

## Electrochemistry

### Definitions

- Galvanic cells are electrochemical cells in which redox reactions occur spontaneously to generate electrical energy.
- Absolute electrode potential is the potential difference between the metal and the solution, as a result of the separation of charge between the metal strip and ions in the solution.
- (/ $E$ ) Standard electrode (/ $\text{reduction}$ ) potential of an electrode is the relative potential of this electrode under standard conditions compared with the standard hydrogen electrode, whose electrode potential is assigned as 0.00V<sup>1</sup>.
- Standard hydrogen electrode consists of  $H_2(g)$  at 1 bar bubbling over platinum electrode<sup>2</sup> coated with finely divided platinum<sup>3</sup>, which is dipped in  $1\text{ mol dm}^{-3} H^+(aq)$  at 298K.
- (/ $E$ ) Standard cell potential is the electromotive force of a galvanic cell which consists of two half cells connected under standard conditions. The  $E_{cell}^\ominus$  value is the difference between the two standard electrode potential.
- Electrolysis is a process in which electrical energy (from an electrical source) is used to bring about non-spontaneous reactions.
- Faraday's first law of electrolysis states that the mass of substance liberated or dissolved from an electrode is proportional to the quantity of electricity.
- Faraday's second law of electrolysis states that the mass of different elements liberated by the same quantity of electricity form simple whole number ratios when divided by their relative atomic masses

	Galvanic cell	Electrolytic cell
Nature of redox rxn	Spontaneous	Non-spontaneous
Energy conversion	Chemical to electrical	Electrical to chemical
Electrode processes	Reduction at cathode Oxidation at anode	
Electrode polarity	Cathode: +ve Anode: -ve	Cathode: -ve Anode: +ve
Presence of battery	No	Yes
May water be involve?	No	Yes
N.B. Non-spontaneous reactions can be made spontaneous with electrical current.		

### Galvanic Cell (= electrochemical cell)

- An-Ox, Red-Cat
- Electrons flow from anode (negative) to cathode (positive)
- Salt bridge can contain  $NaNO_3$  or  $K_2SO_4$ 
  - Salt must not react with other ions in half cell, thereby maintaining electrical neutrality
  - Ends of salt bridge stuffed with porous plugs: prevent direct mixing of 2 solns but allow passage of ions through them to complete the electrical circuit

<sup>1</sup> If standard conditions **not** used, electrode potential **not** 0.

<sup>2</sup> Chosen for its **inert** property

<sup>3</sup> So eqm between  $H_2(g)$  and  $H^+(aq)$  can be established **rapidly**

Deducing standard electrode potential:

Metal in contact with its ions in aq soln	Non-metal in contact with its ions in aq soln	Ions of same element but in different oxidation state
$Zn^{2+}, Zn$ half cell	$Cl_2, Cl^-$ half cell	$Fe^{3+}, Fe^{2+}$ half cell
<p>Zn electrode decreases in mass with time → oxidation → -ve electrode</p> $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ <p>Bubbles of <math>H_2(g)</math> formed at surface of Pt electrode → reduction → +ve electrode</p> $2H^+(aq) + 2e^- \rightarrow H_2(g)$	<p>No bubbles formed at surface of both electrode</p> <p>Oxidation: <math>H_2(g) \rightarrow 2H^+(aq) + 2e^-</math> → this Pt electrode is anode → -ve electrode</p> <p>Reduction: <math>Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)</math> → this Pt electrode is cathode → +ve electrode</p>	<p>Solution in <math>Fe^{3+}/Fe^{2+}</math> half-cell turned from yellow to pale green → reduction → cathode → +ve electrode</p> $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ <p>No bubbles observed at Pt electrode → oxidation → anode → -ve electrode</p> $0.5H_2(g) \rightarrow H^+(aq) + e^-$ <p>N.B. Put <u>all relevant ions</u> in the half equation into the electrolyte with electrode being Pt electrode</p>

Electrode Potential: $E(M^{n+}(aq)/M(s))$	
$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$ $E(M^{n+}(aq)/M(s)) = \underline{\hspace{2cm}} \text{ V}$	
Positive	POE right → reduction favoured
Negative	POE left → oxidation favoured
Factors	<p>1. Nature of metal Highly electropositive metal → greater <b>tendency to lose electrons and become positive ions</b> → POE left, oxidation reaction favoured → electrode potential become more negative</p> <p>2. Concentration of <math>M^{n+}</math> ions Concentration of hydrated metal ion decrease → POE left, favour oxidation reaction → <b>replenish some of the metal ions removed</b> → electrode potential become more negative</p> <p>3. Temperature Higher temperature → increase in <b>tendency for metal to dissolve in solution to form hydrated metal ions</b> → POE left, oxidation reaction favoured → electrode potential become more negative</p> <p>4. Pressure of gaseous species <math>Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)</math>, <math>E(M^{n+}(aq)/M(s)) = +1.36 \text{ V}</math> Pressure of <math>Cl_2(g)</math> increase → POE right, favour reduction reaction → <b>reduce number of gaseous molecules</b> → electrode potential become more positive</p> <p>N.B. Independent of the number of electrons being transferred</p>
Strength of OA/ RA	<p><b>More positive/ less negative <math>E^\circ \rightarrow</math> stronger OA/ more easily reduced</b> as fwd rxn more favourable → greater tendency for species on LHS to be reduced</p> <p><b>More negative / less positive <math>E^\circ \rightarrow</math> stronger RA / most easily oxidised</b> as bwd rxn more favourable → greater tendency for species on RHS to be oxidised</p>

To deduce galvanic cell reaction:

- ① Identify species present
- ② Identify relevant equations from data booklet
- ③ Select the more favourable oxidation and reduction reaction
- ④ Construct half equation and overall equation

Take note that when you write the reduction/ oxidation equations and the overall cell reaction, use → instead of  $\rightleftharpoons$ .

- Format of writing half-cell/  $E^\ominus$  value: **more oxidised cell/ less oxidised species**
- May not be important to write state symbols for half equations** if for e.g. the subsequent parts do not involve shifting of POE.
- May not be important to quote  $E^\ominus$  value alongside ion-electron half-equations** if that part of the question did not require you to evaluate whether a species will be preferentially oxidised or reduced.

*Only have*

Example (Pg 18)  
A mixture containing  $I_2(aq)$  and  $Fe^{2+}(aq)$

$$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq) \quad E^\ominus = +0.54 \text{ V}$$

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

$$E^\ominus_{\text{cell}} = +0.54 - (+0.77) = -0.23 \text{ V}$$

From data booklet, there is only 1 reaction where  $Fe^{2+}$  may be oxidised.

$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77

**Context of the question matters.** If you are restricted by the species available for you to oxidise/ reduce, you are forced to reduce  $I_2(aq)$ , because data booklet only provides you with this half equation involving  $I_2(aq)$ :  $I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ ,  $E^\ominus = +0.54V$ . The only way is to make half equation proceed is fwd. Now, we are left with  $Fe^{2+}$ , which must be oxidised (see text box). If it cannot be oxidised, there will be **no reaction because no 2 species can be oxidised or reduced at the same time**. This reaction is actually non-spontaneous, but it is okay.

When you connect voltmeter in reverse polarity to battery source, voltmeter may display negative reading.

$I^-(aq) + I_2(s) \rightleftharpoons I_3^-(aq)$  and a solution containing  $I_3^-(aq)$  reacts as if it were a solution of iodine in water i.e.  $I_3^-(aq) \equiv I_2(aq)$ . N.B. Iodine i.e.  $I_2(s)$  is not very soluble in water.

- If question require **calculation**, you'll use  $I_2$ , because DB contains no information on  $I_3^-$ 's reduction potential. H
- However, if question require you to construct **electrochemical cell**, you may have to consider a half cell of  $1moldm^{-3} I^-, I_3^-$  at 298K instead of  $I_2$ .

There may be **further redox reactions** after the first one.

Example: Using the data booklet, explain why both components of brass (zinc and copper) are soluble in Iron (III) chloride.

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76 \text{ V}$   
 For the reduction of  $Fe^{3+}(aq)$  to  $Fe^{2+}(aq)$  by  $Zn(s)$ ,  
 $E^\ominus_{\text{cell}} = +0.77 - (-0.76) = +1.53 \text{ V} > 0$ , therefore the reaction is spontaneous. Hence  $Zn(s)$  is soluble in  $FeCl_3(aq)$ .  
 [For the further reduction of  $Fe^{2+}(aq)$  to  $Fe(s)$  by  $Zn(s)$ ,  
 $E^\ominus_{\text{cell}} = -0.44 - (-0.76) = +0.32 \text{ V} > 0$ , which is also spontaneous. Hence  $Zn(s)$  will reduce  $Fe^{2+}(aq)$  to  $Fe(s)$ .]

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\ominus = +0.34 \text{ V}$   
 For the reduction of  $Fe^{3+}(aq)$  to  $Fe^{2+}(aq)$  by  $Cu(s)$ ,  
 $E^\ominus_{\text{cell}} = +0.77 - (+0.34) = +0.43 \text{ V} > 0$ , therefore the reaction is spontaneous. Hence  $Cu(s)$  is soluble in  $FeCl_3(aq)$ .  
 [For the further reduction of  $Fe^{2+}(aq)$  to  $Fe(s)$  by  $Cu(s)$ ,  
 $E^\ominus_{\text{cell}} = -0.44 - (+0.34) = -0.78 \text{ V} < 0$ , which is non-spontaneous and will not take place.]

## Electrode Potential and Gibbs Free Energy Change:

$$E_{cell}^{\ominus} = E_{red}^{\ominus}(reduction) - E_{red}^{\ominus}(oxidation)$$

just substitute values accordingly from data booklet, no manipulation required

$$\Delta G^{\ominus} = -nFE_{cell}^{\ominus}, F = 9.65 \times 10^4 \text{ Cmol}^{-1}$$

$\Delta G^{\ominus}$	$E_{cell}^{\ominus}$	Spontaneity	Energetic feasibility of fwd rxn
-ve	+ve	spontaneous	Feasible
0	0	rxn system at eqm (no current flows in Gcell)	-
+ve	-ve	non-spontaneous (reverse rxn is spontaneous)	Not feasible

N.B. There's still kinetic feasibility to be considered

## Limitations of Standard Electrode Potential:

- High activation energy might mean that a reaction is energetically feasible, but not kinetically feasible.

Factors which may effect changes to  $E^{\ominus}$  value

- Affect  $E_{red}^{\ominus}(reduction)$  and/ or  $E_{red}^{\ominus}(oxidation)$ - less/ more positive/ negative
- Affect  $E_{cell}^{\ominus}$

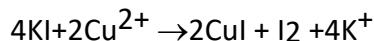
### Change in concentration

- Addition of compound which causes ion in half cell to ppt  
Example: Adding NaOH (aq) to  $Cu^{2+}/Cu$  half cell causes  $Cu^{2+}$  to be ppt as  $Cu(OH)_2$
- Addition of compound which directly affects concentration of ion in half cell  
Example: Adding  $FeCl_2(aq)$  increases concentration of  $Fe^{2+}$
- Addition of water to half cell  
May or may not have effect- depends on the proportion of concentration terms on LHS and RHS of half equation in consideration

### Others: Change in temperature/ pressure

[LCP + ECM] Using relevant equations and the Answer:

Le Chatelier's Principle, explain the following observation.



Adding KI(aq) to a solution containing  $Cu^{2+}(aq)$  produces a solution of brown iodine and a cream precipitate of copper(I) iodide,  $CuI$ , even though the standard cell potential value ( $E_{cell} = -0.39$  V) indicates that this reaction should be non-spontaneous. [2]

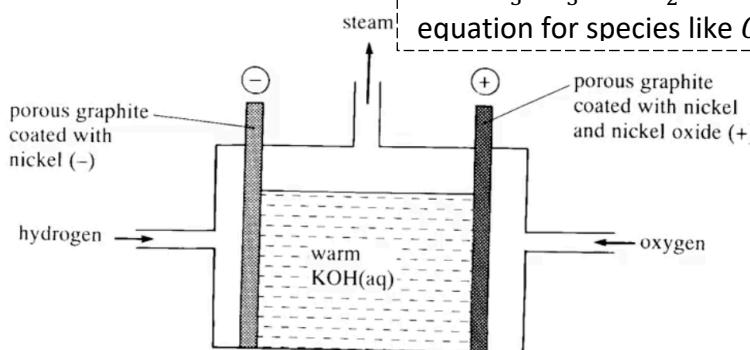
Through the precipitation as  $CuI(s)$ , the concentration of  $Cu^{+}(aq)$  decreases and causes equilibrium position in  $Cu^{2+}(aq) + e^- \rightleftharpoons Cu^{+}(aq)$  to shift to the right, and hence reaction becomes spontaneous.

<sup>4</sup> Need not strictly be  $E_{cell}$  can be standard reduction potential as well



### Fuel Cells:

- Reagents are continuously replaced as they are consumed
- Products are continuously removed as they are formed
- Possible fuels in various contextual questions that may require calculation of  $E_{cell}^{\ominus}$ :  
**hydrogen, hydrocarbon, alcohol**
- Hydrogen fuel cell:



Need to be familiar with formulating redox eqn!

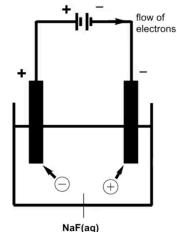
→ Product may be  $CO_2$   
For  $CH_3CH_3$  and  $O_2$  fuel cell, won't be able to find half equation for species like  $CH_2CH_2$  in data booklet.

Surface of porous graphite electrodes coated with Ni and NiO which act as **catalyst**  
Alternatives: Pt/ Pd

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>- Pollution free</li> <li>- High power to mass ratio</li> <li>- Highly efficient</li> </ul>	<ul style="list-style-type: none"> <li>- Expensive due to large amt of catalyst</li> <li>- Catalyst are easily poisoned by impurities</li> <li>- High temperature needed to initiate reaction in half cell</li> </ul>

If question specify acidic/alkaline electrolyte, eliminate half equations from data booklet accordingly.

N.B. Regardless of acidic/alkaline electrolyte, overall equation and  $E_{cell}^{\ominus}$  value will stay the same.



## Electrolytic Cell

Factors affecting the identity of substances liberated:

Factors	Effect
State of electrolyte (molten/aqueous)	<p>Molten electrolyte → contain only constituent ions → <b>cation reduced at cathode; anion reduced at anode</b></p> <p>Aqueous electrolyte → contain cation, anion and water → <b>cation or water reduced at cathode; anion or water oxidised at anode (selective liberation of substances)</b></p> <div style="border: 1px dashed black; padding: 5px;">           Reduction of <math>H_2O</math>: <math>2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)</math>            Oxidation of <math>H_2O</math>: <math>2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-</math> </div>
Position of species in redox series	<p><b>More positive <math>E^\ominus</math> value</b> → more readily <b>reduced</b></p> <p><b>Less positive <math>E^\ominus</math> value</b> → more readily <b>oxidised</b></p> <div style="border: 1px dashed black; padding: 5px;">           Auto-ionisation of water gives <math>H^+</math> and <math>OH^-</math>. H/w, as they are present in low concentrations and hence not considered.  <b>Note: Reduction of <math>H^+</math> and oxidation of <math>OH^-</math> is only considered when there is an external source of <math>H^+</math> or <math>OH^-</math>.</b> </div>
Concentration of species in electrolyte	<p>Species with <b>higher concentration</b> may be <b>preferentially oxidised or reduced</b>, even though its position in redox series may not be as favourable. This is because POE of half equation may be shifted, resulting in changes to the <math>E^\ominus</math> value.</p> <p>N.B. Anions like <math>NO_3^-(aq)</math> and <math>SO_4^{2-}(aq)</math> have a low tendency to be oxidised due to high <math>E^\ominus</math> value, even at high concentrations. <math>H_2O</math> will be oxidised.</p> <p>N.B. For preferential oxidation or reduction to occur due to change in concentration, <b>difference in <math>E^\ominus</math> value of species must be within 0.2-0.3V approximately.</b></p>
Nature of electrode	<p><b>Inert electrodes</b> (Pt, graphite) → <b>do not participate</b> in rxns at electrodes</p> <p><b>Active electrodes</b> (Cu) → <b>participate in rxns</b> at electrodes</p> <div style="border: 1px dashed black; padding: 5px;"> <b>Note:</b> Graphite electrode may <u>burn</u> and produce <math>CO_2(g)</math> and/ or <math>CO(g)</math>. Condition: <u><math>O_2(g)</math> is liberated</u> and electrolysis is carried out at high temperature.         </div>

N.B. Ions with the same charge as the polarity of electrodes will never be able to come in contact with electrodes

Calculations:

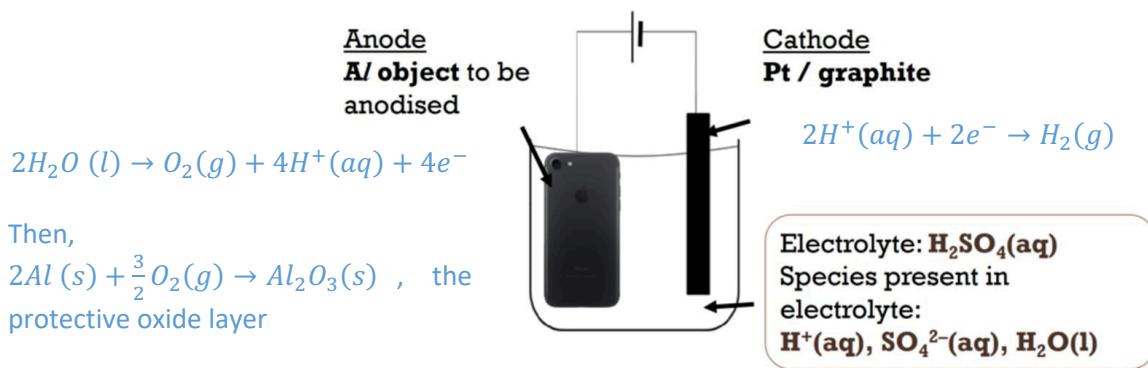
From  $I = \frac{Q}{t}$ ,  $Q = It = nF$ , where F (Faraday's constant) =  $F = 9.65 \times 10^4 \text{ C mol}^{-1}$ .

N.B. Faraday's constant is the amount of charge of 1 mole of electrons. (i.e.  $\text{Avogadro's constant} \times \text{charge on 1 electron} = 6.02 \times 10^{23} \text{ mol} \times 1.60 \times 10^{-19} \text{ C}$ )

For calculation:

- Remember to write out relevant half equations  
Useful when asked to calculate Avogadro's constant from amount of metal reduced.  
If don't write, prone to careless mistake where you don't know the amount of electrons consumed (may not ≠ amount of metal reduced)
- Why may calculated values of constants (e.g. Avogadro's and Faraday's constant not be same as theory:
  - Difficulty keeping current constant
  - Not all metal ions reduced will be deposited on the cathode; some may be dispersed in the electrolyte as fine powder
- Charge of ions is to be written in form e.g.  $3+$  not  $+3$

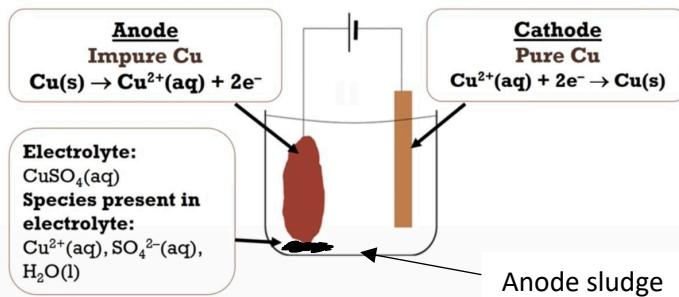
Anodising of aluminium:



- Aluminium → reactive metal → readily oxidised by oxygen in air → form layer of aluminium oxide → resistant to corrosion
- Oxide layer initially porous → allow dye pigment to be adsorbed during anodising → sealed by immersing aluminium object into boiling hot deionised water

N.B. Electroplating non-metals (e.g. plastic), would likely be to give plastic objects a shiny appearance appealing to consumers instead of increasing corrosion resistance. Also, before plastics are electroplated, they'll also be coated with e.g. graphite to allow the article to conduct electricity, since plastic does not conduct electricity while graphite is a good electrical conductor.

## Electrolytic purification of copper:



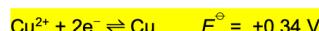
### Observations:

- Concentration of electrolyte remains relatively constant
- Mass of anode decreases, mass of cathode increases

### Possible Question

When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with nickel and silver as minor impurities. It contained no other metal. In order to purify it, this alloy was made the anode of an electrolysis cell, with a pure copper cathode and aqueous  $\text{CuSO}_4$  as electrolyte.

Explain, with reference to relevant  $E^\ominus$  values, what happens to the nickel and silver impurities during this purification process. [3]

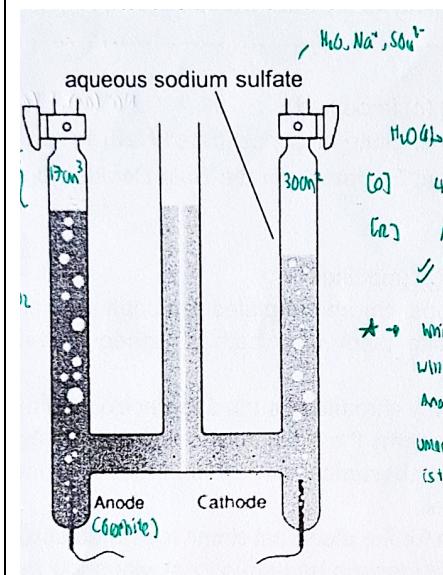


Since  $E^\ominus(\text{Ni}^{2+}/\text{Ni})$  is more negative than  $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ , Ni (and Cu too) would be preferentially oxidised to  $\text{Ni}^{2+}$  at the anode. However, at the cathode,  $\text{Cu}^{2+}$  is preferentially reduced due to  $E^\ominus(\text{Cu}^{2+}/\text{Cu})$  being more positive. Thus  $\text{Ni}^{2+}$  would remain dissolved in the solution/electrolyte.

Since  $E^\ominus(\text{Ag}^+/\text{Ag})$  is more positive than  $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ , so Ag will not be oxidised at the anode but it will fall off the anode as anode sludge during electrolysis.

(Note that question requires candidates to explain specifically what happens to both Ni and Ag during the entire purification process. Hence it is not sufficient to just explain which metal is preferentially oxidised at the anode.)

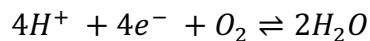
### Example:



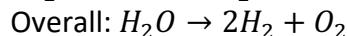
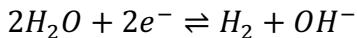
Given that graphite anode is used in this electrolytic cell, gas liberated is  $17\text{cm}^3 \text{O}_2, \text{CO}_2, \text{CO}$ .  $30\text{cm}^3$  of gas formed above the inert cathode, and  $17\text{cm}^3$  of gas above the anode. The anode gas was collected and its volume reduced to  $9\text{cm}^3$  when shaken with  $\text{NaOH}(\text{aq})$ .

Species present:  $\text{H}_2\text{O}, \text{Na}^+, \text{SO}_4^{2-}$

Deduce that  $\text{H}_2\text{O}(\text{l})$  will be preferentially oxidised at anode over  $\text{SO}_4^{2-}(\text{aq})$  due to less +ve  $E^\ominus$  value.



Deduce that  $\text{H}_2\text{O}(\text{l})$  will be preferentially reduced at cathode over  $\text{Na}^+(\text{aq})$  due to less -ve  $E^\ominus$  value.



N.B. Even if concentrated sodium sulfate is used,  $\text{H}_2\text{O}$  will still be preferentially oxidised at anode.

Litmus indicator will turn blue in the cathode compartment due to  $\text{OH}^-$  formed, making the solution around cathode alkaline. Litmus indicator will turn red at anode due to  $\text{H}^+$  formed, making solution around anode acidic.

$\text{CO}_2$  and  $\text{CO}$  are produced at the anode because oxygen reacts with the graphite anode (graphite electrode can burn) to form  $\text{CO}_2$  and  $\text{CO}$ .  $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$  and  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

Explain why the volume of gas collected at the anode is larger than expected with the aid of an equation.

This is because  $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ . 1 mol of  $O_2$  can react to form 2 mol of  $CO$ .  $CO$  produced resulted in the volume of gas collected being larger than expected.

What volume of carbon dioxide was present in 17cm<sup>3</sup> of the anode?

Ans:  $17 - 9 = 8.00\text{cm}^3$

How much oxygen would you expect to be produced at the anode using an inert electrode?

Since overall equation:  $2H_2O \rightarrow 2H_2 + O_2$

Volume of oxygen =  $30/2 = 15\text{cm}^3$ , since  $30\text{cm}^3$  of hydrogen is collected at the cathode

What was the volume of  $CO$  and  $O_2$  respectively in the anode gas?

Initially, in  $17\text{cm}^3$  of anode gas,  $8\text{ cm}^3$  is  $CO_2$ ,  $x\text{ cm}^3$  is  $O_2$  and  $(9-x)\text{ cm}^3$  is  $CO$ . If we were to account for the  $O_2$  used to produce the above 3 gases, they will be  $8\text{cm}^3$ ,  $x\text{ cm}^3$  and  $(9 - x)/2\text{ cm}^3$  respectively. From the previous part, we know that using inert electrode (i.e. get only  $O_2$  gas as anode gas) will yield  $15\text{cm}^3 O_2$  gas. Hence,  $8 + x + (9-x)/2 = 15$ . Solving,  $x = 5\text{cm}^3$ .