

# CHEMISTRY

# LEVEL 4C

(CHM415115)

## ELECTROCHEMICAL CELLS

## THEORY SUMMARY

&

## REVISION QUESTIONS

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# CHEMISTRY LEVEL 4C (CHM 415115)

## ELECTROCHEMICAL CELLS

(CRITERION 5)

### INTRODUCTION:

We are all familiar with the energy supply units that we use in watches, radios 'phones, cameras,..... and commonly refer to as **batteries**. In more correct terminology these are referred to as **electrochemical cells** or sometimes as 'voltaic' or 'galvanic' cells.

These cells **RELEASE** chemical energy by way of a spontaneous redox reaction occurring.

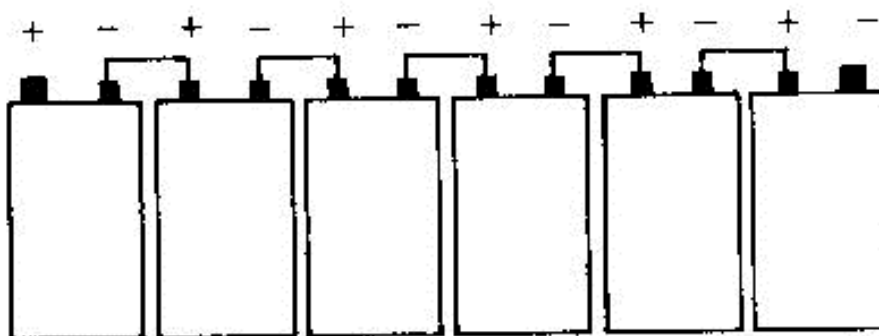
These redox reactions are in many instances ones involving various metal/metal ion reactions and hence the type of cell is often identified by names such as:

- nickel~ cadmium or 'nicad' cells
- mercury~zinc button cells
- silver~zinc cells used in cameras and watches
- zinc~carbon "dry" cells
- manganese dioxide~zinc "alkaline" cells
- lead~sulfuric acid car batteries

Any device that converts chemical energy into electrical energy is described as an electrochemical cell.

The term "battery" which we use really refers to a collection of cells working in series and/or parallel to produce either a greater EMF (voltage) or longer energy supply time.

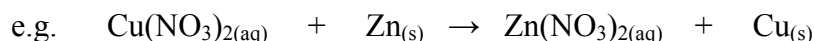
e.g. a standard car "battery" consists of 6 separate electrochemical cells each of which produces an EMF of 2.0 volts. With 6 of these cells in series, the battery gives a total output EMF of 12.0 volts.



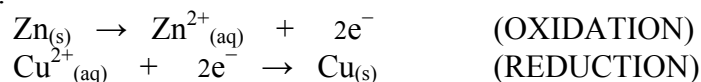
**SIX SEPARATE CELLS MAKE A CAR "BATTERY"**

## THE DANIELL CELL (an example of one electrochemical cell)

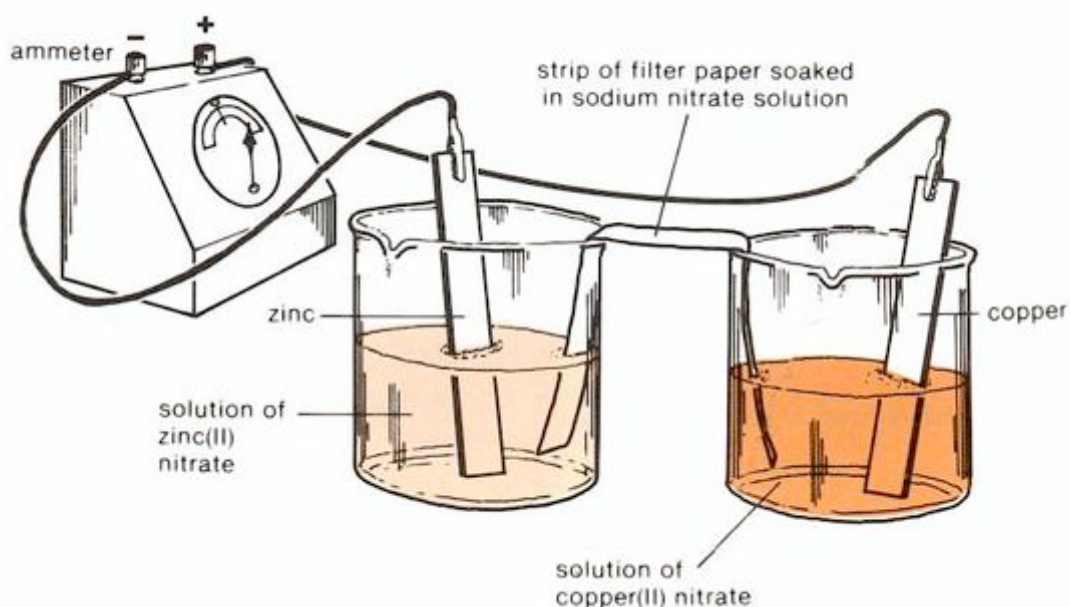
If we immerse a strip of metallic zinc into a beaker containing an aqueous solution of copper(II)nitrate, a spontaneous redox reaction occurs in which the zinc metal is oxidised and the aqueous copper ions are reduced; i.e.



The half-equations being:



Now, suppose that instead of having this chemical reaction occurring in a single beaker, we have two separate beakers set up as shown below. The same reaction occurs as did in the situation above but now we have created an **ELECTROCHEMICAL CELL**. This particular cell based on the copper/zinc combination is called a Daniell Cell.



The key difference is that now the oxidation and reduction half-reactions are taking place at *different sites*.

In this case, oxidation of  $\text{Zn}(\text{s})$  metal is occurring in the left-hand beaker and reduction of the  $\text{Cu}^{2+}(\text{aq})$  ions is taking place in the right-hand beaker.

The two separate beakers are described as 'HALF-CELLS'.

As the spontaneous redox reaction takes place (i.e. one where  $E > 0$ ), electrical energy is given out and this released energy may be used to power a light globe or some other electrical appliance.

**ELECTROCHEMICAL CELLS RELEASE ELECTRICAL ENERGY BY WAY OF A SPONTANEOUS REDOX REACTION OCCURRING.**

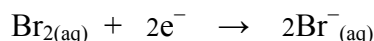
## DEFINITIONS:

### ELECTRODES:

Each of the two half-cells will usually involve an electrically conductive metal strip immersed into a solution. These metallic strips are referred to as electrodes.

e.g. in the Daniell Cell, the electrodes are the two metals  $Zn_{(s)}$  and  $Cu_{(s)}$ .

In some electrochemical cells the metallic strip used is the inert (extremely unreactive) metal platinum (Pt) and this is used where the redox half-equation does not involve a metal; e.g.



In other circumstances, rods of **graphite** (an electrically conducting allotrope of carbon) are used as electrodes.

### ELECTROLYTES:

An electrolyte is an electrically conducting **liquid** which principally means one of two types of liquid; i.e.

- an aqueous solution of an ionic compound e.g.  $Zn(NO_3)_{2(aq)}$ ,  $NaCl_{(aq)}$ ,.....etc
- a molten ionic compound e.g.  $ZnCl_{2(l)}$  (note the “liquid” subscript)

For most electrochemical cells that we will encounter, the electrolytes are aqueous solutions. In most electrochemical cells, each half-cell has its own electrolyte.

e.g. in the Daniell Cell, the electrolytes are the two aqueous solutions  $Zn(NO_3)_{2(aq)}$  and  $Cu(NO_3)_{2(aq)}$ .

### ANODE:

This is defined as the electrode at which **OXIDATION** occurs and is the **NEGATIVE** electrode in an electrochemical cell.

e.g. in the Daniell Cell, the zinc electrode is the **ANODE** and the combination of the zinc metal dipped into the  $Zn(NO_3)_{2(aq)}$  electrolyte is referred to as the **ANODE HALF-CELL**.

### CATHODE:

This is defined as the electrode at which **REDUCTION** occurs and is the **POSITIVE** electrode in an electrochemical cell.

e.g. in the Daniell Cell, the copper electrode is the **CATHODE** and the combination of the copper metal dipped into the  $Cu(NO_3)_{2(aq)}$  electrolyte is referred to as the **CATHODE HALF-CELL**.

### ELECTRON FLOW IN THE EXTERNAL CIRCUIT:

There is a potential difference set up between the anode and cathode half-cells. This is measured as an EMF or ‘cell voltage’.

Electrons are ‘lost’ at the **ANODE** and flow through the external wire towards the **CATHODE**. This results in a current flowing (i.e. a flow of electrons) in the connecting wire.

**ELECTRONS ALWAYS FLOW FROM THE ANODE → THE CATHODE**

## THE SALT BRIDGE:

In order to ‘complete’ the electrical circuit, all electrochemical cells must have some internal linkage between the two half-cells. (see the diagram of the Daniell Cell on p.4)

This completion of the internal circuit is achieved by using a **SALT BRIDGE**. The salt bridge is usually a porous barrier or “U” tube filled with an electrolyte which is normally either  $\text{NaNO}_{3(\text{aq})}$  or  $\text{KNO}_{3(\text{aq})}$ .

The salt bridge has several functions but the principal ones are to:

- provide a barrier between the two half cells and thus to prevent the general mixing of the two half-cells’ electrolytes.
- complete the electrical circuit.
- allow the movement of ions between the two half-cells so as to prevent a build up of electrical charge on either electrode.

Note that in the external wire, electrons are flowing from the anode to the cathode and if this was the only process occurring, the cathode would become increasingly ‘negatively’ charged and the anode would become increasingly ‘positively’ charged. In practice, this doesn’t occur because ion movement through the salt-bridge cancels out this potential charge build-up.

In all instances, negative ions (anions) flow through the salt-bridge towards the anode and positive ions (cations) flow through the salt-bridge towards the cathode.

i.e.

IN ALL SALT-BRIDGES:

ANIONS FLOW TOWARDS THE ANODE  
CATIONS FLOW TOWARDS THE CATHODE

Q. Why do most electrochemical cells use either sodium nitrate solution or potassium nitrate solution as the electrolyte in the salt bridge?

ANS.

Both  $\text{NaNO}_{3(\text{aq})}$  and  $\text{KNO}_{3(\text{aq})}$  solutions are strong electrolytes and thus, being good electrical conductors they ensure the completion of the electrical circuit.

In addition, practically **ALL** sodium and potassium compounds are water soluble as are **ALL** nitrate compounds and thus there will be no likelihood of precipitates forming when other ions flow through the salt bridge.

Note that if precipitates were to form, this would result in non-electrically conducting solids forming and thus the electrical circuit would be incomplete. This is described as resulting in the cell having too high an “internal resistance” and thus the cell’s output voltage is diminished to near zero.

## HALF-CELLS:

1. An electrochemical cell can be regarded as a combination of two half-cells in which:

- one half-cell is the site where OXIDATION occurs and is called the ANODE half-cell.
- the other half-cell is the site where REDUCTION occurs and is called the CATHODE half-cell.

It follows that the ANODE HALF-CELL will involve the *oxidation* process which always occurs to a *reducing agent*; i.e. the anode half-cell will be the half-cell with the stronger reducing agent present. Conversely, the CATHODE HALF-CELL will involve the *reduction* process which always occurs to an *oxidising agent*; i.e. the cathode half-cell will be the half-cell with the stronger oxidising agent present.

2. As the relative strengths of oxidising and reducing agents are of critical concern we now need to focus on the Electrochemical Series (“ECS”) which we encountered in the earlier unit Introduction to Redox Chemistry.

3. Because each half-cell involves an oxidising agent or a reducing agent, the ECS provides valuable guidance to determining which is the anode and which is the cathode in any combination of half cells.

4. Half-cells are usually written in a shorthand form where the redox states are indicated but spectator ions are omitted. These are called a “redox conjugate pairs”.

e.g. 1 The half cell where a strip of magnesium metal is immersed in aqueous magnesium nitrate is specified as:  $\text{Mg}_{(s)}/\text{Mg}^{2+}_{(aq)}$

e.g. 2 The half cell where a strip of copper metal is immersed in aqueous copper(II)sulfate is specified as:  $\text{Cu}_{(s)}/\text{Cu}^{2+}_{(aq)}$

e.g. 3 The half cell where a strip of silver metal is immersed in aqueous silver acetate is specified as:  $\text{Ag}_{(s)}/\text{Ag}^{+}_{(aq)}$

5. Sometimes a half-cell will involve a redox half-equation where *no* metallic component is present and in order to create an electrical circuit, an inert electrical conductor (usually platinum metal or graphite) will provide the surface on which the redox process can occur. The inert metal Pt (or graphite) plays *no* role in the functioning of the redox reaction apart from providing an electrically conducting surface on which electron transfer can take place.

e.g. 1 If the half-cell redox equation involved  $\text{Fe}^{2+}_{(aq)}$  changing to  $\text{Fe}^{3+}_{(aq)}$  then there needs to be a metal to allow this aqueous redox reaction to be connected into the external circuit. This is where the Pt metal is used.

The half-cell would be specified as  $\text{Fe}^{2+}_{(aq)}/\text{Fe}^{3+}_{(aq)}/\text{Pt}_{(s)}$ .

e.g. 2 If the half-cell redox equation involved chlorine gas  $\text{Cl}_{2(aq)}$  changing to aqueous chloride ions ( $\text{Cl}^{-}_{(aq)}$ ) then there needs to be a conducting surface to allow this aqueous redox reaction to be connected into the external circuit. This is where the Pt metal (or graphite) is used.

The half-cell would be specified as  $\text{Cl}_{2(aq)}/\text{Cl}^{-}_{(aq)}/\text{Pt}_{(s)}$  or  $\text{Cl}_{2(aq)}/\text{Cl}^{-}_{(aq)}/\text{C}_{(s)}$ .

# THE ELECTROCHEMICAL SERIES (ECS)

AQUEOUS IONS (1.00 mol L<sup>-1</sup> and 25°C)

		REDUCTION HALF EQUATIONS				
VERY STRONG OXIDISERS	↑	$F_2(g) + 2e^-$	$\rightleftharpoons$	$2F^-(aq)$	VERY WEAK REDUCERS	+2.87
		$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$2H_2O(l)$		+1.78
		$Au^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Au(s)$		+1.50
		$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O(l)$		+1.49
		$Cl_2(g) + 2e^-$	$\rightleftharpoons$	$2Cl^-(aq)$		+1.36
		$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\rightleftharpoons$	$2Cr^{3+}(aq) + 7H_2O(l)$		+1.36
		$MnO_2(s) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 2H_2O(l)$		+1.28
		$O_2(g) + 4H^+(aq) + 4e^-$	$\rightleftharpoons$	$2H_2O(l)$		+1.23
		$Br_2(l) + 2e^-$	$\rightleftharpoons$	$2Br^-(aq)$		+1.09
		$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\rightleftharpoons$	$NO(g) + 2H_2O(l)$		+0.96
		$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$		+0.80
		$Hg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Hg(l)$		+0.78
		$NO_3^-(aq) + 2H^+(aq) + e^-$	$\rightleftharpoons$	$NO_2(g) + H_2O(l)$		+0.78
		$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$		+0.77
		$O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O_2(aq)$		+0.68
		$I_2(s) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$	INCREASING STRENGTH AS REDUCERS	+0.54
		$O_2(g) + 2H_2O(l) + 4e^-$	$\rightleftharpoons$	$4OH^-(aq)$		+0.40
		$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$		+0.34
		$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$SO_2(g) + 2H_2O(l)$		+0.17
		$Sn^{4+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn^{2+}(aq)$		+0.15
		$S(s) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2S(g)$		+0.14
INCREASING STRENGTH AS OXIDISERS	↓	$2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2(g)$		0.00
		$Pb^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s)$		-0.13
		$Sn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn(s)$		-0.14
		$Ni^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ni(s)$		-0.25
		$Co^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Co(s)$		-0.28
		$Cd^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cd(s)$		-0.40
		$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$		-0.41
		$Cr^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Cr(s)$		-0.74
		$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$		-0.76
		$2H_2O(l) + 2e^-$	$\rightleftharpoons$	$2OH^-(aq) + H_2(g)$		-0.83
		$Mn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mn(s)$		-1.18
		$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$		-1.71
		$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$		-2.38
		$Na^+(aq) + e^-$	$\rightleftharpoons$	$Na(s)$		-2.71
		$Ca^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ca(s)$		-2.87
		$Sr^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Sr(s)$		-2.89
		$K^+(aq) + e^-$	$\rightleftharpoons$	$K(s)$		-2.92
VERY WEAK OXIDISERS		$Li^+(aq) + e^-$	$\rightleftharpoons$	$Li(s)$	VERY STRONG REDUCERS	-3.05
		OXIDATION HALF EQUATIONS				



## USING THE ELECTROCHEMICAL SERIES (ECS)

Normally in this course unit on electrochemical cells you will be considering cells that are using  $1.0 \text{ mol L}^{-1}$  aqueous solutions as electrolytes and functioning at  $25^\circ\text{C}$ . This means that the Electrochemical Series (and in particular  $E^\circ$  values) will be a valuable guide as to determining the half-cell reactions occurring.

Without a careful consideration of the relative strengths of oxidising and reducing agents present, the functioning of the cell is not easily determined.

The key steps to success in this problem solving area are:

- identify all oxidisers (oxidising agents) present.
- identify all reducers (reducing agents) present.
- use the ECS to determine which is the stronger/strongest oxidising agent present. This species will undergo REDUCTION AT THE CATHODE.
- use the ECS to determine which is the stronger/strongest reducing agent present. This species will undergo OXIDATION AT THE ANODE.
- Once these key features have been identified, the drawing, labelling and general description of the cell becomes straight forward.

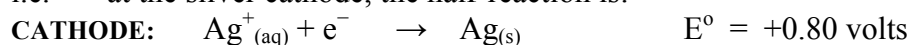
### TYPICAL EXAMPLES:

e.g.1 An electrochemical cell is constructed with one half-cell involving a strip of shiny chromium metal immersed in a  $1.0 \text{ mol L}^{-1}$  aqueous solution of chromium(III)nitrate and the other half-cell involving a strip of silver metal immersed in a  $1.0 \text{ mol L}^{-1}$  aqueous solution of silver nitrate. The cell is connected internally with a "U" tube salt-bridge filled with  $\text{NaNO}_3(\text{aq})$ . The chromium and silver electrodes are connected externally with a wire. What are the anode and cathode half-equations occurring and what initial cell voltage is generated by this cell?

ANSWER.

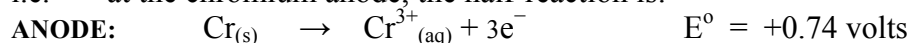
(i) The two oxidisers present are  $\text{Cr}^{3+}(\text{aq})$  and  $\text{Ag}^+(\text{aq})$  and by referring to the ECS,  $\text{Ag}^+(\text{aq})$  is the stronger oxidiser and thus  $\text{Ag}^+(\text{aq})$  undergoes reduction at the cathode;

i.e. at the silver cathode, the half-reaction is:

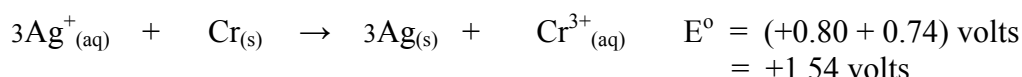


(ii) The two reducers present are  $\text{Cr}(\text{s})$  and  $\text{Ag}(\text{s})$  and by referring to the ECS,  $\text{Cr}(\text{s})$  is the stronger reducer and thus  $\text{Cr}(\text{s})$  undergoes oxidation at the anode;

i.e. at the chromium anode, the half-reaction is:



(iii) Now by combining the two half-equations, we get the net cell equation;



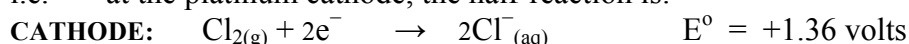
e.g. 2 An electrochemical cell is constructed with one half-cell involving a strip of tin metal  $\text{Sn}_{(s)}$  immersed in a  $1.0 \text{ mol L}^{-1}$  aqueous solution of tin(II)nitrate and the other half-cell involving a strip of platinum metal  $\text{Pt}_{(s)}$  immersed in a  $1.0 \text{ mol L}^{-1}$  aqueous solution of sodium chloride  $\text{NaCl}_{(aq)}$ . Chlorine gas  $\text{Cl}_{2(g)}$  is bubbled over the  $\text{Pt}_{(s)}$  surface. The cell is connected internally with a “U” tube salt-bridge filled with  $\text{KNO}_{3(aq)}$ . The tin and platinum electrodes are connected externally with a wire.

What are the anode and cathode half-equations occurring and what initial cell voltage is generated by this cell?

ANSWER

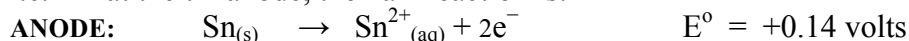
(i) The oxidisers present are  $\text{Na}^+_{(aq)}$ ,  $\text{Sn}^{2+}_{(aq)}$  and  $\text{Cl}_{2(g)}$  and by referring to the ECS,  $\text{Cl}_{2(g)}$  is the strongest oxidiser and thus  $\text{Cl}_{2(g)}$  undergoes reduction at the cathode;

i.e. at the platinum cathode, the half-reaction is:



(ii) The two reducers present are  $\text{Sn}_{(s)}$  and  $\text{Cl}^-_{(aq)}$  and by referring to the ECS,  $\text{Sn}_{(s)}$  is the stronger reducer and thus  $\text{Sn}_{(s)}$  undergoes oxidation at the anode;

i.e. at the tin anode, the half-reaction is:



(iii) Now by combining the two half-equations, we get the net cell equation;



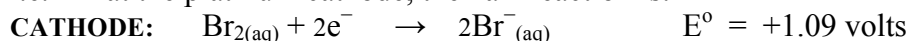
e.g. 3 An electrochemical cell is constructed with one half-cell involving a strip of platinum metal  $\text{Pt}_{(s)}$  immersed in a solution containing bromine  $\text{Br}_{2(aq)}$  and  $1.0 \text{ mol L}^{-1}$  aqueous potassium bromide  $\text{KBr}_{(aq)}$ . The other half-cell involves a strip of cadmium metal  $\text{Cd}_{(s)}$  immersed in a  $1.0 \text{ mol L}^{-1}$  aqueous solution of cadmium sulfate  $\text{CdSO}_{4(aq)}$ . The cell is connected internally with a “U” tube salt-bridge filled with  $\text{KNO}_{3(aq)}$ . The cadmium and platinum electrodes are connected externally with a wire.

What are the anode and cathode half-equations occurring and what initial cell voltage is generated by this cell?

ANSWER.

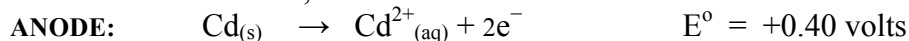
(i) The oxidisers present are  $\text{K}^+_{(aq)}$ ,  $\text{Cd}^{2+}_{(aq)}$  and  $\text{Br}_{2(aq)}$  and by referring to the ECS,  $\text{Br}_{2(aq)}$  is the strongest oxidiser and thus  $\text{Br}_{2(aq)}$  undergoes reduction at the cathode;

i.e. at the platinum cathode, the half-reaction is:

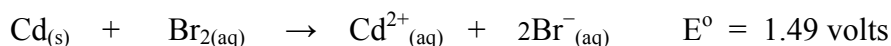


(ii) The two reducers present are  $\text{Cd}_{(s)}$  and  $\text{Br}^-_{(aq)}$  and by referring to the ECS,  $\text{Cd}_{(s)}$  is the stronger reducer and thus  $\text{Cd}_{(s)}$  undergoes oxidation at the anode;

i.e. at the tin anode, the half-reaction is:



(iii) Now by combining the two half-equations, we get the net cell equation;



## SHORTHAND NOTATION

Chemists have agreed to a method of specifying any electrochemical cell in terms of a shorthand notation.

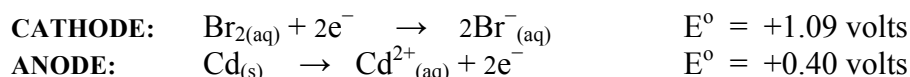
There are a few general rules to note when using this shorthand. These are:

- The anode is shown to the left
- The cathode is shown on the right
- The salt-bridge is represented by two parallel lines, i.e. //
- The oxidation half-equation reactants and products are shown to the left of the // and separated by a single slash, i.e. /
- The reduction half-equation reactants and products are shown to the right of the // and separated by a single slash, i.e. /
- The extreme left and right positions are the actual metals that comprise the anode and cathode electrodes respectively and in some cases will be platinum.
- Spectator ions are not included in the shorthand representation.
- Half-equation coefficients (balancing numbers) are not included.

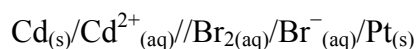
e.g. Refer to example 3 on the preceding page.

An electrochemical cell is constructed with one half-cell involving a strip of platinum metal  $\text{Pt}_{(s)}$  immersed in a solution containing bromine  $\text{Br}_{2(aq)}$  and  $1.0 \text{ mol L}^{-1}$  aqueous potassium bromide  $\text{KBr}_{(aq)}$ . The other half-cell involves a strip of cadmium metal  $\text{Cd}_{(s)}$  immersed in a  $1.0 \text{ mol L}^{-1}$  aqueous solution of cadmium sulfate  $\text{CdSO}_{4(aq)}$ . The cell is connected internally with a "U" tube salt-bridge filled with  $\text{KNO}_{3(aq)}$ . The cadmium and platinum electrodes are connected externally with a wire.

The use of the ECS led us to determine that the two half-equations occurring were:



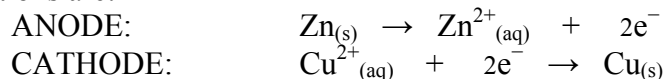
Thus the shorthand for this electrochemical cell will be:



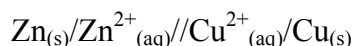
Q. What is the shorthand representation for the Daniell Cell?

(see page 4)

The half-equations are:



Thus the shorthand for the Daniell Cell will be:



## REVIEW QUESTION

An electrochemical cell is constructed as follows. One half-cell involves a piece of silver metal ( $\text{Ag}_{(s)}$ ) immersed in a  $1.0 \text{ mol L}^{-1}$  aqueous solution of silver nitrate ( $\text{AgNO}_{3(aq)}$ ).

The other half-cell involves a piece of platinum metal immersed in a solution containing aqueous tin(II)chloride and tin(IV)chloride with  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  ions at concentrations of  $1.0 \text{ mol L}^{-1}$ . The two half-cells are connected by a salt-bridge "U" tube filled with  $\text{NaNO}_{3(aq)}$ .

(a) Identify the anode and cathode half-reactions occurring in this cell and hence give the net cell equation. (4 marks)

(b) Under standard state conditions, what would be the initial cell voltage (EMF) produced? (2 marks)

(c) Draw a neat, labelled diagram of the cell. On your diagram indicate the anode, cathode, salt bridge, direction of electron flow in the external circuit and direction of ion flow through the salt bridge. Label the appropriate electrodes positive or negative. (6 marks)

(d) Give the "shorthand" representation for the cell. (2 marks)

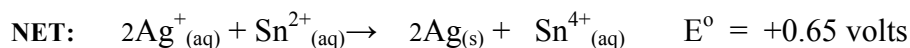
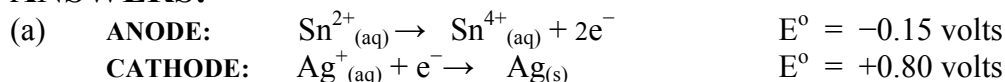
(e) As the cell continues to operate, the voltage produced decreases until it eventually reaches zero. Explain the chemical reasons for this decrease to zero. (2 marks)

(f)(i) If the  $\text{Ag}_{(s)}/\text{Ag}^+_{(aq)}$  half-cell was replaced by a  $\text{Cl}_{2(g)}/\text{Cl}^-_{(aq)}/\text{Pt}_{(s)}$  half-cell, would the EMF produced initially be greater or smaller than when  $\text{Ag}_{(s)}/\text{Ag}^+_{(aq)}$  was used? Explain.

(f)(ii) If the  $\text{Ag}_{(s)}/\text{Ag}^+_{(aq)}$  half-cell was replaced by a  $\text{Zn}_{(s)}/\text{Zn}^{2+}_{(aq)}$  half-cell, would the EMF produced initially be greater or smaller than when  $\text{Ag}_{(s)}/\text{Ag}^+_{(aq)}$  was used? Explain.

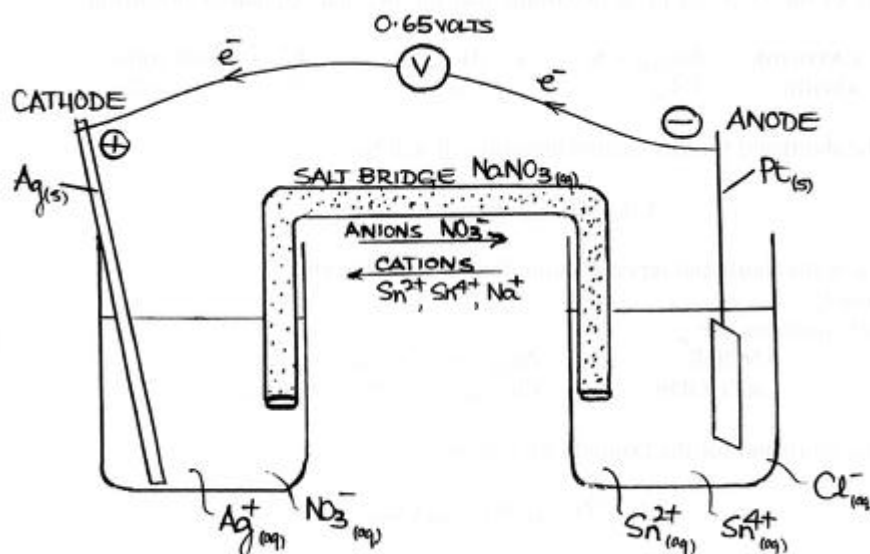
(6 marks)

### ANSWERS:



(b) Initial EMF = 0.65 volts

(c)

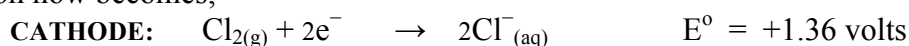


(d) Shorthand representation:  $\text{Pt}_{(s)}/\text{Sn}^{2+}_{(aq)}/\text{Sn}^{4+}_{(aq)}//\text{Ag}^{+}_{(aq)}/\text{Ag}_{(s)}$

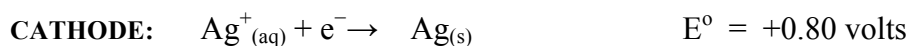
(e) The net cell equation is:  $2\text{Ag}^{+}_{(aq)} + \text{Sn}^{2+}_{(aq)} \rightarrow 2\text{Ag}_{(s)} + \text{Sn}^{4+}_{(aq)}$   $E^{\circ} = +0.65$  volts  
As the cell operates, the concentrations of  $\text{Ag}^{+}_{(aq)}$  and  $\text{Sn}^{2+}_{(aq)}$  ions progressively decrease as these are the reactants for the forward reaction and are being consumed. At the same time as the reactants are being used up, the  $[\text{Sn}^{4+}_{(aq)}]$  is increasing.

As  $[\text{Ag}^{+}_{(aq)}]$  and  $[\text{Sn}^{2+}_{(aq)}]$  decrease, the net 'driving force' for the forward reaction decreases too and because the  $[\text{Sn}^{4+}_{(aq)}]$  is increasing, the driving force for the reverse reaction starts to increase. Eventually, the rates of the forward and reverse reactions become equal and 'equilibrium' is achieved where the net EMF is now zero; i.e. the cell is described as "flat".

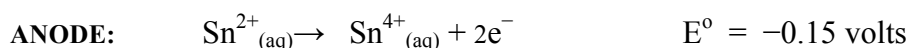
(f)(i) Chlorine ( $\text{Cl}_{2(g)}$ ) is an even stronger oxidising agent than  $\text{Ag}^{+}_{(aq)}$  so the cathode half-equation now becomes;



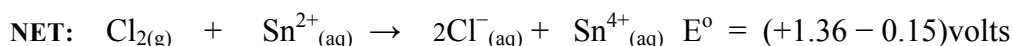
instead of:



And the anode half-equation remains:

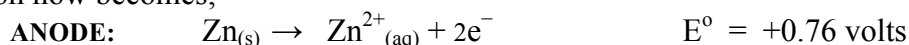


So the new net equation becomes:

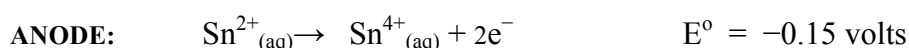


and the EMF generated initially is now +1.21 volts which is greater than with the  $\text{Ag}_{(s)}/\text{Ag}^{+}_{(aq)}$  cathode.

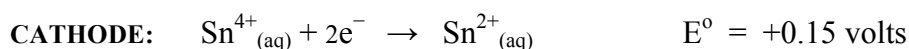
(f)(ii) Zinc metal ( $\text{Zn}_{(s)}$ ) is an even stronger reducing agent than  $\text{Sn}^{2+}_{(aq)}$  so the anode half-equation now becomes;



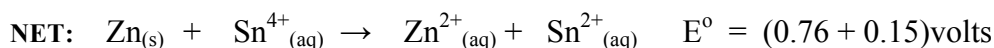
instead of;



and the cathode half-equation now becomes:



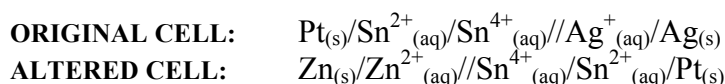
So the new net equation becomes:



and the EMF generated initially is now +0.91 volts.

Note that by replacing the silver half-cell with the zinc half cell, we have not only altered the initial EMF developed by the cell but we have reversed the polarity of the cell because the  $\text{Sn}^{2+}/\text{Sn}^{4+}$  half-cell was the anode initially but now is the cathode.

i.e.



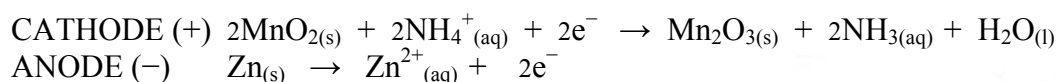
# COMMON ELECTROCHEMICAL CELLS

Some of the commonly encountered electrochemical cells include:

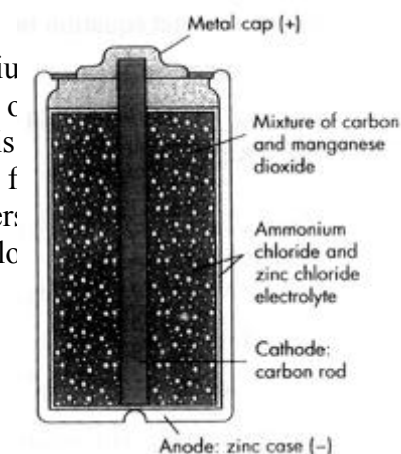
- zinc~carbon “dry” cells
- mercury~zinc button cells
- silver~zinc cells used in cameras and watches
- nickel~ cadmium or ‘nicad’ cells
- manganese dioxide~zinc “alkaline” cells
- lead~sulfuric acid car batteries
- lithium ion batteries

## 1. DRY CELLS:

These cells have a zinc outer (anode) casing and a carbon (cathode) rod immersed in a manganese dioxide ( $\text{MnO}_2$ ) and carbon mixture. The half-equations occurring are:

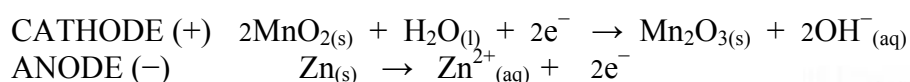


These cells have an electrolyte of zinc chloride and ammonium chloride paste. A new cell produces about 1.5 volts but this drops due to polarisation if the cell is used for a long period of time. This is due to the build up of products around the electrodes. If not used for some time, these products migrate away and the cell ‘recovers’. These dry cells are best used for torches and radios where a low current is required and infrequent use is involved.



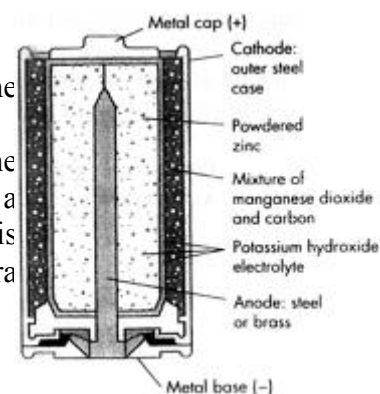
## 2. ALKALINE CELLS:

At the central metal anode rod, zinc powder is oxidised and in the alkaline environment, forms zinc hydroxide. Manganese dioxide is reduced at the outer steel cathode.



Once the  $\text{Zn}^{2+}_{(aq)}$  ions form, they react with the alkaline electrolyte to form zinc hydroxide ( $\text{Zn}(\text{OH})_{2(s)}$ )

These cells have an electrolyte of potassium hydroxide and hence the term ‘alkaline’ cell. Alkaline cells have about 5 times the life of a standard ‘dry-cell’ and are particularly useful where a high current is required for fairly short periods such as occurs with camera flashguns and cassette recorders.



### 3. BUTTON CELLS:

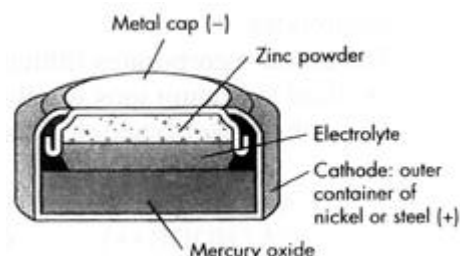
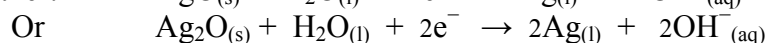
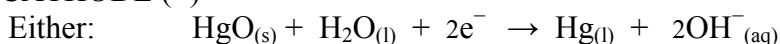
These cells are used where a very small cell is required such as in hearing aids, cameras and watches. If the current drawn is small, then these cells can deliver a near constant current for a prolonged period. There are two main types.

- Mercury-zinc cells (see diagram)
- Silver-zinc cells

In both types, powdered zinc is oxidised at the anode:



CATHODE (+)



A new mercury/zinc cell produces about 1.35 volts whereas the silver/zinc cell gives out about 1.6 volts during discharge.

### 4. LEAD-ACID CAR BATTERY:

These “storage cells” are used extensively in cars, trucks, boats, ..... and can deliver large currents together with the capacity for being rechargeable (i.e. they are secondary cells). The standard car battery consists of 6 cells each developing about 2 volts and with these cells connected in series, overall 12 volts is produced.

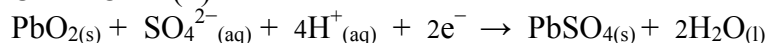
The electrolyte is sulfuric acid.

At the anodes, lead metal is oxidised to  $\text{Pb}^{2+}$  and in the presence of the electrolyte it forms lead(II)sulfate; i.e.

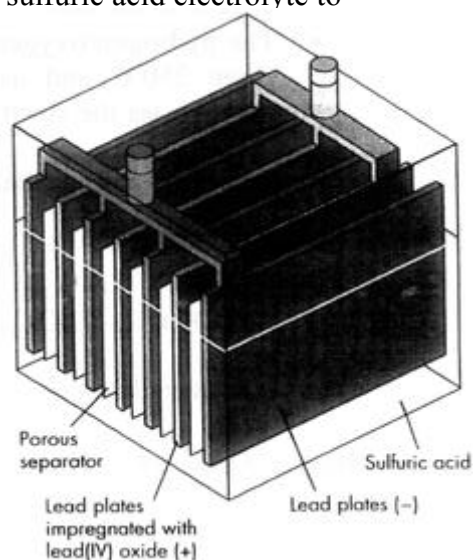


At the cathodes, lead(IV)oxide is reduced in the presence of the sulfuric acid electrolyte to form lead(II)sulfate; i.e.

CATHODE (+)



The product of both half-reactions is lead(II)sulfate which accumulates on the surfaces of the anodes and cathodes. The battery can be recharged by applying an external power source and reversing the half-reactions above. During discharge, the sulfuric acid electrolyte is used up and the density of the electrolyte thus decreases. Thus the state of charge of a car battery can be fairly reliably determined by using a hydrometer for measuring the electrolyte’s density.



## 5. LITHIUM ION CELLS:

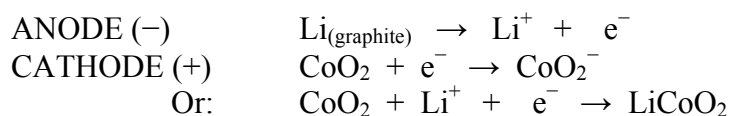
These lightweight and high efficiency cells are now commonly found in mobile phones, digital cameras and camcorders. They represent the latest in rechargeable battery technology combining efficiency with a high energy output.

Lithium is a very strong reducing agent and reacts explosively with water so most aqueous electrolytes are unsuitable. The problem is overcome by using a non-aqueous electrolyte or at least one that doesn't react with lithium metal such as lithium hydroxide solution ( $\text{LiOH}_{(\text{aq})}$ ). Thionyl chloride ( $\text{SOCl}_2$ ) and liquefied  $\text{SO}_2$  have also been used as solvents for non-reacting electrolytes.

The anode incorporates lithium metal adsorbed onto a graphite surface. The lithium metal is oxidised to lithium ions which then migrate towards the cathode.

The cathode half-reaction usually involves a metal oxide or sulfide undergoing reduction.

i.e.



## 6. FUEL CELLS:

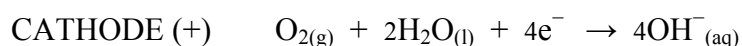
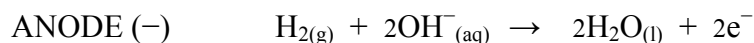
Most cells we have encountered so far are ones that eventually go 'flat' and are discarded or ones that need repeated recharging for further usage.

Fuel cells have the great advantage that they operate continuously supplying electrical energy at a constant rate.

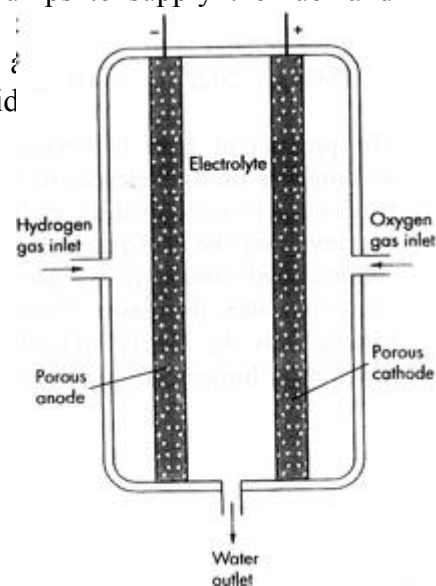
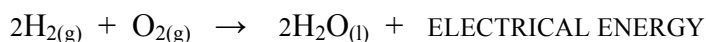
This is achieved by having the reactants (fuel + oxygen) continually supplied (usually pumped) to the cell.

- The fuels used are normally hydrogen or hydrocarbons and they are oxidised about 30% more efficiently than would occur in a direct combustion process.
- Fuel cells vary significantly in size but medium to large sized cells are used in cars, general transport, satellites and industry where a constant and long term energy supply is required.
- The disadvantage of fuel cells is that they require pumps to supply the fuel and oxygen to the cell.
- The hydrogen/oxygen fuel cell (see below) operates at about  $250^\circ\text{C}$  and uses aqueous potassium hydroxide ( $\text{KOH}_{(\text{aq})}$ ) as the electrolyte.

In the fuel cell shown, the half-equations are:



Making the overall reaction:





# ELECTROCHEMICAL CELLS

## THEORY SUMMARY

1. Electrochemical cells involve *spontaneous* redox reactions occurring and energy is released in the form of electrical energy.
2. Oxidation always occurs at the anode.
3. Reduction always occurs at the cathode.
4. The stronger oxidising agent present will be reduced at the cathode.
5. The stronger reducing agent present will be oxidised at the anode.
6. The half-equation (from the E.C.S.) which is further up the page, represents the reduction half-equation (following the forward arrow). This because it involves the stronger oxidiser!
7. The half-equation (from the E.C.S.) which is further down the page, represents the oxidation half-equation (following the reverse arrow). This because it involves the stronger reducer!
8. The anode is assigned a negative(-) polarity.
9. The cathode is assigned a positive(+) polarity.
10. Electrons flow in the external circuit from anode to cathode.
11. In the salt bridge; anions (negative ions) flow towards the anode and cations (positive ions) flow towards the cathode.
12. The shorthand for an electrochemical cell has the anode electrode metal on the left and cathode electrode metal on the right.  
e.g.  $\text{Cu}/\text{Cu}^{2+} // \text{Fe}^{3+} / \text{Fe}^{2+} / \text{Pt}$
13. Electrochemical cells ultimately cease to function (“flat battery”) when the concentrations of the reactant ions and surface areas of electrodes decrease to a limit point where the driving force (EMF) of the cell becomes zero. Equilibrium has been reached.
14. Some electrochemical cells can be recharged by the application of an external power supply. Familiar examples of these rechargeable ‘batteries’ are ‘nicads’, mobile phone batteries, lead/acid car batteries,.....  
Cells that can be recharges are described as **SECONDARY CELLS** whereas others that can’t be recharged are described as **PRIMARY CELLS**.

# ELECTROCHEMICAL CELLS

## REVIEW QUESTIONS

Q1. What are the main functions of a salt bridge in an electrochemical cell?

Q2. The EMF of a new dry-cell is normally about 1.5 volts. If in a particular dry-cell, the species involved in the cell reaction were at equilibrium, what would be the EMF of the cell?

Q3. Which one of the following materials would be the **least** suitable chemically for use as an electrode material in a standard  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half cell?

- A. platinum                      B. iron                      C. carbon                      D. gold

Q4. Given that nickel metal (Ni) has a reducing strength greater than lead but less than zinc, which species would act as an **oxidising agent** in an electrochemical cell composed of  $\text{Ni}^{2+}/\text{Ni}$  and  $\text{Pb}^{2+}/\text{Pb}$  standard half cells?

Q5. Silver oxide cells are used for watches and hearing aids.

The cell reaction is:  $\text{Ag}_2\text{O} + \text{Zn} + \text{H}_2\text{O} \rightarrow 2\text{Ag} + \text{Zn}(\text{OH})_2$

What is the half-equation for the reaction occurring at the **cathode** of this cell?

Questions 6 and 7 refer to the following information. Consider the electrochemical cell represented by the shorthand:



Q6. What is the direction of electron flow in the external circuit?

Q7. Which electrode is the positive electrode?

Q8. If an electrochemical cell is formed by coupling a  $\text{Ni}^{2+}/\text{Ni}$  and a  $\text{Cd}/\text{Cd}^{2+}$  standard half cells, what reaction would occur at the cathode?

Q9. A Daniell Cell is constructed by immersing a strip of zinc metal into a beaker containing an aqueous solution of  $\text{ZnSO}_4$  and connecting this by way of a sodium nitrate filled salt-bridge to a beaker of  $\text{CuSO}_4$  into which is immersed a strip of Cu.

In this cell, describe the anion and cation movement through the salt-bridge.

Q10. Which of the following combinations of half cells would generate the greatest cell EMF (voltage)?

- A.  $\text{Ni}/\text{Ni}^{2+} // \text{Fe}^{3+}/\text{Fe}^{2+}/\text{Pt}$       B.  $\text{Fe}^{3+}/\text{Fe}^{2+}/\text{Pt} // \text{Br}_2/\text{Br}^-/\text{Pt}$       C.  $\text{Ni}/\text{Ni}^{2+} // \text{Br}_2/\text{Br}^-/\text{Pt}$

Q11. An electrochemical cell is formed by coupling  $\text{Ag}/\text{Ag}^+$  and  $\text{Sn}/\text{Sn}^{2+}$  standard half cells. What is the direction of electron flow in the external circuit?

Q12. The EMF of a cell composed of  $\text{Pb}^{2+}/\text{Pb}$  and  $\text{Br}_2/\text{Br}^-$  standard half cells is 1.22 volts and the lead electrode is assigned negative polarity. Show the correct representation of this cell in shorthand?

Q13. For the standard "dry-cell" used in clocks, torches, (etc) what is the change in oxidation number of manganese?

Q14. The standard car battery or "lead-acid accumulator" is classed as a *secondary cell*. Explain the meaning of this term.

Q15. In the standard car battery of the lead-acid type, which of the following statements is correct?

- A. Pb is oxidised and  $\text{PbO}_2$  is reduced.                      B. Pb and  $\text{PbO}_2$  are both oxidised.  
C. Hydrogen ions undergo reduction to water.                D.  $\text{H}^+$  ions react with the lead to produce  $\text{H}_2$  gas.

Q16. An electrochemical cell is to be constructed so as to generate as high an EMF as possible. One of the half cells used is to incorporate  $\text{Au}/\text{Au}^{3+}$ . Which of the following half-cells would be most appropriate in order to gain the maximum voltage?

- A.  $\text{Pb}/\text{Pb}^{2+}$                       B.  $\text{Ag}/\text{Ag}^+$                       C.  $\text{Mg}/\text{Mg}^{2+}$                       D.  $\text{Cl}_2/\text{Cl}^-$

Q17. An electrochemical cell is constructed as follows. One half-cell involves a piece of lead metal (Pb) immersed in a 1.0 mol/L aqueous solution of lead(II)nitrate ( $\text{Pb}(\text{NO}_3)_2$ ). The other half-cell involves a piece of platinum metal immersed in a solution containing aqueous acidified potassium permanganate ( $\text{KMnO}_4(\text{aq})$ ) and manganese sulfate ( $\text{MnSO}_4$ ). All ions are initially at concentrations of 1.0 mol/L. The two half-cells are separated by a salt-bridge barrier filled with  $\text{NaNO}_3(\text{aq})$ .

- (a) Give the anode and cathode half-equations occurring in this cell.  
(b) By combining the two half equations, give the net cell equation.  
(c) At standard conditions, what would be the initial cell voltage produced?  
(d) Draw a neat, labelled diagram of the cell. On your diagram indicate the anode, cathode, salt bridge, direction of electron flow in the external circuit and direction of ion flow through the salt bridge. Label the appropriate electrodes positive or negative.  
(e) Give the "shorthand" representation for the cell.  
(f) What was the function of the piece of platinum (Pt) metal electrode in the cell?

Q18. Why are fuel cells seen as a key way of combating the atmospheric pollution problem referred to as "The Greenhouse Effect"?

Q19. Using diagrams, show how 4 electrochemical cells with individual EMFs = 1.5 volts should be connected so as to produce a *battery* with

- (i) EMF = 6 volts  
(ii) EMF = 1.5 volts  
(iii) EMF = 4.5 volts

# CHEMISTRY (LEVEL 4C)

## ELECTROCHEMICAL CELLS

## TEST 4

Answer the questions in the spaces provided. (Criteria assessed = Cr. 7 & 2)

An electrochemical cell is constructed as follows. One half-cell involves a piece of tin metal (Sn) immersed in a 1.0 mol/L aqueous solution of tin(II)sulfate ( $\text{SnSO}_4$ ).

The other half-cell involves a piece of platinum metal immersed in a solution containing aqueous sodium chloride ( $\text{NaCl}_{(\text{aq})}$ ). Chlorine gas ( $\text{Cl}_{2(\text{g})}$ ) is bubbled over the surface of the platinum electrode.

All ions are initially at concentrations of 1.0 mol/L. The two half-cells are separated by a salt-bridge barrier filled with  $\text{NaNO}_{3(\text{aq})}$ .

(a) Give the anode and cathode half-equations occurring in this cell.

**ANODE:** .....

**CATHODE:** ..... (4 marks)

(b) By combining the two half equations, give the net cell equation.

(2 marks)

(c) Under standard state conditions, what would be the initial cell voltage (EMF) produced?

Cell EMF = ..... (1 mark)

(d) Draw a neat, labelled diagram of the cell. On your diagram indicate the anode, cathode, salt bridge, direction of electron flow in the external circuit and direction of ion flow through the salt bridge. Label the appropriate electrodes positive or negative.

(6 marks)

(e) Give the "shorthand" representation for the cell.

(2 marks)

(f) What was the function of the piece of platinum (Pt) metal electrode in the cell?

(2 marks)

(g) As the cell continues to operate, the voltage produced decreases until it eventually reaches zero. Explain the *chemical reasons* for this decrease to zero.

(2 marks)

(h) If the tin ( $\text{Sn}/\text{Sn}^{2+}$ ) half-cell had been replaced by a standard state silver half-cell ( $\text{Ag}/\text{Ag}^+$ ), what happens to the direction of electron flow through the external circuit? Explain by referring to the "electrochemical series".

(3 marks)

(i) During the operation of this electrochemical cell, it was found that 1.00 g of chlorine had been consumed at that electrode. What would have been the mass change of tin at the other electrode? Show your workings.

(3 marks)

**TOTAL MARKS = ...../25**

# TEST ANSWERS

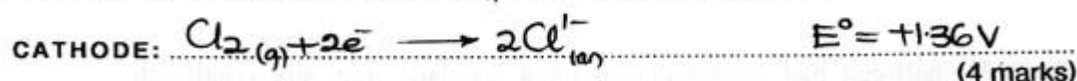
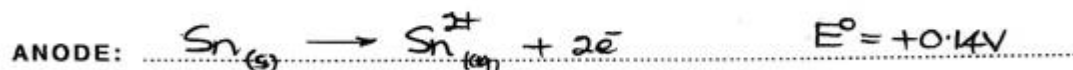
NAME (ANSWERS)  
**CHEMISTRY 12C**  
**ELECTROCHEMICAL CELLS**

## TEST 4

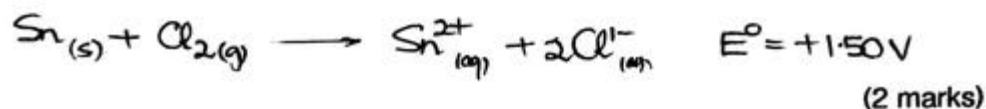
Answer the questions in the spaces provided. (Criteria assessed = Cr. 7 & 2)

An electrochemical cell is constructed as follows. One half-cell involves a piece of tin metal (Sn) immersed in a 1.0 mol/L aqueous solution of tin(II)sulfate (SnSO<sub>4</sub>). The other half-cell involves a piece of platinum metal immersed in a solution containing aqueous sodium chloride (NaCl<sub>(aq)</sub>). Chlorine gas (Cl<sub>2(g)</sub>) is bubbled over the surface of the platinum electrode. All ions are initially at concentrations of 1.0 mol/L. The two half-cells are separated by a salt-bridge barrier filled with NaNO<sub>3(aq)</sub>.

(a) Give the anode and cathode half-equations occurring in this cell.



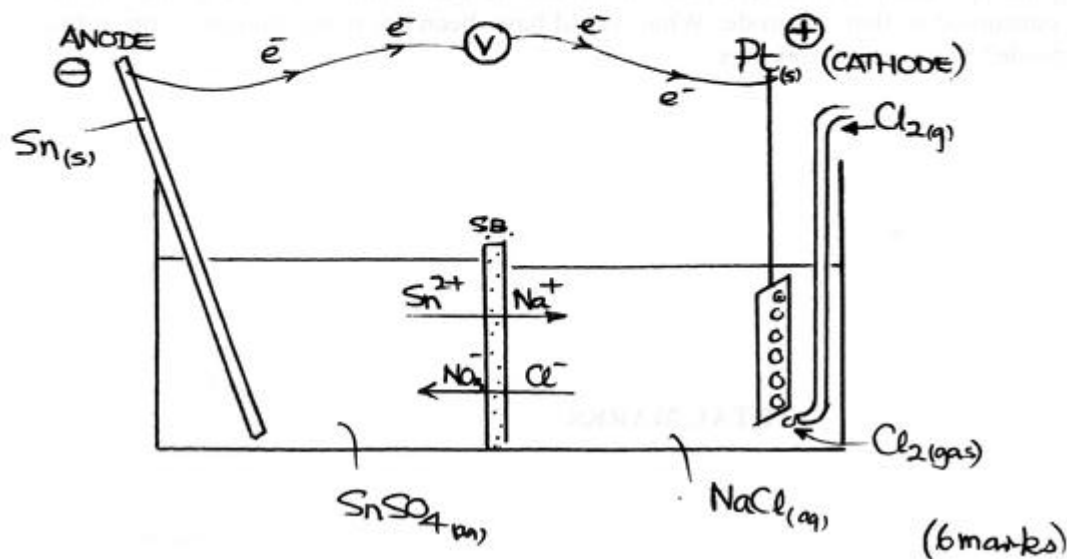
(b) By combining the two half equations, give the net cell equation.



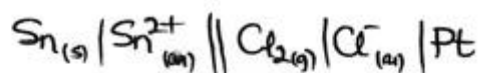
(c) Under standard state conditions, what would be the initial cell voltage (EMF) produced?

Cell EMF = 1.50 V (1 mark)

(d) Draw a neat, labelled diagram of the cell. On your diagram indicate the anode, cathode, salt bridge, direction of electron flow in the external circuit and direction of ion flow through the salt bridge. Label the appropriate electrodes positive or negative.



(e) Give the "shorthand" representation for the cell.



(2 marks)

(f) What was the function of the piece of platinum (Pt) metal electrode in the cell?

To provide an electrically conductive surface which is effectively INERT i.e. it doesn't interfere with the redox reactions occurring. On the surface  $\text{Cl}_2$  gas is reduced to  $\text{Cl}^-$  ions.

(2 marks)

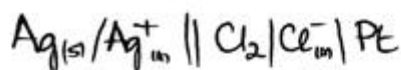
(g) As the cell continues to operate, the voltage produced decreases until it eventually reaches zero. Explain the chemical reasons for this decrease to zero.

As the surface area of the Sn anode decreases and the concentrations of  $\text{Sn}^{2+}$  and  $\text{Cl}^-$  ions increase, the net driving force (EMF) decreases and the cell reaches equilibrium.  $\Rightarrow$

(2 marks)

(h) If the tin ( $\text{Sn}/\text{Sn}^{2+}$ ) half-cell had been replaced by a standard state silver half-cell ( $\text{Ag}/\text{Ag}^+$ ), what happens to the direction of electron flow through the external circuit? Explain by referring to the "electrochemical series".

The  $\text{Ag}/\text{Ag}^+$  electrode would still be the anode because  $\text{Cl}_2$  is a more powerful oxidiser than  $\text{Ag}^+$  or  $\text{Sn}^{2+}$ .  
 $\therefore$  The cell becomes



$\therefore$  direction of  $e^-$  flow is unaltered i.e. from  $\text{Ag} \rightarrow \text{Pt}$

(3 marks)

(i) During the operation of this electrochemical cell, it was found that 1.00 g of chlorine had been consumed at that electrode. What would have been the mass change of tin at the other electrode? Show your workings.

$$\begin{aligned} n(\text{Cl}_2) \text{ consumed} &= \frac{\text{mass}}{M_r} \\ &= \frac{1.00}{71.0} = 0.0141 \text{ mole} \end{aligned}$$

$$\therefore n(\text{Sn}) = (0.0141 \times \frac{1}{1}) \text{ mole}$$

$$\begin{aligned} \rightarrow \text{mass of tin} &= (\text{moles} \times M_r) \text{ g} \\ &= 0.0141 \times 119 \text{ g} \\ &= 1.67 \text{ g} \end{aligned}$$

(3 marks)

TOTAL MARKS = ...../25