

# RAFFLES INSTITUTION YEAR 6 H2 CHEMISTRY 2025 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,  $E_{cell}^{\ominus}$ , 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<sub>2</sub>/O<sub>2</sub> 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.

- <u>Note:</u> 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 <u>positive</u> change in oxidation state indicates that <u>oxidation</u> (loss of electrons) has occurred e.g. +1, +2.
- A <u>negative</u> change in oxidation state indicates that <u>reduction</u> (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,  $I_2$ ,  $S_8$  or  $P_4 = 0$
- 2. The oxidation number of a monoatomic ion is simply the charge on the ion. Example: O.N. of  $Cl^{-} = -1$ ; O.N. of  $Ca^{2+} = +2$
- 3. The sum of the oxidation numbers of all the atoms or ions in an electrically neutral compound = 0.

Examples:

CaBr <sub>2</sub>	+2 + 2(–1) = 0
$Al_2O_3$	2(+3) + 3(-2) = 0
CO <sub>2</sub>	+4+2(-2)=0

4. In polyatomic ions, the sum of the oxidation numbers = the <u>charge</u> on the ion. Examples:

> $SO_4^{2-}$ : The sum of the oxidation numbers (O.N of S = +6, O.N. of O = -2) = +6 + 4(-2) = -2 = charge on the ion

 $CrCl_6^{3-}$ : 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 <u>more electronegative</u> atom has the <u>negative</u> oxidation number while the <u>less electronegative</u> atom has the <u>positive</u> 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  $OF_2 = -1$  O.N. of O in  $OF_2 = +2$ 

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	$Al_2O_3$	
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 in $ClF = +1$
Hydrogen	Usually +1	HC <i>l</i>	<ul> <li>1 in metal hydrides such as NaH (since Na is more electropositive than H)</li> </ul>
Oxygen	Usually –2	CaO	<ul> <li>-1 in peroxides* such as H<sub>2</sub>O<sub>2</sub></li> <li>(hydrogen peroxide) and BaO<sub>2</sub> (barium peroxide)</li> <li>*Peroxide ion is O<sub>2</sub><sup>2-</sup></li> </ul>
			<ul> <li>-0.5 in KO<sub>2</sub> (potassium superoxide*)</li> <li>*Superoxide ion is O<sub>2</sub>-</li> </ul>
			+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.			
	To each half-equation,		ľ	_
2	Balance the element reduced or oxidised in each half-equation.			Jnd
3	Balance <b>oxygen atoms</b> by adding <b>H₂O</b> molecules. Only H₂O. H⁺ or e <sup>-</sup> can be			er a
4	Balance hydrogen atoms by adding H <sup>+</sup> ions. added, either as 'reactant'		Х	cidio
5	Balance <b>overall charges</b> by adding e⁻ or 'product'. (Check that oxidation half- <u>egns</u> have e⁻ on RHS and reduction half- <u>egns</u> have e⁻ on LHS.)			c med
6	Multiply each balanced half-equation by appropriate integers so that no. of electrons gained = no. of electrons lost.			Ĩ
7	Add the 2 balanced half-equations and eliminate any common terms to obtain the overall balanced equation (with no $e^{-}$ ).	J	ſ	
	In alkali medium, do steps A-C after step 5, followed by steps 6 and 7.			Unde
A	"Neutralise" the H <sup>+</sup> ions by adding the required number of OH <sup>-</sup> ions to <b>both</b> sides of a half- equation.			r <u>alkali</u> r
В	Combine the H <sup>+</sup> and OH <sup>-</sup> ions on the same side of the equation to form $H_2O$ .		K	<u>le</u> m
С	Re-balance the half-equation by eliminating any common terms, such as $H_2O$ .			ediur
				3

### A. REDOX PROCESSES & ELECTROLYTES

#### A.1 Redox: Reduction & Oxidation

#### 1.

Oxidation	Reduction
$\circ$ Increase in oxidation state of the	<ul> <li>Decrease in oxidation state of the</li> </ul>
element involved	element involved
<ul> <li>Loss of electron(s)</li> </ul>	<ul> <li>Gain of electron(s)</li> </ul>
<ul> <li>Occurs at anode (AN OX)</li> </ul>	<ul> <li>Occurs at cathode (RED CAT)</li> </ul>
Reducing Agent	Oxidising Agent
Reducing Agent           o         A substance that reduces another	<ul> <li>Oxidising Agent</li> <li>A substance that oxidises another</li> </ul>
<ul> <li>Reducing Agent</li> <li>A substance that reduces another substance</li> </ul>	<ul> <li>Oxidising Agent</li> <li>A substance that oxidises another substance</li> </ul>
<ul> <li>Reducing Agent</li> <li>A substance that reduces another substance</li> <li>Is itself oxidised</li> </ul>	<ul> <li>Oxidising Agent</li> <li>A substance that oxidises another substance</li> <li>Is itself reduced</li> </ul>

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.

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

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

 $\begin{array}{ccc} Cu^{2*}(aq) + Zn(s) & \longrightarrow & Cu(s) + Zn^{2*}(aq) \\ \text{reduction half-equation:} & Cu^{2*}(aq) + 2e^{-} & \longrightarrow & Cu(s) \\ \text{oxidation half-equation:} & Zn(s) & \longrightarrow & Zn^{2*}(aq) + 2e^{-} \end{array}$ 

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.

 $2H^{+}(aq) + 2NO_{2}^{-}(aq) \longrightarrow H_{2}O(I) + NO(g) + NO_{2}(g)$ 

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 <u>aqueous</u> <u>solution or in the molten state</u>. An electrolyte conducts electricity due to the <u>flow of charge</u> <u>carried by its ions</u>.
- 2. A <u>strong electrolyte</u> is a compound which is <u>fully ionised</u> 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),  $PbCl_2(I)$ .

sodium hydroxide:	$NaOH(aq) \longrightarrow Na^{+}(aq) + OH^{-}(aq)$
molten lead(II) chloride:	$PbCl_2(I) \longrightarrow Pb^{2+}(I) + 2Cl^{-}(I)$

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

 $\begin{aligned} &\mathsf{HC}l(\mathsf{g}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \xrightarrow{} \mathsf{H}_3\mathsf{O}^+(\mathsf{aq}) + \mathsf{C}l^-(\mathsf{aq}) \\ &\mathsf{HNO}_3(\mathsf{I}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \xrightarrow{} \mathsf{H}_3\mathsf{O}^+(\mathsf{aq}) + \mathsf{NO}_3^-(\mathsf{aq}) \end{aligned}$ 

- 3. A <u>weak electrolyte</u> only <u>partially ionises</u> in aqueous solution. E.g. water, aqueous ammonia, most organic acids and organic bases
- A <u>non-electrolyte does not ionise</u> 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

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Av	veedkil	ler can l 3NaC <i>l</i> O	be prep	eat 21	ing a bleach NaCl + NaC	solution.	Soc an e to c	lium thi excess o hloride	iosulphate of chlorine ions.	is used in the from bleachin	textile inc ng process	Justry to remove es by reducing it
		Dieach			weed	aller		S <sub>2</sub> C	$D_{1}^{2-} + 4Cl_{2}$	+ 5H <sub>2</sub> O $\rightarrow$ 2H	1SOT + 8F	-1+ + 8C/-
Wh	at are	the ox	idation	states of a	chlorine in	these three		-2-	3	20 / 20		
con	npound	ls?					In t	his rea	ction, how	many moles	of electro	ons are supplied
۸	_1	1	.5				per	mole of	f thiosulph	ate?		
A	-1	-1	ŦJ							~		
В	+1	-1	+5				А	1		С	4	
С	+1	-1	+7				B	2		D	8	J95/IV/I
D	+2	+1	+7			N99/III/17						
	Χ.											
Ans	s: (	)					Ans	51 (	)			
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**IVY Lecture Check Point** 

### 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.	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.
Mg (s) $\longrightarrow$ Mg <sup>2+</sup> (aq) + 2e <sup>-</sup>	$Mg^{2+}$ (ag) + 2e <sup>-</sup> $\longrightarrow Mg$ (s)
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.	

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

$$Mg^{2+}(aq) + 2e^{-} \rightleftharpoons Mg(s)$$

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 <u>electrode potential</u>, *E*, of the metal.
- 3. This configuration of electrode and solution is called a <u>half-cell</u>. 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

- 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 <u>potential difference</u> 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 <u>gas involved in the reaction</u>.
- 3. Hence, the measurement of the standard electrode potential of a half–cell requires:
  - i. <u>standard conditions</u>,
  - ii. a <u>standard electrode</u> as a *reference* electrode,

### **B.2.1 Standard Conditions**

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

Note: The symbol "  $^{\circ}$  " 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 H<sub>2</sub>(g) to be adsorbed on its surface and establish the following equilibrium:

 $2H^{+}(aq) + 2e^{-} \rightleftharpoons H_{2}(g), \qquad E^{\ominus} = 0.00 V$ 

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

Note:

- i. The platinum electrode is coated with finely divided platinum to increase the surface area of the electrode so that equilibrium between  $H_2(g)$  and  $H^+(aq)$  can be established rapidly.
- ii. Other reference electrodes also exist e.g. the calomel electrode ( $E^{\ominus}$  = +0.244 V) and the silver/silver chloride electrode ( $E^{\ominus}$  = +0.199 V).



#### **IVY Lecture Check Point**



### B.3 Common Half-cell Systems

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



Note: i. Each system primarily contains the same element in different oxidation states.

ii. In the absence of a metal in the half–cell, platinum is used as the inert electrode.

The standard redox potential for the half-cell reaction

 $Fe^{3+} + e^{-} = Fe^{2+}$  is +0.77 V.

Which cell would be used to determine this standard value?

- A Fe electrode in 1 mol dm<sup>-3</sup> Fe<sup>3+</sup> against Fe electrode in 1 mol dm<sup>-3</sup> Fe<sup>2+</sup>.
- B Pt electrode in 1 mol dm<sup>-3</sup> Fe<sup>3+</sup> against Pt electrode in 1 mol dm<sup>-3</sup> Fe<sup>2+</sup>.
- C Fe electrode in a solution containing 1 mol dm<sup>-3</sup> Fe<sup>3+</sup> and 1 mol dm<sup>-3</sup> Fe<sup>2+</sup> against a standard hydrogen electrode.
- D Pt electrode in a solution containing 1 mol dm<sup>-3</sup> Fe<sup>3+</sup> and 1 mol dm<sup>-3</sup> Fe<sup>2+</sup> against a standard hydrogen electrode. J95/IV/7

Ans: (

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

Candi	ates 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 <u>298 K</u>, between the <u>half–cell</u> and the <u>standard hydrogen electrode</u>, in which the concentration of any reacting species in solution is <u>1 mol dm<sup>-3</sup></u> and any gaseous species is at a pressure of <u>1 bar</u>.

Note: Standard electrode potential is commonly written as standard <u>reduction potential</u> or standard <u>redox potential</u>. 3. The electrode potentials of half–cells, *E*, are often called <u>redox</u> potentials. By convention, a standard electrode potential always refers to the half-reaction written as a reduction. redox potentials are written as *reduction* processes.

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

When standard conditions are employed, the potentials are termed

- standard electrode potentials
- standard electrode (redox) potentials
- standard reduction potentials
- 4. The standard electrode potential is a measure of the tendency of <u>reduction</u> (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<sup>o</sup> values also give an indication of the <u>position of equilibrium</u> of a reaction.
 A more <u>positive E<sup>o</sup> value</u> indicates that the position of equilibrium lies to the <u>right</u>.
 A more <u>negative E<sup>o</sup> value</u> indicates that the position of equilibrium lies to the <u>left</u>.

The m	ore positive the $E^{\ominus}$ value,	The more negative the $E^{\ominus}$ value, $\rightarrow$ the backward reaction is more favoured
$\Rightarrow$	the more likely reduction occurs.	$\Rightarrow$ the more likely oxidation occurs,
$\Rightarrow$	the higher is the tendency to gain $e^-$ ,	$\Rightarrow$ the higher is the tendency to lose e <sup>-</sup> ,
$\Rightarrow$	the stronger is the oxidising agent.	$\Rightarrow$ 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  $\Delta H$  in Energetics). E.g.

Zn²+(aq) + 2e⁻	$\rightleftharpoons$	Zn(s),	<i>E</i> <sup>⇔</sup> = −0.76 V
Zn(s)	$\rightleftharpoons$	Zn²+(aq) + 2e⁻	<i>E</i> <sup>⇔</sup> = +0.76 V
2Zn <sup>2+</sup> (aq) + 4e <sup>_</sup>	⇒	2Zn(s),	<i>E</i> <sup>⇔</sup> = –0.76 V

Note: Doubling the coefficients does not double the  $E^{\Theta}$  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<sup>-3</sup>, 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. Cu<sup>2+</sup>(aq) / Cu(s) half-cell



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

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

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 H<sup>+</sup>(aq) | H<sub>2</sub>(g) half–cell to the Cu<sup>2+</sup>(aq) | Cu(s) half–cell; i.e. Cu<sup>2+</sup> is more easily reduced than H<sup>+</sup> and the reduction potential for the Cu<sup>2+</sup>(aq) | Cu(s) half–cell is +0.34 V.

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



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

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

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  $Zn^{2+}(aq) | Zn(s)$  half-cell to the H<sup>+</sup>(aq) | H<sub>2</sub>(g) half-cell; i.e. H<sup>+</sup> is more easily reduced than  $Zn^{2+}$  and the reduction potential for the  $Zn^{2+}(aq) | Zn(s)$  half-cell is -0.76 V.

### (ii) gas / ion system

e.g. F₂(g) / F⁻(aq) half–cell



### (iii) ion / ion system

e.g. MnO4-(aq) / Mn2+(aq) half-cell



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

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

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

(a) alphabetical order:		(b) order of decreasing E <sup>⊖</sup> value (i.e. decreasing order of oxidisin	g power):
Electrode reaction	E <sup>⊕</sup> N	Electrode reaction	E↔N
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66	$S_2O_8^{2^-} + 2e^- \rightleftharpoons 2SO_4^{2^-}$	+2.01
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	-2.90	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07	$MnO_4^- + 8H^+ + 5e^- \implies Mn^{2+} + 4H_2O$	+1.52
$Ca^{2+} + 2e^{-} \rightleftharpoons Ca$	-2.87	$PbO_2 + 4H^+ + 2e^- \implies Pb^{2+} + 2H_2O$	+1.47
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

2. 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:

5.	Relationship between E and Reactivity Series of Metals.	M <sup>n+</sup>	Μ	E⇔
		Li+	Li	-3.04
	From Ag to Li.	K+	Κ	-2.92
	<ul> <li>reactivity increases</li> </ul>	Ca <sup>2+</sup>	Ca	-2.87
	<ul> <li>E<sup>o</sup> becomes more negative</li> </ul>	Na⁺	Na	-2.71
	<ul> <li>lose electrons more readily</li> </ul>	Mg <sup>2+</sup>	Mg	-2.38
	<ul> <li>form positive ions more readily</li> </ul>	Al <sup>3+</sup>	A	-1.66
	<ul> <li>metal oxidizes more readily</li> </ul>	Zn <sup>2+</sup>	Zn	-0.76
	<ul> <li>become stronger reducing agents</li> </ul>	Fe <sup>2+</sup>	Fe	-0.44
		Sn <sup>2+</sup>	Sn	-0.14
		Pb <sup>2+</sup>	Pb	-0.13
Exer	cise 4	H⁺	$H_2$	0.00
With	reference to $E^{\ominus}$ values in the Data Booklet on Section 4 pages 46–50.	<sup>—</sup> Cu <sup>2+</sup>	Cu	+0.34
(i)	Name the strongest oxidising agent	Ag⁺	Ag	+0.80
(ii)	Give the symbol of the strongest reducing agent			
(11)	One the symbol of the strongest reducing agent.			1

### Exercise 5

a.	Fill in the standard electrode (redox) poter	ntials for the following:	
	$Br_2 + 2e^- \rightleftharpoons 2Br^-,  E^{\ominus} = 2Br^-$	$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s),$	<i>E</i> ⇔ =
	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-, E^{\ominus} = $	$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s),$	<i>E</i> <sup>⇔</sup> =
b.	For the halogens, is a stronge For the metals, is a stronge	er oxidising agent than er reducing agent than	

#### Exercise 6 IVY Lecture Check Point

Based on the $E^{\ominus}$ data below,					
F <sub>2</sub> (g)	+	2e-	⇒	2F⁻(aq)	<i>E</i> <sup>⇔</sup> = +2.87 V
Cl <sub>2</sub> (g)	+	2e⁻	⇒	2C <i>l</i> ⁻(aq)	<i>E</i> <sup>⇔</sup> = +1.36 V
Ag⁺(aq)	+	e-	⇒	Ag(s)	<i>E</i> <sup>⇔</sup> = +0.80 V
2H⁺(aq)	+	2e-	⇒	H <sub>2</sub> (g)	$E^{\ominus}$ = 0.00 V
Mg²+(aq)	) +	2e-	≓	Mg(s)	$E^{\ominus} = -2.38$ V

Decide if these statements are correct.

- (1) Ag<sup>+</sup> 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, $E^{\Theta}_{cell}$

### 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:

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

- 2. In the reaction, electrons are basically moving from Zn atoms to Cu<sup>2+</sup> 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.)





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

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

- 2. Since the  $E^{\ominus}$  of  $Zn^{2+}$  | 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 Cu<sup>2+</sup> | Cu half–cell is more positive, Cu<sup>2+</sup> is more easily reduced than Zn<sup>2+</sup>, i.e. Cu<sup>2+</sup> has a higher tendency to gain electrons compared to Zn<sup>2+</sup>.
- 3. Zn loses 2 electrons and enters the solution as  $Zn^{2+}$ :

 $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$  (anode, oxidation)

Cu<sup>2+</sup> ions in the solution near the copper metal surface will take up electrons and are reduced to Cu metal:

 $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$  (cathode, reduction)

Overall redox equation:  $Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$ 

**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. <u>direction of electron flow is from Zn to Cu</u>). 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 <u>salt bridge</u> completes the circuit. (see the next section D.3)
- 6. The electrode where <u>oxidation</u> takes place is called the <u>anode</u>. (**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 <u>reduction</u> takes place is called the <u>cathode</u>. (**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. <u>To maintain electrical (charge) neutrality of each half-cell</u>
  - In the Daniell Cell, as Zn<sup>2+</sup> continues to be produced, the Zn<sup>2+</sup> ion solution builds up a positive charge. Similarly, as Cu<sup>2+</sup> deposit as metal atoms on the copper electrode, the solution depletes in positive charge (i.e. becomes increasingly negative since SO<sub>4</sub><sup>2-</sup> remain in solution).



The ions in the salt bridge migrate so as to <u>neutralise the increasing charge</u> 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<sup>+</sup>) which enter the Cu<sup>2+</sup> solution and negative ions (e.g.  $NO_3^-$ ) which enter the Zn<sup>2+</sup> solution.

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

### D.4 Standard Cell Potential, $E^{\ominus}_{cell}$

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,  $E^{\ominus}_{cell}$ , is the <u>potential difference</u> between two half-cells under <u>standard conditions</u>. 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  $E^{\Theta}$  given in Data Booklet!!!

where  $E_{\text{cathode}}^{\ominus}$  is the <u>reduction</u> potential of the half–cell undergoing reduction  $E_{\text{anode}}^{\ominus}$  is the <u>reduction</u> potential of the half–cell undergoing oxidation

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

Equation:  $Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$   $Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s), \quad E^{\ominus} = -0.76 \text{ V} \text{ (this is } E^{\ominus}_{anode})$  $Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s), \quad E^{\ominus} = +0.34 \text{ V} \text{ (this is } E^{\ominus}_{cathode})$ 

 $E_{\text{cell}}^{\Theta} =$ 

### Exercise 7

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

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

	Voltaic C	ell 1	Voltaic Cell 2	
half-	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ ,	<i>E</i> <sup>⇔</sup> = +1.36 V	$Cr_2O_7^{2-}$ + 14H <sup>+</sup> + 6e <sup>-</sup> $\Rightarrow$ 2Cr <sup>3+</sup> + 7H <sub>2</sub> O, $E^{\ominus}$ = -	⊦1.33 V
cells	$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$ ,	<i>E</i> <sup>⇔</sup> = +0.77 V	$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O, \qquad E^{\ominus} = +$	·0.17 V
cathode				
reaction				
anode				
reaction				
cell				
reaction				
E <sup>⇔</sup> <sub>cell</sub>				



# D.5 Effects of Changing Conditions on Cell Potential, *E*<sub>cell</sub>

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

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

### Exercise 8

Consider the electrochemical cell ma	ade up of the following half-cells:
Cu²+ (aq) + 2e⁻ ≓ Cu (s),	<i>E</i> <sup>⇔</sup> = +0.34 V
$Fe^{3+}$ (aq) + $e^{-} \rightleftharpoons Fe^{2+}$ (aq),	<i>E</i> ⇔ = +0.77 V

a. Calculate  $E_{cell}^{\ominus}$  and write the overall equation of the electrochemical cell.

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  $E^{\ominus}_{cell}$ .

 $2Fe^{3+}(aq) + Cu(s) \Rightarrow 2Fe^{2+}(aq) + Cu^{2+}(aq)$  equilibrium I

Change	Effect on position of equilibrium I	Effect on <i>E</i> <sub>cell</sub>
① Adding water to Cu <sup>2+</sup> /Cu half-cell*		
② Adding NaOH(aq) to Cu <sup>2+</sup> /Cu half-cell <sup>#</sup>		
IVY Lecture Check Point		
③ Using a smaller piece of Cu in Cu <sup>2+</sup> /Cu half–cell		
④ Adding water to Fe <sup>3+</sup> /Fe <sup>2+</sup> half-cell*		
IVY Lecture Check Point		
$\$ Adding some FeCl <sub>2</sub> (s) to Fe <sup>3+</sup> /Fe <sup>2+</sup> half–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  $Fe^{3+}/Fe^{2+}$  half–cell. This is because the number of ions is the same for both forward and backward reaction for  $Fe^{3+}/Fe^{2+}$  half–cell.

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

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

Candidates should be able to use standard cell potentials to:

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

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

Under standard conditions,				
$E^{\ominus}_{cell}$	> (	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:

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

 $E^{\ominus}_{\text{cell}} < 0$ : reaction is non-spontaneous

#### Exercise 9

1. Are the following reactions spontaneous when the substances are mixed together?

2. Calculate  $E^{\Theta}_{cell}$  and write equations for any reactions if appropriate.

From Data Booklet: $Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s), E^{\ominus} = -0.76 V$ $Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s), E^{\ominus} = +0.34 V$				
Substances mixed	Is reaction spontaneous? Why?	<b>E</b> <sup>⊖</sup> <sub>cell</sub>	Equation	
(i) Cu <sup>2+</sup> & Zn <sup>2+</sup>				
(ii) Cu & Zn				
(iii) Cu <sup>2+</sup> & Zn				
(iv) Cu & Zn <sup>2+</sup>				

### 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.

1. 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:

 $\Delta \boldsymbol{G}^{\ominus} = -\boldsymbol{n} \boldsymbol{F} \boldsymbol{E}^{\ominus}$ 

units of  $\Delta G^{\ominus}$  is **J mol**<sup>-1</sup> 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<sup>-1</sup> (given in section 1 of Data Booklet)

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

Under standard conditions,  $E_{cell}^{\ominus} > 0; \ \Delta G^{\ominus} < 0 \implies$  reaction is thermodynamically feasible and spontaneous.  $E_{cell}^{\ominus} = 0; \ \Delta G^{\ominus} = 0 \implies$  reaction is at equilibrium  $E_{cell}^{\ominus} < 0; \ \Delta G^{\ominus} > 0 \implies$  reaction is not thermodynamically feasible and not spontaneous. e.g. In the reaction  $Pb(s) + 2Ag^{+}(aq) \longrightarrow Pb^{2+}(aq) + 2Ag(s)$ ,

Ag⁺ + e⁻  $\rightleftharpoons$  Ag, $E^{\ominus}$  = +0.80 VPb²⁺ + 2e⁻  $\rightleftharpoons$  Pb, $E^{\ominus}$  = -0.13 V

*E*<sup>⇔</sup><sub>cell</sub> = +0.80 − (−0.13) = +0.93 V

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

Number of moles of electrons transferred in the equation, n = 2  $\Delta G^{\Theta} = -nFE^{\Theta} = -2 \times 96500 \times 0.93 = -179000 \text{ J mol}^{-1} = -179 \text{ kJ mol}^{-1}$ 

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  $\Delta G^{\Theta}$ ,  $E^{\Theta}$  and the equilibrium constant, K.

#### Exercise 10

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

Species mixed	Half-equations	E <sup>⊖</sup> <sub>cell</sub> , ∆ <i>G</i> <sup>⊖</sup> , Spontaneity	Equation
C <i>l</i> ⁻ and MnO₄⁻ / H⁺	$Cl_2 + 2e^- \rightleftharpoons 2Cl^ E^{\ominus} = +1.36$ V MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> ⇔ Mn <sup>2+</sup> + 4H <sub>2</sub> O $E^{\ominus} = +1.52$ V		*This is also the reason why KMnO₄ should not be acidified with HC/
Br <sub>2</sub> & Fe <sup>2+</sup>	Br <sub>2</sub> + 2e <sup>-</sup> $\rightleftharpoons$ 2Br <sup>-</sup> , $E^{\ominus}$ = +1.07 V Fe <sup>3+</sup> + e <sup>-</sup> $\rightleftharpoons$ Fe <sup>2+</sup> , $E^{\ominus}$ = +0.77 V Fe <sup>2+</sup> + 2e <sup>-</sup> $\rightleftharpoons$ Fe, $E^{\ominus}$ = -0.44 V		
I2 & H2O2	IVY Lecture Check Point $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O, E^{\ominus} = +1.77 \vee 2H^+ + O_2 + 2e^- \rightleftharpoons H_2O_2, E^{\ominus} = +0.68 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \rightleftharpoons 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \bowtie 2I^-, E^{\ominus} = +0.54 \vee I_2 + 2e^- \blacksquare 2E^$		

By referring to the following reduction half-equations,

$Cl_2 + 2e^- \rightleftharpoons 2C\Gamma$	+1.36 V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33 V
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23 V
$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$	+0.77 V
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54 V
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+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  $Cr_2O_7^{2-} / H^+$  (e)  $I^-$  and  $O_2 / H_2O$ 

(b)  $I^-$  and  $Fe^{3+}$  (d)  $I^-$  and  $O_2 / H^+$ 

Hence, explain why:

- Iron(III) iodide does not exist in aqueous solution.
   Reason:
- ② Potassium manganate(VII) should not be acidified using dil HC*l* but potassium dichromate(VI) may be acidified using dil HC*l*. Reason: \_\_\_\_\_\_

Potassium iodide solution turns yellow in the presence of acid.
 Reason:

### D.8 Limitations of Spontaneity Predictions Based on $E_{cell}^{\Theta}$

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

#### 1. Kinetic factor is not taken into consideration: $\overline{E^{\circ}}$ is a measure of the position of equilibrium but gives no indication of

 $E^{\ominus}_{cell}$  is a measure of the position of equilibrium but gives no indication of rate.

- In the reaction of H<sub>2</sub> with Cu<sup>2+</sup>,  $E^{\ominus}_{cell}$  = +0.34 0.00 = +0.34V
- $\Rightarrow$  reaction is thermodynamically feasible and the reaction

 $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$  is expected to occur spontaneously.

However, no reaction takes place when  $H_2(g)$  is passed into  $CuSO_4(aq)$  as the activation energy for the reaction is high. Hence, even though the reaction is thermodynamically feasible, it is kinetically not feasible.

Reaction takes place under non-standard conditions. 2.  $E_{\text{cell}}^{\Theta}$  is the cell potential at standard conditions. Predictions using  $E_{\text{cell}}^{\Theta}$  under non-standard conditions may not be valid. In the reaction between Cu<sup>2+</sup> and V<sup>3+</sup>, ----- $Cu^{2+} + 2e^{-} \rightleftharpoons Cu$ ,  $E^{\ominus} = +0.34 \text{ V}$  $VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O_1$ *E*<sup>⊕</sup> = +0.34 V  $E^{\ominus}_{\text{cell}} = +0.34 - (+0.34) = 0 \text{ V}$  $\Rightarrow$  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<sup>3+</sup> can reduce Cu<sup>2+</sup> by increasing concentration of V<sup>3+</sup> or increasing concentration of Cu<sup>2+</sup>. \_\_\_\_\_ 3. Side reactions may occur. If a side reaction occurs, especially with insoluble ionic solid formation, a non-spontaneous reaction may become spontaneous. ----------For example, reaction between Cu<sup>2+</sup> and I<sup>-</sup>,  $\begin{array}{ll} I_2 \ (aq) + 2e^- \rightleftharpoons 2I^- (aq), & E^{\ominus} = +0.54 \ V ---- \ (1) \\ Cu^{2+} \ (aq) + e^- \rightleftharpoons Cu^+ \ (aq), & E^{\ominus} = +0.15 \ V ---- \ (2) \end{array}$  $E^{\ominus}_{\text{cell}}$  = +0.15 – (+0.54) V = -0.39 V  $\Rightarrow$  no reaction is expected when aqueous solutions of Cu<sup>2+</sup> and I<sup>-</sup> are mixed. • However, a reaction does occur:  $2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$ . When blue Cu<sup>2+</sup> (aq) is mixed with colourless I<sup>-</sup> (aq), a cream precipitate (CuI) in a brown solution  $(I_2)$  is observed. Refer to QA3. • Due to the precipitation of CuI, [Cu<sup>+</sup>(aq)] becomes very low, such that the P.O.E. of (2) favours the R.H.S. Thus,  $E_{Cu2+/Cu+} > E_{Cu2+/Cu+}^{\ominus}$  and  $E_{cell}$  may become > 0 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

- 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: Cathode reaction: Overall cell reaction: (Note that since the electrolyte is KOH(aq), the half equations should be balanced in basic medium)
- 6. Electrolyte: dil H<sub>2</sub>SO<sub>4</sub> Anode reaction: Cathode reaction: Overall cell reaction: (Note that since the electrolyte is H<sub>2</sub>SO<sub>4</sub>(aq), the half equations should be balanced in acidic medium)
- 7. Advantages:
  - i. Able to attain maximum power with <u>minimum weight and volume</u>, important e.g. for space flights.
  - ii. <u>High efficiency</u> 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 <u>reactants are supplied continuously</u> 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 <sub>2</sub> H <sub>6</sub>	ethane, C <sub>2</sub> H <sub>6</sub>
oxidising agent	air	air
electrolyte	dil H <sub>2</sub> SO <sub>4</sub>	NaOH (aq)
rxn at anode	$C_2H_6 (g) + 4H_2O (I)$ $\rightarrow 2CO_2 (g) + 14H^+ (aq) + 14e^-$	
rxn at cathode	O <sub>2</sub> (g) + 4H <sup>+</sup> (aq) + 4e <sup>-</sup> → 2H <sub>2</sub> O (I)	
overall rxn	$2C_2H_6(g) + 7O_2(g)$ $\rightarrow 4CO_2(g) + 6H_2O(I)$	

### E.2 Development of Other Types of Cells

- 1. Improvement of cells are sought in terms of <u>smaller size</u>, <u>lower mass</u>, <u>higher voltage</u>, longer life, greater reliability, quicker recharging e.g. for electric vehicles, mobile phones, portable PCs, watches, cardiac pace–makers etc.
- 2. 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.
- 3. Electric Car

Reasons for electric car:

Shrinking oil supplies

Concern about environmental pollution

Advantages			Disadvantages	
i.	zero emission of polluting exhaust	i.	limited range (about 120 km) & speed	
	gases		(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:

i. ii.

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