ALL SAINTS' COLLEGE

Science Department

Year 12 Chemistry ATAR

Test 5: Electrochemistry – Commercial Cells and Electrolysis

Name: Solutions

Instructions to Students:

1. 50 minutes permitted
2. Attempt all questions
3. Write in the spaces provided
4. Show all working when required
5. All answers to be in blue or black pen, diagrams in pencil.

TOTAL	Final Percentage
/48	

ALL SAINTS' COLLEGE

Year 12 Chemistry ATAR

Electrochemistry – Commercial Cells and Electrolysis

Commercial Cells

1. One of the many practical applications of electrochemical cell theory is in the construction of dry cell "batteries". Over the years, companies have tried different chemical compounds to move beyond the original zinc/carbon primary cell to rechargeable secondary cells of more advanced construction.

One such cell is the nickel-cadmium, or "ni-cad" cells. These cells are known as secondary cells and are used in video cameras, phones and other cordless electrical devices

The equations involved with this type of cell are:

1. $Cd_{(s)} + 2OH^{-1}{}_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^{-1}$ $\quad E° = +0.88V$

2. $NiO(OH)_{(s)} + H_2O_{(l)} + e^{-1} \rightarrow Ni(OH)_{2(s)}$ $\quad E° = +0.52V$

(a) Give the overall cell reaction.

$Cd_{(s)} + 2OH^{-1}{}_{(aq)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)}$ 1

(b) State the expected EMF of the cell. ***1.40V*** 1

(c) Despite their popularity, there are concerns with these type of cells, and all carry a safety warning specifically about their disposal. What is a potential safety concern with this type of battery?

Cadmium is a heavy metal and significant health concern if disposed of in land fill. 1

(d) These type of cells are known as "secondary" cells. Why is this?

Secondary Cells are rechargeable and can be used more than once. 1

(e) List two advantages and disadvantages of secondary cells (especially the lead-acid accumulator) as opposed to traditional primary cells.

Advantages	Disadvantages
Rechargeable	***Initial Cost***
Lower cost in long term	***safety issues***
High Cell Voltage	***Low Energy density***
1	1

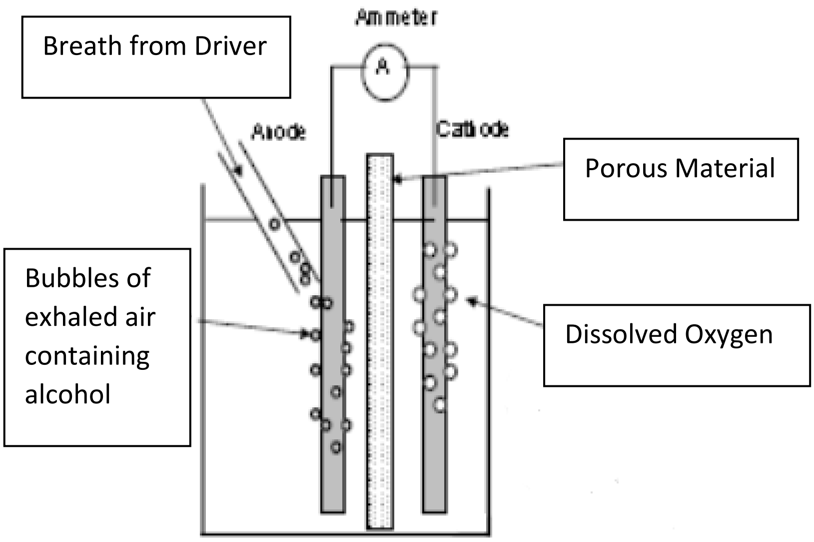
[6 marks]

2. Breathalysers work by analysing the amount of ethanol (C_2H_5OH) present in a driver's breath. Most modern breathalysers are based on fuel cell technology which is described below.

The fuel cell has two platinum electrodes with a porous acid-electrolyte material sandwiched between them. As the exhaled air from the driver flows past one side of the fuel cell, any alcohol in the breath is reacted at the other side at the platinum electrode producing ethanoic acid (acetic acid), hydrogen ions and electrons.

The electrons flow through a wire between the platinum electrodes. The oxygen moves to the lower portion of the fuel cell and is reacted to form hydroxide ions.

The more alcohol that is oxidised, the greater the electrical current. The current fed into a microprocessor and a digital reading of the blood alcohol level is shown on a screen on the device.



(a) Write the half-equation for the reaction of ethanol.

$C_2H_5OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$ 1

(b) Is this oxidation or reduction and at which electrode will this reaction take place?

Oxidation at the anode 1

(c) Write the half-equation for the reaction of oxygen at the other electrode.

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ 1

(d) Is this oxidation or reduction and at which electrode will this reaction take place?

Reduction at the cathode 1

(e) Why must the acid-electrolyte material be porous?

So that ions can move between electrodes to prevent polarisation of electodes.

1

(f) What is the purpose of having electrodes made of platinum?

So they are inert and take no part in the reaction. 1

(g) The ethanol cell produces a voltage of around 1.2V. Using a table of standard reduction potentials, predict the standard reduction potential of the ethanol/ethanoic half- cell.

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ***is +0.40V so (1.2V + 0.4V) = +1.6V*** 1

(h) Why is this estimate of the standard reduction potential only approximate?

The E° values only apply at standard conditions of pressure and temperature. 1

(8 marks)

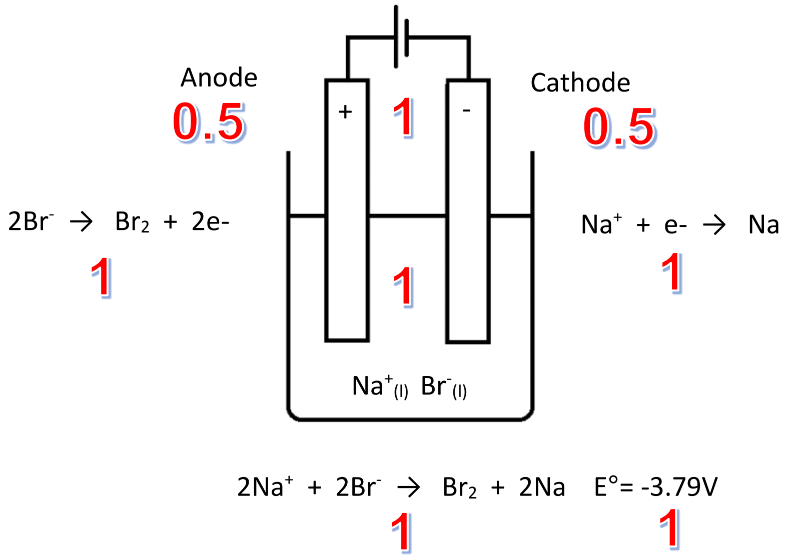
Continued on next page

Electrolysis

3.

(a) Draw a diagram to show the electrolysis of molten NaBr with platinum electrodes. Indicate the following:

(i) Anode and cathode.
(ii) Anode half equation.
(iii) Cathode half equation.
(iv) Overall reaction.
(v) E° for the process.
(vi) Positive and negative terminal.



(b) Why must the products of each half equation mentioned above be separated from one another?

If they are not separated the products will react spontaneously in a redox reaction to produce the original reactants. 1

(8 marks)

4. In 1807 Sir Humphry Davy electrolysed molten potassium hydroxide to produce the first drops of potassium metal. Bubbles of gas were observed at the anode. Write half-equations for the two electrode reactions.

$K^+ + e^- \rightarrow K$ 1

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ 1

(2 marks)

5. Write two half equations and a balanced cell reaction to explain the observations that a brown stream forms around one electrode and bubbles of gas are given off at the other when a strongly acidified aqueous solution of potassium iodide is electrolysed.

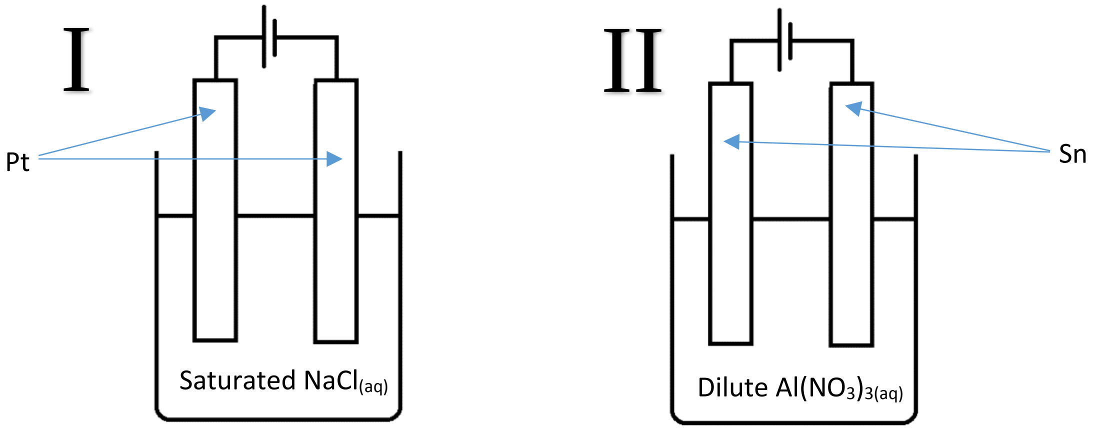
$2I^- \rightarrow I_2 + 2e^-$ 1

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ 1

$2I^- + 2H_2O \rightarrow I_2 + H_2 + 2OH^-$ 1

(3 marks)

6. Examine the two electrolytic cells below.



(a) Write the anode and cathode half-reactions and overall reaction for both cells immediately they are switched on.

Cell I Anode: *$2Cl^- \rightarrow Cl_2 + 2e^-$* 1

Cathode: *$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$* 1

Overall: *$2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^-$* 1

(3 marks)

Cell II **Anode:** $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ 1

Cathode: $H_2O + 2e^- \rightarrow H_2 + 2OH^-$ 1

Overall: $2H_2O \rightarrow 2H_2 + O_2$ 1

(3 marks)

(b) Calculate the minimum E.M.F. needed to electrolyse each solution under standard conditions.

Cell I Anode –1.36V Cathode – 0.83V 1 Overall – 2.19V EMF Required +2.19V 1	Cell II Anode –1.23V Cathode – 1.68V 1 Overall – 2.91V EMF Required +2.91V 1

(4 marks)

7. Copper metal is usually purified in an electrolytic cell with copper sulfate solution as the electrolyte. A raw copper bar containing many impurities (among them iron and silver metals) is used as the anode while the cathode is composed of pure copper.

(a) At the positive electrode the iron and copper are converted to ions but the silver is not - it falls to the bottom of the cell and is periodically removed. Briefly explain this difference in behaviour.

Silver is harder to oxidise than Fe or Cu. 1

The Fe would oxidise before the Cu in the electrode but the Cu would be entirely oxidised before any of the Ag impurity which would fall to the bottom (anode mud) 1

(2 marks)

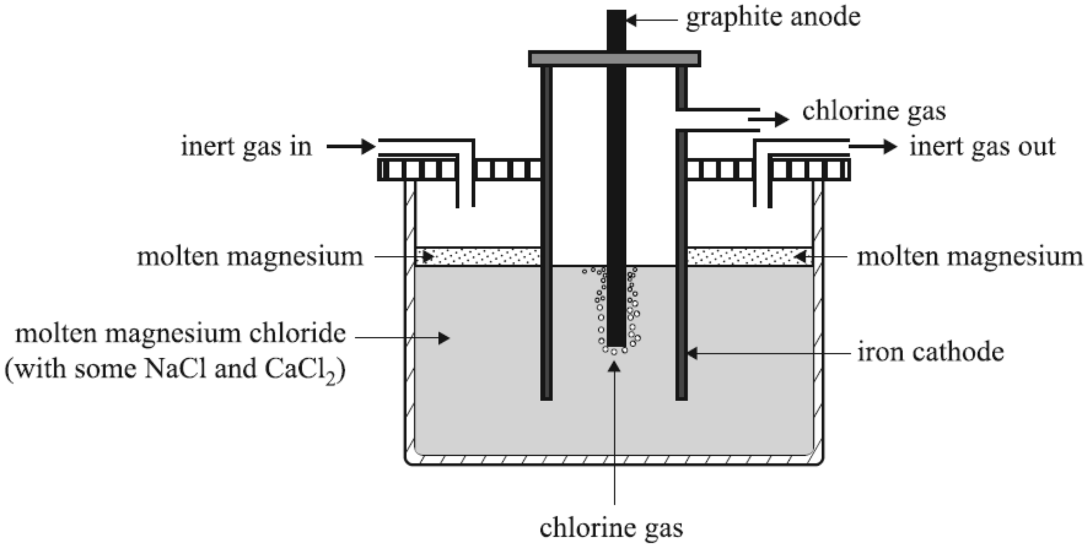
(b) At the other electrode, copper is deposited but iron is not. Briefly explain why this is so.

Cu^{2+} ions are more easily reduced than Fe^{2+}. They are better competitors for electrons. The reduction has a more positive E° value. 1

(1 mark)

8. Magnesium is one of the most abundant elements on Earth. It is used extensively in the production of magnesium-aluminium alloys. It is produced by the electrolysis of molten magnesium chloride.

A schematic diagram of the electrolytic cell is shown below.



The design of this cell takes into account the following properties of both magnesium metal and magnesium chloride:

- Molten magnesium reacts vigorously with oxygen.
- At the temperature of molten magnesium chloride, magnesium is a liquid.
- Molten magnesium has a lower density than molten magnesium chloride and forms a separate layer on the surface.

a. Write a balanced half-equation for the reaction occurring at each of

the cathode $Mg^{2+}_{(l)} + 2e^- \rightarrow Mg_{(l)}$ 1

the anode $2Cl^- \rightarrow Cl_2 + 2e^-$ 1

(2 marks)

b. Explain why an inert gas is constantly blown through the cathode compartment.

To prevent: molten Mg reacting with oxygen in the air and/or contact between Mg and air/oxygen

1

(1 mark)

c. The melting point of a compound can often be lowered by the addition of small amounts of other compounds. In an industrial process, this will save energy. In this cell, NaCl and $CaCl_2$ are used to lower the melting point of $MgCl_2$.

Why can NaCl and $CaCl_2$ be used to lower the melting point of $MgCl_2$ but $ZnCl_2$ cannot be used?

According to the electrochemical series:

- ***both Na^+ and Ca^{2+} are weaker oxidants than Mg^{2+} and so are unlikely to interfere with the production of Mg at the cathode.*** 1
- ***Zn^{2+} is a stronger oxidant than $Mg^{2+}_{(aq)}$ and could be reduced to Zn, thus either preventing the production of Mg or contaminating the Mg produced.*** 1

(2 marks)

d. What difference would it make to the half-cell reactions if the graphite anode were replaced with an iron anode? Write the half-equation for any different half-cell reaction. Justify your answer.

According to the electrochemical series Fe is a stronger reductant than Cl^-

At the anode, Fe would be oxidised instead of Cl^-/Fe^{2+} would be produced rather than Cl2.

Half-equation: $Fe(s) \rightarrow Fe^{2+}(l) + 2e^-$

The cations $Fe^{2+}(l)$ would migrate to the cathode/Fe^{2+} is a stronger oxidant than Mg^{2+} hence Fe could be produced/cathode half-equation would be $Fe^{2+}(l) + 2e^- \rightarrow Fe(s)$.

One mark each was awarded for:
- explaining why Fe2+ is produced at the anode
- the correct anode half-equation
- explanation of, or half-equation for, production of Fe at the cathode or other valid consequence of the production of Fe at the anode.

(3 marks)

End of test