



RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2023
Lecture Notes 21a – Electrochemistry 1

A Content

- Redox processes: electron transfer and changes in oxidation number (oxidation state)
- Electrode potentials
 - (i) Standard electrode (redox) potential, $E^\ominus$; the redox series
 - (ii) Standard cell potentials, $E_{\text{cell}}^\ominus$, and their uses
 - (iii) Batteries and fuel cells

B Learning outcomes

Candidates should be able to:

- (a) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)
- (b) define the terms:
 - (i) *standard electrode (redox) potential*
 - (ii) *standard cell potential*
- (c) describe the standard hydrogen electrode
- (d) 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
- (e) calculate a standard cell potential by combining two standard electrode potentials
- (f) use standard cell potentials to:
 - (i) explain/deduce the direction of electron flow from a simple cell
 - (ii) predict the spontaneity of a reaction
- (g) understand the limitations in the use of standard cell potentials to predict the spontaneity of a reaction
- (h) construct redox equations using the relevant half-equations
- (i) state and apply the relationship $\Delta G^\ominus = -nFE^\ominus$ to electrochemical cells, including the calculation of $E^\ominus$ for combined half reactions
- (j) predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion
- (k) 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

C References

1. Chemistry for Advanced Level by Peter Cann and Peter Hughes
2. Chemistry the Central Science by T L Brown and H E Lemay
3. Chemistry by Zumdahl

PRE-REQUISITE KNOWLEDGE

Candidates should be able to describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state).

Please refer to Lecture Notes 1b Redox Reactions pages 2 – 8 to refresh your understanding on redox reactions and how to balance redox equations.

An oxidation number is a number which is assigned to an element in a substance to show its state of oxidation.

Note: The oxidation number of an element in a substance is related to the number of electrons lost, gained, or shared as a result of chemical bonding.

- A positive change in oxidation state indicates that oxidation (loss of electrons) has occurred e.g. +1, +2.
- A negative change in oxidation state indicates that reduction (gain of electrons) has occurred e.g. -1, -2.

Rules for Assigning Oxidation Number

1. The oxidation number of an atom in the elemental state = 0.
Example: O.N. of Ca, I₂, S₈ or P₄ = 0
2. The oxidation number of a monoatomic ion is simply the charge on the ion.
Example: O.N. of Cl⁻ = -1; O.N. of Ca²⁺ = +2
3. The sum of the oxidation numbers of all the atoms or ions in an electrically neutral compound = 0.
Examples:

CaBr ₂	+2 + 2(-1) = 0
Al ₂ O ₃	2(+3) + 3(-2) = 0
CO ₂	+4 + 2(-2) = 0
4. In polyatomic ions, the sum of the oxidation numbers = the charge on the ion.
Examples:

SO₄²⁻ : The sum of the oxidation numbers (O.N. of S = +6, O.N. of O = -2)
 = +6 + 4(-2) = -2 = charge on the ion

CrCl₆³⁻ : The sum of the oxidation numbers (O.N. of Cr = +3, O.N. of Cl = -1)
 = +3 + 6(-1) = -3 = charge on the ion
1. In a covalent bond, the more electronegative atom has the negative oxidation number while the less electronegative atom has the positive oxidation number.
 - Electronegativity is the ability of an atom in a molecule to attract shared electrons in a bond.
 - Electronegativity values: F > O > N > C > H

Examples: O.N. of F in OF₂ = -1 O.N. of O in OF₂ = +2

6. The oxidation numbers of groups 1, 2, 13 and 17 elements, hydrogen and oxygen are listed in the table. Note the exceptions.

Element	O.N.	Examples	Exception
Group 1 (e.g. Na)	Always +1	NaBr	--
Group 2 (e.g. Mg)	Always +2	MgO	--
Group 13 (e.g. Al)	Always +3	Al ₂ O ₃	--
Group 17	Usually -1 (F is always -1)	NaF	Except when forming compounds with more electronegative atom E.g. O.N. for Cl in ClO ₂ = +4 O.N. for Cl in CCl ₄ = +1
Hydrogen	Usually +1	HCl	-1 in metal hydrides such as NaH (since Na is more electropositive than H)
Oxygen	Usually -2	CaO	-1 in peroxides* such as H ₂ O ₂ (hydrogen peroxide) and BaO ₂ (barium peroxide) *Peroxide ion is O ₂ ²⁻ -0.5 in KO ₂ (potassium superoxide*) *Superoxide ion is O ₂ ⁻ +2 in OF ₂ (fluorine monoxide) since F is more electronegative than O

Balancing Redox Equations

Candidates should be able to construct redox equations using the relevant half-equations.

1	Construct unbalanced oxidation and reduction half-equations by writing the reagent and product involved in each half-equation.	Only H ₂ O, H ⁺ or e ⁻ can be added, either as 'reactant' or 'product'. (Check that oxidation half-eqns have e ⁻ on RHS and reduction half-eqns have e ⁻ on LHS.)
	To each half-equation,	
2	Balance the element reduced or oxidised in each half-equation.	
3	Balance oxygen atoms by adding H ₂ O molecules.	
4	Balance hydrogen atoms by adding H ⁺ ions.	
5	Balance overall charges by adding e ⁻ . (Check that oxidation half-eqns have e ⁻ on RHS and reduction half-eqns have e ⁻ on LHS.)	
6	Multiply each balanced half-equation by appropriate integers so that no. of electrons gained = no. of electrons lost.	
7	Add the 2 balanced half-equations and eliminate any common terms to obtain the overall balanced equation (with no e ⁻).	
	In alkali medium, do steps A-C after step 5, followed by steps 6 and 7.	
A	"Neutralise" the H ⁺ ions by adding the required number of OH ⁻ ions to both sides of a half-equation.	Under alkaline medium
B	Combine the H ⁺ and OH ⁻ ions on the same side of the equation to form H ₂ O.	
C	Re-balance the half-equation by eliminating any common terms, such as H ₂ O.	

Under acidic medium

Under alkaline medium

A. REDOX PROCESSES & ELECTROLYTES

A.1 Redox: Reduction & Oxidation

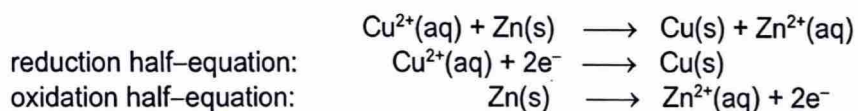
1.

Oxidation	Reduction
- o Increase in oxidation state of the element involved - o Loss of electron(s) - o Occurs at anode (AN OX)	- o Decrease in oxidation state of the element involved - o Gain of electron(s) - o Occurs at cathode (RED CAT)
Reducing Agent	Oxidising Agent
- o A substance that reduces another substance - o Is itself oxidised - o Electron donor, i.e. loses e^-	- o A substance that oxidises another substance - o Is itself reduced - o Electron acceptor, i.e. gains e^-

2. A redox reaction is one in which both reduction and oxidation occur. In fact, both processes must occur at the same time i.e. one cannot occur without the other.

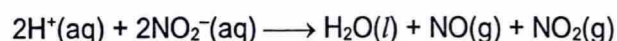


3. The equation for a redox reaction may be separated into two half-equations:



The half-equations show the transfer of electrons that occurs between the relevant species in a redox reaction. Note that the number of electrons lost must be equal to the number of electrons gained in the reaction. Thus, a balanced redox equation does not contain any electrons.

4. A disproportionation reaction is a redox reaction in which the same element in a substance is simultaneously oxidised and reduced.



In this reaction, some NO_2^- ions are being reduced to NO while simultaneously, other NO_2^- ions are being oxidised to NO_2 .

Oxidation number of N increases from +3 in NO_2^- to +4 in NO_2 .

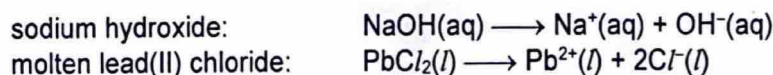
Oxidation number of N decreases from +3 in NO_2^- to +2 in NO .

5. Some everyday examples of redox reactions include rusting, respiration and combustion, reactions in batteries and cells, extraction of ores, and electroplating.

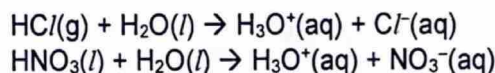
A.2 Electrolytes

1. An electrolyte is a compound which will conduct an electric current when it is in aqueous solution or in the molten state. An electrolyte conducts electricity due to the flow of charge carried by its ions.
2. A strong electrolyte is a compound which is fully ionised in aqueous solution.

All ionic compounds are strong electrolytes since they are made up of ions which become mobile in the molten or aqueous state. E.g. NaOH(aq) , $\text{PbCl}_2(l)$.



Some covalent compounds ionise completely in water and are also strong electrolytes. E.g. hydrogen chloride or HNO_3 .



3. A weak electrolyte only partially ionises in aqueous solution.
E.g. water, aqueous ammonia, most organic acids and organic bases
4. A non-electrolyte does not ionise at all and does not conduct electricity.
E.g. most organic compounds such as hydrocarbons (e.g. methane, ethene, benzene), alcohols, sugars, halogenoalkanes (e.g. chloromethane).

Exercise 1

A weedkiller can be prepared by heating a bleach solution.



What are the oxidation states of chlorine in these three compounds?

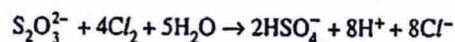
- | | | | |
|---|----|----|----|
| A | -1 | -1 | +5 |
| B | +1 | -1 | +5 |
| C | +1 | -1 | +7 |
| D | +2 | +1 | +7 |

N99/III/17

Ans: (**B**)

IVY Lecture Check Point

Sodium thiosulphate is used in the textile industry to remove an excess of chlorine from bleaching processes by reducing it to chloride ions.



In this reaction, how many moles of electrons are supplied per mole of thiosulphate?

- | | | | |
|---|---|---|---|
| A | 1 | C | 4 |
| B | 2 | D | 8 |

J95/IV/1

Ans: (**D**)

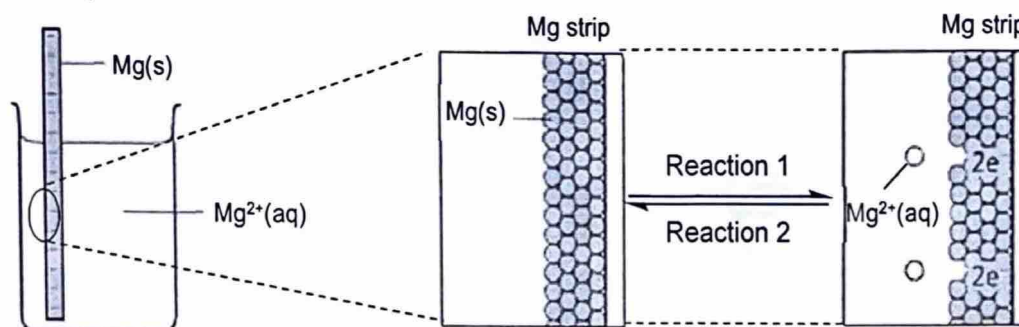
B. ELECTRODE POTENTIALS

B.1 Electrode Potentials

1. If a metal electrode is immersed in an aqueous solution containing a metal cation, an equilibrium is established which leads to negative charge formation on the electrode.

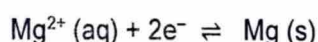
Using Mg as an example:

When a piece of magnesium is placed in an aqueous solution of its ions, two possible electron transfer processes can occur:



Reaction 1	Reaction 2
The magnesium atoms have a certain tendency to lose electrons. Hence, some atoms will go into solution as magnesium ions. $\text{Mg (s)} \longrightarrow \text{Mg}^{2+} \text{ (aq)} + 2\text{e}^{-}$ The electrons will be left behind on the metal. Over time, there will be a build-up of electrons on the magnesium surface, and the metal inside the solution will be surrounded by a layer of positive ions.	The positive ions in the solution may also gain back electrons. Hence, some ions will deposit back onto the metal surface i.e. reforming the metal. $\text{Mg}^{2+} \text{ (aq)} + 2\text{e}^{-} \longrightarrow \text{Mg (s)}$

When the rates of the two reactions are equal, a dynamic equilibrium is established:



At equilibrium, there will be a constant negative charge on the metal, and a constant number of ions present in the solution around the metal.

2. Over time, the metal becomes negatively charged and the solution becomes positively charged. There is a separation of charge across the metal-solution interface and there is a potential difference between the metal and the solution. This potential difference is known as the electrode potential, E , of the metal.
3. This configuration of electrode and solution is called a half-cell. There are other types of half-cells, e.g. gas / ion systems, ion / ion systems (refer to B.3).

B.2 Measurement of Electrode Potentials

1. The electrode potential, E , of an electrode (half-cell) i.e. its absolute potential, cannot be measured directly. Another electrode is required, and this new electrode will introduce its own potential. The potential difference between two electrode systems can be measured directly. What we need to do is to assign one electrode system as a reference, and measure all other electrode systems against this standard.
2. It has been found that electrode potential is dependent on the following conditions:
 - i. **temperature**,
 - ii. **concentration of ions** in aqueous solution,
 - iii. **partial pressure of any gas involved in the reaction**.
3. Hence, the measurement of the standard electrode potential of a half-cell requires:
 - i. standard conditions,
 - ii. a standard electrode as a *reference* electrode,

B.2.1 Standard Conditions

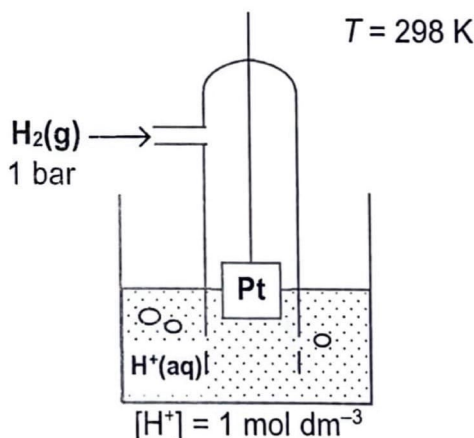
Temperature:	25 °C or 298 K
Pressure (of any gases involved):	1 bar
Concentration (of <i>all</i> ions involved in half eqn):	1 mol dm ⁻³

Note: The symbol "°" denotes standard conditions and is written as a superscript.

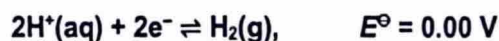
B.2.2 Standard Hydrogen Electrode

Candidates should be able to describe the standard hydrogen electrode.

1. The standard hydrogen electrode (S.H.E.) consists of
 - i. a platinum electrode coated with finely divided platinum
 - ii. immersed in a solution where $[H^+] = 1 \text{ mol dm}^{-3}$,
 - iii. hydrogen gas at 1 bar is bubbled over the platinum electrode,
 - iv. temperature is kept at 25 °C or 298 K.



2. Platinum is used because it is inert. The electrode allows $\text{H}_2(\text{g})$ to be adsorbed on its surface and establish the following equilibrium:



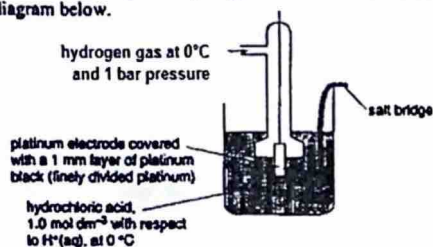
A potential develops on the surface of the platinum electrode and it is *arbitrarily* assigned a value of 0.00 V.

Note:

- The platinum electrode is coated with finely divided platinum to increase the surface area of the electrode so that equilibrium between $\text{H}_2(\text{g})$ and $\text{H}^+(\text{aq})$ can be established rapidly.
- Other reference electrodes also exist e.g. the calomel electrode ($E^\ominus = +0.244 \text{ V}$) and the silver/silver chloride electrode ($E^\ominus = +0.199 \text{ V}$).

Exercise 2

A student set up the hydrogen electrode shown in the diagram below.



What would have to be changed to make this a standard hydrogen electrode?

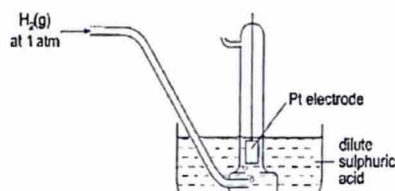
- the temperature of the gas and the acid solution
- the pressure of the hydrogen gas
- the metal comprising the electrode
- the thickness of the layer of platinum black
- the concentration of the hydrochloric acid

N89/11/5; J96/11/8

Ans: (D)

IVY Lecture Check Point

The diagram represents an electrode that, at 298 K, could be used to measure standard electrode potentials.



What should be the condition of the surface of the platinum electrode and the concentration of the sulphuric acid when making the measurement?

	Pt electrode	$[\text{H}_2\text{SO}_4(\text{aq})]/\text{mol dm}^{-3}$
A	platinised	0.5
B	platinised	1.0
C	polished	0.5
D	polished	1.0

N06/1/8

Ans: (B)

B.3 Common Half-cell Systems

The following are three common types of half-cell systems:

i. metal / metal ion e.g. $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ $\text{Cu}^{2+}(\text{aq}) / \text{Cu}(\text{s})$ half-cell	ii. gas / ion e.g. $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$ $\text{Cl}_2(\text{g}) / \text{Cl}^-(\text{aq})$ half-cell	iii. ion / ion e.g. $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ $\text{Fe}^{3+}(\text{aq}) / \text{Fe}^{2+}(\text{aq})$ half-cell
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- Note:
- Each system primarily contains the same element in different oxidation states.
 - In the absence of a metal in the half-cell, platinum is used as the inert electrode.

Exercise 3

The standard redox potential for the half-cell reaction



Which cell would be used to determine this standard value?

- A Fe electrode in $1 \text{ mol dm}^{-3} \text{ Fe}^{3+}$ against Fe electrode in $1 \text{ mol dm}^{-3} \text{ Fe}^{2+}$.
- B Pt electrode in $1 \text{ mol dm}^{-3} \text{ Fe}^{3+}$ against Pt electrode in $1 \text{ mol dm}^{-3} \text{ Fe}^{2+}$.
- C Fe electrode in a solution containing $1 \text{ mol dm}^{-3} \text{ Fe}^{3+}$ and $1 \text{ mol dm}^{-3} \text{ Fe}^{2+}$ against a standard hydrogen electrode.
- D Pt electrode in a solution containing $1 \text{ mol dm}^{-3} \text{ Fe}^{3+}$ and $1 \text{ mol dm}^{-3} \text{ Fe}^{2+}$ against a standard hydrogen electrode.

J95/1V/7

Ans: (D)

B.4 Standard Electrode Potential, $E^{\ominus}$

Candidates should be able to define the terms:

- (i) standard electrode (redox) potential
- (ii) standard cell potential

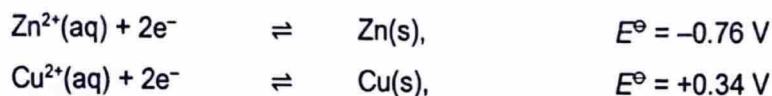
1. If a half-cell is connected to a hydrogen electrode (which is also a half-cell), the resultant cell has a potential difference i.e. electromotive force (e.m.f.) which can be measured by a voltmeter.
2. If this e.m.f. is measured under standard conditions, its value is known as the *standard electrode potential*, $E^{\ominus}$, of the half-cell.

Definition:

The *standard electrode potential* of a half-cell is the electromotive force, measured at 298 K, between the half-cell and the standard hydrogen electrode, in which the concentration of any reacting species in solution is 1 mol dm^{-3} and any gaseous species is at a pressure of 1 bar.

Note: *Standard electrode potential* is commonly written as *standard reduction potential* or *standard redox potential*.

3. The electrode potentials of half-cells, E , are often called redox potentials. By convention, a standard electrode potential always refers to the half-reaction written as a reduction. redox potentials are written as *reduction* processes.



When standard conditions are employed, the potentials are termed

- standard electrode potentials
 - standard electrode (redox) potentials
 - standard reduction potentials
- } $E^{\ominus}$

4. The standard electrode potential is a measure of the tendency of reduction (i.e. gaining electrons) occurring.

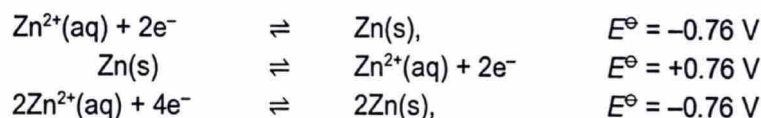
The more positive the value of $E^{\ominus}$, the more *likely* reduction is to occur (w.r.t. the standard hydrogen electrode.)

5. $E^{\ominus}$ values also give an indication of the position of equilibrium of a reaction.
A more positive $E^{\ominus}$ value indicates that the position of equilibrium lies to the right.
A more negative $E^{\ominus}$ value indicates that the position of equilibrium lies to the left.

The more positive the $E^{\ominus}$ value,
 $\Rightarrow$ the forward reaction is more favoured,
 $\Rightarrow$ the more likely reduction occurs,
 $\Rightarrow$ the higher is the tendency to gain e^{-} ,
 $\Rightarrow$ the stronger is the oxidising agent.

The more negative the $E^{\ominus}$ value,
 $\Rightarrow$ the backward reaction is more favoured,
 $\Rightarrow$ the more likely oxidation occurs,
 $\Rightarrow$ the higher is the tendency to lose e^{-} ,
 $\Rightarrow$ the stronger is the reducing agent.

6. Whenever the direction of a half-reaction is reversed, the sign of $E^{\ominus}$ must also be reversed. The value of $E^{\ominus}$ is not affected even if the half-reaction is multiplied by coefficients (unlike for ΔH in Energetics). E.g.



Note: Doubling the coefficients does not double the $E^{\ominus}$ value as the standard electrode potential is the ratio of energy to charge. When we change the coefficients, the amount increases but the energy and charge increase proportionately, so their ratio stays the same. This is similar to the density, which does not change as the amount of substance increases because the mass and volume increase proportionately.

B.5 Measurement of Standard Electrode (Redox) Potentials, $E^{\ominus}$

Candidates should be able to describe methods used to measure the standard electrode potentials of:

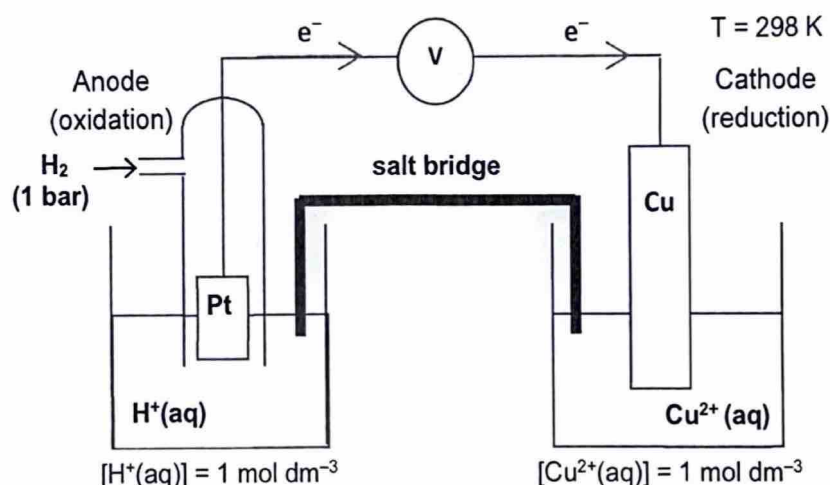
- (i) metals or non-metals in contact with their ions in aqueous solution
- (ii) ions of the same element in different oxidation states.

- Step 1: Connect the given half-cell to the S.H.E. and ensure that all concentrations of solutions are 1 mol dm^{-3} , the temperature is 298 K and the pressure of gases (if any) is 1 bar.
- Step 2: Connect the two solutions in the two half-cells with a salt bridge, commonly made up of saturated potassium nitrate solution.
- Step 3: Measure the potential difference between the given half-cell and the S.H.E. using a high-resistance voltmeter. The value shown on the voltmeter is the standard electrode potential (or e.m.f.) of the half-cell concerned.

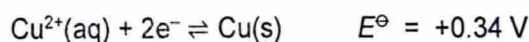
Note: The first reading shown on the voltmeter the moment the two half-cells are connected is the actual e.m.f. If current is allowed to flow in a closed circuit, chemical reactions will occur and the concentration of the reactants will start to decrease and will no longer be at standard conditions. The reading on the voltmeter will eventually drop to zero when the cell goes flat (i.e. the system has reached equilibrium and there is no longer any potential difference between the two half-cells).

(i) metal / metal ion system

e.g. $\text{Cu}^{2+}(\text{aq}) / \text{Cu}(\text{s})$ half-cell



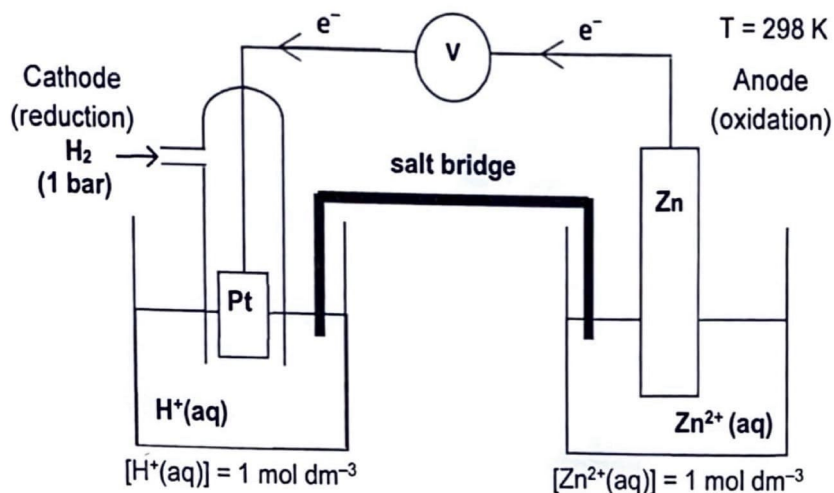
At standard conditions, the reading on the voltmeter gives the standard electrode potential of the $\text{Cu}^{2+}(\text{aq}) / \text{Cu}(\text{s})$ half-cell:



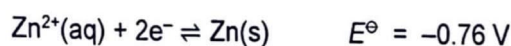
Note: The voltmeter reading gives an indication of the direction of electron flow. A positive value in the above set-up shows that electrons flow from the $\text{H}^{+}(\text{aq}) / \text{H}_2(\text{g})$ half-cell to the $\text{Cu}^{2+}(\text{aq}) / \text{Cu}(\text{s})$ half-cell; i.e. Cu^{2+} is more easily reduced than H^{+} and the reduction potential for the $\text{Cu}^{2+}(\text{aq}) / \text{Cu}(\text{s})$ half-cell is +0.34 V.

You need to be able to draw the experimental setup for measuring standard electrode potentials.

e.g. $\text{Zn}^{2+}(\text{aq}) / \text{Zn}(\text{s})$ half-cell



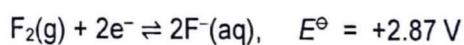
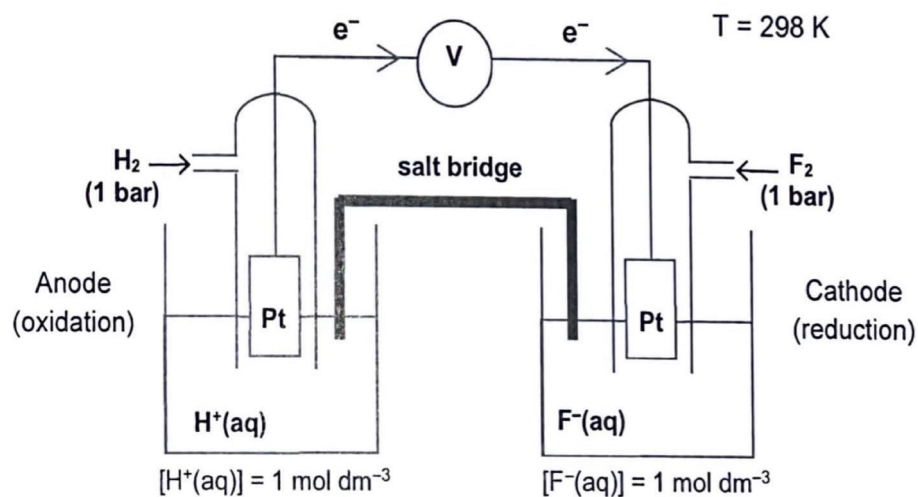
At the standard conditions, the reading on the voltmeter gives the standard electrode potential of the $\text{Zn}^{2+}(\text{aq}) | \text{Zn}(\text{s})$ half-cell:



Note: The voltmeter reading gives an indication of the direction of electron flow. A negative value in the above set-up shows that electrons flow from the $\text{Zn}^{2+}(\text{aq}) | \text{Zn}(\text{s})$ half-cell to the $\text{H}^{+}(\text{aq}) | \text{H}_2(\text{g})$ half-cell; i.e. H^{+} is more easily reduced than Zn^{2+} and the reduction potential for the $\text{Zn}^{2+}(\text{aq}) | \text{Zn}(\text{s})$ half-cell is -0.76 V .

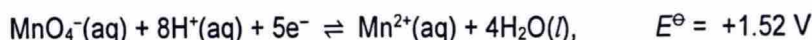
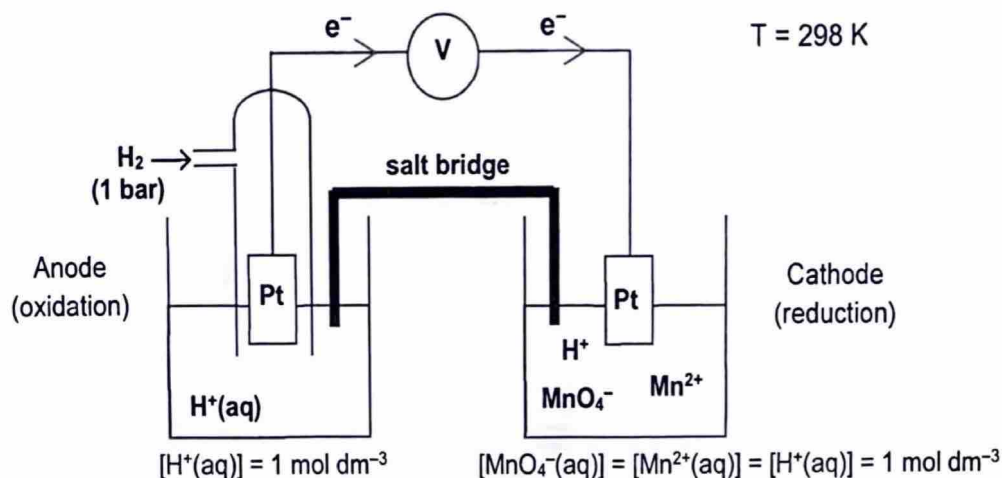
(ii) gas / ion system

e.g. $\text{F}_2(\text{g}) / \text{F}^{-}(\text{aq})$ half-cell



(iii) ion / ion system

e.g. $\text{MnO}_4^-(\text{aq}) / \text{Mn}^{2+}(\text{aq})$ half-cell



Checklist for the general labels to include when drawing the setups:

in each half-cell		connecting 2 half-cells	
☐	identity of electrode	☐	external wire with voltmeter
☐	identity and concentration of electrolyte	☐	direction of electron flow
☐	gas jar, identity and partial pressure of gas (if any)	☐	salt bridge
		☐	temperature

Note: Question may also ask for the labelling of anode (–) or cathode (+).

C. THE REDOX SERIES

- The redox series is a compilation of standard electrode (*redox*) potentials. There are two tabulations in the *Data Booklet*:

(a) alphabetical order:

Electrode reaction	$E^\ominus/\text{V}$
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.80
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	–1.66
$\text{Ba}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ba}$	–2.90
$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+1.07
$\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca}$	–2.87
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36

(b) order of decreasing $E^\ominus$ value

(i.e. decreasing order of oxidising power):

Electrode reaction	$E^\ominus/\text{V}$
$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	+2.87
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2.01
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.77
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	+1.47
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36

- For the series arranged in order of decreasing $E^\ominus$ value, the species on the L.H.S. at the top are strong oxidising agents while those on the R.H.S. at the bottom are strong reducing agents.

3. Relationship between $E^\ominus$ and Reactivity Series of Metals:

From Ag to Li,

- reactivity increases
- $E^\ominus$ becomes more negative
- lose electrons more readily
- form positive ions more readily
- metal oxidizes more readily
- become stronger reducing agents

M^{n+}	M	$E^\ominus$
Li^+	Li	-3.04
K^+	K	-2.92
Ca^{2+}	Ca	-2.87
Na^+	Na	-2.71
Mg^{2+}	Mg	-2.38
Al^{3+}	Al	-1.66
Zn^{2+}	Zn	-0.76
Fe^{2+}	Fe	-0.44
Sn^{2+}	Sn	-0.14
Pb^{2+}	Pb	-0.13
H^+	H_2	0.00
Cu^{2+}	Cu	+0.34
Ag^+	Ag	+0.80

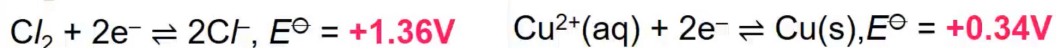
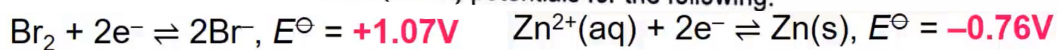
Exercise 4

With reference to $E^\ominus$ values in the Data Booklet on Section 4 pages 46–50,

- Name the strongest oxidising agent. F_2
- Give the symbol of the strongest reducing agent. Li

Exercise 5

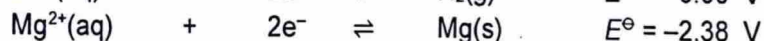
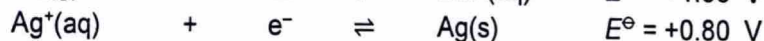
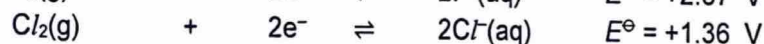
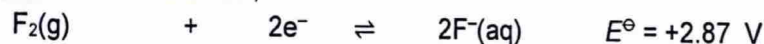
a. Fill in the standard electrode (redox) potentials for the following:



b. Cl_2 is a stronger O.A. than Br_2 . Zn is a stronger R.A. than Cu .

Exercise 6 IVY Lecture Check Point

Based on the $E^\ominus$ data below,



Decide if these statements are correct.

- (1) Ag^+ has a higher tendency to gain electrons compared to H^+ . ✓
- (2) Mg has a higher tendency to lose electrons compared to H_2 . ✓
- (3) Mg^{2+} is a stronger oxidising agent than Ag^+ . ✗
- (4) F_2 has a higher tendency to gain electrons compared to Cl_2 . ✓
- (5) Cl^- is a weaker reducing agent than F^- . ✗

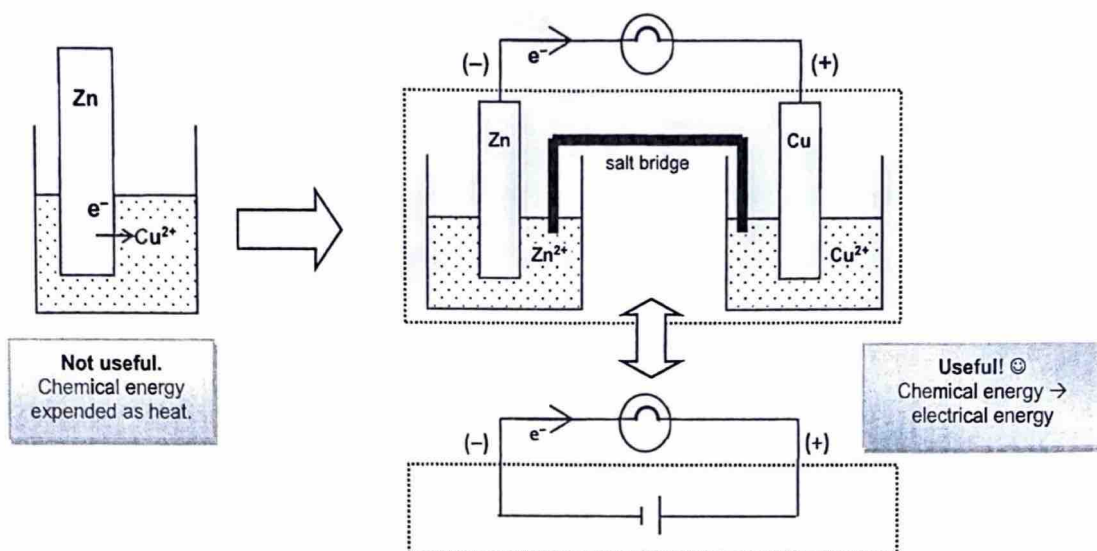
D. STANDARD CELL POTENTIALS, $E^\ominus_{\text{cell}}$

D.1 Electrochemical (Voltaic) Cell

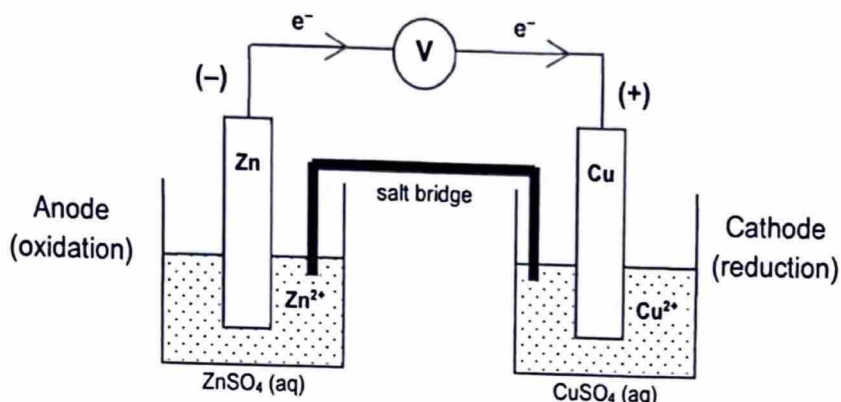
1. When a strip of zinc foil is dipped into copper(II) sulfate solution for some time, it is found that some zinc has dissolved and a brown deposit of copper metal is formed on the zinc foil. The reaction is exothermic and heat is given out. A redox reaction has occurred and this can be represented by the equation:



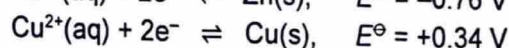
2. In the reaction, electrons are basically moving from Zn atoms to Cu^{2+} ions via the metal-solution interface. By simply "extending the route of electron travel", the chemical energy of this reaction could be converted to electrical energy.
3. This is explained by making use of the inherent *potential difference* between the zinc half-cell and the copper half-cell. This cell is an example of an electrochemical (voltaic) cell or simply, *batteries*. (This Zn-Cu cell is also known as a Daniell cell.)



D.2 The Daniell Cell



1. The Daniell cell is made up of a $\text{Zn}^{2+} | \text{Zn}$ half-cell and a $\text{Cu}^{2+} | \text{Cu}$ half-cell. The two relevant redox half-equations are:

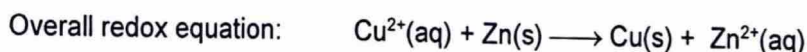


2. Since the $E^{\ominus}$ of $\text{Zn}^{2+} | \text{Zn}$ half-cell is more negative, Zn is more easily oxidised than Cu, i.e. Zn has a higher tendency to lose electrons compared to Cu. Alternatively, we can say that since the $E^{\ominus}$ of $\text{Cu}^{2+} | \text{Cu}$ half-cell is more positive, Cu^{2+} is more easily reduced than Zn^{2+} , i.e. Cu^{2+} has a higher tendency to gain electrons compared to Zn^{2+} .

3. Zn loses 2 electrons and enters the solution as Zn^{2+} :



Cu^{2+} ions in the solution near the copper metal surface will take up electrons and are reduced to Cu metal:



Note: For the half-equations and overall redox equation, use ' $\longrightarrow$ ' instead of ' $\rightleftharpoons$ '.

4. Electrons leave the Zn electrode and travel via the connecting wire (i.e. the external circuit) to the Cu electrode (i.e. direction of electron flow is from Zn to Cu).
Note: Current (I) is said to flow from the Cu electrode to the Zn electrode i.e. in a direction opposite to electron flow.
5. The salt bridge completes the circuit. (see the next section D.3)
6. The electrode where oxidation takes place is called the anode. (**An Ox**). It is the negative electrode (i.e. the (-) terminal of a battery) since electrons are produced at the anode and exit the cell via the anode. In the Daniell cell, the Zn electrode is the anode.

The electrode where reduction takes place is called the cathode. (**Red Cat**). It is the positive electrode (i.e. the (+) terminal of a battery) since electrons are absorbed at the cathode when they re-enter the cell via the cathode. In this case, the Cu electrode is the cathode.

7. In general, the half-cell with a more positive $E^\ominus$ is the reduction half-cell and the half-cell with a less positive (or more negative) $E^\ominus$ is the oxidation half-cell. This is because the more positive the $E^\ominus$ value, the more readily reduction occurs.

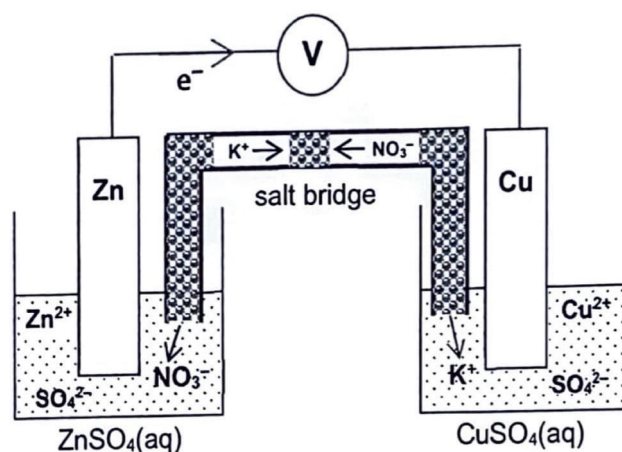
D.3 Salt Bridge

For the electrochemical cell, electrons flow in the external circuit from the anode to the cathode.

The two half-cells are connected internally by a salt bridge – a U-tube that contains an electrolytic solution, such as KNO_3 , whose ions do not react with other ions in the cell or with electrodes.

Role of salt bridge

1. To maintain electrical (charge) neutrality of each half-cell
In the Daniell Cell, as Zn^{2+} continues to be produced, the Zn^{2+} ion solution builds up a positive charge. Similarly, as Cu^{2+} deposit as metal atoms on the copper electrode, the solution depletes in positive charge (i.e. becomes increasingly negative since SO_4^{2-} remain in solution).



The ions in the salt bridge migrate so as to neutralise the increasing charge in the two half-cells. In the salt bridge, cations migrate to the cathode while anions migrate to the anode. The salt bridge provides positive ions (e.g. K^+) which enter the Cu^{2+} solution and negative ions (e.g. NO_3^-) which enter the Zn^{2+} solution.

2. To complete the circuit by allowing ions to flow without the mixing of electrolytes.

D.4 Standard Cell Potential, $E^\ominus_{\text{cell}}$

Candidates should be able to calculate a standard cell potential by combining two standard electrode potentials.

1. An electrochemical (or voltaic) cell converts the energy change of a spontaneous reaction (chemical energy) into electrical energy. This electrical energy can do work and is proportional to the difference in potential between the two electrodes. *(For the applications of electrochemical cells, refer to Section E – Fuel cells and other types of cells)*

The standard cell potential, $E^\ominus_{\text{cell}}$, is the potential difference between two half-cells under standard conditions. It gives a measure of the e.m.f. (electromotive force) of the cell.

2. The standard potential of any electrochemical cell can be calculated by the following:

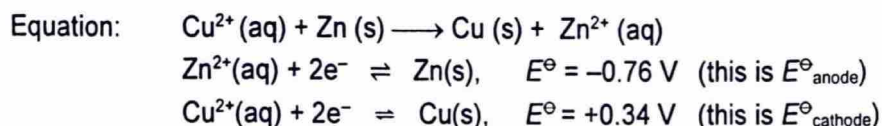
$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{cathode}} - E^{\ominus}_{\text{anode}}$$



Do NOT change the sign of $E^{\ominus}$ given in Data Booklet!!!

where $E^{\ominus}_{\text{cathode}}$ is the reduction potential of the half-cell undergoing reduction
 $E^{\ominus}_{\text{anode}}$ is the reduction potential of the half-cell undergoing oxidation

e.g. calculate the $E^{\ominus}_{\text{cell}}$ for Daniell cell (page 16):



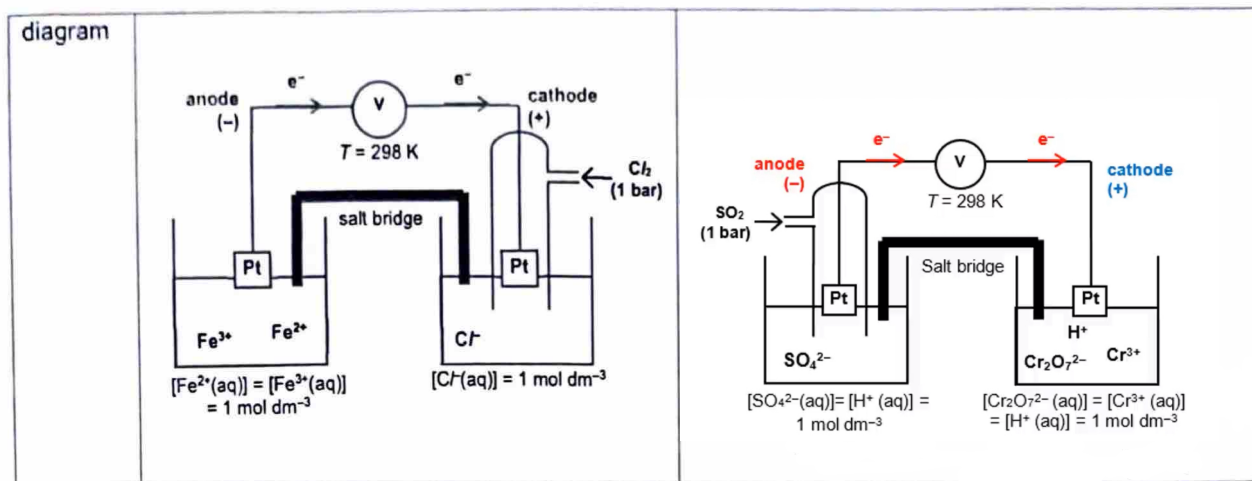
$$E^{\ominus}_{\text{cell}} = +0.34 - (-0.76) = +1.10 \text{ V}$$

Exercise 7

For the voltaic cells made up of the following half-cells,

- Write equations for reactions at cathode, anode and the overall cell reaction.
- Calculate $E^{\ominus}_{\text{cell}}$.
- Draw a labelled diagram for each cell, indicating the anode and cathode, and the direction of electron flow in the external circuit.

	Voltaic Cell 1	Voltaic Cell 2
half-cells	$\text{Cl}_2 + 2\text{e}^{-} \rightleftharpoons 2\text{Cl}^{-}, \quad E^{\ominus} = +1.36 \text{ V}$ $\text{Fe}^{3+} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}, \quad E^{\ominus} = +0.77 \text{ V}$	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^{+} + 6\text{e}^{-} \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}, \quad E^{\ominus} = +1.33 \text{ V}$ $\text{SO}_4^{2-} + 4\text{H}^{+} + 2\text{e}^{-} \rightleftharpoons \text{SO}_2 + 2\text{H}_2\text{O}, \quad E^{\ominus} = +0.17 \text{ V}$
cathode reaction	$\text{Cl}_2(\text{g}) + 2\text{e}^{-} \rightarrow 2\text{Cl}^{-}(\text{aq})$	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^{+}(\text{aq}) + 6\text{e}^{-} \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$
anode reaction	$\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^{-}$	$\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 2\text{e}^{-}$
cell reaction	$\text{Cl}_2(\text{g}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow 2\text{Cl}^{-}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 2\text{H}^{+}(\text{aq}) + 3\text{SO}_2(\text{g}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 3\text{SO}_4^{2-}(\text{aq})$
$E^{\ominus}_{\text{cell}}$	$E^{\ominus}_{\text{cell}} = +1.36 - (+0.77) = +0.59 \text{ V}$	$E^{\ominus}_{\text{cell}} = +1.33 - (+0.17) = +1.16 \text{ V}$



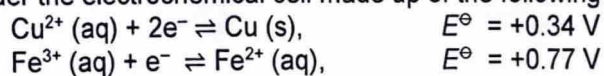
D.5 Effects of Changing Conditions on Cell Potential, E_{cell}

Candidates should be able to predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion.

- Under non-standard conditions, $E \neq E^{\ominus}$
- Consider the half-cell: $Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$, $E^{\ominus} = +0.77 \text{ V}$
 - If the $[Fe^{3+}(aq)]$ is increased such that it becomes greater than 1 mol dm^{-3} (i.e. conditions are no longer standard), the position of equilibrium will shift to the right and $E > +0.77 \text{ V}$ (i.e. $E > E^{\ominus}$).
 - If the $[Fe^{3+}(aq)]$ is decreased such that it becomes less than 1 mol dm^{-3} (i.e. conditions are no longer standard), the position of equilibrium will shift to the left and $E < +0.77 \text{ V}$ (i.e. $E < E^{\ominus}$).
- Similarly, for an electrochemical (voltaic) cell (i.e. made up of two half-cells) under non-standard conditions, $E_{\text{cell}} \neq E^{\ominus}_{\text{cell}}$.

Exercise 8

Consider the electrochemical cell made up of the following half-cells:

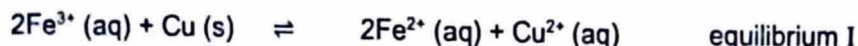


- a. Calculate $E^{\ominus}_{\text{cell}}$ and write the overall equation of the electrochemical cell.

At the anode:	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
At the cathode:	$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}$
Overall equation:	$2Fe^{3+}(aq) + Cu(s) \rightarrow 2Fe^{2+}(aq) + Cu^{2+}(aq)$

$$E^{\ominus}_{\text{cell}} = +0.77 - (+0.34) = +0.43 \text{ V}$$

- b. The above electrochemical cell is initially set up under standard conditions. The following changes are made to the electrochemical cell. Predict whether the new E_{cell} is higher or lower than $E^{\ominus}_{\text{cell}}$.



Change	Effect on position of equilibrium I	Effect on E_{cell}
① Adding water to Cu^{2+}/Cu half-cell*	shifts right	$E_{\text{cell}} > E^{\ominus}_{\text{cell}}$
② Adding $\text{NaOH}(\text{aq})$ to Cu^{2+}/Cu half-cell#	shifts right	$E_{\text{cell}} > E^{\ominus}_{\text{cell}}$
IVY Lecture Check Point		
③ Using a smaller piece of Cu in Cu^{2+}/Cu half-cell	no change	no change
④ Adding water to $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell*	no change	no change
IVY Lecture Check Point		
⑤ Adding some $\text{FeCl}_2(\text{s})$ to $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell	shifts left	$E_{\text{cell}} < E^{\ominus}_{\text{cell}}$

*Note: By LCP, addition of water would cause position of equilibrium to shift to the side with more ions. On adding water, position of equilibrium shifts to the left for Cu^{2+}/Cu half-cell but there is no change in position of equilibrium for $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell. This is because the number of ions is the same for both forward and backward reaction for $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell.

#Note: The addition of $\text{NaOH}(\text{aq})$ results in the precipitation of insoluble $\text{Cu}(\text{OH})_2$ precipitate, causing $[\text{Cu}^{2+}]$ to drop. By LCP, the position of equilibrium shifts to the right to increase $[\text{Cu}^{2+}]$ resulting in the increase in E_{cell} .

D.6 Predicting Spontaneity of a Redox Reaction Using $E^{\ominus}_{\text{cell}}$

Candidates should be able to use standard cell potentials to:

- explain/deduce the direction of electron flow from a simple cell
- predict the spontaneity of a reaction.

When predicting the spontaneity of a redox reaction, the sign of $E^{\ominus}_{\text{cell}}$ indicates the spontaneity of the reaction:

Under standard conditions,

$E^{\ominus}_{\text{cell}} > 0 \Rightarrow$ reaction is thermodynamically feasible and spontaneous.

$= 0 \Rightarrow$ reaction is at equilibrium

$< 0 \Rightarrow$ reaction is not thermodynamically feasible and not spontaneous.

Steps in predicting spontaneity of a redox reaction:

- Identify which species is reduced and which is oxidised.
- Write down the two relevant half-equations and their $E^{\ominus}$ values.
- Identify $E^{\ominus}_{\text{cathode}}$ and $E^{\ominus}_{\text{anode}}$ based on which species undergoes reduction/oxidation.
- Calculate $E^{\ominus}_{\text{cell}}$.
- $E^{\ominus}_{\text{cell}} > 0$: reaction is spontaneous
 $E^{\ominus}_{\text{cell}} < 0$: reaction is non-spontaneous

Exercise 9

- Are the following reactions spontaneous when the substances are mixed together?
- Calculate $E^\ominus_{\text{cell}}$ and write equations for any reactions if appropriate.

From Data Booklet: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s}), E^\ominus = -0.76 \text{ V}$
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s}), E^\ominus = +0.34 \text{ V}$

Substances mixed	Is reaction spontaneous? Why?	$E^\ominus_{\text{cell}}$	Equation
Cu^{2+} & Zn^{2+}	No. Both species are oxidising agents.		
Cu & Zn	No. Both species are reducing agents.		
Cu^{2+} & Zn	Yes. $E^\ominus_{\text{cell}} > 0$	$E^\ominus_{\text{cell}} = +0.34 - (-0.76)$ $= +1.10 \text{ V}$	$\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s})$ $\rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$
Cu & Zn^{2+}	No. $E^\ominus_{\text{cell}} < 0$	$E^\ominus_{\text{cell}} = -0.76 - 0.34$ $= -1.10 \text{ V}$	

D.7 Relationship between $E^\ominus$ and Gibbs Free Energy

Candidates should be able to state and apply the relationship $\Delta G^\ominus = -nFE^\ominus$ to electrochemical cells, including the calculation of $E^\ominus$ for combined half reactions.

- In Energetics II (Lecture Notes 5b), the concept of using the change in Gibbs free energy, $\Delta G^\ominus$, to predict the spontaneity of reaction was introduced. If $\Delta G^\ominus < 0$, the reaction is said to be spontaneous; if $\Delta G^\ominus > 0$, the reaction is said to be non-spontaneous; if $\Delta G^\ominus = 0$, the reaction is said to be at equilibrium.

The relationship between $E^\ominus$ and $\Delta G^\ominus$ is:

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

units of $\Delta G^\ominus$ is J mol^{-1} and $E^\ominus$ is V

where n is the number of moles of electrons transferred in the redox equation
 F is the Faraday constant, 96500 C mol^{-1} (given in section 1 of Data Booklet)

- The signs of $\Delta G^\ominus$ and $E^\ominus$ are opposite for any reaction.
 - A spontaneous reaction has a negative Gibbs free energy change ($\Delta G^\ominus < 0$) and positive cell potential ($E^\ominus_{\text{cell}} > 0$).
 - A non-spontaneous reaction has a positive Gibbs free energy change ($\Delta G^\ominus > 0$) and negative cell potential ($E^\ominus_{\text{cell}} < 0$).

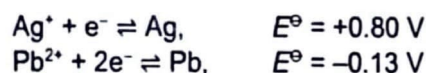
Under standard conditions,

$E^\ominus_{\text{cell}} > 0; \Delta G^\ominus < 0 \Rightarrow$ reaction is thermodynamically feasible and spontaneous.

$E^\ominus_{\text{cell}} = 0; \Delta G^\ominus = 0 \Rightarrow$ reaction is at equilibrium

$E^\ominus_{\text{cell}} < 0; \Delta G^\ominus > 0 \Rightarrow$ reaction is not thermodynamically feasible and not spontaneous.

e.g. In the reaction $\text{Pb(s)} + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{Ag(s)}$,



$$E^\ominus_{\text{cell}} = +0.80 - (-0.13) = +0.93 \text{ V}$$

Number of moles of electrons transferred in the equation, $n = 2$

$$\Delta G^\ominus = -nFE^\ominus = -2 \times 96500 \times 0.93 = -179000 \text{ J mol}^{-1} = -179 \text{ kJ mol}^{-1}$$

Note:
n represents the no. of moles of electrons transferred in the redox equation

Note: In Chemical Equilibrium (Lecture Notes 7), we saw that the position of equilibrium is also dependent on the change in Gibbs free energy. Thus, there exists an interrelationship between $\Delta G^\ominus$, $E^\ominus$ and the equilibrium constant, K .

Exercise 10

For the following, identify the relevant half-equations from the species that are mixed together, calculate $E^\ominus_{\text{cell}}$ and $\Delta G^\ominus$, and predict if the reaction is spontaneous. Write any equation for any reaction that occurs.

Species mixed	Half-equations	$E^\ominus_{\text{cell}}$, $\Delta G^\ominus$, Spontaneity	Equation
Cl^- and $\text{MnO}_4^- / \text{H}^+$	$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^- \quad E^\ominus = +1.36 \text{ V}$ $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E^\ominus = +1.52 \text{ V}$	$E^\ominus_{\text{cell}} = +1.52 - 1.36 = +0.16 \text{ V} > 0$ $\Delta G^\ominus = -10(96500)(0.16)$ $= -154400 \text{ J mol}^{-1}$ $= -154 \text{ kJ mol}^{-1}$ Since $\Delta G^\ominus < 0$, reaction is spontaneous. $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{Cl}_2$	*This is also the reason why KMnO_4 should not be acidified with HCl
Br_2 & Fe^{2+}	$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-, \quad E^\ominus = +1.07 \text{ V}$ $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}, \quad E^\ominus = +0.77 \text{ V}$ $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}, \quad E^\ominus = -0.44 \text{ V}$	$E^\ominus_{\text{cell}} = +1.07 - 0.77 = +0.30 \text{ V} > 0$ $\Delta G^\ominus = -2(96500)(0.30)$ $= -57900 \text{ J mol}^{-1}$ $= -57.9 \text{ kJ mol}^{-1}$ Since $\Delta G^\ominus < 0$, reaction is spontaneous. $\text{Br}_2 + 2\text{Fe}^{2+} \rightarrow 2\text{Br}^- + 2\text{Fe}^{3+}$	
I_2 & H_2O_2	IVY Lecture Check Point $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}, \quad E^\ominus = +1.77 \text{ V}$ $2\text{H}^+ + \text{O}_2 + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2, \quad E^\ominus = +0.68 \text{ V}$ $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-, \quad E^\ominus = +0.54 \text{ V}$	The two relevant equations are: $2\text{H}^+ + \text{O}_2 + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2, \quad E^\ominus = +0.68 \text{ V}$ $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-, \quad E^\ominus = +0.54 \text{ V}$ $E^\ominus_{\text{cell}} = +0.54 - 0.68 = -0.14 \text{ V}$ $\Delta G^\ominus = -2(96500)(-0.14)$ $= +27020 \text{ J mol}^{-1}$ $= +27.0 \text{ kJ mol}^{-1}$ Since $\Delta G^\ominus > 0$, the reaction is not spontaneous.	NIL

Exercise 11

By referring to the following reduction half-equations,

$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36 V
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33 V
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23 V
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77 V
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54 V
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$	+0.40 V

tick reactions that are spontaneous and cross out those that are not when the following are mixed:

- (a) I_2 and Fe^{2+} ✗ (c) Cl^- and $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$ ✗ (e) I^- and $\text{O}_2 / \text{H}_2\text{O}$ ✗
 (b) I^- and Fe^{3+} ✓ (d) I^- and O_2 / H^+ ✓

Hence, explain why:

- Iron(III) iodide does not exist in aqueous solution.
Reason: Fe^{3+} oxidises I^- to I_2 and is reduced to Fe^{2+} .
- Potassium manganate(VII) should not be acidified using dil HCl but potassium dichromate(VI) may be acidified using dil HCl .
Reason: Cl^- is oxidised by KMnO_4 to Cl_2 (from ex 10) but is not oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$.
- Potassium iodide solution turns yellow in the presence of acid.
Reason: I^- is oxidised to I_2 by O_2 in air under acidified conditions.

D.8 Limitations of Spontaneity Predictions Based on $E^\ominus_{\text{cell}}$

Candidates should be able to understand the limitations in the use of standard cell potentials to predict the spontaneity of a reaction.

- Kinetic factor is not taken into consideration:
 $E^\ominus_{\text{cell}}$ is a measure of the position of equilibrium but gives no indication of rate.

In the reaction of H_2 with Cu^{2+} , $E^\ominus_{\text{cell}} = +0.34 - 0.00 = +0.34\text{V}$

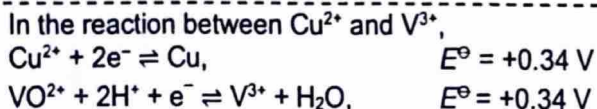
$\Rightarrow$ reaction is thermodynamically feasible and the reaction

$\text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}^+(\text{aq})$ is expected to occur spontaneously.

However, no reaction takes place when $\text{H}_2(\text{g})$ is passed into $\text{CuSO}_4(\text{aq})$ as the activation energy for the reaction is high. Hence, even though the reaction is thermodynamically feasible, it is kinetically not feasible.

2. Reaction takes place under non-standard conditions.

$E^\ominus_{\text{cell}}$ is the cell potential at standard conditions. Predictions using $E^\ominus_{\text{cell}}$ under non-standard conditions may not be valid.



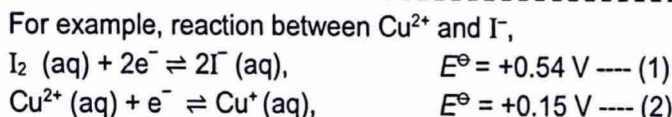
$$E^\ominus_{\text{cell}} = +0.34 - (+0.34) = 0 \text{ V}$$

$\Rightarrow$ A reversible reaction takes place until equilibrium is reached.

However, by varying conditions such as concentration, the reaction may be made to proceed. Hence, V^{3+} can reduce Cu^{2+} by increasing concentration of V^{3+} or increasing concentration of Cu^{2+} .

3. Side reactions may occur.

If a side reaction occurs, especially with insoluble ionic solid formation, a non-spontaneous reaction may become spontaneous.



$$E^\ominus_{\text{cell}} = +0.15 - (+0.54) \text{ V} = -0.39 \text{ V}$$

$\Rightarrow$ no reaction is expected when aqueous solutions of Cu^{2+} and I^- are mixed.

- However, a reaction does occur: $2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^-(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq})$. When blue $\text{Cu}^{2+}(\text{aq})$ is mixed with colourless $\text{I}^-(\text{aq})$, a cream precipitate (CuI) in a brown solution (I_2) is observed. Refer to QA3.
- Due to the precipitation of CuI , $[\text{Cu}^+(\text{aq})]$ becomes very low, such that the P.O.E. of (2) favours the R.H.S. Thus, $E_{\text{Cu}^{2+}/\text{Cu}^+} > E^\ominus_{\text{Cu}^{2+}/\text{Cu}^+}$ and E_{cell} may become $> 0 \text{ V}$.
- Thus, the reaction becomes spontaneous.

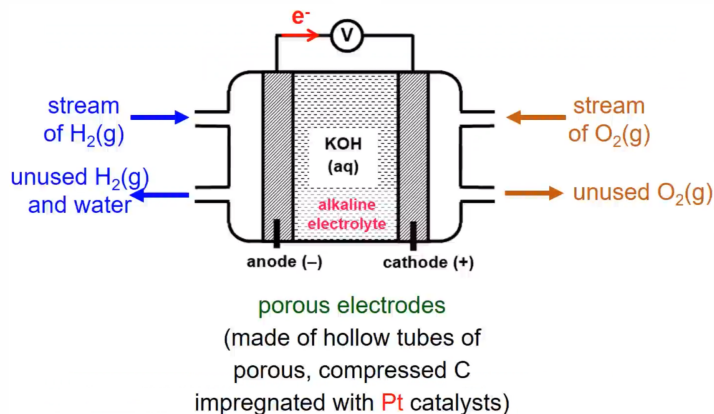
E FUEL CELLS & OTHER TYPES OF CELLS

Candidates should be able to 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.

E.1 Fuel Cell

1. Fuel cells use combustion reactions to produce electricity. The fuel does not burn because, as in other batteries, the reactants undergo separate half-reactions, and the electrons are transferred through an external circuit. This converts chemical energy into electrical energy. A fuel (e.g. hydrogen, methane etc.) is continuously supplied to one electrode and an oxidant (usually oxygen), to the other.
2. At the anode: the fuel is oxidised and electrons are released to the external circuit.
At the cathode: oxygen is reduced by electrons received from the external circuit.

3. The energy produced in the reaction is converted into electrical energy very efficiently.
4. Hydrogen–oxygen fuel cell:



5. Electrolyte: KOH(aq)

Anode reaction: $\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-$

Cathode reaction: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$

Overall cell reaction: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

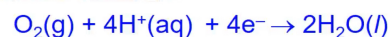
$$E^\ominus_{\text{cell}} = +0.40 - (-0.83) = +1.23 \text{ V} > 0$$

Electrolyte: dil H_2SO_4

Anode reaction:

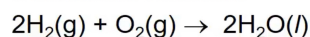


Cathode reaction:



$$E^\ominus_{\text{cell}} = +1.23 - 0.00 = +1.23 \text{ V}$$

Overall cell reaction:



7. Advantages:

- i. Able to attain maximum power with minimum weight and volume, important e.g. for space flights.
- ii. High efficiency of conversion of chemical energy to electrical energy (up to 75% vs. about 40% for power stations).
- iii. Fuel cells do not 'go dead' as reactants are supplied continuously and products are continually removed. An ordinary battery stops working as soon as the electrode materials are used up.
- iv. The product of reaction is non-polluting. The water produced by the fuel cells on the U.S. space laboratory was used for drinking and washing.

8. Disadvantages:

- i. Expensive due to the use of Pt as catalyst at the graphite electrodes.
- ii. Most fuels require a high temperature to react in a fuel cell.
- iii. Hydrogen is potentially explosive.

Exercise 12

Two fuel cells using ethane but different electrolytes:

fuel cell	1	2 (IVY Lecture Check Point)
fuel used	ethane, C_2H_6	ethane, C_2H_6
oxidising agent	air	air
electrolyte	dil H_2SO_4	$NaOH$ (aq)
rxn at anode	$C_2H_6(g) + 4H_2O(l) \rightarrow 2CO_2(g) + 14H^+(aq) + 14e^-$	$C_2H_6 + 14OH^- \rightarrow 2CO_2 + 10H_2O + 14e^-$
rxn at cathode	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
overall rxn	$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$	$2C_2H_6 + 7O_2 \rightarrow 6H_2O + 4CO_2$

E.2 Development of Other Types of Cells

- Improvement of cells are sought in terms of smaller size, lower mass, higher voltage, longer life, greater reliability, quicker recharging e.g. for electric vehicles, mobile phones, portable PCs, watches, cardiac pace-makers etc.
- For example: the lithium-ion battery has a mass about half that of a Ni-Cd battery providing similar energy. Extremely high energy/mass ratio, and avoids the toxicity of cadmium in Ni-Cd battery.
- Electric Car
Reasons for electric car:
 - Shrinking oil supplies
 - Concern about environmental pollution

Advantages	Disadvantages
i. zero emission of polluting exhaust gases	i. limited range (about 120 km) & speed (80km/h)
ii. quiet	ii. batteries are heavy, bulky and expensive
iii. easier mechanical maintenance	iii. recharging takes time (> 3 hours)

Criteria for batteries suitable for electric vehicle:

High energy density (i.e. carry a large amount of energy yet very light), long life and good durability, reliable and quick recharge.



RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2023
Tutorial 21a: Electrochemistry 1

SELF-CHECK QUESTIONS

- 1 Define the terms:
(a) standard electrode potential, $E^\ominus$ (b) standard cell potential, $E^\ominus_{\text{cell}}$
- 2 [N2012/III/2(a)]
Chlorine and iodine differ in their relative reactivity as oxidising agents. Chlorine is a gas under standard conditions. Although iodine is not very soluble in water, it is freely soluble in KI(aq), according to the following equilibrium.
- $$\text{I}^-(\text{aq}) + \text{I}_2(\text{s}) \rightleftharpoons \text{I}_3^-(\text{aq})$$
- A solution containing $\text{I}_3^-(\text{aq})$ reacts as if it were a solution of iodine in water.
- (a) Draw a fully labelled diagram of the electrochemical cell you would set up in order to measure the relative oxidising powers of chlorine and iodine under standard conditions.
(b) Describe the measurements you would make and explain their significance.
(c) Write a balanced equation for the reaction that would take place if the electrodes of the cell were connected together by an external circuit.
- 3 For the two given half-cells: $\text{Co}^{2+} / \text{Co}$ and $\text{Cl}_2 / \text{Cl}^-$.
(a) State which half-cell undergoes reduction when the two are connected.
(b) Write the equation for the cell reaction.
(c) Calculate the value of $E^\ominus_{\text{cell}}$.

PRACTICE QUESTIONS

Electrochemical (Voltaic) Cell

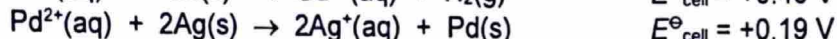
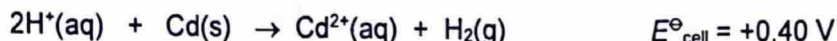
- 4 (a) Cell (1) is made up of two half-cells: $\text{Cu}^{2+} / \text{Cu}$ and $\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+}$
Cell (2) is made up of two half-cells: $\text{O}_2 / \text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2 / \text{H}_2\text{O}$

For each cell,

- (i) Write half-equations of the reactions occurring at the cathode and anode and suggest the electrodes to be used in each half-cell. Write the overall cell reaction.
(ii) Calculate $E^\ominus_{\text{cell}}$.
(iii) Draw a fully labelled diagram of the electrochemical cell you would set up to measure $E^\ominus_{\text{cell}}$. Indicate on your drawing the direction of electron flow in the external circuit.
- (b) For Cell (1), predict the effect on E_{cell} if the following changes are imposed:
(i) Adding $\text{Na}_2\text{CO}_3(\text{aq})$ to the $\text{Cu}^{2+} / \text{Cu}$ half-cell.
(ii) Adding some potassium bromide pellets to the $\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+}$ half-cell.
- (c) For Cell (2), suggest two different changes which would decrease E_{cell} (i.e. $E_{\text{cell}} < E^\ominus_{\text{cell}}$).

5 [RI 2016 CT2 A2 (modified)]

Various half-cells were connected to determine the $E^\ominus_{\text{cell}}$ values. The results are as follows:

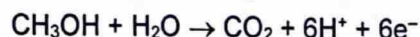


What is the potential of the palladium electrode relative to the cadmium electrode?

6 [N2010/III/3 (modified)]

The direct oxidation of alcohols in a fuel cell represents potentially the most efficient method of obtaining useful energy from a renewable fuel.

- (a) The first alcohol to be used successfully in a fuel cell was methanol. At the anode, methanol and water undergo the following reaction.



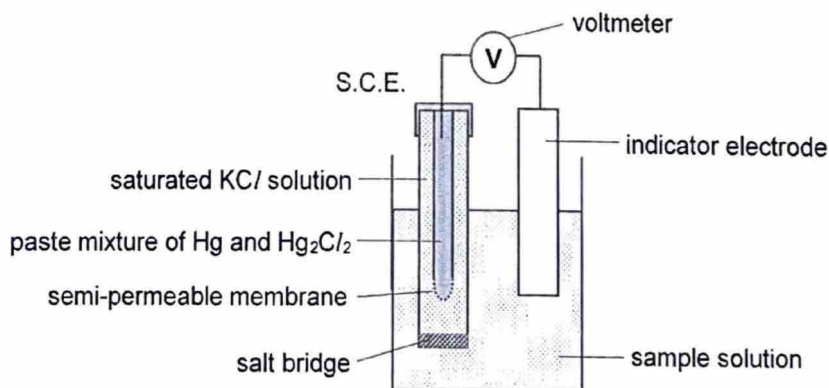
The electrons pass around the external circuit to the cathode.

The protons move through the conducting polymer electrolyte to the cathode, where they react with oxygen, producing water.

- Construct an equation for the cathode reaction.
 - Hence, construct the equation for the overall reaction, showing your working.
 - The cell is capable of producing an e.m.f. of 1.18 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the $\text{CO}_2/\text{CH}_3\text{OH}$ electrode reaction.
 - Suggest a possible advantage of using the methanol fuel cell compared to a hydrogen-oxygen fuel cell.
- (b) Ethanol is also being investigated as a possible fuel in fuel cells.
- Write the equation for the complete combustion of 1 mol of ethanol.
 - The standard enthalpy change of combustion of ethanol, $\Delta H_c^\ominus$, has a value of $-1367 \text{ kJ mol}^{-1}$ and the entropy change for the same process is $-140 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the combustion of ethanol.
 - Hence, calculate the $E^\ominus_{\text{cell}}$ for the ethanol/oxygen fuel cell.

7 [RI 2019 CT2 B2 (modified)]

The concentration of an ion in solution can be measured using an indicator electrode paired to a reference electrode, such as the saturated calomel electrode (S.C.E.), in a voltaic cell. A diagram of the setup is shown below.

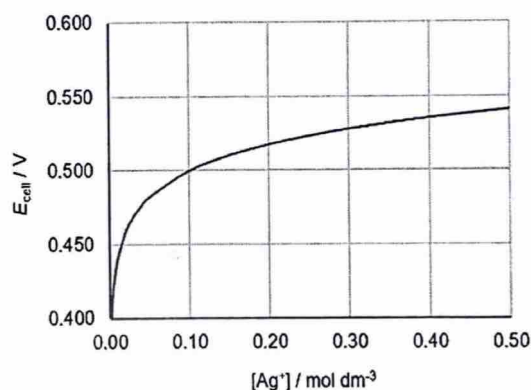


The indicator electrode responds to the ion being analysed in the sample solution and produces a potential that is dependent on the concentration of the ion.

A reference electrode is one with a fixed composition and constant potential. The S.C.E. comprises a saturated potassium chloride solution and a paste mixture of Hg and Hg_2Cl_2 .

The half-equation for the S.C.E. is as follows: $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq})$
 $E = +0.241 \text{ V}$

- (a) (i) Suggest why a saturated potassium chloride solution was used in the S.C.E.
 (ii) The E value of the S.C.E. is not a standard potential. Predict whether the $E^\ominus$ value of the S.C.E. is higher or lower than $+0.241 \text{ V}$ and briefly explain why.
- (b) In an experiment, a silver electrode was used as the indicator electrode to measure Ag^+ concentration in the sample solution. The S.C.E. was used as the reference electrode. The concentration of Ag^+ ions in the sample solution was found to be 1.00 mol dm^{-3} .
- (i) By using relevant data from the Data Booklet, determine which electrode, silver or S.C.E., is the anode.
 (ii) Determine the potential, E_{cell} , recorded in the experiment.
 (iii) The graph below shows the relationship between E_{cell} (using S.C.E.) and the concentration of Ag^+ ions.



By considering the shape of the graph, suggest why the silver electrode is useful for measuring small changes at very low concentrations of Ag^+ .

Using the sign of $E_{\text{cell}}^\ominus$ to predict the spontaneity of a reaction

- 8 Deduce the spontaneity of the reaction between
- | | |
|--|---|
| (a) Ag^+ and Cu | (e) H_2O_2 and MnO_4^- (in an acidic medium) |
| (b) Br_2 and Fe^{2+} | (f) MnO_4^- and Ca^{2+} |
| (c) Al^{3+} and Cl^- | (g) Zn and $\text{Cr}_2\text{O}_7^{2-}$ |
| (d) $[\text{Co}(\text{NH}_3)_6]^{2+}$ and H_2 (in an alkaline medium) | |

Note: The context of the question is not about setting up an electrochemical cell with half-cells here. Instead, you are to use the sign of E_{cell} to predict if a reaction occurs when two compounds are mixed (in a test-tube).

For part (g), the reaction involves more than one step. You should consider the reacting species and calculate the $E_{\text{cell}}^\ominus$ for each step to show the feasibility of that step.

9 By calculating the $E^\ominus_{\text{cell}}$ and predicting the spontaneity of all the possible reactions, explain the following statements.

- (a) Potassium dichromate(VI), but not potassium manganate(VII), can be used for the titrimetric determination of iron(II) ions when dilute HCl(aq) is used to acidify the reaction mixture.
- (b) A solution of hydrogen peroxide gives off bubbles of oxygen on standing.

10 [N2010/P1/17]

Use of the Data Booklet is relevant to this question.

If iron is heated separately with chlorine, bromine and iodine, what are the likely products?

	chlorine	bromine	iodine
A	FeCl_2	FeBr_2	FeI_2
B	FeCl_3	FeBr_2	FeI_2
C	FeCl_3	FeBr_3	FeI_2
D	FeCl_3	FeBr_3	FeI_3

Application of relationship between $\Delta G^\ominus$ and $E^\ominus$

11 The equation for dissolving AgCl(s) in an aqueous solution is $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

- (a) Determine the $E^\ominus_{\text{cell}}$ of the dissolution reaction, given the following data
 $\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag(s)} \quad E^\ominus = +0.80 \text{ V}$
 $\text{AgCl(s)} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-(\text{aq}) \quad E^\ominus = +0.22 \text{ V}$
- (b) Hence determine the standard free energy change of the reaction.
- (c) Given that for any reaction, $\Delta G^\ominus = -RT \ln K$, determine the K_{sp} of AgCl at 298 K.
 Note: The units of $\Delta G^\ominus$ should be in J mol^{-1} when this formula is used.

12 An electrochemical cell is constructed of one half-cell in which a platinum plate is placed into an aqueous solution of $1.00 \text{ mol dm}^{-3} \text{ Fe(NO}_3)_2$ and $1.00 \text{ mol dm}^{-3} \text{ Fe(NO}_3)_3$, and the other half-cell consists of a nickel electrode in an aqueous solution of $\text{Ni(NO}_3)_2$ that is also 1.00 mol dm^{-3} .

- (a) Calculate the standard cell potential of this electrochemical cell and write the overall equation for the reaction that takes place.
- (b) State the observations in each half-cell when the cell was allowed to run.
- (c) Calculate the $\Delta G^\ominus$ for this cell.

Standard cell potential $E^\ominus$ are calculated under standard conditions. However, most cells do not operate under standard conditions. To calculate E_{cell} under non-standard conditions, the **Nernst Equation** given below can be used.

For the Ni^{2+}/Ni half-cell, the **Nernst equation** can be written as:

$$E_{\text{Ni}^{2+}/\text{Ni}} = E^\ominus_{\text{Ni}^{2+}/\text{Ni}} - (9.916 \times 10^{-5})T \log \frac{1}{[\text{Ni}^{2+}]}$$

- (d) After running the electrochemical cell for 10 h under standard conditions, 0.373 mol of Ni^{2+} was formed in the Ni^{2+}/Ni half-cell. Given the volume of each half-cell was 1 dm^3 , calculate the half-cell potential of the Ni^{2+}/Ni half-cell at 298 K.

The equation below can be used to calculate the cell potential under non-standard conditions.

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - (9.916 \times 10^{-5})T \log \left(\frac{[\text{Ni}^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2} \right)$$

- (e) What would the E_{cell} value be at 35.0°C when $[\text{Ni}^{2+}]$ is 0.20 mol dm^{-3} and $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 0.40 \text{ mol dm}^{-3}$?
- (f) Given that the cell stops working when the overall cell reaction reaches **equilibrium**, calculate the equilibrium constant K_c for the overall cell reaction at 35.0°C .
 [Hint: You may begin by writing the K_c expression for the cell reaction in (a).]