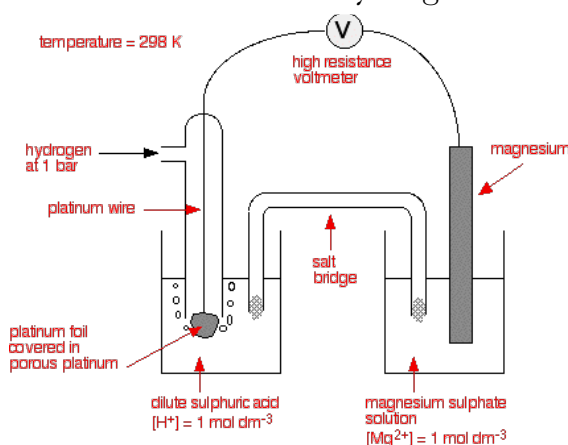


- Since hydrogen is not a metal, platinum foil covered in porous platinum is used as the electrode. Platinum also catalyses the set up of the equilibrium.
- Hydrogen gas at 100 kPa** is bubbled over the platinum. On the surface of the platinum, the equilibrium is set up. The **concentration of hydrogen ions is at 1 mol dm⁻³**.



Standard electrode potential, E°

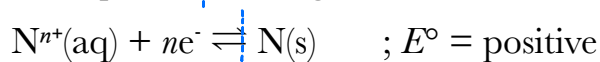
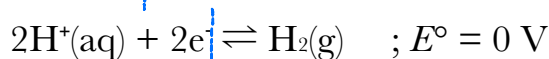
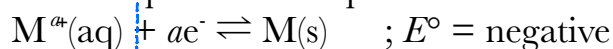
- 1) *Standard electrode potential, E°* is the e.m.f. of a cell when a half-cell is connected to a standard hydrogen electrode under standard conditions.
- 2) The standard conditions are:
 - i. A pressure of **100 kPa** (approximately atmospheric pressure).
 - ii. A temperature of **298 K or 25 °C**.
 - iii. The ions at a concentration of **1.0 mol dm⁻³**.
- 3) A standard condition is required because all these factors will affect the position of equilibrium of the reaction, therefore the magnitude of E° will also be affected.
- 4) The standard electrode potential of a cell can be measured by connecting a half-cell to a standard hydrogen electrode like this:



Note:

- 1) A high resistance voltmeter is used so that **no current** flows through the external circuit and the maximum voltage (the e.m.f.) can be recorded.
- 2) A salt bridge physically separates the half-cells but **allows the passage of electricity between the electrodes**. It contains ions that do not react with the solution.
- 2) 1 bar = 100 kPa \approx 1 atm

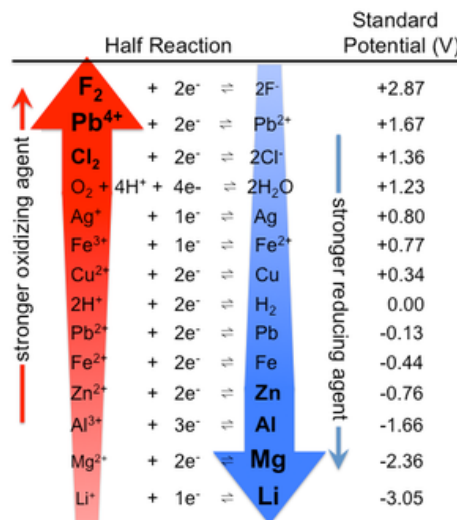
- 5) Recall that electrode potential measures the tendency of a metal to lose its electrons. Standard electrode potential compares this tendency with the tendency of hydrogen to release its electrons.
- 6) i. A negative value of E° implies that the metal loses electrons more readily than hydrogen does. Therefore the position of equilibrium lies further to the left.
 ii. A positive value of E° implies that the metal loses electrons less readily than hydrogen does. Therefore the position of equilibrium lies further to the right.



- 7) Remember that standard electrode potential is all about comparing. A positive E^\ominus does not mean the position of equilibrium is exactly at the right. It is further to the right compared to the position of equilibrium of SHE.
- 8) i. The bigger the negative value, the further the position of equilibrium is to the left and the more reactive that metal is.
 ii. The bigger the positive value, the further the position of equilibrium is to the right, and the less reactive that metal is.

The electrochemical series

Half Reaction	Standard Potential (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$Au^+(aq) + e^- \rightarrow Au(s)$	+1.68
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe_3^+(aq) + e^- \rightarrow Fe_2^+(aq)$	+0.77
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$Cu_2^+(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb_2^+(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Sn_2^+(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Ni_2^+(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Co_2^+(aq) + 2e^- \rightarrow Co(s)$	-0.28
$Fe_2^+(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Zn_2^+(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al_3^+(aq) + 3e^- \rightarrow Al(s)$	-1.67
$Mg_2^+(aq) + 2e^- \rightarrow Mg(s)$	-2.34
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Ca_2^+(aq) + 2e^- \rightarrow Ca(s)$	-2.87
$K^+(aq) + e^- \rightarrow K(s)$	-2.93



- The electrochemical series is built up by arranging various redox equilibria in order of their standard electrode potentials.
- The figures above show some common redox equilibria arranged according to their standard electrode potentials. The full list can be found in the *Data Booklet*.
- From the top to the bottom, the position of equilibrium shifts from right to left. This is because the value of E^\ominus changes from the most positive to the most negative.
- This implies that the **ease of losing electrons by the element increases** from top to bottom (or the **ease of gaining electrons by the ion decreases** from top to bottom).
- Ions at the top (with more positive E^\ominus value) gain electrons and get reduced more readily, hence they are **good oxidising agents**.
 - Elements (metals) at the bottom (with more negative E^\ominus value) lose electrons and get oxidised more readily, hence they are **good reducing agents**.

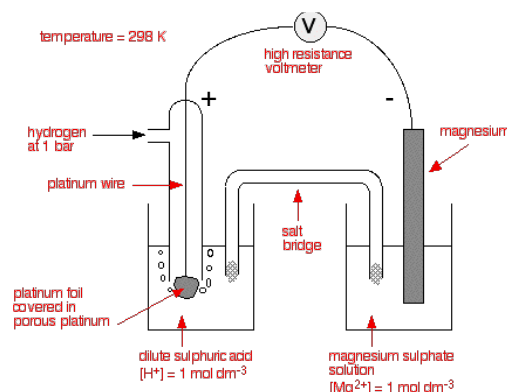
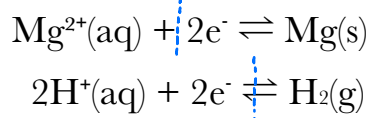
21.2 Measuring Standard Electrode Potential

The big picture

- 1) The standard electrode potential of the following system will be considered:
 - i. A metal/metal ion half-cell with SHE.
 - ii. A non-metal/non-metal ion half-cell with SHE.
 - iii. An ion/ion(with different oxidation states) half-cell with SHE.
 - iv. The combination of the above three half-cells.

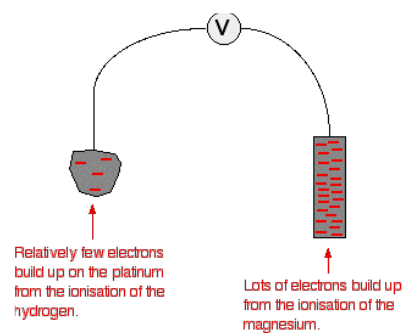
Metal/metal ion half-cell

- 1) Take magnesium as an example of a metal. The equilibrium set up on both electrodes are:



- 2) From the voltmeter reading, the $E^{\circ}_{\text{cell}} = 2.34 \text{ V}$. Thus, the standard electrode potential of Mg/Mg^{2+} half-cell is **-2.34 V**.

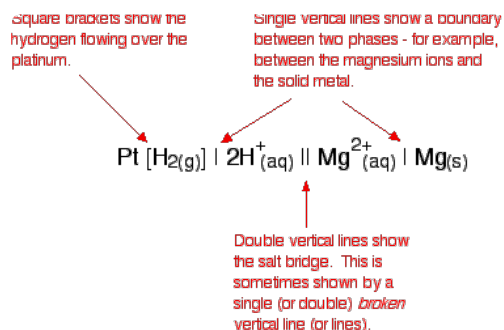
- 3) i. Cathode, which is the positive terminal is platinum of the H_2/H^{+} half-cell. This is because more electrons are being accepted here due to the position of equilibrium of the H_2/H^{+} being further to the right.
 - ii. Anode, which is the negative terminal is magnesium of the Mg/Mg^{2+} half-cell. This is because more electrons are being released here due to the position of equilibrium of the Mg/Mg^{2+} half-cell being further to the left.



- 4) The full cell can be represented using a cell diagram. A simple cell diagram is as shown beside.

Note:

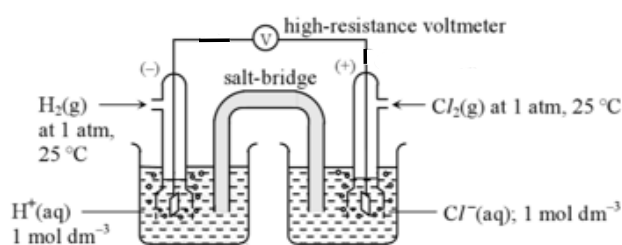
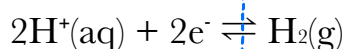
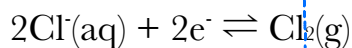
- i. The positive electrode is always written on the left side.
- ii. The species with lowest oxidation state is written next to the inert electrode.



- 5) A negative E° value implies that **magnesium loses electrons more readily than hydrogen does.**
- 5) If magnesium is replaced by copper, the value of E° will be +0.34 V. Copper of Cu/Cu²⁺ half-cell will be the positive terminal while platinum of H₂/H⁺ half-cell will be the negative terminal.
- 6) A positive E° value implies that **copper ions gain electrons more readily than hydrogen ions does.**

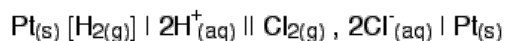
Non-metal/non-metal ion half-cell

- 1) Take chlorine as an example of a non-metal. The equilibrium set up on both electrodes are:



- 2) Since chlorine is not a metal, the electrical contact with the solution is made by using platinum as the electrode (same as SHE).
- 3) From the voltmeter reading, the $E^\circ_{\text{cell}} = 1.36 \text{ V}$. Thus, the standard electrode potential of Cl₂/Cl⁻ half-cell is **+1.36 V**.
- 4) i. Cathode, which is the positive terminal is platinum of the Cl₂/Cl⁻ half-cell. This is because more electrons are being accepted here due to the position of equilibrium of the Cl₂/Cl⁻ being further to the right.
 ii. Anode, which is the negative terminal is platinum of the H₂/H⁺ half-cell. This is because more electrons are being released here due to the position of equilibrium of the H₂/H⁺ half-cell being further to the left.
- 5) A positive E° value implies that **chloride ions gain electrons more readily than hydrogen ions does.**

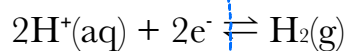
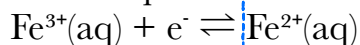
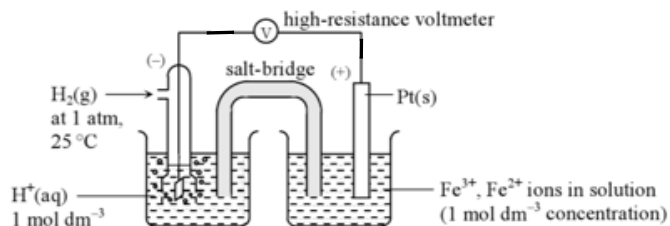
- 6) The cell diagram of this cell is:



$$E^\circ = +1.36 \text{ v}$$

Ion/ion half-cell

- 1) Two different ions of the same element with two different oxidation states can also be used as a half-cell. Take iron(II) and iron(III) ions as example. The equilibrium set up on both electrodes are:



- 2) Since there is no solid metal as an electrode, electrical contact the solution is made by using platinum as the electrode.
- 3) From the voltmeter reading, the $E^{\circ}_{\text{cell}} = 0.77 \text{ V}$. Thus, the standard electrode potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ half-cell is **+0.77 V**.
- 4) i. Cathode, which is the positive terminal is platinum of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ half-cell. This is because more electrons are being accepted here due to the position of equilibrium of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ being further to the right.
 ii. Anode, which is the negative terminal is platinum of the H_2/H^{+} half-cell. This is because more electrons are being released here due to the position of equilibrium of the H_2/H^{+} half-cell being further to the left.
- 5) A positive E° value implies that **iron(III) ions gain electrons more readily than hydrogen ions does.**
- 6) The cell diagram of this cell is:



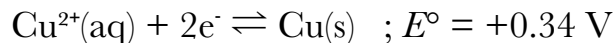
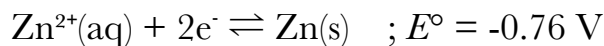
$$E^{\circ} = + 0.77 \text{ v}$$

Combination of half-cells

- 1) In fact, the SHE shown in previous examples can be replaced by other half-cells.
- 2) When this happens, the standard cell potential, E°_{cell} will also change, the new E°_{cell} is simply **the difference between the E° values of the two half-cells.**

$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{bigger value}) - E^{\circ}(\text{smaller value})$$

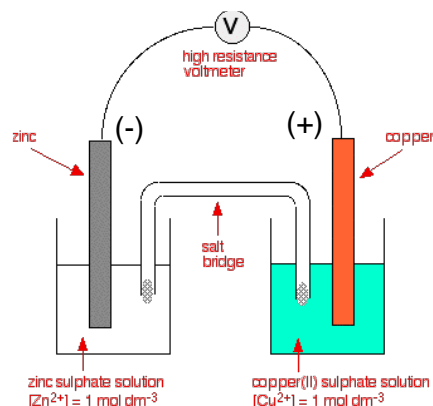
- 3) For example, when Zn/Zn²⁺ half-cell is connected to Cu/Cu²⁺ half-cell, the equilibrium set up on both electrodes are:



- 4) From the voltmeter reading, the $E^{\circ}_{\text{cell}} = 1.10 \text{ V}$.

This can also be calculated, using:

$$E^{\circ}_{\text{cell}} = 0.34 - (-0.76) = 1.10 \text{ V}$$



- 4) i. Cathode, which is the positive terminal is copper of the Cu/Cu²⁺ half-cell.
This is because more electrons are being accepted here due to the position of equilibrium of the Cu/Cu²⁺ being further to the right.
- ii. Anode, which is the negative terminal is platinum of the Zn/Zn²⁺ half-cell.
This is because more electrons are being released here due to the position of equilibrium of the Zn/Zn²⁺ half-cell being further to the left.

20.3 Using E° Values

The usage of E° values

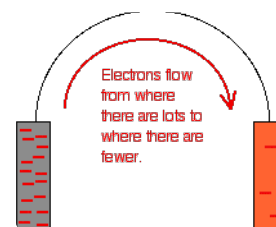
- 1) The value of standard electrode potential, E° can be used in some ways:
 - i. To predict standard cell potentials, E°_{cell} .
 - ii. To determine the direction of electron flow.
 - iii. To predict the feasibility of reactions.
 - iv. To determine the strength of reducing and oxidising agents.

Predicting standard cell potentials, E°_{cell}

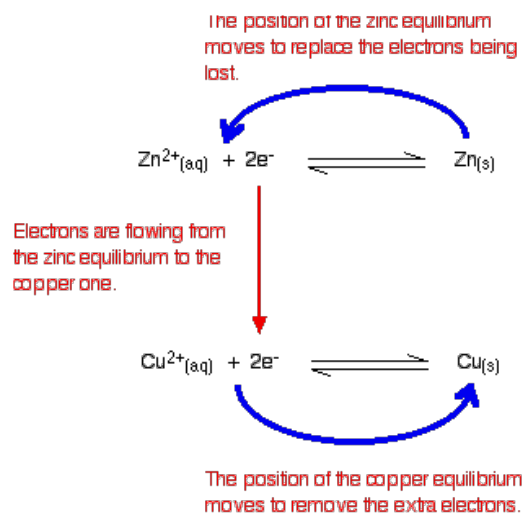
- 1) The standard cell potential, E°_{cell} of a cell consisting of two half-cells can be predicted by connecting them together using wires with a voltmeter.
- 2) i. Find from the *Data Booklet* the required equilibrium equation.
ii. Copy down the equilibrium equations and their corresponding E° values.
iii. Use the formula $E^{\circ}_{\text{cell}} = E^{\circ}(\text{bigger value}) - E^{\circ}(\text{smaller value})$.

Determining the direction of electron flow

- 1) When the high-resistance voltmeter of a cell is removed, electrons will flow from one cell to another. The electron will flow from the half-cell **with more electrons(anode)** to the half-cell **with less electrons(cathode)**.



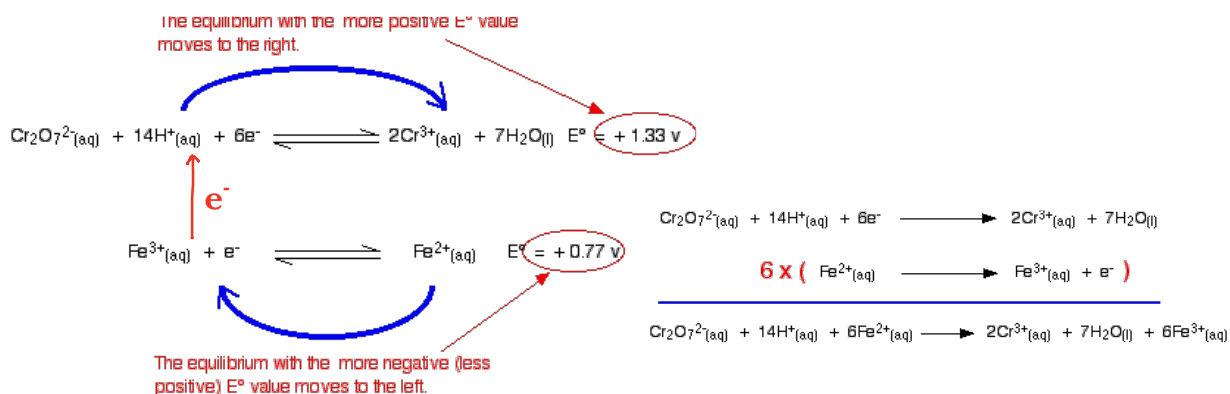
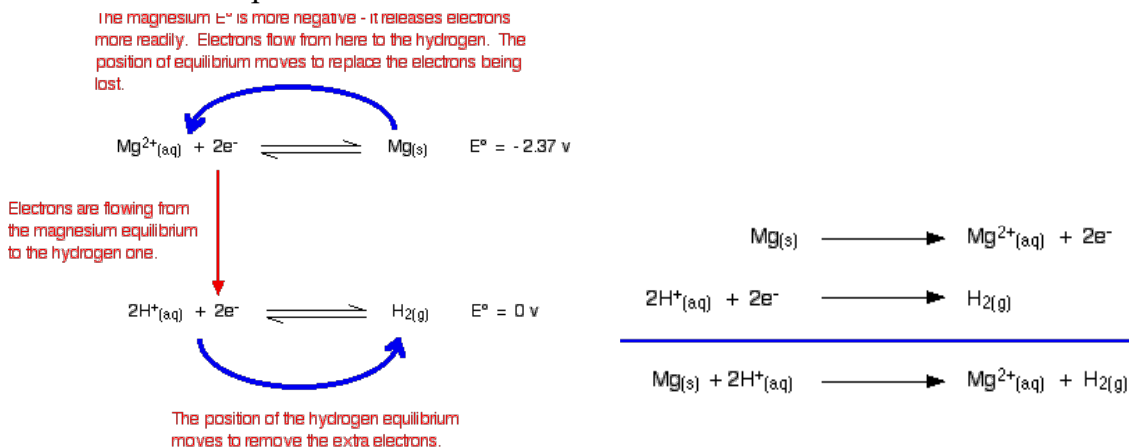
- 2) For example, if the voltmeter in the Zn/Zn²⁺ half-cell and Cu/Cu²⁺ half-cell is removed, electrons will flow from zinc electrode to copper electrode.
- 3) Due to the fact that the system is equilibrium, the decrease in electron concentration in the Zn/Zn²⁺ equilibrium will be accompanied by some changes. The same goes to the increase in electron concentration in Cu/Cu²⁺ half-cells. This comes from Le Chatelier's principle.



- 4) If the electrons continue to flow, the position of equilibrium keeps shifting, eventually producing **a one-way reaction**.
- $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$, releases electrons to the Cu/Cu²⁺ half-cell
- $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$, accepts electrons from the Zn/Zn²⁺ half-cell
- ...combining these two equations:
- $$\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$$

- 5) Electrons will always flow from the half-cell **with lower(more negative or less positive) E° value** to the half-cell **with higher(less negative or more positive) E° value**.

6) Two more examples:

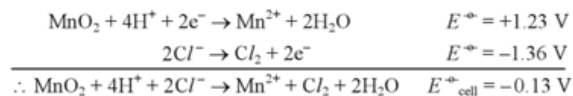


Predicting the feasibility of reactions(two methods)

- 1) Reactions **with positive E^\ominus value** is said to be thermodynamically feasible.
- 2) Sometimes this prediction fails because:
 - i. the actual conditions of the reaction are **not standard conditions**.
 - ii. the reaction has **high activation energy**.
- 3) Remember:
 - i. E^\ominus value gives no information about the reaction rates.
 - ii. E^\ominus value applies to standard conditions only.
- 4) i. If you are given an equation, split the equation into two half-equations, the find the corresponding E^\ominus values from the *Data Booklet*.
 - ii. **Add the two E^\ominus values** together and determine whether the sum is positive or negative.
 - iii. Reverse the equation may be necessary, remember to reverse the sign too.

5) Examples:

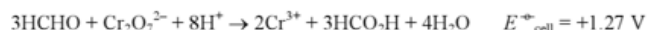
e.g. 1: Oxidation of concentrated HCl by MnO₂



Since E^\ominus_{cell} is negative, the reaction is predicted to be *not feasible*.
However, Cl₂ can be prepared by *heating* MnO₂ with *concentrated* HCl.

The prediction fails because E^\ominus value does *not* apply when *non-standard* conditions are used. (Here, [HCl] ≠ 1.0 mol dm⁻³ and temperature ≠ 25 °C).

e.g. 2: Oxidation of methanal to methanoic acid by acidified K₂Cr₂O₇



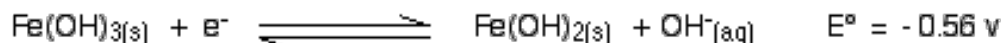
Since E^\ominus_{cell} is positive, the reaction is predicted to be *feasible*.
However, in practice, there is *no reaction* at room temperature due to *high activation energy*. Heating is required for the reaction to occur.

The prediction fails because E^\ominus value gives no information about the kinetics of the reaction.

6) Alternatively, it can also be predicted by looking at the reactants and products of the equation.

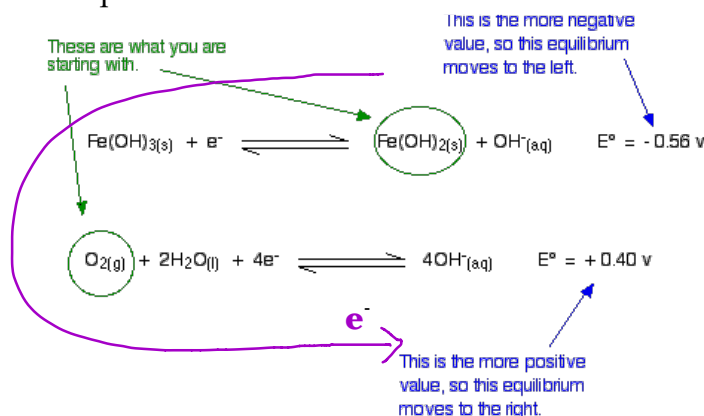
7) Example 1: Will oxygen oxidise iron(II) hydroxide to iron(III) hydroxide under alkaline conditions?

i. Find from the *Data Booklet* the equations involving the reactants and products stated and write down their corresponding E^\ominus values.



ii. Determine the direction of electron flow. Remember that electrons flow from the half-cell with more negative E^\ominus value to the half-cell with more positive E^\ominus value.

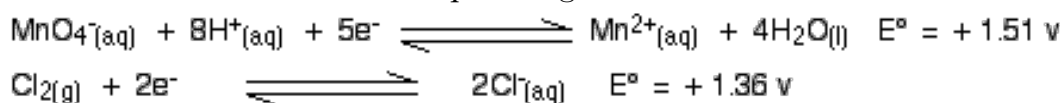
iii. Determine the shift of position of equilibrium, and see whether it tallies with the reactants and products.



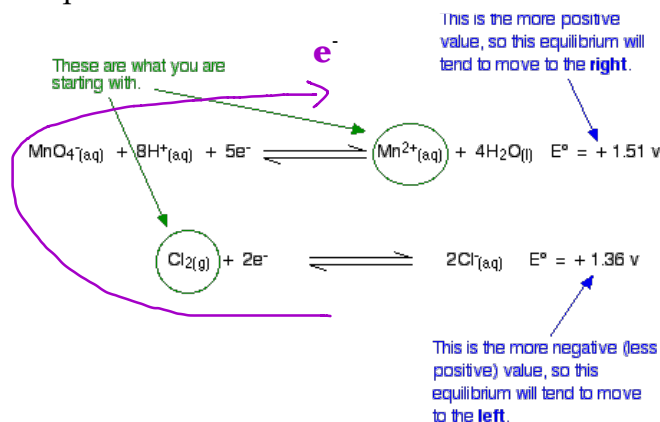
- iv. From the direction of electron flow and shift of equilibrium, we can deduce that:
- iron(II) hydroxide will be oxidised to iron(III) hydroxide because the position of equilibrium of first reaction shifts to the left.
 - oxygen will accept electrons from the first reaction and will be reduced to hydroxide ions because the position of equilibrium of second reaction shifts to right.

8) Example 2: Will chlorine oxidise manganese(II) ions to manganate(VII) ions?

- i. Find from the *Data Booklet* the equations involving the reactants and products stated and write down their corresponding E° values.



- ii. Determine the direction of electron flow. Remember that electrons flow from the half-cell with more negative E° value to the half-cell with more positive E° value.
- iii. Determine the shift of position of equilibrium, and see whether it tallies with the reactants and products.



- iv. From the direction of electron flow and shift of equilibrium, we can deduce that:
- manganese(II) ions will not be oxidised to manganate(VI) ions because if it were to occur the position of equilibrium of first reaction will shift to the left. However, it shifts to the right because the first reaction has a more positive E° value.
 - chlorine will not be reduced to chloride ions because if it were to occur the position of equilibrium of the second reaction will shift to the right. However, it shifts to the left because the second reaction has a more negative E° value.

Determining the strength of oxidising and reducing agents

- 1) From the last example, the scenario can also be interpreted as:
 - i. Chlorine is a weaker oxidising agent than manganate(VI) ion, hence it will not oxidise manganese(II) ion to manganate(VI) ion.
 - ii. Manganese(II) ion is a weaker reducing agent than chloride ion, hence it will not reduce chlorine to chloride ion.

- 2) From the second last example, the scenario can also be interpreted as:
 - i. Iron(II) hydroxide is a stronger reducing agent than hydroxide ion, hence it will reduce oxygen to hydroxide ion.
 - ii. Oxygen is a stronger oxidising agent than iron(III) hydroxide, hence it will oxidise iron(II) hydroxide to iron(III) hydroxide.

Effect of temperature, pressure and concentration on E° value

- 1) Since redox equilibria are equilibria, a change in temperature, concentration and pressure will have an effect on its position of equilibrium. This will also affect the value of E° because E° indicates the position of equilibrium of a redox equilibrium.

- 2)
 - i. If a change causes the position of equilibrium to shift to the right, the value of E° increases.
 - ii. If a change causes the position of equilibrium to shift to the left, the value of E° decreases.

21.4 Cells and Batteries

Rechargeable and non-rechargeable cells

- 1) Batteries are electrochemical cells used as portable sources of electricity.

- 2)
 - i. Primary cells **cannot be recharged** and are discarded once the supply of electric current decreases. This happens when the concentration of reactants becomes too low.
 - ii. Secondary cells **can be recharged** over and over again. This involves converting the products back to the reactants produced when delivering the current by electric current.

Dry cells

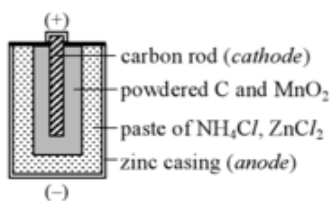
1)

A dry cell generates between 1.25 V and 1.50 V.

Electrolyte : paste of NH_4Cl , ZnCl_2 and water.

Anode (-): zinc casing

Cathode (+): C rod surrounded by a layer of MnO_2 .



Anode reaction : $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

Cathode reaction : $2\text{MnO}_2(\text{s}) + 2\text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{NH}_3(\text{aq}) + 2\text{MnO}(\text{OH})(\text{s})$

Overall reaction : $\text{Zn} + 2\text{MnO}_2 + 2\text{NH}_4^+ \rightarrow \text{Zn}^{2+} + 2\text{NH}_3 + 2\text{MnO}(\text{OH})$

Advantage: The dry cell is a *convenient portable source of electricity* since it is tightly sealed and so does not leak.

Disadvantages:

1. *Corrosion of zinc* by the acidic electrolyte.
2. The voltage *drops* during rapid discharge due to the build-up of products at the electrodes.
3. It *cannot* be recharged.

Lead-acid accumulator

1)

The lead-acid accumulator is used in cars and normally consists of *six* cells arranged in *series* to provide 12 V.

Electrolyte : sulfuric acid.

Anode (-): lead (*spongy lead*)

Cathode (+): PbO_2 on a lead frame.

Anode reaction : $\text{Pb(s)} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4(\text{s}) + 2\text{e}^-$

Cathode reaction : $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-} + 2\text{e}^- \rightleftharpoons \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

Overall reaction : $\text{Pb} + \text{PbO}_2 + 4\text{H}^+ + 2\text{SO}_4^{2-} \xrightleftharpoons[\text{charging}]{\text{discharging}} 2\text{PbSO}_4 + 2\text{H}_2\text{O}$

The battery is recharged by applying an external current. The relative density of sulfuric acid indicates the state of charge in the battery. When the battery is fully charged, the sulfuric acid has a relative density of about 1.275. Upon discharge, the relative density of sulfuric acid decreases as sulfuric acid is consumed and PbSO_4 forms at both electrodes.

Advantage: The battery is *rechargeable* (since the products formed remained in contact with the electrodes).

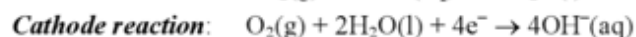
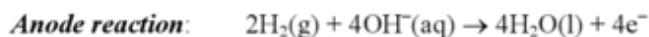
Disadvantage: It is *very heavy* due to the lead.

Hydrogen-oxygen fuel cells

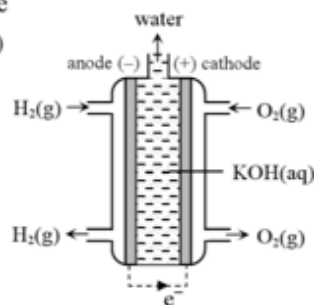
- The **fuel cell** is an electrochemical device that converts chemical energy of conventional fuels (such as hydrogen or methane) into electrical energy *directly* and *continuously* by oxidation with oxygen from the air.
- Fuel cells do not have the limited capacity of primary batteries (caused by small quantities of reactants present) or the storage capacity of secondary batteries where oxidant and reductant can be regenerated by recharging.

In a fuel cell, a *continuous supply* of reactants (fuel and oxygen) is needed.

- In this cell, hydrogen and oxygen are bubbled through *porous* carbon electrodes (which contain a *Pt catalyst*) into a concentrated solution of an alkali such as KOH.



At the negative electrode (*anode*), H_2 adsorbed by the porous carbon reacts with OH^- (from the electrolyte) to form water and releases electrons which flows through the external circuit.



Advantages:

- Fuel cells are *highly efficient*.
- Fuel cells are virtually *pollution-free* since water is the only product formed.
[In the spacecraft, water is removed and consumed by the astronauts.]
- Fuel cells *work indefinitely* as long as the reactants are supplied.
[An ordinary battery has a fixed life span; it stops working as soon as the electrode materials are used up.]

Disadvantages:

- Fuel cells are *expensive* since large amounts of Pt metals are required as catalysts for the electrode reactions.
- Most fuels require a *high temperature* to react. Hence, fuel cells are not yet being used as a major source of electricity. Their main use is in spacecraft.

Electric cars

- Reasons to support the use of electric car:
 - reduction in air pollution**
– since the electric car has *no exhaust* and so, produces *no air pollution*.
 - lower maintenance costs**
– since there are few parts to wear out and no oil to change.
- It is an *illusion* to think that the electric car, which releases no exhaust gases, offers a complete solution to the problem of air pollution associated with petrol-driven cars.
This is because the manufacture of batteries and their recharging are likely to involve the *combustion of fossil fuels* in a power station and hence, the release of CO_2 (the main greenhouse gas).
- To date, electric cars have had little success because of
 - high mass of batteries**
– accounts for half the mass of an electric car (using lead-acid batteries).
 - short driving ranges**
– due to the low energy storage capacity of the battery.
 - low recharging rates**
– hence, long times are required for recharging the batteries.
 - high replacement costs** of batteries
– the batteries cannot be recharged indefinitely and have to be replaced.

[In fact, the heavy, expensive, short-lived lead-acid batteries make the cost of running electric cars twice that of the petrol-powered type.]

21.5 Quantitative Electrolysis

E° value in electrolysis

- 1) Recall that the selective discharge of ions during electrolysis is affected by:
 - i. the position of ions in the electrochemical series.
 - ii. the concentration of ions.
- 2) Cations lower in the electrochemical series will be selectively discharged(reduced). This is because they have a more positive E° value and hence it favours reduction more.
- 3) Cations with higher concentration will be selectively discharged(reduced). This is because the value of E° becomes more positive as the concentration of ions increases. A more positive E° favours reduction.

electro-chemical series

Potassium	-2.92
Calcium	-2.87
Sodium	-2.71
Magnesium	-2.37
Aluminium	-1.66
Zinc	-0.76
Iron	-0.44
Tin	-0.14
Lead	-0.13
Hydrogen	0.00
Copper	+0.34
Silver	+0.80
Mercury	+0.85
Gold	+1.68

Faraday's laws of electrolysis

- 1) The quantity of charge, Q passed during electrolysis is given by this equation. Q is measured in Coulombs, C

$$Q = It$$

where I = Current/A
 t = Time/s

- 2) *Faraday's first law of electrolysis* states that the mass of a substance liberated during electrolysis is directly proportional to the quantity of charge passed through during electrolysis.

$$m \propto Q \quad \text{or} \quad m \propto I \times t \quad \text{since } Q = I \times t$$

where m = mass of substance liberated in grams, g.
 Q = quantity of electricity in coulombs, C.

- 3) *Faraday's second law of electrolysis* states that the number of Faradays required to discharge one mole of ion at an electrode equals to the number of charges on the ion.
- 4) Faraday, F is the amount of charge carried by one mole of electrons.

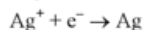
$1 \text{ electron} \rightarrow 1.60 \times 10^{-19} \text{ C}$
 $\therefore 6.02 \times 10^{23} \text{ electrons} \rightarrow 96500 \text{ C}$

Therefore, $1 F = 96500 C$

5) Calculation examples:

e.g. 1: To calculate the mass of silver deposited at the cathode when a current of 0.5 A is passed through a solution of silver nitrate for 15 minutes.

$$\text{Quantity of electricity, } Q = I \times t = (0.5 \times 15 \times 60) C = 450 C$$

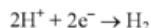


From equation, 1 F (or 96,500 C) of electricity deposits 1 mol of Ag.

$$\therefore \text{ mol of Ag deposited by } 450 C = \frac{450}{96500} = 4.66 \times 10^{-3} \text{ mol}$$

$$\text{Hence, mass of Ag deposited} = nA_r = (4.66 \times 10^{-3} \times 108) g = 0.503 g$$

e.g. 2: To calculate the volume of hydrogen liberated at s.t.p. if a second beaker containing aqueous sulfuric acid is connected in series to that in e.g. 1.



From equation, 2 F (or $2 \times 96,500 C$) of electricity liberates 1 mol of H_2 .

$$\therefore \text{ mol of } H_2 \text{ liberated by } 450 C = \frac{450}{2 \times 96500} = 2.33 \times 10^{-3} \text{ mol}$$

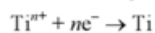
$$\text{Hence, vol of } H_2 \text{ liberated} = (2.33 \times 10^{-3} \times 22.4) dm^3 = 0.0522 dm^3$$

[NB. The *same current* passes through the two beakers connected in *series*.]

e.g. 3: To deduce the charge on the titanium ion in an aqueous solution of a titanium salt given that 5.60 g of metallic titanium was deposited at the cathode in an electrolysis by passing a current of 5.00 A for 2.5 hours.

$$\begin{aligned} \text{Quantity of electricity, } Q &= I \times t \\ &= (5.00 \times 2.5 \times 60 \times 60) C = 45,000 C \end{aligned}$$

$$\Rightarrow \text{ no. of Faraday} = \frac{45000}{96500} F = 0.466 F$$



$$\text{mol of Ti deposited} = \frac{m}{A_r} = \frac{5.60}{47.9} = 0.117 \text{ mol}$$

\therefore 0.117 mol of Ti is deposited by 0.466 F of electricity.

$$\Rightarrow 1 \text{ mol of Ti is deposited by } \frac{0.466}{0.117} = 4 F \text{ of electricity.}$$

Hence, $n = 4$. The charge on titanium ion is 4+.

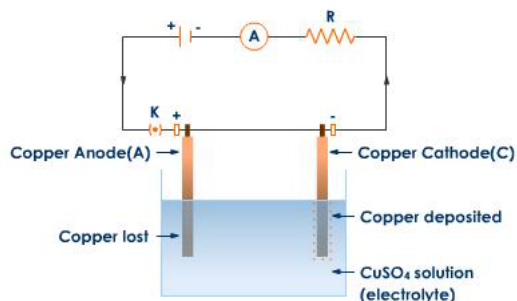
Determining the value of Avogadro's constant, L by means of electrolysis

1) The Avogadro's constant can be determined using electrolysis. This is done by calculating the charge associated with one mole of electrons. Then, Avogadro's constant can be calculated using:

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

2) The charge on one electron is $1.60 \times 10^{-19} C$, this is done using physics calculation.

3) The charge on one mole of electrons is then found from a simple electrolysis experiment.



- 4) The procedure is
- Weigh the pure copper anode and pure copper cathode separately.
 - Arrange the apparatus as shown. The variable resistor is used to keep the current constant.
 - Pass a constant electric current for a measured time interval.
 - Remove the cathode and anode and wash and dry them with distilled water and then with propanone.
 - Reweigh the copper cathode and anode
- 5) The cathode increases in mass because copper is deposited, the anode decreases in mass because the copper goes into the solution as ions. The decrease in mass of anode is preferably measured, this is because copper does not always 'stick' to the cathode very well, resulting in inaccurate gain in mass.
- 6) Suppose a sample set of experiment data is as shown below:
- Mass of anode at the beginning = 56.53 g
 - Mass of anode at the end = 56.40 g
 - Mass of copper removed from anode = 0.13 g
 - Quantity of charge passed = 408 C
- 7) i. $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$
- $0.13 \text{ g} \rightarrow 408 \text{ C}$
 - $\therefore 63.5 \text{ g} \rightarrow 63.5 \times 408 \div 0.14 = 185057.143 \text{ C}$, for two moles of electrons
 - Therefore, charge on one mole of electrons = $185057.143 \div 2 = 99600 \text{ C}$
 - Therefore, $L = 99600 \div 1.60 \times 10^{-19} \text{ C} = 6.2 \times 10^{23}$
 - This is a good agreement with the accurate value, 6.02×10^{23} .